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UNIVERSITY OF CALIFORNIA SAN DIEGO

Organic Diradicals as Resources for Quantum Technologies

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy

in

Chemistry

by

Yong Rui Poh

Committee in charge:

Professor Joel Yuen-Zhou, Chair
Professor Rommie E Amaro
Professor Francesco Paesani
Professor Andrew Brian Pun
Professor Wei Xiong

2025

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The Dissertation of Yong Rui Poh is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2025

DEDICATION

To my fiancée,
for her strong and unwavering support during uncertain times.

EPIGRAPH

By distance, you know the true power of a horse;
with time, you see the true colour of people.

Unknown, *Chinese idiom*

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ABSTRACT OF THE DISSERTATION

Organic Diradicals as Resources for Quantum Technologies

by

Yong Rui Poh

Doctor of Philosophy in Chemistry

University of California San Diego, 2025

Professor Joel Yuen-Zhou, Chair

Electron spins are promising resources for quantum technologies, and molecules offer additional advantages of higher tunability and scalability. In particular, organic diradicals host electron spins that are relatively long-lived, offering more avenues for engineered interactions with their environment. In the first few chapters of this Dissertation, I will discuss our recent works on designer organic diradicals that can function as optically addressable molecular spin qubits in quantum information science. These light-initiated platforms have traditionally been hosted in metallic complexes, and our design principles for an organic analogue have been supported by *ab initio* calculations and experimental implementations. Subsequently, I will discuss how triplet carbenes, which also exhibit diradical-like electronic structures, can display larger spin polarisations and improved

spin readout mechanisms. This will be illustrated with a few realistic carbene candidates, designed with existing synthetic strategies in mind. Finally, in the fifth chapter of this Dissertation, I will discuss how diradicals in the excited state, also known as radical pairs or electron donor-acceptor complexes, can be harnessed for chemical control, particularly chiral resolution under an applied magnetic field. The principles are analogous to the chirality-induced spin selectivity (CISS) effect, whereby a broken time-reversal symmetry is intricately linked to a broken mirror symmetry via the electron spin. Through these theoretical endeavours, I hope to motivate further explorations of spin dynamics to achieve unprecedented goals in quantum technology. This may include quantum computing, quantum sensing, and quantum control.

Chapter 1

Introduction: Electron Spins in Physics and Chemistry

The exploration of an additional two-valued quantum number in electrons began shortly after the development of quantum mechanics in the early 20th century. First proposed by Wolfgang Pauli in 1924 to explain the emission spectra of atoms, it was followed by many rounds of debate until an agreement was finally achieved with the help of relativity. Today, this extra degree of freedom is well-established as having originated from the electron rotating about its own axis. Such a motion has been christened as the electron *spin*.

In addition to its significance in fundamental science, this discovery has ushered in new ages for adjacent fields. Interestingly, the implications of the electron spin are varied across scientific disciplines. In Physics, spins have been instrumental for understanding properties such as magnetism and atomic fine structure. They have also been exploited for materials development, like in superconductivity, topological materials, and quantum spin liquids. Most recently, quantum information scientists have proposed the use of spins as basis states for quantum computation, opening up new opportunities in related fields, including quantum sensing and communication. By contrast, the electron spin has impacted the Chemistry community by offering an explanation for chemical bonding. In particular, the Pauli exclusion principle helped justify the existence of otherwise empirical rules for chemical stability, such as the octet rule. Having deciphered the quantum nature of molecular structures, chemists proceeded to use electron spins for reactions. This took the

forms of both basic science investigations, such as mechanistic studies in spectroscopy and analytical chemistry, and real-world applications, like in catalysis and enzyme chemistry.

I find it amazing how the same fundamental quantum property of *spins* has evolved into such distinct applications when approached from different perspectives. Moreover, each of these disciplines is fully developed, standing in its own right. Therefore, my goal with this Dissertation is to be at the scientific intersection and borrow ideas from both fields. In the first few chapters, I will discuss how *Chemistry* can influence *Physics* in the context of optically addressable diradical qubits. There, the hope is to use organic diradical molecules to mimic a state-of-the-art quantum sensor in *Physics* – the nitrogen-vacancy defect centre – and contribute to a long-standing problem of scalability and tunability in solid-state spin defects. Following that, I will improve on these designs using diradical-like carbenes, which, despite being the cornerstone of organometallic catalysis, have yet to be explored as quantum materials. Finally, in the fifth chapter, I will explore how the concepts that I have learnt from *Physics* can also influence *Chemistry*. Specifically, I will discuss how the interaction of radical pairs with an external magnetic field can separate enantiomers in a racemic mixture. Such chemical transformations are valuable to drug design, where opposite molecular chirality can exhibit different therapeutic properties.

Chapter 2

Alternant Hydrocarbon Diradicals as Optically Addressable Molecular Qubits

2.1 Introduction

There has been sustained interest in designing optically addressable electron spins that can be both initialised (polarised) and read out by optical means [19]. Known as optically-detected magnetic resonance (ODMR), this technique offers precise control of a single qubit and has found numerous applications in quantum sensing [6] and quantum information science [178]. The platform, referred to as a colour centre, is often a solid-state spin defect such as a nitrogen-vacancy (NV) centre in diamond [216, 51, 194, 85, 41, 158, 135, 136]. However, because these defects are introduced post-synthesis and often without control over their locations, defect-based colour centres suffer from poor scalability and tunability.

These problems can be tackled with molecular spin systems because they can be synthesised from bottom-up and extended into macromolecular systems [76, 18, 230, 246, 132, 199, 237, 242]. Metal complexes have seen the most advancements, particularly with transition metals [234, 27, 65, 151, 119, 133, 11, 28, 82, 117, 118, 159]. By contrast, little progress has been made with fully organic molecules [206, 56, 84, 173, 149, 205] which, being metal-free, will be more cost-efficient and sustainable than their metal-based counterparts. Pioneering efforts were made by Gorgon et al. using excited organic radicals

[84]; however, a drawback of microwave spin manipulation in an excited electronic state is the limited lifetime of the latter. As for ground-state organic systems, the same (and only) work [84] also showed light-induced selective preparation of a diradical in the triplet ground state over its degenerate singlet counterpart. In this case, it is unclear if the triplet magnetic sublevels were differentially populated, which is key towards coherent spin control. To this end, we present the first theoretical analysis for a general class of organic spin-optical interfaces, focusing on attaining spin polarisation in the ground-state magnetic sublevels.

In diamond-NV centres, ODMR is achieved via the following procedure [57]: Upon photoexcitation of the triplet ground state to the excited state (also a triplet), intersystem crossing (ISC) to a singlet excited state occurs with a change in magnetic quantum number M_S . This increases the relative population of the excited triplet $M_S = 0$ level, the photoluminescence (PL) of which transfers the spin polarisation to the ground state (optical initialisation). The PL intensity also indicates the ground-state polarisation (optical readout). As for the singlet excited state, its population decays non-radiatively to the triplet $M_S = 0$ ground state, its irreversibility being the key towards overall purification of the ground state spins [Fig. 5.2a]. There are thus three elements to engineer in a metal-free molecular system: (1) a high-spin ground state, (2) spin-selective interactions among the excited states, and (3) irreversible relaxation to the ground state.

Element (1) suggests the use of an organic diradical. Thus far, most luminescent diradicals have involved some degree of π -conjugation [94, 121, 235, 72, 103, 3, 148, 2], which has proven useful in the chemical assembly of spin arrays [121]. However, large spatial separation between the two paramagnetic centres is often necessary to minimise radical-radical interactions and achieve a high-spin ground state [Fig. 5.2b] [4, 38, 208, 161, 243]. In most cases, this separation extends to the excited states as well, which is disadvantageous for element (2). Indeed, in Gorgon et al.’s seminal work, interrational interaction was achieved via a charge transfer to the spacer’s triplet state, generating a complicated manifold of 12 coupled electronic levels [84]. One solution would be to

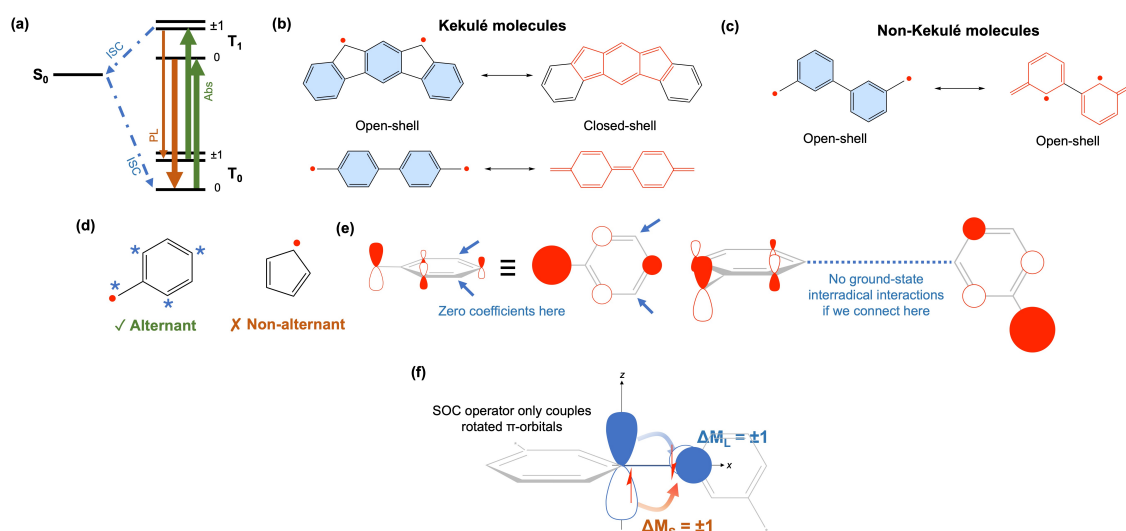


Figure 2.1. (a) Colour centres like diamond-NV defects can be spin polarised by multiple photoexcitation (Abs) cycles, the intensity of PL being an indicator of the ground-state spin polarisation. This procedure is known as ODMR. (b) Kekulé hydrocarbons are conjugated π -systems with at least one closed-shell Kekulé structure. These molecules tend to have lower diradical characters. (c) Non-Kekulé structures have no closed-shell Kekulé structures and are hence more likely to have open-shell ground states. (d) Alternant hydrocarbons are π -systems whereby the π -contributing atoms may be divided into two classes, starred [*] and unstarred [], such that no two atoms from the same class are adjacent. (e) Within the Hückel framework, radicals constructed with alternancy symmetry (termed AHRs) have their SOMOs localised on the starred atoms (the class with more atoms). As such, two AHRs covalently bonded via the unstarred atoms will have vanishing radical-radical interactions. These molecules are non-Kekulé, as shown in (c). (f) In π -electron systems, SOC-mediated ISC can only occur between rotated π -orbitals, in line with the El-Sayed rules. Due to conservation of angular momentum, an electron spin flip must occur concomitantly, making a triplet-singlet ISC process spin-selective.

reduce (improve) the stability of the molecule’s closed-shell (open-shell) Kekulé structures, with a crude measure being the number of Clar sextets minus the number of unpaired electrons [183]. In the most extreme case, the π -diradical may have no closed-shell Kekulé structures at all; such molecules are termed “non-Kekulé” [4, 161] and an example has been shown in Fig. 5.2c. However, this analysis is purely qualitative and there exist non-Kekulé molecules with appreciable closed-shell characters [208]. (Interestingly, alkaline earth metal complexes [120], commonly used as optical cycling centres [55, 256], as well as nitrenes [79] have also been investigated for luminescent diradical properties and are useful candidates of molecular colour centres as well.)

Alternant hydrocarbon radicals (AHRs) are a special type of hydrocarbon π -electron radicals. In AHRs, atoms contributing to the π framework may be divided into two classes such that no two atoms from the same class are adjacent [Fig. 5.2d]. Importantly, within Hückel theory of nearest-neighbour hopping, the singly occupied molecular orbital (SOMO) is localised on atoms from only one class – the class containing more atoms [Fig. 5.2e]. As such, by covalently tethering two AHRs via atoms of the *other* class, radical-radical interactions may be avoided in the ground state, that is, the resulting diradical is non-Kekulé and quantitatively predicted to be open-shell within the Hückel framework. Note that interrational interactions are retained in the excited states because the occupied and virtual molecular orbitals (MOs) are in general delocalised across both atom classes; this is necessary for element (2).

Thus far, we have not addressed the spin selectivity component of element (2). This was achieved in NV centres via an ISC process mediated by spin-orbit coupling (SOC) [57], but these rates are negligible if the π -conjugated system is fully planar. The reason may be found in the SOC operator, which in its mean-field Breit-Pauli form has the structure of $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{L}_z \hat{S}_z + \hat{L}_+ \hat{S}_- / 2 + \hat{L}_- \hat{S}_+ / 2$, where $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are the orbital and spin angular momentum vector operators respectively [177]. The first operator vanishes when acting on $2p_z$ atomic orbitals (AOs), while the other two operators rotate $2p_z$ orbitals into linear combinations of $2p_x$ and $2p_y$ orbitals. Therefore, the SOC operator only connects

between rotated $2p$ (or π) orbitals [Fig. 5.2f]. This is essentially the statement of El-Sayed [61] and implies that torsion between the radical π -systems is important for element (2) [99, 195, 22, 248]. Finally, since orbital rotation constitutes a $\Delta M_L = \pm 1$ transition, to conserve total angular momentum the spin must also change by $\Delta M_S = \pm 1$, giving rise to the spin selectivity of ISC in π -electron systems [99, 22, 248].

Therefore, through a qualitative analysis, we find potential in realising an NV centre analogue by attaching two AHRs covalently at selected atoms and with significant torsion. We call them AHR m -dimers, referencing the fact that most luminescent π -radicals have benzylic structures and thus should be dimerised via atoms at the *meta* position. In this work, we make further progress by analysing the electronic structure of AHR m -dimers and the symmetries of their excited wavefunctions. By adopting a mean-field approach to the Pariser-Parr-Pople (PPP) model [175, 182, 138] (also known as the extended Hubbard model), we find that not all excitations are absorptive and only few within the subset can undergo triplet-singlet ISC. This makes the excited state kinetics highly selective and useful for generating robust ODMR mechanisms leading towards ground-state spin polarisation. While general to any AHR m -dimer, our observations are also set in the context of two existing AHRs – a methylated benzylic radical and the tris(2,4,6-trichlorophenyl)methyl (TTM) radical – using parameters estimated from density functional theory (DFT). For the methylated benzylic radical, our DFT-parametrised excited states also matched the results from a multi-configurational level of theory. These ab initio calculations further demonstrate the possibility of designing a molecular colour center with AHR m -dimers.

The paper is organised as such: In Sec. 2.1, the electronic structure of AHR m -dimers is analysed using the PPP framework. This section is technical and the reader may safely skip it at the first pass. In Sec. 2.2, ODMR mechanisms resulting in ground-state spin polarisation are proposed based on results from the PPP model. In Sec. 2.3, the PPP predictions are verified by ab initio calculations. Finally, in Sec. 2.4, a mapping between a polarised ground-state triplet and an operational qubit is proposed.

2.2 Results and Discussions

2.2.1 Electronic structure analysis

The PPP model [175, 182, 138] is an extension of the Hückel model to include additional Coulomb interactions. It partially resolves the electron-electron correlation problem and continues to be the reference model for π -conjugated hydrocarbons. By considering only the minimal basis of $2p$ AOs that constitute the π -electron system, the PPP Hamiltonian reads

$$\begin{aligned} \hat{H}_{\text{PPP}} = & \sum_{\mu} \alpha_{\mu} \hat{n}_{\mu} - \sum_{\langle v > \mu \rangle} \sum_{\sigma} \beta_{\mu v} \left(\hat{a}_{\mu \sigma}^{\dagger} \hat{a}_{v \sigma} + \hat{a}_{v \sigma}^{\dagger} \hat{a}_{\mu \sigma} \right) \\ & + \sum_{\mu} \gamma_{\mu \mu} \hat{n}_{\mu \alpha} \hat{n}_{\mu \beta} + \sum_{v > \mu} \gamma_{\mu v} \hat{n}_{\mu} \hat{n}_v, \end{aligned} \quad (2.1)$$

with $\hat{a}_{\mu \sigma}^{\dagger}$ ($\hat{a}_{\mu \sigma}$) being the fermionic creation (annihilation) operator for an electron in the $2p$ AO of atom μ with spin σ ($= \alpha, \beta$), $\hat{n}_{\mu \sigma} \equiv \hat{a}_{\mu \sigma}^{\dagger} \hat{a}_{\mu \sigma}$ being the number operator and $\hat{n}_{\mu} \equiv \sum_{\sigma=\alpha, \beta} \hat{n}_{\mu \sigma}$. Here, we have used α (β) to denote spin-up (spin-down) electrons. The parameters are defined as followed: α_{μ} is the on-site energy of atom μ , $\beta_{\mu v}$ is the hopping amplitude between atoms μ and v , and $\gamma_{\mu v}$ represents the effective Coulombic repulsion between an electron on atom μ and another electron on atom v . Finally, $\langle \cdot \rangle$ denotes nearest neighbours.

Its application towards AHRs was explored by Longuet-Higgins and Pople using a mean-field approach similar to Hartree-Fock theory [142, 52, 141]. The results remain qualitatively the same as the Hückel approach, that is, if we label the alternacy class containing more atoms by stars [*] [Fig. 5.2d], then each HOMO- j has the same atomic coefficients as the corresponding LUMO+ j , except with opposite signs on the unstarred atoms. This is known as the pairing theorem and, consequently, the SOMO has nodes on the unstarred atoms. An excellent review on this topic has been provided by Hele [95] and we shall not rederive the results. Instead, we will briefly mention that, within the aforementioned mean-field treatment, the AHR's electronic ground state (GS) is a doublet

described by the following (Slater) determinants:

$$|\Psi; +1/2\rangle = |\cdots 2\bar{2}1\bar{1}0\rangle, \quad |\Psi; -1/2\rangle = |\cdots 2\bar{2}1\bar{1}0\rangle, \quad (2.2)$$

that is, determinants with one electron in the SOMO ($j = 0$) and two electrons in each HOMO- j ($j = 1, 2, \dots$). In this work, we shall follow standard electronic structure theory notation [213]. In addition, the second state index labels the spin magnetic number $M_S \in \{+1/2, -1/2\}$.

Yet another consequence of alternacy symmetry is the invariance of $\hat{H}_{\text{PPP}}$ [Eq. (C.32)] under particle-hole transformation (PHT) $\hat{a}_{\mu\sigma}^\dagger \rightarrow f_\mu \hat{a}_{\mu\bar{\sigma}}$ with f_μ being +1 if μ is starred and -1 otherwise ($\bar{\sigma}$ is the spin complementary to σ). As such, it is apt to label electronic states of AHRs by their symmetries under PHT, be it odd or even. For instance, when considering an α -spin excitation from SOMO to LUMO+ j , labelled $|\Psi_0^{j'}; +1/2\rangle$, one should take a linear combination with the β -spin HOMO- j to SOMO transition $|\Psi_j^{\bar{0}}; +1/2\rangle$, which is related to the latter by PHT, such that the resulting state has a well-defined symmetry under PHT. Following the notation set by Pariser [174, 96], we label these symmetry-adapted states by “+” and “-” representing symmetric and antisymmetric combinations respectively:

$$|\Psi_{0j}^\pm; +1/2\rangle \equiv \frac{|\Psi_j^{\bar{0}}; +1/2\rangle \pm |\Psi_0^{j'}; +1/2\rangle}{\sqrt{2}}. \quad (2.3)$$

We note that due to differences in origin (Pariser was considering configuration interactions), some “+” states may be odd (instead of even) under PHT and the same can happen to “-” states too. Despite that, there is a one-to-one mapping between the two notations, justifying our choice of Pariser’s (see Supplementary Information S1).

Our m -dimer system comprises two AHRs covalently tethered via the unstarred atoms (the class containing fewer atoms) [Fig. 2.2a]. The entire π -electron system is modelled by the PPP Hamiltonian. Because the monomers are rotated relative to each

other by sterics, any intermonomer couplings due to π -orbital overlaps may be treated perturbatively. As such, we partition the Hamiltonian into monomeric components:

$$\begin{aligned}\hat{H}_r = & \sum_{\mu \in \mathcal{N}_r} \alpha_\mu \hat{n}_\mu - \sum_{\langle \nu > \mu \in \mathcal{N}_r \rangle} \sum_{\sigma} \beta_{\mu\nu} \left(\hat{a}_{\mu\sigma}^\dagger \hat{a}_{\nu\sigma} + \hat{a}_{\nu\sigma}^\dagger \hat{a}_{\mu\sigma} \right) \\ & + \sum_{\mu \in \mathcal{N}_r} \gamma_{\mu\mu} \hat{n}_{\mu\alpha} \hat{n}_{\mu\beta} + \sum_{\nu > \mu \in \mathcal{N}_r} \gamma_{\mu\nu} \hat{n}_\mu \hat{n}_\nu,\end{aligned}\quad (2.4)$$

and perturbative intermonomer couplings:

$$\begin{aligned}\hat{V}_{AB} = & - \sum_{\langle \mu \in \mathcal{N}_A, \nu \in \mathcal{N}_B \rangle} \sum_{\sigma} \beta_{\mu\nu} \left(\hat{a}_{\mu\sigma}^\dagger \hat{a}_{\nu\sigma} + \hat{a}_{\nu\sigma}^\dagger \hat{a}_{\mu\sigma} \right) \\ & + \sum_{\mu \in \mathcal{N}_A, \nu \in \mathcal{N}_B} \gamma_{\mu\nu} \hat{n}_\mu \hat{n}_\nu,\end{aligned}\quad (2.5)$$

such that the full Hamiltonian reads $\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}_{AB}$. Here, $r \in \{A, B\}$ labels the two monomers and $\mathcal{N}_r$ denotes the set of atoms in monomer r .

Before solving the Hamiltonian $\hat{H}$, it is useful to understand the types of electronic states to expect. We note that all dimers have a C_2 rotational symmetry and both $\hat{H}_A + \hat{H}_B$ and $\hat{V}_{AB}$ are symmetric under this transformation. Furthermore, the m -dimer is also alternant so both $\hat{H}_A + \hat{H}_B$ and $\hat{V}_{AB}$ are symmetric under PHT as well. As such, focusing on the zeroth-order term $\hat{H}_A + \hat{H}_B$ for now, the zeroth-order electronic states may be organised by eigenvalues of the molecule's spin and symmetry operators, namely (1) the spin numbers, S and M_S , (2) symmetry under PHT, $P \in \{+, -\}$, and (3) irreducible representations (irreps) of the C_2 point group, $\Gamma \in \{A, B\}$, presented in typewriter font to avoid confusion with the monomer index. In this work, we packed them into the following notation for electronic states:

$$\left| {}^{2S+1}\Phi_{\Gamma}^{jk,P}; M_S \right\rangle, \quad (2.6)$$

with Φ labelling the class of excitation and $\{j, k\}$ labelling the MOs involved in the excitation (more to follow).

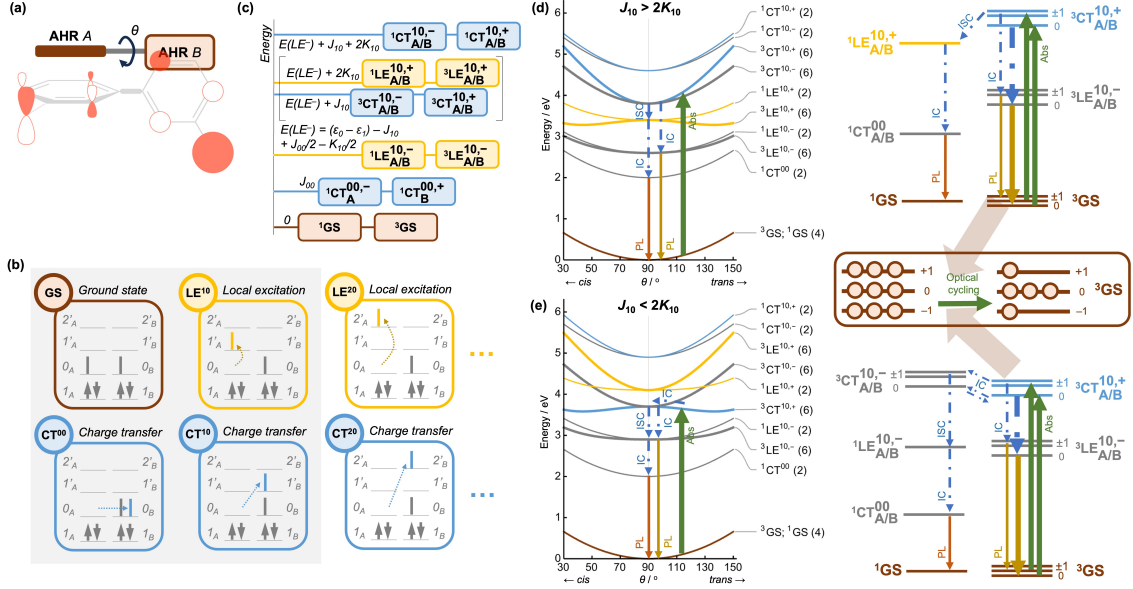


Figure 2.2. (a) Schematic of an AHR m -dimer, which contains two AHRs (indexed $r \in \{A, B\}$) covalently tethered at the unstarred atoms (the class of fewer atoms) with torsional angle θ . (b) Ground and excited state configurations of AHR m -dimers, expressed in the basis of MOs localised completely on either monomer A, i.e. $\{\dots, 1_A, 0_A, 1'_A, \dots\}$, or monomer B, i.e. $\{\dots, 1_B, 0_B, 1'_B, \dots\}$. LEs keep the excited electron on the same monomer (e.g. $0_A \rightarrow 1'_A$), while CTs excite electrons across monomers (e.g. $0_A \rightarrow 1'_B$). Labels “ $\pm$ ” represent linear combinations of SOMO-to-LUMO and HOMO-to-SOMO transitions, i.e. particle-hole symmetries. (c) Energies of ground and excited electronic states at $\hat{V}_{NN} = 0$, presented in ascending order. The energy ordering between the $LE^{10,+}$ states and the ${}^3CT^{10}$ states depends on the relative values of $J_{10} \equiv (11|00)$ and $2K_{10} \equiv 2(10|01)$. ZFS is not being considered by this work. (d,e) Plots of representative PESs based on perturbation theory calculations for (d) $J_{10} > 2K_{10}$ and (e) $J_{10} < 2K_{10}$. Non-absorptive states are drawn in grey and degeneracies are indicated in parenthesis. Also illustrated are two possible ODMR mechanisms, one for each case. In both cases, spin polarisation is attained in the triplet GS by transferring its $M_S = \pm 1$ populations into the singlet GS. Parameters for (d): $E_{steric} = 0.6$ eV; $\theta_{eq} = 90.0^\circ$; $\beta_{AB}^0 = 2.5$ eV; $\gamma_{AB}^0 = 0$ eV; SOMO-LUMO gap = 3.0 eV; $c_{A1_A} = c_{B1_B} = 0.5$; $J_{00} = 2.0$ eV; $J_{10} = 1.2$ eV; $K_{10} = 0.4$ eV. Parameters for (e): Same as (d) except $J_{10} = 0.8$ eV and $K_{10} = 0.6$ eV. Abs: Photoexcitation.

To solve the Hamiltonian, we note that the monoradical terms $\hat{H}_A$ and $\hat{H}_B$ each admit the same mean-field solutions as those obtained by Longuet-Higgins and Pople, described by Eq. (2.2). As such, because the two monomers are non-interacting at $\hat{V}_{AB} = 0$, the approximate zeroth-order electronic ground states ($\Phi = \text{GS}$) to the full zeroth-order Hamiltonian $\hat{H}_A + \hat{H}_B$ will be (tensor) products of the monoradical’s mean-field solutions. This yields a singlet state $|^1\text{GS}; 0\rangle$ and a set of triplet states $\{|^3\text{GS}; M_S\rangle | M_S = -1, 0, +1\}$, all of which have “–” particle-hole symmetry. Note that we continue to use the basis of MOs localised on each monomer; for instance, $|^3\text{GS}; +1\rangle = |\cdots 1_A \bar{1}_A 0_A \cdots 1_B \bar{1}_B 0_B\rangle$, with j_r being the j -th MO of monomer r .

As for the zeroth-order low-lying excited states, they are approximated by single excitations from the GS, just like the monoradical case [Eq. (2.3)]. With dimers, there can be two types of excited states: local excitations ($\Phi = \text{LE}$), which move electrons within the same monomer, and charge transfers ($\Phi = \text{CT}$), which excite electrons to the other monomer. Fig. 2.2b provides a diagrammatic representation of these excitations. For simplicity, we consider only the $1 \rightarrow 0$ and $0 \rightarrow 1'$ transitions (j' labels LUMO+ j), even though the subsequent analysis applies to higher-lying excitations as well (such as $2 \rightarrow 0$ and $0 \rightarrow 2'$). This totals up to 35 states and their expressions have been compiled in Supplementary Information S2 after taking symmetry- and spin-adapted linear combinations, as described by Eq. (2.6).

We then compute the zeroth-order excitation energies by taking expectation values over $\hat{H}_A + \hat{H}_B$, the results being compiled in Fig. 2.2c. We highlight that the singlet CT^P state is higher in energy than the triplet ones because, unlike LE^P , the unpaired spins in CT^P experience intramonomer exchange interactions that do not vanish with $\hat{V}_{AB} \rightarrow 0$. Also, the $\{|^1\text{LE}_T^{10,+}; 0\rangle\}$ and $\{|^3\text{CT}_T^{10,+}; \pm 1\rangle\}$ sets may have opposite energy rankings depending on the relative values of $J_{10} \equiv (11|00)$ and $2K_{10} \equiv 2(10|01)$ (in chemists’ notation [213]). Finally, while the LE^+ and LE^- states are separated in energy due to configuration interaction between the $1 \rightarrow 0$ and $0 \rightarrow 1'$ transitions, this separation is not present in the CT states because the two MO transitions, being intermonomer in nature, are

non-interacting at $\hat{V}_{AB} = 0$. These, as we shall see, are crucial to the ODMR mechanism.

With regard to the linear absorption spectrum, we find that out of all 35 zeroth-order low-lying excitations, only the LE^+ states are bright with non-vanishing transition dipole moments. The reason lies in the form of the dipole operator within the neglect of differential overlap assumption invoked by the PPP model [174]:

$$\hat{\boldsymbol{\mu}} = \sum_{v \in \mathcal{N}_A \cup \mathcal{N}_B} \boldsymbol{\mu}_v \hat{n}_v, \quad (2.7)$$

which has “−” particle-hole symmetry and does not excite between monomers. Hence, the GS, being of “−” symmetry, can only be photoexcited locally and to “+” states. (An alternative interpretation is to realise that the $j \rightarrow 0$ and $0 \rightarrow j'$ transitions have identical transition dipole moments, so they cancel when taking antisymmetric combinations in Eq. (2.3) [1, 95].)

Next, we consider perturbative effects on the approximate zeroth-order eigenstates due to $\hat{V}_{AB}$. Because $\hat{V}_{AB}$ is a spin-preserving intermonomer operator of “+” particle-hole symmetry and A irrep [Eq. (2.5)], only CT-type mixing between states of like symmetry can occur:

$$\left| {}^{2S+1}\text{LE}_{\Gamma}^{10,P}; M_S \right\rangle \xleftrightarrow{\hat{V}_{AB}} \left| {}^{2S+1}\text{CT}_{\Gamma}^{10,P}; M_S \right\rangle. \quad (2.8)$$

This suggests that CT^+ excitations can also be partially bright depending on the extent of LE^+ mixing. We note that while $\hat{V}_{AB}$ can in principle connect GS to CT states and also CT^{00} to LE states, these matrix elements are small because $\hat{V}_{AB}$ is largest near the dimer linkage where nodes of the SOMOs reside, thus any excitations involving SOMO electrons will be negligible. This is consistent with the notion that, in AHR m -dimers, π -bonding – described by mixing of covalent (LE) and ionic (CT) wavefunctions [196] – only occurs in the excited states. Formally, we extend the nearest neighbour approximation to the Coulomb interaction parameter $\gamma_{\mu\nu}$ (which scales inversely with the distance between μ and ν) and expand $\hat{V}_{AB}$ in terms of MO fermionic operators using $\hat{a}_{\mu\sigma}^{\dagger} = \sum_{j_r} c_{\mu j_r}^* \hat{b}_{j_r\sigma}^{\dagger}$ (r

indexes the monomer containing μ). The result, labelled $\hat{V}_{\text{NN}}$, reads [Eq. (2.5)]

$$\begin{aligned}\hat{V}_{AB} &\approx \hat{V}_{\text{NN}} \\ &\equiv -\beta_{\mathcal{A}\mathcal{B}} \sum_{\sigma} \left(\hat{a}_{\mathcal{A}\sigma}^{\dagger} \hat{a}_{\mathcal{B}\sigma} + \hat{a}_{\mathcal{B}\sigma}^{\dagger} \hat{a}_{\mathcal{A}\sigma} \right) \\ &\quad + \gamma_{\mathcal{A}\mathcal{B}} \hat{n}_{\mathcal{A}} \hat{n}_{\mathcal{B}}\end{aligned}\tag{2.9}$$

in the AO basis and

$$\begin{aligned}\hat{V}_{AB} &\approx \hat{V}_{\text{NN}} \\ &\equiv -\beta_{\mathcal{A}\mathcal{B}} \sum_{j_A, k_B} \sum_{\sigma} \left(c_{\mathcal{A}j_A}^* c_{\mathcal{B}k_B} \hat{b}_{j_A\sigma}^{\dagger} \hat{b}_{k_B\sigma} \right. \\ &\quad \left. + c_{\mathcal{B}k_B}^* c_{\mathcal{A}j_A} \hat{b}_{k_B\sigma}^{\dagger} \hat{b}_{j_A\sigma} \right) \\ &\quad + \gamma_{\mathcal{A}\mathcal{B}} \sum_{j_A, l_A, k_B, m_B} \sum_{\sigma\tau} c_{\mathcal{A}j_A}^* c_{\mathcal{A}l_A} c_{\mathcal{B}k_B}^* c_{\mathcal{B}m_B} \\ &\quad \times \hat{b}_{j_A\sigma}^{\dagger} \hat{b}_{l_A\sigma} \hat{b}_{k_B\tau}^{\dagger} \hat{b}_{m_B\tau}\end{aligned}\tag{2.10}$$

in the MO basis, with $\mathcal{A}$ and $\mathcal{B}$ being the unstarred atoms linking the two AHRs. Because unstarred atoms are where the SOMO's nodes are located, we find that $c_{\mathcal{A}0_A} = c_{\mathcal{B}0_B} = 0$, restricting the sum over $\{j_A, l_A, k_B, m_B\}$ in Eq. (2.10) to only non-zero values. This leaves $\hat{V}_{\text{NN}}$ with no excitations connected to the SOMO (index $j = 0$), in line with the above analysis. Importantly, all of these suggest a negligible GS singlet-triplet gap despite $\hat{V}_{\text{NN}} \neq 0$, a sign of a true diradical.

Corrections to the states and energies are then evaluated to second order in the approximate perturbation $\hat{V}_{\text{NN}}$, the results being presented in Supplementary Information S3. Importantly, because $\hat{V}_{\text{NN}}$ scales with the degree of π -orbital overlap between the two AHRs, we expect its effects to be quantified by an intermonomer torsional angle θ [Fig. 2.2a] such that the π -interactions are maximal when the two monomers are coplanar at

$\theta = 0^\circ$ or 180° . To this end, we parametrise $\hat{V}_{\text{NN}} = \hat{V}_{\text{NN}}(\theta)$ by substituting

$$\beta_{\mathcal{A}\mathcal{B}} = \beta_{\mathcal{A}\mathcal{B}}(\theta) \approx \beta_{\mathcal{A}\mathcal{B}}^0 \cos \theta, \quad (2.11)$$

$$\gamma_{\mathcal{A}\mathcal{B}} = \gamma_{\mathcal{A}\mathcal{B}}(\theta) \approx \gamma_{\mathcal{A}\mathcal{B}}^0 \cos^2 \theta. \quad (2.12)$$

Here, $\cos \theta$ represents the projection of one AHR's local axis of quantisation (the “z-axis”) onto the other's, and two of such terms are necessary for any two-electron integral. An additional parabolic potential is also introduced to model steric effects in the GS:

$$V_{\text{steric}}(\theta) \approx E_{\text{steric}} (\theta - \theta_{\text{eq}})^2, \quad (2.13)$$

which we assume to be the same in the excited states. In general, we expect $\theta_{\text{eq}} \approx 90^\circ$ due to the lack of π -bonding in the GS.

Based on the perturbation theory results and the above θ parametrisation, we plotted two representative potential energy surfaces (PESs) in Fig. 2.2d,e. Indeed, the singlet and triplet GSs are degenerate over the entire range of θ , consistent with the lack of radical-radical interactions in the GS. The same holds for LE states at $\theta = 90^\circ$ (because $\hat{V}_{AB} = 0$). However, away from this angle, mixing with the CT states opens up a gap between the two spin multiplicities – a sign of π -bonding [196].

The ODMR cycle is only complete with a spin-selective ISC, the key towards spin polarisation. At the heart of this effect is the SOC operator that controls the ISC rate and, as mentioned earlier, only links rotated π -orbitals [99, 195, 22, 248]. Because AHRs are mostly planar, SOC will have to be an intermonomer effect that is largest at the maximum torsion of $\theta = 90^\circ$. Furthermore, we expect this operator to act locally at the dimer connection since its matrix elements scale inversely with the cube of the interatomic distance. Given these restrictions, we further examine the nature of SOC by adapting the

single-electron Breit-Pauli SOC operator in PPP theory [22] to our system. We obtain

$$\hat{V}_{\text{SOC}}(\theta) = \sum_{\sigma} B \sin(\theta) \left(\hat{a}_{\mathcal{A}\sigma}^{\dagger} \hat{a}_{\mathcal{B}\bar{\sigma}} - \hat{a}_{\mathcal{B}\bar{\sigma}}^{\dagger} \hat{a}_{\mathcal{A}\sigma} \right), \quad (2.14)$$

or, in terms of MO operators,

$$\begin{aligned} \hat{V}_{\text{SOC}}(\theta) = \sum_{j_A \neq 0_A, k_B \neq 0_B} \sum_{\sigma} B \sin(\theta) & \left(c_{\mathcal{A}j_A}^* c_{\mathcal{B}k_B} \hat{b}_{j_A\sigma}^{\dagger} \hat{b}_{k_B\bar{\sigma}} \right. \\ & \left. - c_{\mathcal{B}k_B}^* c_{\mathcal{A}j_A} \hat{b}_{k_B\bar{\sigma}}^{\dagger} \hat{b}_{j_A\sigma} \right), \end{aligned} \quad (2.15)$$

where B is a purely imaginary value defined in Supplementary Information S4. Similar to the analysis of $\hat{V}_{AB}$, we find that $\hat{V}_{\text{SOC}}$ only couples LE and CT excitations and leaves the GS and CT^{00} states unperturbed due to the SOMO's nodal structure. It creates spin flips, has “+” particle-hole symmetry and is odd under C_2 rotation. Hence, we find that the only allowed ISC processes are

$$\left| {}^1\text{LE}_{\Gamma}^{10,P}; 0 \right\rangle \xleftrightarrow{\hat{V}_{\text{SOC}}} \left| {}^3\text{CT}_{\bar{\Gamma}}^{10,P}; \pm 1 \right\rangle, \quad (2.16)$$

$$\left| {}^3\text{LE}_{\Gamma}^{10,P}; \pm 1 \right\rangle \xleftrightarrow{\hat{V}_{\text{SOC}}} \left| {}^1\text{CT}_{\bar{\Gamma}}^{10,P}; 0 \right\rangle, \quad (2.17)$$

with $\bar{\Gamma}$ being the irrep opposite to Γ . As an aside, in deriving Eq. (2.15) we have assumed the dimer linkage to be perpendicular to the spin quantisation axis (Supplementary Note S4). When no magnetic field is applied, the latter is determined by the spin-spin interactions intrinsic to the molecule [14]. This implies spin quantisation along the high-symmetry axis of the molecule, making the earlier assumption valid in AHR m -dimers given the orientation of the C_2 axis.

2.2.2 Proposed ODMR mechanisms

To sum it up, a detailed electronic structure analysis of AHR m -dimers revealed important symmetries that affect the ODMR mechanism. Of particular importance are the following:

- a. Excited states may be classified based on their character at torsion $\theta = 90^\circ$ [Fig. 2.2a]. This can be either local excitations (LEs), which promote electrons in an intramonomer fashion, or charge transfers (CTs), which move electrons across monomers [Fig. 2.2b]. Also labelled are the state's particle-hole symmetry (a consequence of alternancy symmetry), which can be either “+” or “−” [Eq. (2.6)]. These states are ordered by energy in Fig. 2.2c. (*Aside:* States are also labelled by their irrep $\Gamma \in \{A, B\}$, but this is inconsequential to the ODMR mechanism.)
- b. Near the equilibrium torsion of $\theta \approx 90^\circ$ [Fig. 2.2a], intermonomer π -bonding is negligible. Therefore, only the CT states have appreciable singlet-triplet gaps due to intramonomer exchange interactions [Fig. 2.2c]. This implies that selective photoexcitation of the triplets (over the singlets) can only occur to CT-dominated states.
- c. Of all lowest-lying LE and CT excitations, only LE states of “+” particle-hole symmetry are bright at $\theta = 90^\circ$ [Eq. (2.7)]. However, CT states of “+” particle-hole symmetry can borrow intensity from these LE states at θ values away from 90° due to intermonomer π -bonding [Eqs. (2.10), (2.11) and (2.12)].
- d. ISC is fastest at $\theta = 90^\circ$, between CT and LE states, between states of like particle-hole symmetry, and when the triplet $M_S = \pm 1$ levels are involved – this aligns with El-Sayed rules [61]. In addition, ISC processes involving the $|^1\text{CT}^{00,-}\rangle$ and $|^1\text{CT}^{00,+}\rangle$ states are slow because the SOMO has a node at the bond connecting the two monomers [Eqs. (2.15), (2.16) and (2.17)].

These observations are consistent with those made in the introduction. From here, we report two possible pathways for ODMR according to the excitation energies [Fig. 2.2c]:

1. In the first case where $J_{10} > 2K_{10}$ [Fig. 2.2d], we propose to directly photoexcite the $|^3\text{CT}^{10,+}\rangle$ states at θ values away from 90° (via thermal effects) where π -bonding with the $|^3\text{LE}^{10,+}\rangle$ states is appreciable. Relaxation to the equilibrium torsion of

$\theta \approx 90^\circ$ is expected. At this point, ISC effects are strongest and couple the $M_S = \pm 1$ sublevels of the $|^3\text{CT}^{10,+}\rangle$ state to the $|^1\text{LE}^{10,+}\rangle$ state, selectively depopulating the triplet $M_S = \pm 1$ levels. Following Kasha's rule, the resulting $|^1\text{LE}^{10,+}\rangle$ population should emit from the $|^1\text{CT}^{00,-}\rangle$ and $|^1\text{CT}^{00,+}\rangle$ states, relaxing to the ground singlet state. As for the remaining $|^3\text{CT}^{10,+}\rangle$ molecules in the $M_S = 0$ level, emission to the ground triplet state should occur through the $|^3\text{LE}^{10,-}\rangle$ states ($M_S = 0$) at a different wavelength from the singlets, offering optical readout of the triplet $M_S = 0$ levels. We note that both non-radiative internal conversions (ICs) and emissions are spin-preserving. Therefore, overall, population from the triplet $M_S = \pm 1$ ground levels have been transferred away to the singlet ground state, creating ground-state spin polarisation. Since ISC rates decay exponentially with the energy gap [62], this mechanism works best when the $|^3\text{CT}^{10,+}\rangle$ and $|^1\text{LE}^{10,+}\rangle$ states lie close in energy, achieved when $J_{10} \approx 2K_{10}$.

2. In the second case where $J_{10} < 2K_{10}$ [Fig. 2.2e], the photoexcited $|^3\text{CT}^{10,+}\rangle$ molecules can, through a single-phonon process, rotate to $\theta \approx 90^\circ$, at which point the $|^3\text{CT}^{10,-}\rangle$ states are near-degenerate and directly accessible via spin-preserving ICs [62]. This is also the geometry with the best ISC, taking $|^3\text{CT}^{10,-}\rangle$ to $|^1\text{LE}^{10,-}\rangle$ through the triplet $M_S = \pm 1$ sublevels, which then relaxes to the ground singlet state. Meanwhile, the remaining triplet $M_S = 0$ population in the $|^3\text{CT}^{10}\rangle$ states have no ISC channel and will return to the ground triplet state, with optical readout being possible because emissions from both spin multiplicities are distinguishable by wavelength (just like in case 1). This mechanism works best with smaller J_{10} values because not only is the rotation barrier on the $|^3\text{CT}^{10,+}\rangle$ surfaces smaller, but also ISC can occur over a smaller energy gap.

A few points are now in order: Firstly, photoexcitation away from the equilibrium torsion of $\theta \approx 90^\circ$ is possible at room temperature, verified by ab initio calculations (more to follow) and with the trade-off of faster spin decoherence. Next, while the $|^1\text{GS}\rangle \rightarrow |^3\text{GS}\rangle$

ISC through the triplet $M_S = \pm 1$ sublevels will lead to spin relaxation, such couplings are not mediated by the single-electron Breit-Pauli SOC due to the operator's CT nature [Eq. (2.15)]. Thirdly, while LE^- and CT states of AHR dimers are, at $\theta \approx 90^\circ$ torsion, less emissive than their LE^+ counterparts [Eq. (2.7)], PL can still be detected; for instance, TTM radicals have quantum yields of around 0.02 with emission from LE^- states [77, 1, 2]. On a related note, we did not explicitly model IC in the PPP framework but only expected them to occur without preserving particle-hole symmetry, as with most AHRs [1, 95]. Finally, because spins are polarised by shelving triplet $M_S = \pm 1$ population into the singlet state, at most 25% of the ensemble will be a triplet $M_S = 0$, unlike the NV centre where this value is 100%.

Note that even though we have described only the $1 \rightarrow 0$ and $0 \rightarrow 1'$ excitations for simplicity, the same selection rules apply to any general $j \rightarrow 0$ and $0 \rightarrow j'$ transitions ($j > 0$), which may be low-lying in some AHR m -dimers.

2.2.3 Validation by ab initio calculations

To set the results in the context of existing systems, we consider two specific AHRs: A methylated benzylic radical [Fig. 2.3a] and TTM [Fig. 2.4a]. Ground-state properties of the AHR m -dimers were calculated using unrestricted DFT at the B3LYP/6-31G(d,p) level. In both cases, significant torsion was found at the equilibrium geometry, with θ_{eq} values of 91.9° and 92.9° respectively. Through calculations converging to the open-shell broken-symmetry (BS) state, we also found small singlet-triplet energy gaps (ΔE_{ST}) at both $\theta = 90^\circ$ (-0.003 eV and -0.053 eV respectively) and $\theta = 110^\circ$ (-0.006 eV and -0.031 eV), indicating weak exchange interactions between the two monoradicals¹. Indeed, the two SOMOs of the BS state were degenerate, each localised on separate monomers [Fig. 2.3,2.4b]. Closed-shell singlet (CS) states were also found, with energies that were at least 1.0 eV higher than the open-shell triplet states (respective

¹These values were calculated using the Q-Chem package (version 6.0.2) [63]. For the same computation on the Gaussian16 software [75], the respective values were -0.005 eV and $+0.001$ eV at $\theta = 90^\circ$, and -0.009 eV and $+0.001$ eV at $\theta = 110^\circ$.

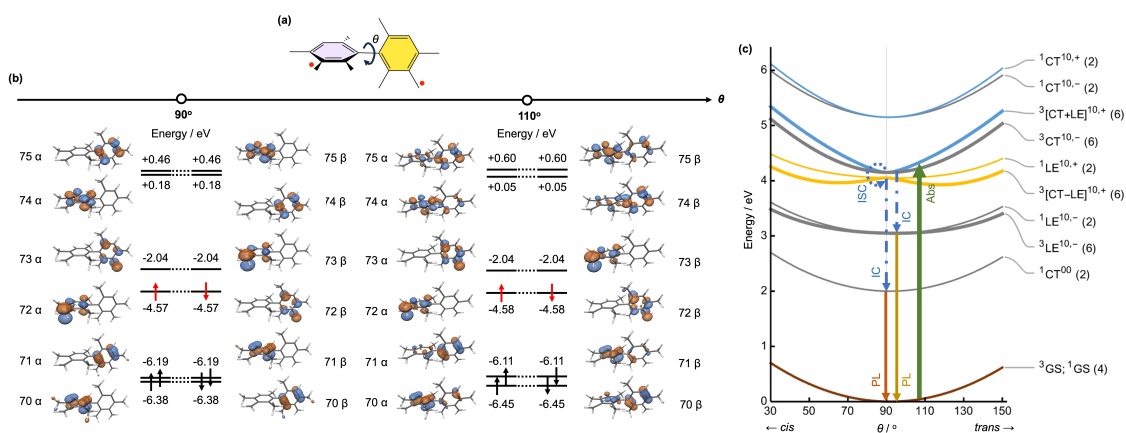


Figure 2.3. (a) Structure of an AHR *m*-dimer constructed using two methylated benzylic radicals. (b) Frontier MOs (isovalue = 0.060) of the dimer in the open-shell BS ground state at two different conformations ($\theta = 90^\circ$ and 110°), calculated using DFT (UB3LYP/6-31G(d,p)). (c) Plots of PESs using parameters from a TDDFT/TDA calculation (UB3LYP/6-31G(d,p)) of the monoradical. Parameters: $E_{\text{steric}} = 0.6$ eV; $\theta_{\text{eq}} = 91.9^\circ$; $\beta_{\mathcal{AB}}^0 = 2.5$ eV; $\gamma_{\mathcal{AB}}^0 = 0$ eV; SOMO-LUMO gap = 3.4 eV; $c_{\mathcal{A}1_A} = c_{\mathcal{B}1_B} = 0.5$; $J_{00} = 2.0$ eV; $J_{10} = 1.1$ eV; $K_{10} = 0.5$ eV.

values: 1.021 eV and 1.031 eV at $\theta = 90^\circ$; 0.974 eV and 1.019 eV at $\theta = 110^\circ$). This suggests that AHR *m*-dimers are likely to be open-shell diradicals in the ground state across different torsional angles θ . Finally, rotating the molecules away from $\theta = 90^\circ$ distributed the HOMOs and LUMOs (but not the SOMOs) of the BS state across the dimer, a sign of interrational interactions in the excited states [Fig. 2.3,2.4b]. These findings are consistent with the analytical results from the PPP Hamiltonian.

For the methylated benzylic radical *m*-dimer, multi-configurational self-consistent field (MCSCF) and configuration interaction (CI) methods were also used to verify the DFT calculations (MCSCF approach: complete active space self-consistent field (CASSCF) method with 10 electrons and 10 orbitals optimised for the ground state; see Methods). ΔE_{ST} was computed to be -0.004 eV at $\theta = 90^\circ$ and -0.009 eV at $\theta = 110^\circ$ with the first excited singlet energies being 2.227 eV and 2.207 eV respectively relative to the triplet ground state. These results agree with those from ground-state DFT (note that the CS energy is approximately half of the first singlet excitation energy; see Methods).

We also approximated the width of the Boltzmann distribution of θ by $\Delta\theta \equiv \sqrt{k_B T / E_{\text{steric}}}$ [Eq. (2.13)] with k_B and T representing the Boltzmann constant and tem-

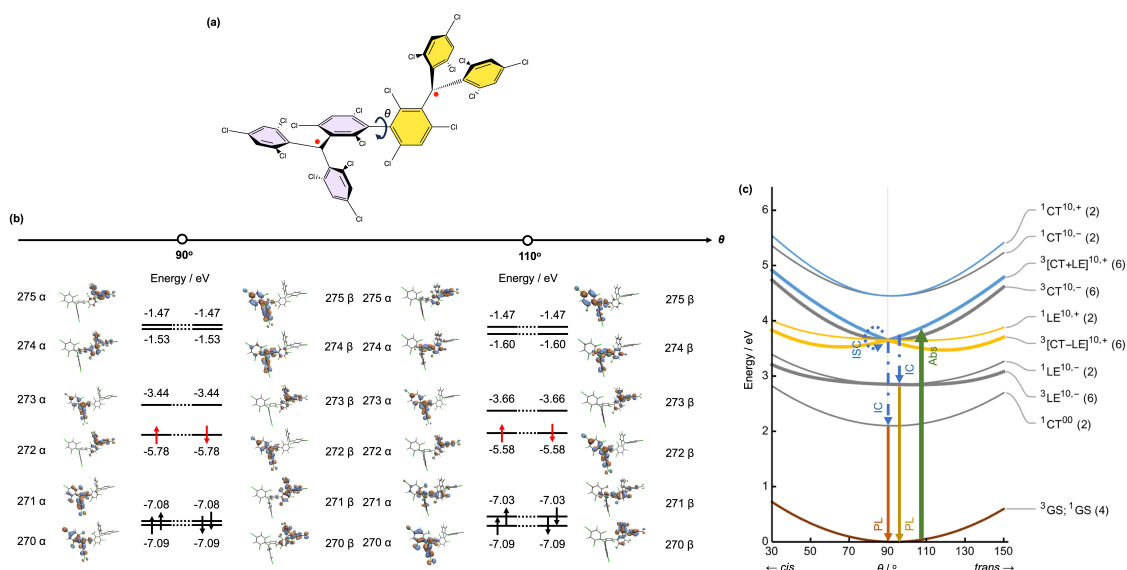


Figure 2.4. (a) Structure of an AHR *m*-dimer constructed using two TTM radicals. (b) Frontier MOs (isovalue = 0.030) of the dimer in the open-shell BS ground state at two different conformations ($\theta = 90^\circ$ and 110°), calculated using DFT (UB3LYP/6-31G(d,p)). (c) Plots of PESs using parameters from a TDDFT/TDA calculation (UB3LYP/6-31G(d,p)) of the monoradical. Parameters: $E_{\text{steric}} = 0.6$ eV; $\theta_{\text{eq}} = 92.9^\circ$; $\beta_{\mathcal{AB}}^0 = 2.5$ eV; $\gamma_{\mathcal{AB}}^0 = 0$ eV; SOMO-LUMO gap = 2.8 eV; $c_{\mathcal{A}1_A} = c_{\mathcal{B}1_B} = 0.5$; $J_{00} = 2.1$ eV; $J_{10} = 0.8$ eV; $K_{10} = 0.4$ eV.

perature respectively. For both AHR *m*-dimers, $\Delta\theta = 12^\circ$ at $T = 298$ K, indicating that excitation away from $\theta = 90^\circ$, required for ODMR [Fig. 2.2d,e], may be achieved by operating at room temperature (at the expense of enhancing deleterious decoherence processes). Importantly, this value can be tuned by modifying the degree of steric hindrance at the dimer linkage. As an example, to the methylated benzylic radical *m*-dimer, we removed the methyl substituents closest to the dimer linkage that are *ortho* to the methylene group. This widened the ground-state PES, yielding the same $\Delta\theta$ value at a lower temperature of $T = 108$ K (Supplementary Information S7).

Coulomb and exchange integrals among the MOs were then estimated from the excited-state properties of the monoradicals using unrestricted time-dependent DFT (TD-DFT) calculations, conducted within the Tamm–Dancoff approximation (TDA) and with the same functional and basis set as the dimers. We note that these excitation energies have poorer accuracies of ~ 0.3 eV than a rigorous multi-reference electron correlation approach [134] but are nevertheless sufficient for the present goal of setting our analytical

results in the correct parameter range. With the methylated benzylic radical, an additional $|\Psi_{02}^-; \pm 1/2\rangle$ state (following the notation of Eq. (2.3)) was found to lie between the $|\Psi_{01}^-; \pm 1/2\rangle$ and $|\Psi_{01}^+; \pm 1/2\rangle$ excitations. Because states of “–” particle-hole symmetry are dark, the $|\Psi_{02}^-; \pm 1/2\rangle$ excitation only contributes an additional intermediate state for non-radiative decay and does not affect the overall ODMR process. Other than that, the methylated benzylic radical is an example of case 1, with $J_{10} \approx 1.1$ eV and $K_{10} \approx 0.5$ eV. We note that given the small energy difference between J_{10} and $2K_{10}$, perturbation theory in $\hat{V}_{\text{NN}}$ between the $|^3\text{LE}_{\Gamma}^{10,+}; M_S\rangle$ and $|^3\text{CT}_{\Gamma}^{10,+}; M_S\rangle$ states breaks down and it is necessary to exactly diagonalise the matrix representation of $\hat{V}_{\text{NN}}$ within this subspace; these eigenstates are labelled $|^3[\text{CT} \pm \text{LE}]_{\Gamma}^{10,+}; M_S\rangle$ (see Supplementary Information S5). Despite that, the ODMR mechanism remains unchanged [Fig. 2.3c].

A smaller J_{10} value is desirable for case 1 because the energy gap for ISC will be reduced. This may be achieved by extending the degree of π -conjugation, which spreads the electron clouds of the valence MOs out, thereby reducing Coulombic repulsion between the occupying electrons. Indeed, the TTM radical, which has a (chlorinated) benzylic radical π -conjugated to two more (chlorinated) phenyl groups, was estimated to have a lower J_{10} value of ≈ 0.8 eV ($K_{10} \approx 0.4$ eV) when averaged over its five near-degenerate lowest energy LUMOs. This places the TTM m -dimer in the most ideal scenario for case 1 of ODMR in AHR m -dimers [Fig. 2.4c].

Because the MCSCF/CI approach fully describes the multi-configurational nature of the methylated benzylic radical m -dimer, we used that to verify the PPP model parameters, which we had obtained earlier from a single-reference TDDFT/TDA calculation of the monoradical. At this level of theory, we estimated SOMO-LUMO gap ≈ 3.4 eV, $J_{00} \approx 2.2$ eV, $J_{10} \approx 1.0$ eV, and $K_{10} \approx 0.6$ eV. PESs plotted using these parameters agree well with the MCSCF/CI calculations [Fig. 2.5a,b]. By placing J_{10} and $2K_{10}$ at slightly different values from TDDFT/TDA (with differences of ≈ 0.1 eV), MCSCF/CI changed the ODMR mechanism to that of case 2 [Fig. 2.5b]. Nevertheless, we believe both mechanisms to be possible given the uncertainty in TDDFT/TDA energies and the sensitivity of

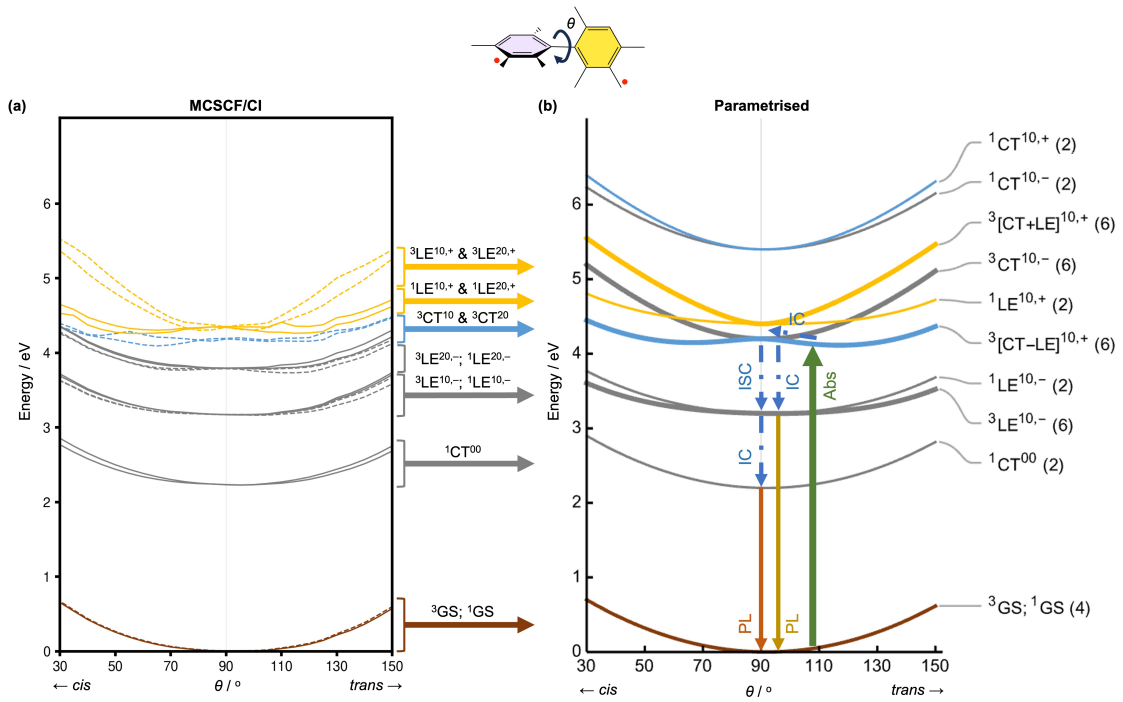


Figure 2.5. (a) PESs of the nine lowest-lying triplet $M_S = +1$ states (dashed lines) and the nine lowest-lying singlet states (solid lines) of the methylated benzylic radical *m*-dimer, obtained with MCSCF/CI/6–31G(d,p) calculations (theory level: CASSCF(10,10)/CASCI/QD-SC-NEVPT2; see Methods). States were assigned based on their characters at $\theta \approx 90^\circ$. (b) Plots of PESs using parameters from MCSCF/CI/6–31G(d,p) calculations of the *m*-dimer. Parameters: $E_{\text{steric}} = 0.6$ eV; $\theta_{\text{eq}} = 91.9^\circ$; $\beta_{\mathcal{AB}}^0 = 2.5$ eV; $\gamma_{\mathcal{AB}}^0 = 0$ eV; SOMO-LUMO gap = 3.4 eV; $c_{\mathcal{A}1_A} = c_{\mathcal{B}1_B} = 0.5$; $J_{00} = 2.2$ eV; $J_{10} = 1.0$ eV; $K_{10} = 0.6$ eV.

MCSCF/CI results to input parameters. Another advantage of the MCSCF/CI method is the possibility for ab initio SOC calculations. Indeed, only CT-type ISCs had appreciable SOC matrix elements with $\Delta M_S = \pm 1$ selectivity, in agreement with Eqs. (2.16) and (2.17) (Supplementary Information S7). All these lend credence to the semiempirical analysis described earlier.

2.2.4 Mapping the triplet ground state to a controllable qubit

Finally, we note that the triplet ground state of AHR *m*-dimers is likely to have minimal zero-field splittings (ZFSs) due to weak spin dipolar interactions between spatially separated radicals [14]. As such, a two-state qubit cannot be isolated by simply applying an external magnetic field, in contrast to the diamond-NV centre. Nevertheless, we propose

for an *effective* qubit with the $M_S = 0$ sublevel being one of the qubit states and the $M_S = \pm 1$ sublevels functioning collectively as an *effective* second qubit state. This is possible because for systems of two non-interacting electron spins experiencing an external magnetic field along its quantisation axis (C_2 axis for AHR m -dimers), circularly-polarised microwave light will produce unitary operations of the 3D rotation group $SO(3)$, that is, it rotates the $|M_S = 0\rangle$ or $|z\rangle$ state into linear combinations of $|x\rangle$ and $|y\rangle$ states, defined as

$$|x\rangle \equiv \frac{|M_S = +1\rangle - |M_S = -1\rangle}{\sqrt{2}}, \quad (2.18)$$

$$|y\rangle \equiv i \frac{|M_S = +1\rangle + |M_S = -1\rangle}{\sqrt{2}}. \quad (2.19)$$

For instance, if an AHR m -dimer were to be spin polarised into an initial quantum state of $|\psi\rangle = |z\rangle$, then a microwave pulse will drive it into

$$|\psi\rangle \rightarrow |\psi'\rangle = a|x\rangle + b|y\rangle + c|z\rangle, \quad (2.20)$$

keeping $a, b, c \in \mathbb{R}$ and preserving the norm of $a^2 + b^2 + c^2 = 1$. In spherical coordinates, this reads

$$|\psi'\rangle = \sin \theta \cos \phi |x\rangle + \sin \theta \sin \phi |y\rangle + \cos \theta |z\rangle, \quad (2.21)$$

with $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi)$. Since two real numbers are sufficient to describe a qubit state, an effective qubit arises here because the normalised state $|\psi'\rangle$ is also characterised by two real-valued coefficients θ and ϕ . In this way, the $M_S = \pm 1$ sublevels have become the second qubit state through either $|x\rangle$ or $|y\rangle$ (with the other state being redundant). This is essentially a statement of the isomorphism between $SO(3)$ and $SU(2)$, the latter of which describes a qubit. Here, our accessible pure state space is a unit 2-sphere with the three Cartesian axes corresponding to $|x\rangle$, $|y\rangle$ and $|z\rangle$ states, analogous to the Bloch sphere for a pure qubit state [Table 2.1].

To see how circularly-polarised microwave pulses result in unitary operations of

Table 2.1. Mapping between a standard qubit and our effective qubit.

	Standard qubit	Our effective qubit
Pure state	$ \psi\rangle = \cos(\theta/2) \uparrow\rangle + e^{i\phi}\sin(\theta/2) \downarrow\rangle$ with $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi)$	$ \psi\rangle = \sin\theta\cos\phi x\rangle + \sin\theta\sin\phi y\rangle + \cos\theta z\rangle$ with $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi)$
Single qubit operator	$\hat{R}_{\mathbf{n}}(\theta) = e^{-i\theta\mathbf{n}\cdot\hat{\boldsymbol{\sigma}}/2}$	$\hat{R}_{\mathbf{n}}(\theta) = e^{-i\theta\mathbf{n}\cdot\hat{\mathbf{S}}}$

A pure qubit state “lives” on a Bloch sphere spanned by eigenstates of the Pauli vector operator $\hat{\boldsymbol{\sigma}}$, denoted here by $\{|\uparrow\rangle, |\downarrow\rangle\}$. The general form of a single qubit operator is thus a rotation on the Bloch sphere, generated by $\mathbf{n} \cdot \hat{\boldsymbol{\sigma}}/2$ for some unit vector $\mathbf{n}$. Because our effective qubit state, if pure, can only access a unit sphere in 3D real space, the corresponding single qubit operator is a 3D rotation, generated by $\mathbf{n} \cdot \hat{\mathbf{S}}$. Here, $\hat{\mathbf{S}}$ is the spin-1 operator with eigenstates $\{|M_S\rangle | M_S = -1, 0, +1\}$, where $|z\rangle \equiv |M_S = 0\rangle$ and $\{|x\rangle, |y\rangle\}$ are linear combinations of $\{|M_S = \pm 1\rangle\}$ states [Eqs. (2.18) and (2.19)].

the SO(3) group, we consider a Hamiltonian $\mathcal{H}$ of two electron spins $\hat{\mathbf{S}}_j$ ($j \in \{A, B\}$) with negligible exchange and spin-dipolar couplings. Both spins are precessing under the influence of both a static magnetic field $B_0\mathbf{z}$ and an oscillating circularly-polarised microwave field $B_1[\cos(\omega t)\mathbf{x} + \sin(\omega t)\mathbf{y}]$ ($\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ are unit vectors of the Cartesian axes). This Hamiltonian reads

$$\mathcal{H}(t) = \sum_{j=A,B} g_j \mu_B [B_0 \hat{S}_{j,z} + B_1 \hat{S}_{j,x} \cos(\omega t) + B_1 \hat{S}_{j,y} \sin(\omega t)], \quad (2.22)$$

where g_j is the g -factor of electron j and μ_B is the Bohr magneton. By substituting $g_A = g_B \equiv g$ for dimers and $\hat{\mathbf{S}} \equiv \hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B$ as the total spin operator, we find $\mathcal{H}$ in the rotating frame of the oscillating field to be

$$\mathcal{H}_{\text{r.f.}} = (g\mu_B B_0 - \hbar\omega) \hat{S}_z + g\mu_B B_1 \hat{S}_x. \quad (2.23)$$

Thus, the time evolution operator at resonance is $\hat{U}(t) = \exp(-i\omega_1 \hat{S}_x t)$, the rotation operator about the x -axis by angle $\omega_1 t$ ($\omega_1 \equiv g\mu_B B_1/\hbar$). Similarly, a y -axis rotation may be obtained by shining light of the opposite polarisation. Thus, through a series of microwave

pulses we can achieve any arbitrary single qubit operation in our effective qubit (for instance, through the X – Y decomposition [168]), satisfying the generality criteria.

We note that general rotations of a three-level system (qutrit) belong to the $SU(3)$ group, which contains the $SO(3)$ group, so the operations proposed above are only a subset of all possible rotations in a qutrit, an observation consistent with our mapping of a qutrit to a qubit.

2.3 Conclusion

In conclusion, we demonstrate AHR m -dimers to be promising sources of fully-organic molecular colour centres. By analysing their electronic structure using the PPP framework, we propose different ODMR mechanisms for different energetic orderings of the excited states. The general principle is the same in all cases: Because the SOC operator, responsible for spin filtering through its $\Delta M_S = \pm 1$ rule, only mediates transitions across two rotated AHRs, charge transfer must be engineered between a triplet and a singlet in the excited states. Moreover, only CT-type excited states have energetically well-separated singlet and triplet levels because an unpaired electron from one monoradical has been excited into the other monomer and thus experiences stronger exchange interactions. Therefore, one may begin with a CT-type photoexcitation of *only* the triplet molecules, which will then see their $M_S = \pm 1$ population reverse the charge transfer via SOC to the singlet excited states, i.e. undergo spin-selective ISC. The excited-state spin polarisation may then be transferred to the ground state via any series of spin-selective relaxation, such as IC or emission. Since the emission probabilities and wavelengths of the triplet M_S levels will be different due to different decay channels (± 1 through the singlets and 0 through the triplets), one can achieve optical readout of the ground-state spin polarisation by observing changes to the emission spectrum. The specific method for optical readout will differ based on the molecular parameters.

To the best of our knowledge, this is the first theoretical analysis on carbon-based ground-state optically-addressable molecular qubits and we hope that our findings can

guide future efforts in this field. To this end, we have outlined the possibility of driving the ZFS-free triplet sublevels using microwave pulses, an example of a single qubit operation. Ongoing efforts include further structural optimisation of AHR m -dimers and generalisation of the qubit pulse protocol using a density matrix formalism.

2.4 Methods

Unless otherwise stated, all DFT-based calculations were performed using the Q-Chem package (version 6.0.2) [63]. In the next two paragraphs, we describe our DFT methods, conducted at the UB3LYP/6-31G(d,p) level and in vacuo. Ground-state geometries of the AHR m -dimers were optimised as triplets and PES scans were performed as triplets over $20^\circ \leq \theta \leq 160^\circ$ (interval = 5°), of which the resulting energies were fitted into V_{steric} [Eq. (2.13)]. Using geometries obtained for $\theta = 90^\circ$ and 110° (*trans*), energies of the open-shell singlet were found by the spin-unrestricted BS approach and used to compute ΔE_{ST} following Yamaguchi et al. [240]:

$$\Delta E_{\text{ST}} \equiv E_{\text{S}} - E_{\text{T}} = \frac{\langle \mathbf{S}^2 \rangle_{\text{T}}}{\langle \mathbf{S}^2 \rangle_{\text{T}} - \langle \mathbf{S}^2 \rangle_{\text{BS}}} (E_{\text{BS}} - E_{\text{T}}). \quad (2.24)$$

Energies of the CS states were also computed at the same conformations. Due to C_2 symmetry, the CS states were described by $|\cdots 1_+ \overline{1}_+ 1_- \overline{1}_- 0_+ \overline{0}_+\rangle$ with $j_{\pm} \approx 2^{-1/2} (j_A \pm j_B)$ ($j = \cdots, 1, 0, 1', \cdots$). Hence, for AHR m -dimers described by the PPP Hamiltonian $\hat{H}$ [Eqs. (2.4) and (2.5)], the CS states will have energies of

$$E_{\text{CS}} \approx E_{\text{T}} + \frac{J_{00}}{2} \quad (2.25)$$

(Supplementary Information S6). From that, we estimated the values of J_{00} .

Geometries of AHR monomers were optimised as doublets, following which unrestricted TDDFT/TDA was applied without further structural changes. For the methylated benzylic radical, the SOMO-LUMO gap (ϵ_{01}) was estimated as half of the HOMO-LUMO gap. Within the mean-field approach set by Longuet-Higgins and Pople [142, 52, 141], we

find J_{10} and K_{10} to have the following expressions:

$$K_{10} = \frac{E_{01}^+ - E_{01}^-}{2}, \quad (2.26)$$

$$J_{10} = -E_{01}^- + \epsilon_{01} + \frac{J_{00}}{2} - \frac{1}{2}K_{10}, \quad (2.27)$$

where $E_{01}^\pm$ are the excitation energies of $|\Psi_{01}^\pm; +1/2\rangle$, estimated using TDDFT/TDA. A similar approach was taken for the TTM radical. However, because the highest-energy HOMOs and lowest-energy LUMOs were (almost) five-fold degenerate each, for simplicity the $\{(j \rightarrow 0) | 1 \leq j \leq 5\}$ and $\{(0 \rightarrow j') | 1 \leq j \leq 5\}$ sets of lowest-lying excitations were each modelled as effective single $1 \rightarrow 0$ and $0 \rightarrow 1'$ excitations with parameters averaged over the five MOs. This is sufficient to place the PPP model parameters in the correct energy range.

For the methylated benzylic radical *m*-dimer, MCSCF calculations were performed on the UB3LYP-optimised triplet ground-state geometry using the CASSCF method. We conducted state-specific CASSCF(10,10) calculations to obtain the ground triplet and singlet states, following which the excited states were estimated using the complete active space configuration interaction (CASSCF) method. All states and energies were corrected by the van Vleck quasi-degenerate (QD) extension to the strongly contracted second-order N-electron valence state perturbation theory (SC-NEVPT2). We were able to classify all lowest-lying excited states into an excitation from Fig. 2.2c by observing the CI vector characters and oscillator strengths. This allowed us to estimate the parameters ϵ_{01} , J_{00} , J_{10} , and K_{10} by comparing the computed energies with the expressions in Fig. 2.2c. In particular, the first singlet excitation had CT⁰⁰ character, placing its energy at approximately J_{00} or twice that of the DFT CS state [Eq. (2.25)]. Meanwhile, SOC matrix elements were computed between singlet and triplet wavefunctions of a CASSCF/QD-SC-NEVPT2 calculation using state-specific orbitals optimised by CASSCF(10,10) for the triplet ground state. Only for this calculation were the orbitals shared between singlets and triplets. Also, the $\hat{S}_z$ eigenbasis was used to express the electron spin states with the *z*-axis aligned to

the molecular C_2 axis – these are the most-likely spin eigenstates of the molecule (see discussion following Eq. (2.17)). Finally, ground and excited PESs were estimated via the same state-specific CASSCF(10,10)/CASCI/QD-SC-NEVPT2 strategy with separate orbitals for singlets and triplets and using the UB3LYP-scanned triplet conformations mentioned earlier. These multi-configurational calculations were performed with the ORCA 5.0 code [166] and the basis set remains unchanged at 6–31G(d,p).

Acknowledgments

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Chapter 3

Enhancing the ODMR Signal of Organic Molecular Qubits

3.1 Introduction

Polarised electron spins are promising quantum bit (qubit) candidates [19] with applications in quantum sensing [6] and quantum information science [178]. Purifying these spin magnetic dipoles into a particular polarisation requires irreversible decays and these have been achieved in solid-state spin defects [216, 51, 194, 85, 41, 158, 135, 58, 218, 136] by coupling the microwave-addressable electron spins with their orbital degrees of freedom [Fig. 5.2a]. Because the latter lies high in the optical regime, this technique has become known as optically-detected magnetic resonance (ODMR) – “detected” because the same optical-spin interface also enables readout of the spin polarisation. Platforms hosting optically addressable spins are then referred to as colour centres.

While early endeavours in this direction have focused on solid-state defects such as nitrogen-vacancy (NV) centres in diamond [57], their poor scalability and tunability have motivated the community to shift towards molecular platforms [76, 18, 230, 246, 132, 199, 237, 242, 104, 254]. Transition metal complexes with high-spin ground states (GSs) offer the most natural starting point and this has been successful in Cr(IV), V(III), Ni(II), and, most recently, Ir(IV) complexes [234, 27, 65, 151, 119, 133, 11, 28, 82, 117, 118, 159, 212]. However, in none of these systems were the spin lifetimes as long as NV centres, essential for applications like qubit operations, and this has been attributed to the larger spin-

orbit couplings (SOCs) introduced by metals. Other challenges include higher costs and poorer sustainability. This has prompted a search for a molecular NV-centre mimic that is metal-free, just like diamond itself, notwithstanding the benefits of metal-based qubit systems such as higher biocompatibility [106, 152] and simpler protocols for multiqubit addressability [8, 156, 18, 157].

As a first step along this path, organic molecules were designed to demonstrate ODMR in high-spin excited states while acknowledging the limited lifetimes of these electronic excitations [206, 56, 84, 173, 149, 205, 184, 241, 137]. Subsequently, our group theoretically proposed a class of organic π -diradicals with optically-addressable high-spin ground states [179] that were also experimentally validated by Chowdhury et al. [46] and Kopp et al. [126]. In all of these systems, spin polarisation was likely attained by shelving the triplet $M_S = \pm 1$ population in the singlet manifold via spin-selective intersystem crossings (ISCs) while utilising the presence of additional singlet charge-recombined states absent from the triplet manifold [Fig. 5.2b]. (Interestingly, such imbalances have recently been proposed as evidence of low-energy electronic spin isomers [201].) Missing from the ODMR cycles are the ISCs between singlets and triplets selective for the $M_S = 0$ triplet sublevel, which the NV centre exhibits. As mentioned in our previous work [179], this limits the maximum possible triplet $M_S = 0$ population to 25% at steady state, constraining the ODMR resolution. Moreover, this increases the risk of metastable singlet molecules returning as $M_S = \pm 1$ triplets, which would negate the accumulated spin polarisation. Indeed, in the aforementioned experimental works, poor ODMR contrasts of $< 1\%$ were observed at temperatures above 5 K. We note in passing that, apart from π -diradicals, alkaline earth metal complexes [120, 233] and nitrenes [79] also display diradical properties and their functions as molecular colour centres have not been fully explored.

Our earlier theoretical model [179] had focused primarily on nearest-neighbour-only (through-bond-only) SOCs, which predicted ISCs to have $\Delta M_S = 0 (\pm 1)$ selectivity for electron spins quantised parallelly (perpendicularly) to the dimer linkage. However, beyond-nearest-neighbour SOC effects have been shown to be experimentally relevant

in ODMR, as in the recent work by Kopp et al. [126] [Fig. 5.2b], and such effects can induce ISC with an opposite spin selectivity. Motivated by this observation, in this work, we design another class of organic π -diradicals, this time capable of ISCs involving both triplet $M_S = \pm 1$ and $M_S = 0$ sublevels of *different* electronic states as facilitated by beyond-nearest-neighbour and nearest-neighbour SOC respectively [Fig. 5.2c]. This way, we create a true analogue of the NV centre, which we predict to demonstrate enhanced ODMR signals by optically pumping the near-degenerate triplet and singlet local excitations. Our design principle stems from a careful group-theoretical analysis of the transitioning orbitals, which coincidentally also solves the problem of singlet-triplet mixing during electron paramagnetic resonance (EPR) measurements of weakly-coupled diradicals (as most π -diradicals are [203, 126]). As a realistic prototypical example of our design, the electronic structure of $\text{PT}_2\text{TM}-p\text{-PT}_2\text{TM}$ [Fig. 5.2c] was shown at both density functional theory (DFT) and multi-configurational (MC) levels of theory to demonstrate an ODMR mechanism similar to the NV centre. The potential for signal enhancement through this ODMR pathway is supported by microkinetic analyses, where we found high ODMR contrasts of around 30% to be experimentally possible (as compared to $< 1\%$ in earlier theoretical [179] and experimental [46, 126] studies). In this regime, the steady-state triplet population exceeds 25%, which is the upper bound of prior works [179, 46, 126]. While not explored by the present work, we expect further mesitylation [Fig. 5.2c] to improve the luminescence quantum yield via geometrical relaxation [162, 81], as exemplified by Chowdhury et al. [46] to produce near-unity photoluminescence yields. This paves the way towards better designs of optically-addressable organic spins. Note that the alternancy symmetry of $\text{PT}_2\text{TM}-p\text{-PT}_2\text{TM}$ is not important to our design, which should be separated from our earlier work [179].

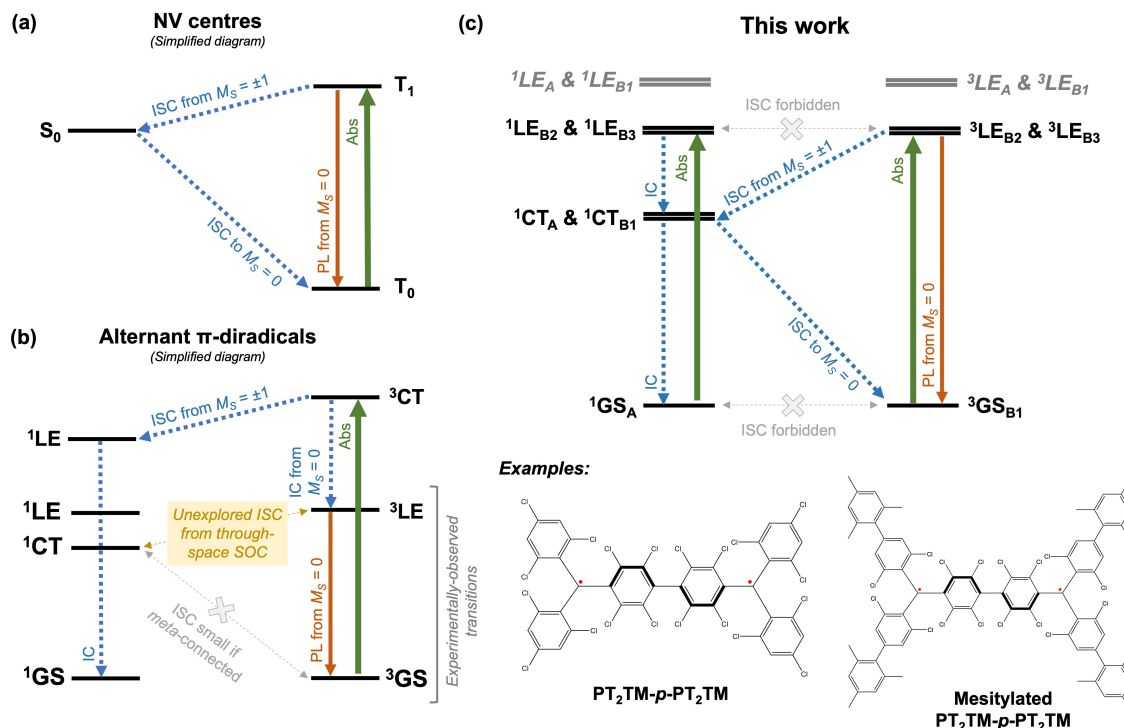


Figure 3.1. (a) Simplified ODMR mechanism typical of diamond-NV defects. (b) Simplified ODMR mechanism of alternant π -diradicals as explored by our previous work [179]. Note that the CT-to-GS ISC rates are small if the two benzylic radicals are tethered at their *meta* positions, which is avoided by our new design (see main text). (c) ODMR mechanism of our new design, which more closely resembles the spin polarisation pathway of NV centres. Also drawn are the PT_2TM - p - PT_2TM diradical and its mesitylated counterpart, both of which satisfy our design requirements. (Abbreviations of electronic transitions: Abs = absorption; PL = photoluminescence; IC = internal conversion; ISC = intersystem crossing. Labels for electronic states: GS = ground state; LE = local excitation; CT = charge transfer. These labels are inherited from our previous analysis of the π -diradical electronic structure [179] with subscripts A, B₁, B₂, and B₃ signifying the state irreps.)

3.2 Results and Discussions

3.2.1 Investigating the role of beyond-nearest-neighbour SOC

As we have previously shown [179], when two benzylic radicals are covalently connected with a significant torsion (as is the way most π -diradicals are experimentally constructed [94, 121, 235, 72, 161, 103, 3, 197, 148, 140, 183, 2, 255, 40, 153, 229, 247, 203]), its SOC matrix elements are dominated by nearest-neighbour interactions between the two $2p$ atomic orbitals (AOs) of opposite π -rings (reason: El-Sayed rule ¹) that are closest to the dimer linkage (reason: SOC is a local effect). Henceforth, we refer solely to π AOs. Furthermore, if the spin quantisation axis lies parallel (perpendicular) to the line connecting the two $2p$ AO centres, then the ISC spin selectivity arising from the SOC matrix elements is strictly $\Delta M_S = 0 (\pm 1)$ due to symmetry [179]. Note that the last condition is satisfied for interactions at the dimer bond because the spin axes (without applying any magnetic fields) coincide with the dimer's high symmetry axes. However, ISCs in π -diradicals occur not between pairs of $2p$ AOs but between pairs of *delocalised* molecular orbitals (MOs) that are each a linear combination of a few $2p$ AOs. When one of the transitioning MOs contains a node at the dimer linkage, the relevant SOC matrix elements necessarily involve next-nearest-neighbour couplings not considered by the above analysis. Such effects are generally small following the local nature of SOC, yet they can be appreciable if most of the transitioning MO's amplitude is piled up at these next-nearest-neighbour sites (as opposed to nearest-neighbour couplings weighted by small MO amplitudes). Importantly, next-nearest-neighbour interactions involve two $2p$ AO centres that are not colinear with the spin quantisation axis, causing the ISC selectivity to break down [Fig. 3.2a]. Indeed, for two benzylic radicals covalently tethered at the *para* positions with 90° torsion (hereafter called benzyl-*p*-benzyl), the next-nearest-neighbour SOC evaluated over singly-occupied $2p$ AOs biases the $\Delta M_S = \pm 1$ transitions with 68.1% selectivity (noting that the spin quantisation (z -)axis lies parallel to the dimer linkage due

¹The El-Sayed rule states that the SOC matrix elements are the largest when the transitioning orbitals adopt different orientations [61].

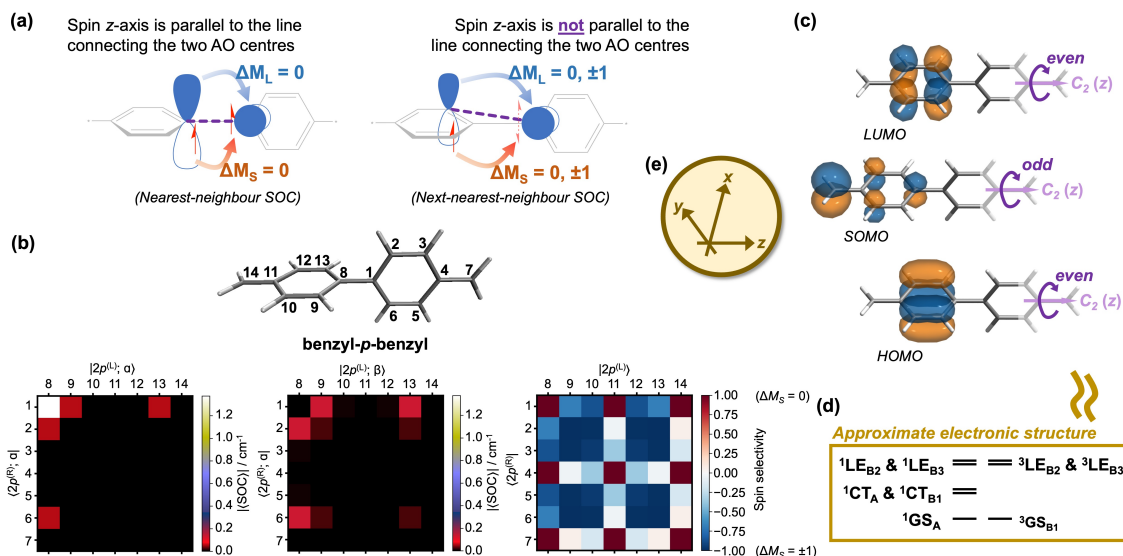


Figure 3.2. (a) Breakdown of the spin selection rule for ISCs involving next-nearest-neighbour SOCs. (b) Amplitudes of the SOC matrix elements evaluated between two carbon $2p$ AOs centred on opposite π -systems of the benzyl- p -benzyl diradical. Each $2p$ AO is assumed to be occupied by one full electron with either the same or opposite spin as its counterpart on the other benzylic fragment. Taking the difference between the matrix elements-squared of the two spin alignments and weighing the result by their sums give the spin selectivity. (c) Sketches of the frontier Hückel MOs for the benzylic monoradical. Also illustrated are their parities under $C_2(z)$ rotation. (d) Approximate electronic structure of benzyl- p -benzyl obtained from the Hückel theory analysis in (c). The excitation labels are inherited from Ref. [179] and the subscripts indicate the state irreps. In this work, all molecular geometries are presented in the coordinate frame depicted in (e).

to the molecular D_{2d} point group symmetry) and this SOC has a significant amplitude of 0.13 cm^{-1} [Fig. 3.2b]. For comparison, the nearest-neighbour analogue has a *perfect* spin selectivity of $\Delta M_S = 0$ with a larger amplitude of 1.37 cm^{-1} . Note that these SOC matrix elements represent upper bounds to the true molecular values because we have assumed one full electron in each AO.

3.2.2 Perfecting the spin selectivity using the molecular point group symmetry

That ISC in π -diradicals can actually occur with both spin selectivities is contrary to most theoretical analyses [99, 22, 248] (including ours [179]) and opens up the possibility of transferring the full electronic structure of NV centres into molecules. Our next step is to perfect the next-nearest-neighbour spin selectivity via symmetry considerations. We

note that by connecting two benzylic radicals at their *para* positions, the resulting diradical has at least a D_2 point group symmetry with irreducible representations (irreps) organised by their characters under $C_2(y)$ and $C_2(z)$ rotations. The irrep of any electronic state is in turn the direct product of its orbital and spin irreps. Focusing on the orbital part, if we continue to align the z -axis along the dimer linkage [Fig. 3.2b,e], then a $C_2(y)$ rotation becomes equivalent to swapping the two monomers. Therefore, for two weakly-interacting π -systems of significant torsion, the low-lying excitations are expected to appear in near-degenerate pairs of $\{A, B_1\}$ and $\{B_2, B_3\}$, each comprising a state of opposite parity under $C_2(y)$, i.e. equal probability of exciting either monomer. These two pairs can be distinguished by their transformations under $C_2(z)$ and, for that, it is easier to think in the basis of *monomeric* π MOs. We first note that $2p$ AOs have π symmetry, that is, their phases change under C_2 rotation about the AO centre. Further, for the two $2p$ AOs at the dimer linkage, that π -symmetry-defining C_2 rotation coincides with the diradical's $C_2(z)$ symmetry element. Hence, a monomeric MO with a non-zero amplitude at the dimer linkage *must* be antisymmetric under $C_2(z)$ rotation. By contrast, for a monomeric MO to be symmetric under $C_2(z)$ rotation, it *must* possess a node at the dimer linkage. For instance, the Hückel method predicts the highest occupied, singly occupied and lowest unoccupied MOs (abbreviated as HOMO, SOMO, and LUMO respectively) of the benzylic radical to have $+1$, -1 , and $+1$ characters under $C_2(z)$ rotation [Fig. 3.2c]. Finally, we recall that the symmetry of the orbital wavefunction is the direct product of the symmetries of all singly occupied orbitals. Therefore, the ground states of benzyl-*p*-benzyl, having two unpaired electrons in the SOMOs, transform as either A or B_1 . Similarly, the lowest charge transfer (CT) singlets with all doubly-occupied orbitals (also known as charge-recombined or zwitterionic states of the two radicals) also transform as either A or B_1 . As for the lowest local excitations (LEs), they are a linear combination of HOMO-to-SOMO and SOMO-to-LUMO excitations (an outcome of alternancy symmetry; see Ref. [179]) and hence transform as either B_2 or B_3 . Including the characters under $C_2(y)$ rotation yields the approximate energy level diagram illustrated in Fig. 3.2d (for a review of the electronic

structure of benzylic diradicals, see our earlier work [179]).

Returning to our goal of attaining perfect ISC spin selectivities, we note that the singlet, triplet $M_S = 0$, and triplet $M_S = \pm 1$ spin sublevels transform as A , B_1 , and $\{B_2, B_3\}$ respectively [50, 214]. For an ISC to be symmetry-allowed, the SOC matrix elements must contain the totally symmetric irrep. Hence, because the SOC Hamiltonian is totally symmetric, ISC processes in benzyl-*p*-benzyl are spin-selective for $\Delta M_S = \pm 1$ when moving between triplet LEs and singlet CTs, and $\Delta M_S = 0$ when moving between singlet CTs and triplet GSs. Actually, we already knew this from the previous section: The first ISC occurs between SOMOs and LUMOs (or HOMOs) of opposite monomers and only the latter has a node at the dimer linkage [Fig. 3.2c]. Thus, this process occurs predominantly via next-nearest-neighbour SOC, which we found before to exhibit $\Delta M_S = \pm 1$ selectivity [Fig. 3.2b]. Similarly, the second ISC connects between two SOMOs of opposite monomers and is mediated mostly by nearest-neighbour SOC with $\Delta M_S = 0$ selectivity [Fig. 3.2b]. Yet, the key improvement achieved by this section is the perfection of ISC spin selectivities to 100% by making the opposite spin channel symmetry-forbidden. From a microscopic perspective, we have destructively interfered any deleterious ISC channels using other higher-nearest-neighbour SOC, treated more generally by the group-theoretical approach. Importantly, this electronic structure produces the ODMR mechanism shown in Fig. 5.2c, where populations in the triplet $M_S = \pm 1$ LEs are moved into the triplet $M_S = 0$ GS via two sequential ISCs of opposite spin selectivities. In other words, such molecules exhibit the ODMR mechanism of NV centres.

As an aside, while it is tempting to consider only symmetry arguments and ignore the discussions made in the previous section, note that symmetry-allowed transitions need not occur with high amplitudes. Therefore, one still needs to check if the allowed ISCs are facilitated by either nearest- or next-nearest-neighbour SOC, which have the largest amplitudes. For example, the *meta*-connected diradicals explored in our previous work [179] have negligible SOC between singlet CTs and triplet GSs [Fig. 5.2b] because they are dominated by third-nearest-neighbour effects with a maximum SOC amplitude of

0.02 cm^{-1} [Fig. 3.2b]. In other words, our plan for enhanced ODMR contrasts requires *para*-connectivity between the two benzylic radicals, consistent with our group-theoretical analysis (*meta*-connectivity does not yield D_2 point group symmetry). We note in passing that vibronic perturbations to the SOC operator, which are not considered by this study, can modify the spin selectivity as well [136, 26]. This will be explored in our upcoming studies.

3.2.3 Our proposal

We now introduce a molecular design that realises the ODMR mechanism described in Fig 5.2c:

1. **The π -diradical should be a dimer centralised around a benzyl-*p*-benzyl-like framework.** This ensures that the diradical’s electronic structure resembles Fig. 3.2d.
2. **Sufficient steric hindrances should be installed around the dimer linkage to maintain a 90° torsion.** Otherwise, *para* connectivity facilitates π -bonding and encourages a singlet ground state [4, 38, 208, 161, 243]. For instance, chloro substituents can be introduced at the *meta* positions, which is common practice when synthesising luminescent benzyl-type radicals [161].
3. **Any additional π -conjugation to the benzylic radical should continue to localise the lowest-lying excitations around the benzylic group.** For instance, phenyl substituents added to the benzylic radical (typically used to improve radical stability and luminescence) should have less-extensive internal π -conjugation so that their lowest transitions are energetically separated from the benzylic fragment’s.
4. **These extra substituents should also maintain the monoradical’s $C_2(z)$ symmetry, where the z -axis lies along the *ipso-para* direction.** The reason is that the $C_2(z)$ axis is the *only* symmetry element discriminating between the monomeric π MOs [Fig. 3.2c], thus their parities under $C_2(z)$ dictate the spin selectivity of their

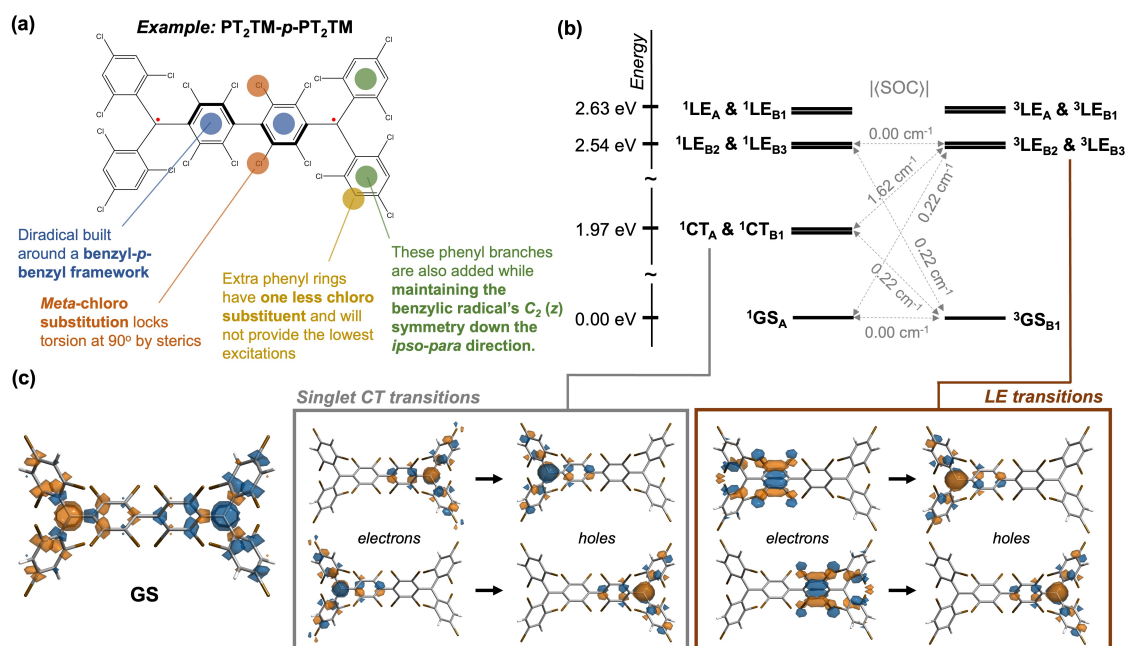


Figure 3.3. (a) Features of our diradical design, demonstrated on the PT₂TM-*p*-PT₂TM diradical. (b) Energy level diagram of PT₂TM-*p*-PT₂TM, computed using TDDFT. Also included are the root-mean-squared SOC matrix elements, averaged over all channels. These calculations were performed using MCSCF/CI methods on the central tetra-chlorinated benzyl-*p*-benzyl fragment. (c) Ground state spin density (isovalue = 0.004) and natural transition orbitals (isovalue = 0.040) for the first few excited states of PT₂TM-*p*-PT₂TM, obtained using BS-DFT/TDDFT.

intermonomer ISCs. (For the same reason, diradicals of D_2 point group symmetry are not the only molecules satisfying our design criteria. Non-dimeric diradicals can also be constructed with C_2 symmetry and the above near-degenerate pairs of $\{A, B_1\}$ and $\{B_2, B_3\}$ excitations will become split in energy, thereby offering a ladder of states through which the singlet molecules can decay. Here, we will focus solely on dimeric diradicals of D_2 symmetry for simplicity.) As an example, when substituting the two hydrogens on the benzylic centre, both hydrogens should be replaced simultaneously and with identical moieties.

These features are summarised in Fig. 3.3a using our prototype PT₂TM-*p*-PT₂TM diradical as an example. Note that its alternacy symmetry is not crucial to our design, which should be distinguished from our earlier work [179].

3.2.4 Ab initio calculations of the prototype PT₂TM-*p*-PT₂TM diradical

To support the above theory, calculations were performed on the PT₂TM-*p*-PT₂TM diradical as a representative example of experimentally-feasible diradicals. Starting with its ground state properties, the triplet equilibrium geometry was found using unrestricted DFT to display a significant torsion of 86.4° around the dimer linkage. At this geometry, the ground singlet state is only 1.08 meV lower in energy (equivalent to thermal energy at 12.5 K) than the ground triplet state, computed using broken-symmetry (BS) DFT. Thus, the *m*-chloro substituents sufficiently minimise π -bonding between the two radicals, that is, we have obtained a true diradical.

Excited state properties were then estimated using unrestricted time-dependent DFT (TDDFT) within the Tamm–Dancoff approximation (TDA). The electronic structure fits our requirements for the ODMR mechanism [Fig. 5.2c] with the exception of another low-lying LE pair of irreps *A* and *B*₁ at around 0.1 eV away from the lowest LEs [Fig. 3.3b]. As eluded in Fig. 5.2c, these excitations are spectroscopically distinguishable from the lowest LEs by wavelength and may be avoided by optically pumping with a single-frequency laser. Otherwise, there is a possibility of avoiding these excitations by aligning the excitation polarisation along the lowest LEs' transition dipole moments, i.e. along the *xy*-plane. *Even if these undesired LEs were photoexcited*, any deleterious $\Delta M_S = 0$ ISC to the lowest singlet CTs are expected to be slower than internal conversions (ICs) to the lowest LEs due to Kasha's rule [62] and will have a minimal impact on the proposed ODMR pathway. Further verification of this energy gap was achieved by applying multi-configurational self-consistent field (MCSCF) and configuration interaction (CI) methods on the monoradical. Here, the dimer linkage was capped with a hydrogen substituent. This approach places the energy separation between the two lowest LEs at 0.21 eV, consistent with the TDDFT/TDA predictions [Fig. 3.3b].

As speculated, the lowest LE transitions are largely localised on the central (tetra-chlorinated) benzyl-*p*-benzyl fragment [Fig. 3.3c]. Hence, for computational efficiency,

the SOC matrix elements were computed for this central fragment instead, capping any open ends with hydrogen. Indeed, the MCSCF/CI results suggest appreciable SOC matrix elements along the proposed ODMR pathway [Fig. 3.3b]. While, strictly speaking, these calculations present only an upper bound to the true SOC matrix elements of the full $\text{PT}_2\text{TM}-p\text{-PT}_2\text{TM}$ diradical, their values should not decrease by much upon weak π -conjugation to the additional trichlorophenyl substituents. Most importantly, these calculations lend credence to the theoretical proposal presented by this work.

3.2.5 Symmetry avoids Zeeman-induced singlet-triplet mixings during EPR spectroscopy

Interestingly, in connecting two identical monoradicals of (at least) C_2 point group symmetry to form a diradical of (at least) D_2 point group symmetry, the resulting structure can avoid undesirable singlet-triplet mixings found in many weakly-coupled diradicals under an applied magnetic field. This would alleviate most magnetic-field-induced decoherence events in the ground state [14, 45] (notice that the singlet and triplet GSs differ by either the coherence or a single spin flip [179]). It also facilitates Rabi nutation experiments in EPR spectroscopy [126], amongst other benefits.

To introduce the problem, we consider the spin Hamiltonian $\hat{H}_{\text{spin}}$ of two electron spins $\hat{\mathbf{S}}_j$ ($j = 1, 2$) under an applied magnetic field $\mathbf{B}$:

$$\begin{aligned} \hat{H}_{\text{spin}} = & \mu_B \mathbf{B} \cdot \mathbf{g}_1 \cdot \hat{\mathbf{S}}_1 + \mu_B \mathbf{B} \cdot \mathbf{g}_2 \cdot \hat{\mathbf{S}}_2 + 2J \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \\ & + \frac{\mu_0 g_e^2 \mu_B^2}{4\pi} \left[\frac{\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2}{|\mathbf{r}|^3} - \frac{3 (\hat{\mathbf{S}}_1 \cdot \mathbf{r}) (\hat{\mathbf{S}}_2 \cdot \mathbf{r})}{|\mathbf{r}|^5} \right]. \end{aligned} \quad (3.1)$$

The first two terms represent each spin's interaction with the magnetic field (i.e. the spin Zeeman terms), characterised by different g -tensors $\mathbf{g}_j$ ($j = 1, 2$). The third term symbolises the exchange interaction between the two spins with coupling $2J$ and is responsible for singlet-triplet splittings. The last term denotes the spin-spin dipolar interaction that gives rise to zero-field splittings in organic diradicals; here, the spatial degrees of freedom (characterised by $\mathbf{r}$) have been integrated over some orbital subspace (for instance, the

ground state). Finally, the symbols μ_B , μ_0 , and g_e represent, respectively, the Bohr magneton, the vacuum magnetic permeability, and the electron g -factor. Implicit to the above expression is the definition of a four-dimensional Hilbert space spanned by tensor products of the two electron spin states. By applying the angular momentum sum rules, one may also express the Hilbert space in the basis of one singlet and three triplet spin states [213, 14]. This amounts to re-expressing Eq. (3.1) in terms of the total spin operator $\hat{\mathbf{S}} \equiv \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$, which yields

$$\begin{aligned} \hat{H}_{\text{spin}} = & \mu_B \mathbf{B} \cdot \mathbf{g}_1 \cdot \hat{\mathbf{S}} + \mu_B \mathbf{B} \cdot (\mathbf{g}_2 - \mathbf{g}_1) \cdot \hat{\mathbf{S}}_2 \\ & + J (\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2) + \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}. \end{aligned} \quad (3.2)$$

The procedure for transforming the last term of Eq. (3.1) into the last term of Eq. (3.2) is presented in most EPR texts [14, 45] with $\mathbf{D}$ being referred to as the zero-field splitting tensor. We now see the problem: If $\mathbf{g}_1 \neq \mathbf{g}_2$, true in most organic systems, then the singlet-triplet basis block-diagonalises every term in Eq. (3.2) (with the triplets forming their own block) except for the second one. In other words, the second term induces mixings between the singlet state and the triplet manifold. This, as mentioned, leads to deleterious effects such as spin decoherence [14, 45] and additional Rabi frequencies [126]. One solution would be to engineer an exchange coupling J that is large enough for the Zeeman-induced singlet-triplet couplings of $\sim \mu_B B |g_2 - g_1|$ to be a perturbation relative to the singlet-triplet gap. However, as explained in our earlier work [179], further enhancement of the exchange coupling in π -diradicals is likely to result in a singlet GS, i.e. J is typically antiferromagnetic [4, 38, 208, 161].

The alternative approach would be to somehow make elements that differ between $\mathbf{g}_1$ and $\mathbf{g}_2$ disappear under experimental conditions. This can be achieved in our diradicals by aligning the magnetic field $\mathbf{B}$ parallelly to the dimer linkage. (We acknowledge that aligning the molecules, say, in a liquid crystal, may be an experimental challenge, although this has been previously demonstrated [12, 60].) To see that, we first note that elements

of the g -tensor have the following approximate expression, obtained from second-order perturbation theory in the SOC: [14, 45]

$$g_{ab} = g_e \delta_{ab} + 2\lambda \sum_{\Psi'} \frac{\langle \Psi | \hat{L}_a | \Psi' \rangle \langle \Psi' | \hat{L}_b | \Psi \rangle}{E_{\Psi} - E_{\Psi'}}. \quad (3.3)$$

Here, λ is an effective SOC constant and $\{|\Psi'\rangle\}$, $\{E_{\Psi'}\}$ respectively denote the orbital eigenfunctions and eigenenergies of the molecule's non-relativistic electronic Hamiltonian, with Ψ being the orbital eigenfunction under consideration (say, the ground state wave-function). The indices a and b run over all three-dimensional coordinates (such as x , y , and z) and $\hat{L}_a$ is the a -th component of the orbital angular momentum operator $\hat{\mathbf{L}}$. Because each monoradical of our proposed system is symmetric about $C_2(z)$ rotation (using the coordinate frame defined by Fig. 3.2e, i.e. z -axis along dimer linkage), the g -tensor must remain invariant under $C_2(z)$ rotation. Such a rotation takes $\{\hat{L}_x, \hat{L}_y, \hat{L}_z\} \rightarrow \{-\hat{L}_x, -\hat{L}_y, \hat{L}_z\}$, hence, using Eq. (3.3), we obtain

$$\mathbf{g} \equiv \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix} = \begin{pmatrix} g_{xx} & g_{xy} & -g_{xz} \\ g_{yx} & g_{yy} & -g_{yz} \\ -g_{zx} & -g_{zy} & g_{zz} \end{pmatrix}. \quad (3.4)$$

By contradiction, it must be that

$$\mathbf{g} = \begin{pmatrix} g_{xx} & g_{xy} & 0 \\ g_{yx} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix}. \quad (3.5)$$

Next, the two monoradicals in the dimer are related by a $C_2(y)$ rotation. Taking Eq. (3.5)

to be the g -tensor of radical 1, we find the g -tensors of both radicals to be

$$\mathbf{g}_1 = \begin{pmatrix} g_{xx} & g_{xy} & 0 \\ g_{yx} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix}, \quad (3.6)$$

$$\mathbf{g}_2 = \begin{pmatrix} g_{xx} & -g_{xy} & 0 \\ -g_{yx} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix}. \quad (3.7)$$

Therefore, because both $\mathbf{g}_1$ and $\mathbf{g}_2$ have the same g_{zz} components, the second term of Eq. (3.2) vanishes when the magnetic field $\mathbf{B}$ falls along the z -axis (the dimer linkage), i.e.

$$\begin{aligned} \hat{H}_{\text{spin}} &= \mu_B g_{zz} |\mathbf{B}| \hat{S}_z \\ &+ J (\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2) + \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}. \end{aligned} \quad (3.8)$$

The singlet-triplet states may now block-diagonalise $\hat{H}_{\text{spin}}$ with no singlet-triplet mixings present. Furthermore, due to the approximate D_{2d} point group symmetry of our system, the zero-field splitting caused by $\mathbf{D}$ also occurs along the z -axis. This may be further rationalised by the cylindrical spin density distribution of the diradical [45]. Therefore, the singlet-triplet basis fully-diagonalises $\hat{H}_{\text{spin}}$ in Eq. (3.8) when the magnetic field is applied along the dimer linkage.

3.2.6 Predicted ODMR contrasts

As a final theoretical piece to this puzzle, we construct a microkinetic model of the excited state kinetics and predict the ODMR contrast at steady state. For simplicity, we shall take the incoherent limit and consider only changes to the eigenstate populations. Also, populations of degenerate eigenstates are pooled into a single variable. Therefore, the relevant eigenstates are

- a. the singlet GS (labelled GS, degeneracy = 1),

- b. the triplet $M_S = 0$ GS (labelled GT0 for ground triplet, degeneracy = 1),
- c. the triplet $M_S = \pm 1$ GS (labelled GT1, degeneracy = 2),
- d. the singlet CTs (labelled CT, degeneracy = 2),
- e. the singlet LEs (labelled ES for excited singlet, degeneracy = 2),
- f. the triplet $M_S = 0$ LEs (labelled ET0 for excited triplet, degeneracy = 2), and
- g. the triplet $M_S = \pm 1$ LEs (labelled ET1, degeneracy = 4).

Here, we continue to assume a spin quantisation axis parallel to the dimer linkage. The kinetic processes connecting these eigenstates and their associated rate constants are presented in Fig. 3.4; there, the symbols adopt their usual meanings. As far as possible, model parameters were selected within experimental reason. Listed below are our justifications for these parameters and the reader may safely skip it at the first pass.

1. Also modelled are the vibrationally-excited LE states, labelled with an asterisk (*). These states represent the wavefunction following an initial Franck-Condon photoexcitation and will, within picoseconds, undergo vibrational relaxation to the ground vibrational level of the respective LE states, labelled without an asterisk ().
2. The experimentally-observed IC rates from LE to GS triplets are between 10^8 and 10^{10} s^{-1} [3, 40, 46, 126]. In our model, we shall pick the upper bound as a conservative estimate. Then, because experiments predict the IC rate from CT to GS singlets to be an order of magnitude slower [46, 126], we place its value at 10^9 s^{-1} . Finally, IC from LE to CT singlets must be faster in view of the smaller energy gap [62] and we estimate this rate to be 10^{11} s^{-1} .
3. The ISC rates are chosen to represent typical organic systems, i.e. around 10^7 s^{-1} between excited states (i.e. triplet LEs to singlet CTs) [123] and 10^5 s^{-1} for relaxation to the ground (i.e. singlet CTs to triplet GSs) [123, 149, 205]. Because the energy gaps between LEs and GSs are larger than between CTs and GSs, we expect their

ISC rates to be scaled down by an order of magnitude to around 10^4 s^{-1} (this is also expected by the El-Sayed rules; see Refs. [179, 126]). Lastly, because the singlet CTs and triplet LEs are relatively close in energy ($\gtrsim 0.05 \text{ eV}$) [179, 46, 126], reverse ISCs are probable with a delayed timescale. By detailed balance, this rate will be around $7 \times 10^5 \text{ s}^{-1}$ if we make a safe assumption of a 0.02 eV energy gap at 85 K – these parameters also produce similar ODMR contrasts as experiments [46, 126] when the CT-to-GS ISC channel is shut (more to follow).

4. The weakly-coupled pair of doublet spins in the GS can mix and decohere which, in the singlet-triplet basis, translates into population transfers among the singlet and triplet GSs. Therefore, we shall assume a uniform rate constant k_{decoh} for mixing between the four near-degenerate magnetic levels (one from the singlet and three from the triplet). This is consistent with Kopp et al. [126], where the singlet to triplet GS ISCs occur at around the same timescale as the triplet spin-lattice and spin-spin relaxations. The same decoherence pathway is also expected among the singlet and triplet LEs. Special attention is given to mixing among the triplet spin sublevels, denoted by a rate constant κ_{decoh} . In our simulations, we will always set $\kappa_{\text{decoh}} = k_{\text{decoh}}$ unless a microwave drive is applied (necessary for finding the ODMR contrast). This introduces additional triplet spin mixing that, assuming a saturating microwave field, is mathematically equivalent to the limit of $\kappa_{\text{decoh}} \rightarrow \infty$, i.e. full mixing between the triplet sublevels [27].

Solving the kinetic model for the steady-state populations yields the ODMR contrast and optically-induced spin polarisation via the following expressions [58, 218, 136]:

$$\begin{aligned} &\text{ODMR contrast} \\ &= \frac{\sum_{j=0,1} n_{\text{ET}j}^{\text{ss},\infty} - \sum_{j=0,1} n_{\text{ET}j}^{\text{ss}}}{\sum_{j=0,1} n_{\text{ET}j}^{\text{ss}}} \times 100\% \end{aligned} \quad (3.9)$$

and

$$\text{Spin polarisation} = \frac{n_{\text{GT0}}^{\text{ss}} - n_{\text{GT1}}^{\text{ss}}/2}{n_{\text{GT0}}^{\text{ss}} + n_{\text{GT1}}^{\text{ss}}/2} \times 100\%, \quad (3.10)$$

where the factor of $1/2$ arises from the double degeneracy of the triplet $M_S = \pm 1$ GSs. Here, n_{Ψ}^{ss} denotes the steady-state population of state Ψ at $\kappa_{\text{decoh}} = k_{\text{decoh}}$, while $n_{\Psi}^{\text{ss},\infty}$ denotes the same quantity at $\kappa_{\text{decoh}} \rightarrow \infty$, i.e. under a microwave resonance. (The rate equations are available in Supplementary Information 1.)

The results are plotted in Fig. 3.5 across experimental ranges of k_{abs} and k_{decoh} . The former represents the optical pump rate and has an experimental upper bound of 10^{12} s^{-1} for our system (see Supplementary Information 2 for estimates of k_{abs} , which is based on a laser used in teaching labs [251]). Meanwhile, the latter denotes the spin relaxation rate, the slowest of which is around 10^4 s^{-1} at temperatures of around 100 K with faster rates expected at higher temperatures [84, 197, 46, 126]. Strikingly, at $k_{\text{abs}} = 10^9 \text{ s}^{-1}$ and $k_{\text{decoh}} = 10^4 \text{ s}^{-1}$, a high ODMR contrast of -27.29% is observed with an optically-induced spin polarisation of 62.76% . The triplet $M_S = 0$ LE population, which is proportional to the photoluminescence intensity, is also appreciable at 7.34% . Importantly, the proportion of molecules in the triplet GSs is above 25% , suggesting that the observed polarisation pathway goes beyond the shelving mechanism described by previous studies [179, 46, 126]. Finally, the above ODMR contrast was obtained at a microwave drive rate of $\kappa_{\text{decoh}} \sim 10^6 \text{ s}^{-1}$, which is experimentally reasonable [58, 218, 136]. For comparison with our earlier theoretical study [179], the predicted ODMR contrast in the absence of CT-to-GS ISC is only -0.24% , in agreement with experimental setups that employ the shelving mechanism [46, 126] (this final result was obtained with $k_{\text{CT-GT}} = 0$).

3.3 Conclusion

By covalently tethering two benzylic radicals at their *para* positions, the resulting diradical of D_2 point group symmetry has a triplet GS of irrep B_1 , lowest singlet CTs of

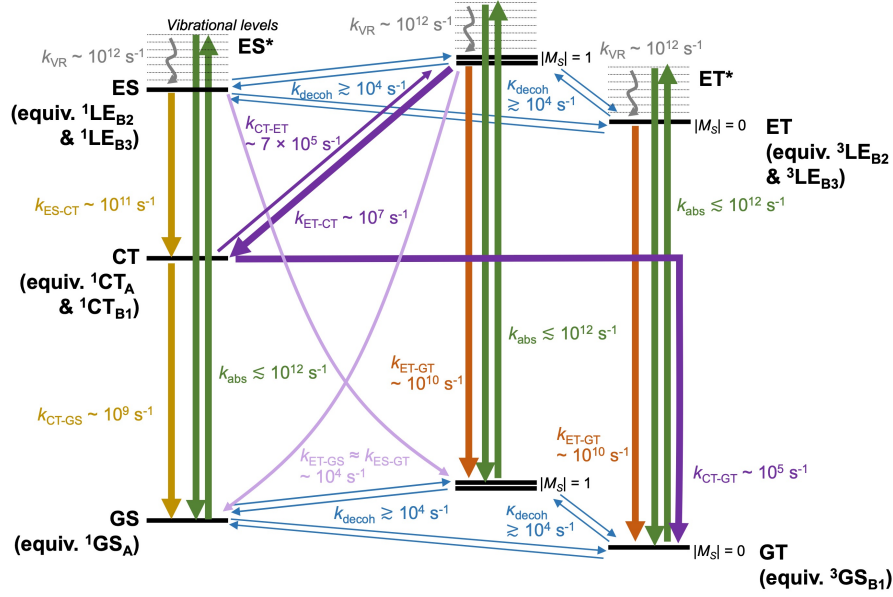


Figure 3.4. Schematic diagram depicting the excited-state transitions being considered by our microkinetic model.

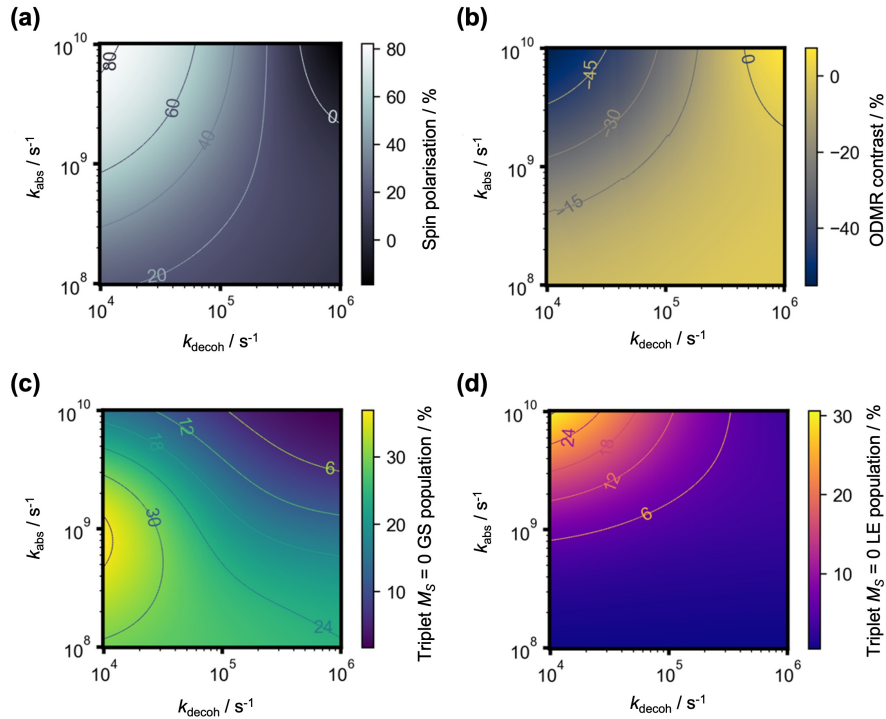


Figure 3.5. Steady-state solutions to the (a) optically-induced spin polarisation, (b) ODMR contrast, (c) triplet $M_S = 0$ GS population, and (d) triplet $M_S = 0$ LE population (which simulates the emission intensity). Plots are made across varying optical pump rates k_{abs} and spin decoherence rates k_{decoh} within experimental ranges. Other parameters are defined in Fig. 3.4, chosen to be as realistic as possible.

irreps A and B_1 , and lowest triplet LEs of irreps B_2 and B_3 . Thus, by group-theoretical considerations, spin polarisation can be achieved via a $\Delta M_S = \pm 1$ ISC from LEs to CTs, followed by a $\Delta M_S = 0$ ISC from CTs to GSs, just like in an NV centre. Moreover, the associated SOC matrix elements are appreciable due to next-nearest-neighbour effects for the former and nearest-neighbour effects for the latter. We expect this success to be generalisable to any diradical based upon two *para*-connected benzylic radicals. This is illustrated in the $\text{PT}_2\text{TM-}p\text{-PT}_2\text{TM}$ diradical: Firstly, the benzylic radicals are *meta*-chlorinated to lock the inter-radical torsion by steric repulsion, ensuring that the GS comprises both triplets and singlets at near-degeneracy. Next, the stabilising phenyl rings are specially chosen to not break the C_2 rotational symmetry down the benzylic *ipso-para* direction, which is the essential symmetry element of the aforementioned benzylic para-dimer. Finally, every benzylic radical has one more chloro substituent than each of its phenyl branches, thereby localising the lowest-lying excitations on the tetra-chlorinated benzylic fragment. Indeed, these expectations are reflected in the *ab initio* results by producing the desired electronic structure for ODMR.

To our best knowledge, our new design has checked most boxes for a robust optical-spin interface [230]. Perhaps a minor problem not addressed by this work is the poor emissive properties of our $\text{PT}_2\text{TM-}p\text{-PT}_2\text{TM}$ prototype due to its alternacy symmetry [1, 95, 179]. For that, we expect techniques of alternacy symmetry breaking [1, 95, 84] and excited-state symmetry breaking [162, 81] employed by the organic light-emitting diode (OLED) community to be useful. In fact, the latter was recently demonstrated by Chowdhury et al. [46], who synthesised trityl-based diradicals of near-unity luminescence quantum yields by mesitylating at the *para* positions. When applied to $\text{PT}_2\text{TM-}p\text{-PT}_2\text{TM}$, a possible diradical would look like Fig. 5.2c, which is a suitable synthetic starting point. Notably, the ODMR contrast for this novel spin polarisation pathway is expected to be around 30% with more than 25% of the population being in the triplet manifold at steady state, an unequivocal improvement from earlier theoretical [179] and experimental [46, 126] works. Regarding qubit operations, our design also overcomes problems of

Zeeman-induced spin decoherence and observations of multiple Rabi frequencies during EPR measurements of weakly-coupled diradicals. These are all crucial steps towards the realisation of optically-addressable molecular spin qubits.

3.4 Methods

The geometry of benzyl-*p*-benzyl was relaxed as a triplet on UB3LYP-D3BJ/def2-SVP [86, 87] while enforcing D_{2d} point group symmetry. Due to the lack of steric hindrances, the optimisation converged to a saddle point on the potential energy surface with a single imaginary frequency of amplitude 57.8 cm^{-1} . These calculations were done using the ORCA 5.0 code [166]. We then computed the SOC matrix elements between carbon $2p$ AOs of opposite π -systems using the single-electron form of the SOC operator [147], taking each AO to be singly-occupied and using a carbon effective nuclear charge of 3.9 [71]. These integrals were computed using PySCF 2.5.0 [211] and the carbon $2p$ AOs were represented by the STO-6G basis set.

Hereafter, all ab initio calculations were performed with the ORCA 5.0 code [166]. Geometries of $\text{PT}_2\text{TM-}p\text{-PT}_2\text{TM}$ and its central tetra-chlorinated fragment (labelled $\text{Cl}_4\text{M-}p\text{-Cl}_4\text{M}$) were optimised as triplets on UB3LYP-D3BJ/def2-SVP [86, 87] with harmonic vibrational frequency analyses done to ensure no imaginary frequencies. The resulting geometries had at least D_2 point group symmetries. For the full $\text{PT}_2\text{TM-}p\text{-PT}_2\text{TM}$ diradical, its electronic structure was estimated by spin-unrestricted TDDFT/TDA at the UB3LYP/def2-SVPD level using both triplet and BS singlet ground states as reference. In cases where the latter approach yielded BS solutions of $\langle \mathbf{S}^2 \rangle \approx 1$, we assumed negligible discrepancies to the singlet energies from spin contamination because the results were similar to the triplet excitations (within 0.1 eV), which are the most-probable spin contaminants [240]. Excited state irreps were then inferred from the polarisations of the respective transition dipoles. In performing a BS-DFT calculation, we had also obtained

the open-shell singlet GS energy via the following expression from Yamaguchi et al. [240]:

$$E_S - E_T = \frac{\langle \mathbf{S}^2 \rangle_T}{\langle \mathbf{S}^2 \rangle_T - \langle \mathbf{S}^2 \rangle_{BS}} (E_{BS} - E_T), \quad (3.11)$$

where E_T , E_{BS} , and E_S are the energies of the triplet, BS singlet, and open-shell singlet states while $\langle \mathbf{S}^2 \rangle_T$ and $\langle \mathbf{S}^2 \rangle_{BS}$ are the respective expectations of the total spin-squared. The smaller $\text{Cl}_4\text{M-}p\text{-Cl}_4\text{M}$ fragment was then used to compute the SOC matrix elements at the MCSCF/CI level, also using the def2-SVPD basis set. For that, we first performed a complete active space self-consistent field (CASSCF) calculation with 10 active electrons and 10 active orbitals, state-averaging the energy over the ground triplet and singlet states (i.e. SA2). Thereafter, the excited states were estimated using the complete active space configuration interaction (CASCI) method, among which the SOC matrix elements were computed. In this work, the electron spin states are expressed in the symmetry-aligned coordinate frame shown in Fig. 3.2e. Finally, with the monoradical of $\text{PT}_2\text{TM-}p\text{-PT}_2\text{TM}$ (labelled $\text{PT}_2\text{TM-H}$), its geometry was first optimised as a doublet on UB3LYP-D3BJ/def2-SVP [86, 87] and the presence of a local minimum of C_2 point group symmetry was confirmed by harmonic vibrational frequency analysis. Then, using the def2-SVPD basis set, orbitals were optimised by CASSCF(11,11) state-specific to the ground doublet, following which the excited doublet energies were obtained by CASCI. In this last calculation, the RIJCOSX approximation (RIJCOSX = resolution of identity approximation for the Coulomb term and chain-of-spheres approximation for the exchange term) was applied using the def2/JK auxiliary basis set. All CASCI energies were corrected by the strongly contracted second-order N-electron valence state perturbation theory (SC-NEVPT2).

Acknowledgments

Chapter 3, in full, is reprinted with permission from Yong Rui Poh, and Joel Yuen-Zhou, "Enhancing the Optically Detected Magnetic Resonance Signal of Organic Molecular Qubits" published in *ACS Cent. Sci.* 2025, 11, 1, 116–126. Copyright 2025 American Chemical Society. The dissertation author was the primary investigator, first

author, and corresponding author of this paper. He conceptualised the project, completed the semi-empirical and ab initio analyses, and wrote the manuscript.

Chapter 4

Electron Sextets as Optically Addressable Molecular Qubits: Triplet Carbenes

4.1 Introduction

Electron spins have long been proposed as quantum bit (qubit) candidates [19] for use in quantum sensing [6] and quantum information science [178]. These spin magnetic dipoles can be polarised through spin-selective intersystem crossings (ISCs) among the electronically excited states, accessible by optical pumping. Additionally, if some of these electronic states are emissive, then the luminescence intensity can be engineered to reflect the spin information, allowing for optical readout. This technique is known as optically-detected magnetic resonance (ODMR) and has been heavily utilised in solid-state spin defects [216, 51, 194, 85, 41, 158, 135, 58, 218, 136, 130] such as the nitrogen-vacancy (NV) centre in diamond [57]. An archetypal example of this spin polarisation pathway has been drawn in Fig. 4.1.

The lack of scalability and tunability in solid-state colour centres has motivated recent developments in molecular platforms that can host these optically addressable electron spins [76, 18, 230, 246, 132, 199, 237, 242, 104, 254, 217, 120, 233]. Transition metal complexes with high-spin ground states (GSs) take the lead [234, 27, 65, 151, 119, 133, 11, 28, 82, 117, 118, 159, 212] and their excellent biocompatibility [106, 152] and ease of multiqubit addressability [8, 156, 18, 157] also prepare them as next-generation

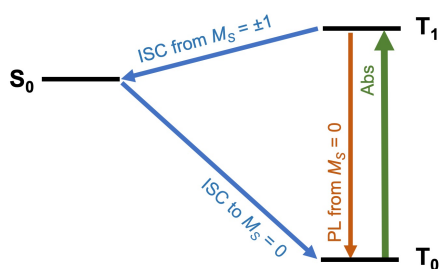


Figure 4.1. An ODMR mechanism paradigmatic of solid-state spin defects such as the diamond-NV centre. Following photoexcitation (Abs) of the ground triplet (T_0) state to the excited triplet (T_1) state, two sequential intersystem crossings (ISCs) via an intermediate singlet state (S_0) bring the $M_S = \pm 1$ excited triplet spins back into the ground triplet state as $M_S = 0$. This leads to spin polarisation in the ground $M_S = 0$ triplet state that accumulates over many successive photoexcitation-decay cycles. Due to the additional non-radiative ISC channel experienced by the excited $M_S = \pm 1$ triplet spins, the photoluminescence (PL) intensity of the T_1 state correlates with the $M_S = 0$ population, thereby encoding the triplet spin information. Together, both spin initialisation and readout are made optically available.

quantum materials. A critical shortcoming of metallic systems is their short *spin* lifetimes, crucial for qubit operations, and metal-free organic platforms with smaller spin-orbit couplings (SOCs) are poised to overcome this hurdle. For instance, ODMR has been shown in the high-spin excited states of organic molecules [206, 56, 84, 173, 149, 205, 184, 241, 137, 204, 88] and its recent incorporation into a protein interface sets the stage for quantum sensing in biological environments [70]. Yet, because such spin qubits are installed in an electronic excitation, they are in turn limited by their short *electronic* (excited-state) lifetimes. Another emerging materials class is that of organic diradicals, in which the two weakly-coupled spins naturally display open-shell GSs as a pair of near-degenerate low-spin singlet and high-spin triplet [179, 46, 126, 181]. In such systems, the two spins must be sufficiently decoupled to sustain a high-spin GS [94, 121, 235, 72, 161, 103, 3, 197, 148, 140, 183, 2, 255, 40, 153, 229, 247, 203, 201, 4, 38, 208, 243, 150], which constrained early endeavours to alternant hydrocarbon π -diradicals. Consequently, these diradical-based colour centres had weak photoluminescence and, hence, poor ODMR resolutions [179, 126]. Also, accumulation of population in the low-spin GS singlet further restricted the ODMR resolution by depleting the high-spin, optically addressable triplet

population [179, 46, 126]. Subsequent designs tackled the first problem with excited-state symmetry breaking [46] and partially alleviated the second by installing a spin-selective ISC channel between the excited singlet and ground triplet states [181]. Even so, the ODMR signal would benefit greatly from the possibility of ground singlet-to-triplet ISCs, which is usually slow due to the small SOC matrix elements between transitioning orbitals of similar characters (i.e. the El-Sayed rule [61]).

Interestingly, no work thus far has explored organic systems with electron sextets (i.e. six valence electrons [35]) as sources of spin-optical interfaces. This is despite recent advancements made from both experimental and theoretical fronts to tame these chemically reactive molecules [97, 232]. Carbenes are a good example – these are molecules bearing a two-coordinate carbon atom with two unshared valence electrons. When the carbene is stabilised by enough π -conjugation to its substituents, each of its unshared electrons can reside in orthogonal valence orbitals, giving it a fused π -diradical-like electronic structure with a triplet GS [219, 114, 220, 221, 222, 200, 115, 236, 167, 97, 155, 164, 131, 98, 103, 145, 48, 89, 209] (a primer on its electronic structure will be provided later). Stable triplet carbenes are experiencing a renaissance with multiple prominent reports of isolated species being made in the past five years [164, 131, 98, 145, 48]. They have many advantages over organic π -diradicals as ground-state optically addressable spin qubits: Firstly, co-localisation of the two electron spins on the same carbon atom allows for stronger exchange interactions, potentially shifting the GS singlet up in energy and out of thermal accessibility. The same feature also leads to larger SOC and faster ISC rates, enhancing the ODMR contrast. Thirdly, because π delocalisation into the carbene substituents places the two electron spins in spatially perpendicular π orbitals, these spins are sufficiently decoupled, providing more freedom for addressing other design criteria such as improved emission and ODMR resolution by incorporating non-alternant substituents. Finally and most importantly, vibronic mixing between the triplet GS, which prefers a carbene sp hybridisation of linear conformation, and the singlet GS, which prefers an sp^2 hybridisation of bent conformation, allows the ground triplet and singlet spatial wavefunctions to have

different and well-characterised orbital characters. To our best knowledge, this is the first organic high-spin colour centre explored hitherto that can demonstrate appreciable ground singlet-to-triplet ISC with a well-understood and controllable spin selectivity.

In this theoretical work, we shall explore the electronic properties of triplet carbenes in relation to ground-state optically addressable spin qubits and propose three carbene molecules as candidates for ODMR. Carbene **1** [Fig. 5.2a] replicates our prior endeavours in organic diradical-based colour centres [179, 126] and we will demonstrate how its alternancy symmetry, which we no longer require given the carbene's triplet ground-state spin multiplicity, can be broken for better photoluminescence [1, 95, 84]. Meanwhile, carbene **2** [Fig. 5.2b] resembles our improved diradical design [181] but with significant ground singlet-to-triplet ISC of excellent spin selectivity. This channel is highly coveted in today's state-of-the-art and is made possible by the expanded ground singlet-triplet gap and the aforesaid vibronic effects. Finally, carbene **3** combines both benefits to offer a bright triplet emitter with an appreciable ground-state ISC [Fig. 5.2b]. Therefore, each carbene prototype curbs the complications faced by their diradical counterparts, which is noteworthy given the experimental success of these diradical platforms [46, 126]. Importantly, all three prototypes are chosen to be as realistic as possible: Not only do they resemble existing emissive radicals, but they also abide by the principles used to stabilise experimentally isolated triplet carbenes, particularly through the use of π -conjugated systems as carbene substituents [220, 236, 98]. As such, we hope that this study will motivate the development of persistent luminescent triplet carbenes and other high-spin electron sextets (such as nitrenes [232, 244, 79, 109, 228] and vinylidenes [131]) as optically addressable molecular spin qubits. (*Aside:* We recognise the perspective of π -stabilised carbenes being more cumulenenic in chemical reactivity and hence more properly considered as "diradicals" [221, 222, 167, 145]. However, given our contrasting focus on the optical and spin properties of fused π -systems, we shall distinguish carbenes from diradicals by their coordinations of two rather than three. Thus, we shall classify "cumulene-like diradicals" as carbenes.)

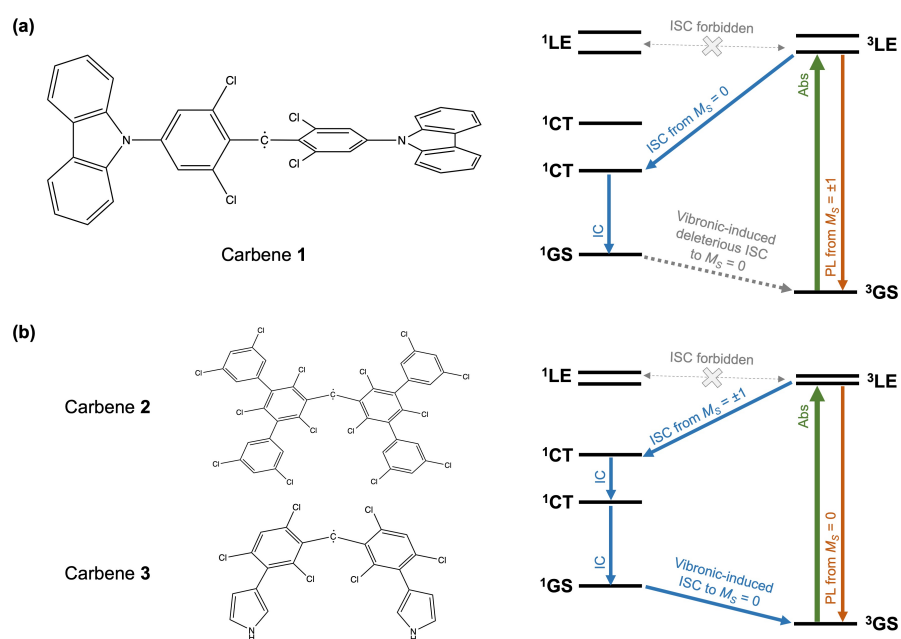


Figure 4.2. Molecular structures and hypothesised ODMR pathways of our representative carbenes, **1** (a), **2**, and **3** (b). The electronic states are labelled by their spin multiplicities (as superscripts) and electronic configurations (GS, CT, and LE). These configurations were introduced during our earlier analyses of π -diradicals [179, 181] and are recapitulated in Fig. 4.3e. (Abbreviations: Abs = absorption; PL = photoluminescence; IC = internal conversion; ISC = intersystem crossing.)

4.2 Results and Discussions

4.2.1 Electronic structure of triplet carbenes in the linear conformation

Roughly speaking (formally, from a valence bond theory perspective), carbenes can be considered as divalent species with two of its four carbon electrons being trapped in σ bonds with the substituents and the remaining two electrons residing in non-bonding orbitals. In the extreme case of a linear geometry around the carbene atom, this atom adopts an sp hybridisation while the remaining pair of $2p$ orbitals form degenerate non-bonding orbitals [Fig. 4.3a]. Hence, by Hund’s rule, the high-spin triplet GS is stabilised over its singlet counterpart to minimise Coulomb and exchange interactions. Bending the geometry causes the hybridisation to switch to sp^n ($n > 1$) with the extra p character arising from *one of* the non-bonding $2p$ orbitals (i.e. bonding occurs). This lifts the degeneracy of the valence orbitals, which are now of p and $(sp)^j p^k$ characters (also loosely called π and σ orbitals [102]) [Fig. 4.3b]. (This phenomenon is reminiscent of the Jahn-Teller geometric distortion (i.e. spontaneous symmetry breaking) due to orbital vibronic coupling [90, 176, 30].) Further, if one of the orbitals is stabilised adequately to overcome the Coulomb and exchange penalties of adopting the low-spin singlet state [213, 198], then the lowest-energy state will be a singlet. As such, the triplet and singlet GSs of carbenes tend to have drastically different geometries with the former (latter) favouring the linear (bent) conformation [221, 222, 236, 167, 155, 89, 209]. For substituents with significant π conjugation to the carbene atom, the valence orbitals will be heavily stabilised by π delocalisation, which is maximised by having minimal s contributions to these orbitals (i.e. by keeping the hybridisation as close to sp as possible). In such scenarios, the GS geometry will not deviate significantly from the linear conformation and the triplet GS will be lower in energy than the singlet GS [221, 222, 236, 167, 155, 89, 209]. This special case will be the focus of this section and will be exemplified by our first carbene prototype; the implications of geometric distortions will be discussed later.

In the linear conformation, each substituent is incentivised to orientate itself perpendicularly to the other and π -stabilise opposite carbene $2p$ orbitals, much like an allene [221, 222, 236, 167, 155, 89, 209]. Thus, the electronic structure closely resembles that of our earlier π -diradical colour centres [179, 126, 181] with two spatially perpendicular and fused π -systems interacting weakly via on-site couplings at the fusing site, i.e. the central carbene atom [Fig. 4.3c]. If we ignore this weak interaction for now, then the electronic structure of the diradical colour centre is fully recovered [179, 126, 181]: The GSs exist as a pair of near-degenerate triplet and singlet while the low-lying excitations are a pair of near-degenerate singlet charge transfers (CTs; also known as zwitterionic or charge-recombined states), a pair of near-degenerate triplet local excitations (LEs), and another pair of near-degenerate singlet LEs. Fig. 4.3d offers a diagrammatic representation of these electronic states. In Supplementary Information S1, we model the carbene on-site couplings using the Pariser-Parr-Pople (PPP) framework [175, 182, 138], which is standard to most semi-empirical analyses of carbenes [32, 53, 124, 10, 107], and introduce the effect of these couplings via time-independent perturbation theory. Interestingly, the state wavefunctions remain largely unchanged, that is, they retain the same characters as their diradical analogues. Meanwhile, the energies of all near-degenerate states are split in support of the triplet GS being the lowest-energy state (this is consistent with Hund’s rule) [Fig. 4.3e]. Therefore, we find that a linear carbene inherits the properties of a π -diradical plus the additional benefits detailed in the introduction. This leads us to our first carbene candidate, which is expected to display the same ODMR pathway as Refs. [179, 126, 46] but with improved photoluminescence due to alternancy symmetry breaking [1, 95, 84].

4.2.2 Triplet carbenes can be bright emitters when non-alternant substituents are installed

Alternant hydrocarbons are π systems in which the π -contributing carbon atoms can be grouped alternately into two distinct classes [95]. This symmetry element endows the π system with special electronic properties, which we used in our first diradical spin-optical interface to selectively minimise typically antiferromagnetic [94, 121, 235, 72, 161,

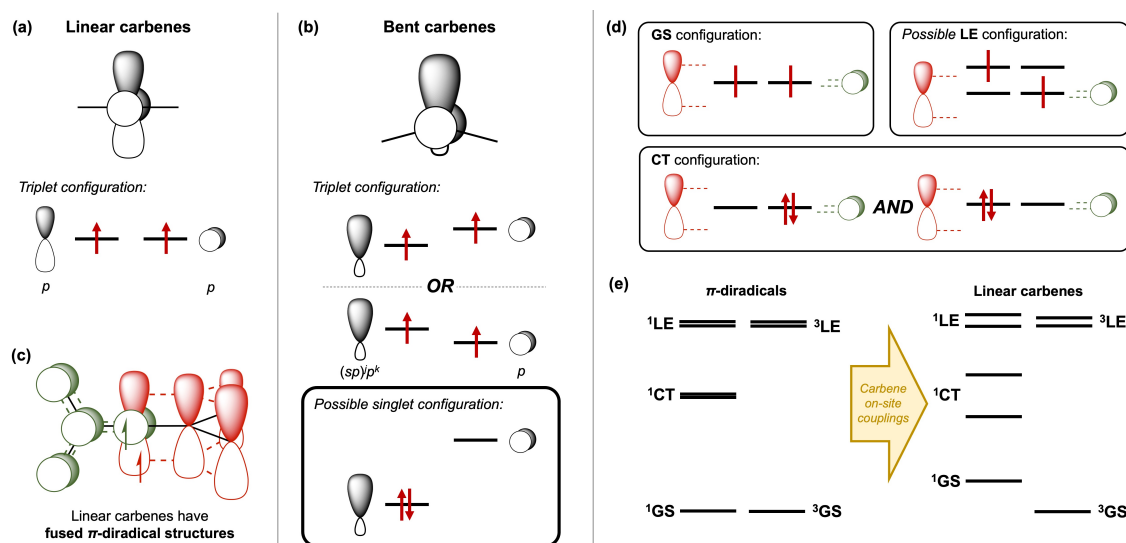


Figure 4.3. (a,b) Sketches of the frontier orbitals of carbenes in the linear (a) and bent (b) conformations. Also illustrated are schematics of the orbital energy level diagram and possible electron occupations. For the bent geometry, the relative ordering of the p and $(sp)^j p^k$ orbitals (also loosely denoted as π and σ orbitals by the community [102]) depends on the stabilising forces imparted by the carbene substituents [219, 114, 220, 221, 222, 200, 115, 236, 167, 97, 155, 164, 131, 98, 103, 145, 48, 89, 209]. (c–e) Spin delocalisation through π -conjugation with the substituents (c) favours a linear triplet carbene with a fused π -diradical-like electronic structure. The ground and excited state configurations are summarised by (d) and the energy ordering in comparison with regular π -diradicals is shown in (e). (Abbreviations: GS = ground state; LE = local excitation; CT = charge transfer.)

103, 3, 197, 148, 140, 183, 2, 255, 40, 153, 229, 247, 203, 201, 4, 38, 208, 243, 150] spin exchange interactions in the GS, thereby guaranteeing a thermally accessible high-spin GS [179]. Unfortunately, this came at the price of poor emission [179, 126], a well-explored consequence of alternancy symmetry [1, 95, 84], and subsequent improvements had to rely on excited-state symmetry breaking [46], which is hard to predict a priori [162, 81]. With triplet carbenes, the ground-state spin multiplicity has been engineered to be high-spin through extensive π delocalisation as discussed earlier. Thus, substituents can be installed to break the alternancy symmetry and yield bright emitters; a common non-alternant fragment for this purpose is a carbazole [1, 95, 84].

Our first proposed carbene (labelled **1**) [Fig. 4.4a] mimicks successful radical emitters used in the organic light-emitting diode (OLED) community [1, 95, 84]. The carbene atom is directly connected to a dichlorophenyl moiety for π -stabilisation, resulting in a near-linear conformation of bond angle 179.95° for the triplet GS [Fig. 4.4a], optimised using density functional theory (DFT). In addition, a carbazole fragment is tethered to the dichlorophenyl group, causing the triplet LE to be bright with an oscillator strength of 0.37 as opposed to around 0.01 for a chlorinated benzylic radical [179, 181]; these values were obtained using time-dependent DFT (TDDFT). All other features of the electronic structure [Fig. 4.4b,c] match our predictions in Fig. 4.3e when computed using broken-symmetry (BS) DFT and TDDFT; these DFT-based results are further verified by multi-configurational (MC) wavefunction-based methods. Similarly, the SOC matrix elements point towards the same ODMR mechanism as our previous diradical colour centre [179, 126], namely, the shelving of the triplet $M_S = 0$ population in the singlet manifold; this is summarised by Fig. 4.4b. Noteworthily, the SOC matrix elements, being around $1 - 10 \text{ cm}^{-1}$ [Fig. 4.4b], are larger than the typical $0.1 - 1 \text{ cm}^{-1}$ values found in regular organic π -diradicals [179, 126]. This agrees with the site-by-site calculation presented in Fig. 2b of Ref. [181] and points towards quicker ISC rates but not debilitating spin relaxation rates, as seen in most transition metal complexes with SOC matrix elements above 100 cm^{-1} [128]. Ultimately, utilising high-spin molecules like carbene **1** as colour

configuration [Fig. 4.5a]. Thus, ISC between these two states is forbidden by the El-Sayed rule. In the bent conformation, one of the $2p$ orbitals mixes with the sp orbitals to form an $(sp)^j p^k$ hybrid valence orbital. While the triplet configuration remains untouched at $\left[(sp)^j p^k\right]^1 [p]^1$, the singlet becomes a linear combination of the $\left[(sp)^j p^k\right]^2$ and $[p]^2$ configurations with unequal amplitudes due to differing orbital energies [Fig. 4.5a]. (Note that these configurations are, respectively, the $\sigma^2 \pi^0$ and $\sigma^0 \pi^2$ configurations familiar to the singlet carbene community [102].) Thus, when the carbene is bent, ISC between the ground singlet and triplet states moves electrons between $(sp)^j p^k$ and $2p$ orbitals with asymmetrical probabilities (due to the skewed amplitudes aforesaid) and is no longer El-Sayed-forbidden. As an example using the σ and π orbital labels [102], in the extreme case of the σ orbital being much lower in energy than the π orbital, the singlet carbene will have a $\sigma^2 \pi^0$ configuration. In this limit, the ISC process to the triplet $\sigma^1 \pi^1$ configuration moves electrons between σ and π orbitals, that is, the orbital character changes, satisfying the El-Sayed rule [61]. This underscores the importance of vibronic effects in carbenes. (Formally, we continue to work in the electronic basis of diradical GS and CT configurations such that the SOC matrix elements between the two GS configurations vanish at all carbene bond angles. However, this basis is not an eigenbasis of the electronic Hamiltonian when the carbene is bent; instead the GS and CT singlets of irrep A mix. Therefore, in the distorted geometry, the lowest-energy singlet picks up some CT character, which contributes to an appreciable SOC with the GS triplet. More details may be found in Supplementary Information S2.)

The above postulates are verified by plotting the low-lying potential energy surfaces (PESs) of carbene **1**, presented in Fig. 4.5b. This plot also affirms the triplet GS to be of lower energy than the singlet GS at their respective energy minima, i.e. carbene **1** is a triplet carbene. While not explicitly discussed, the above analysis can easily be extended to rationalise why all of the excited state energies minimise at the linear conformation. Importantly, this suggests that the excited-state activities will occur mostly at linearity except for the ground singlet-to-triplet ISC. For carbene **1**, this ground-state ISC is dominated

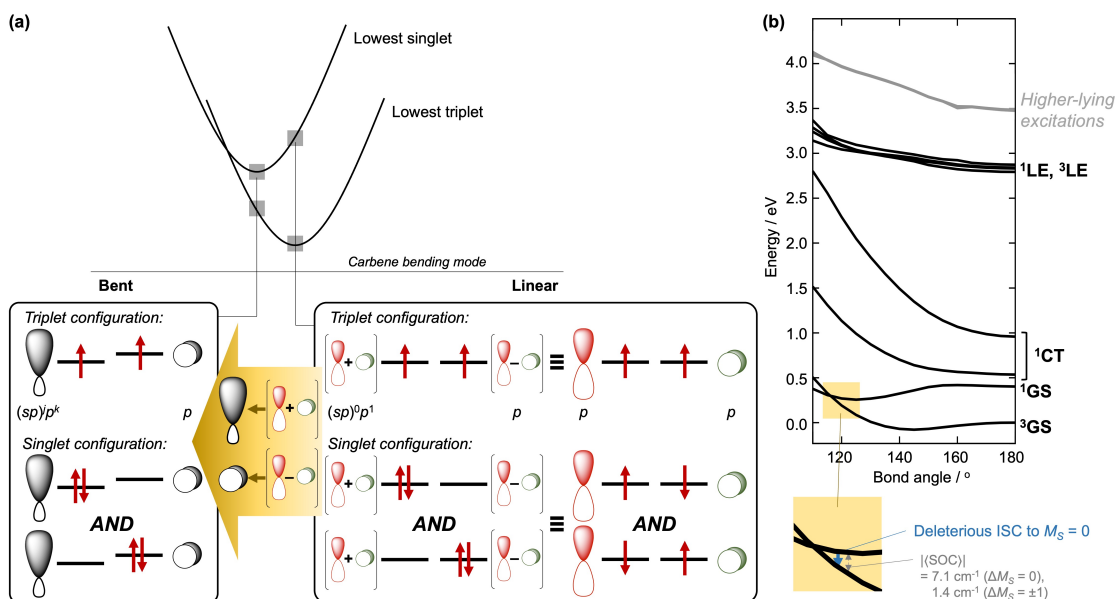


Figure 4.5. (a) Diagrammatic representation of the carbene vibronic coupling using a pair of displaced harmonic oscillators. The dominant electronic configurations at the bent and linear geometries are also depicted. The left- and right-most columns of (a) are the same as Fig. 4.3; the middle column represents the linear-geometry electronic configurations expressed in the symmetry-adapted orbital basis (to be specific, this is the molecular C_2 symmetry that is conserved by the bending motion). This final step ensures continuity in moving between the linear and bent conformations – see Supplementary Information S2 for more details. (b) PESs of the low-lying electronic states of carbene **1** along with the amplitude of the SOC matrix element between the lowest singlet and lowest triplet states at the 120°-bond angle. These results were obtained with MC wavefunction-based methods. The presence of a shallow minimum on the ground triplet surface at an angle away from 180° is an artefact of computing with geometries relaxed for a spin-restricted singlet state (see Methods and Supplementary Information S3).

by on-site SOC with the *same* spin selectivity as the excited-state ISC [99, 22, 248, 179] (see Ref. [179] for a full discussion). Thus, it is detrimental to spin purification [Fig. 4.5b]. Nevertheless, we have previously engineered diradicals with excited-state ISCs facilitated by beyond-nearest-neighbour SOC, which will demonstrate spin selectivities *opposite* from on-site or nearest-neighbour SOC [181]. Therefore, through this approach, the carbene's strong ground-state vibronic coupling can be leveraged for ODMR and our next two carbene prototypes exemplify this point.

4.2.4 Triplet carbenes can achieve the desired ground singlet-to-triplet ISC through vibronic effects

Carbene **2** [Fig. 4.6a] is designed to replicate our follow-up diradical study [181], which is also based upon experimentally-reported luminescent radicals [162, 81, 46]. Coincidentally, the DFT-optimised triplet GS geometry is slightly bent at an angle of 150.88° [Fig. 4.6a] due to weaker π delocalisation than carbene **1** (for instance, the radical-phenyl bond length of the monoradical analogue is longer in carbene **2** by 0.0022). Nonetheless, the key features of our diradical design [181] are inherited by this molecule, especially the possibility for ISC between the triplet LE and excited singlet CT as mediated by next-nearest-neighbour SOC [Fig. 4.6b,c] (these results were computed using BS-DFT, TDDFT, and MC methods). As rationalised earlier, at this bent geometry, a second ISC between the lowest singlet and lowest triplet states should be El-Sayed-allowed; indeed, the ab initio results [Fig. 4.6b] support this hypothesis with the associated SOC amplitude being comparable to and the spin selectivity being opposite to the excited ISC channel (formally, this arises from the 4.3% CT contribution to the lowest singlet). Such a decay pathway is highly desirable as it efficiently funnels singlet population back into the triplet manifold. Moreover, with the specially designed carbene **2**, this channel also leads to overall purification of the electron spins, enhancing the ODMR signal through a newfound mechanism shown in Fig. 4.6b. As far as we are aware, no such pathway has been reported or postulated in organic spin-optical interfaces, hence we expect carbene **2** to be a paradigm-shifting molecular colour centre. Note that linear carbenes of comparable molecular structures should display similarly improved ODMR signals owing to the vibronic effects described earlier [Fig. 4.5a]. To demonstrate this, we conducted further DFT studies and identified the lowest singlet geometry at an even more bent conformation of 127.38° . At this geometry, the lowest singlet remains higher in energy than the lowest triplet by 0.27 eV, supporting carbene **2** as a triplet carbene. Crucially, this energy difference is equivalent to thermal energy at around 3100 K, making the ground singlet-to-triplet ISC largely irreversible under most operating conditions (Boltzmann factor $\approx 10^{-5}$ at 298 K).

Put differently, the lowest singlet is thermally inaccessible.

We note that the LE emission of alternant carbene **2** can be enhanced by excited-state symmetry breaking [162, 81, 46]; this was also mentioned in our diradical work [181]. Alternatively, one can install alternancy-symmetry-breaking substituents strategically at the position meta to the central carbene atom. To rationalise this, we consider carbene **3** as an example, which promises a magnitude-order improvement in the LE oscillator strength from carbene **2** through its non-alternant meta-substituent, computed using TDDFT [Fig. 4.7]. This LE is associated with a HOMO-to-SOMO transition. Unsurprisingly, the HOMO's nodal structure surrounding the carbene atom remains unchanged, i.e. the excited-state ISC is expected to occur through next-nearest-neighbour SOC with a $\Delta M_S = \pm 1$ selectivity. An important consequence of meta-substitution is that the SOMO, which has a node at the meta carbon, remains untouched by this modification. This is unlike carbene **1**, where the LE occurs among orbitals that inherit the nodal structure of the SOMO, which has a large amplitude at the central carbene atom [Fig. 4.4b]. As discussed, this causes the excited-state ISC to occur via the undesired on-site SOC of $\Delta M_S = 0$ selectivity. (Acronyms: HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital; SOMO = singly occupied molecular orbital.)

As an aside, engineering such vibronic couplings in π -diradicals while maintaining the lowest-energy state at a high-spin configuration might be a challenge because π -diradicals have a propensity for their lowest-energy state to be a singlet [94, 121, 235, 72, 161, 103, 3, 197, 148, 140, 183, 2, 255, 40, 153, 229, 247, 203, 201, 4, 38, 208, 243, 150] and these geometric distortions are likely to further lower the low-spin singlet energy [Fig. 4.5a]. Furthermore, the characters of these rehybridised valence orbitals, which impact the spin selectivity, might be difficult to control [162, 81]. Therefore, the paramagnetic occupation of well-defined hybrid orbitals and the strong ferromagnetic exchange coupling between this pair of spins (which originates from their spatial co-localisation on the carbene centre) are both paramount to the anticipated success of carbenes **2** and **3**.

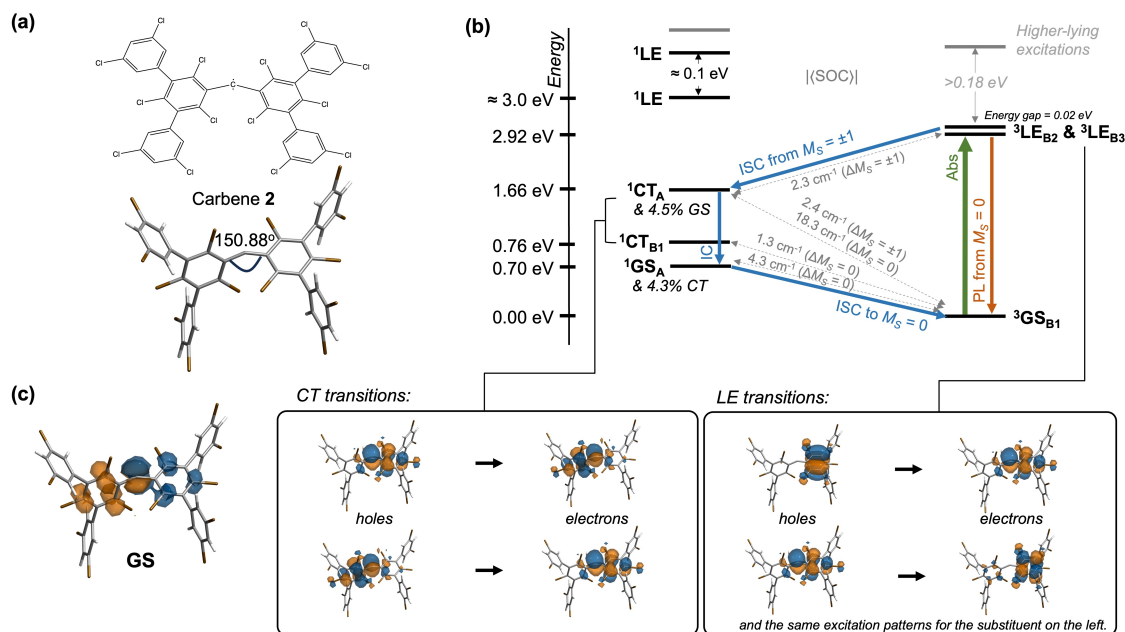


Figure 4.6. Ab initio results for carbene **2**. (a) Molecular structure and DFT-optimised triplet geometry. (b) Excited-state electronic structure, calculated using BS-DFT/TDDFT. The subscripts A, B₁, B₂, and B₃ that accompany the excitation labels signify the state irreps based on the molecule's approximate *D*₂ point group symmetry (where the *z*-axis lies along the two carbene substituents). A formal breakdown of the GS and CT contributions to the low-lying singlets (see main text) is indicated as well. The same panel also shows all SOC matrix elements (more specifically, their amplitudes) of values above 1.0 cm⁻¹, computed using MC wavefunction-based methods. The coloured lines denote our postulated ODMR mechanism. (c) Overlay of the two singly occupied molecular orbitals (isovalue = 0.030), characteristic of the GS, and plots of the transitioning orbitals for the lowest-lying excitations (isovalue = 0.020), obtained using MC wavefunction-based methods.

First two triplet transitions:

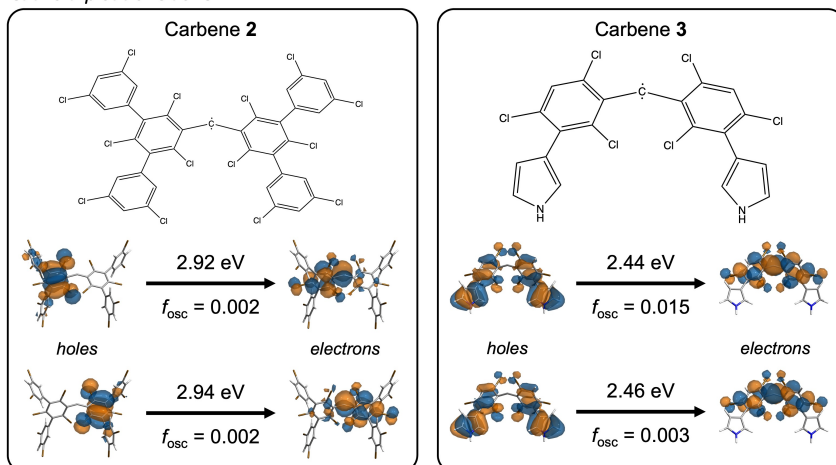


Figure 4.7. Properties associated with the two lowest-lying triplet excitations of carbenes **2** and **3**, including the excitation energies, the oscillator strengths, and the natural transition orbitals (isovalue = 0.020). These results are computed using TDDFT. Here, the hole and electron orbitals resemble the HOMO and SOMO, respectively (see, for instance, Ref. [181]).

4.3 Conclusion

The search for organic high-spin ground states often necessitates the use of electron-deficient systems that break the octet rule, leaving them with possibly unshared electrons that can become unpaired. Radicals, having a septet (seven) of electrons, are excellent precedents [179] and their limitations at being optically addressable are progressively being tackled by the community [46, 126, 181]. This work takes another leap by proposing electron sextets as sources of colour centres. Not to overshadow other electron sextets like nitrenes [232, 244, 79, 109, 228] and vinylidenes [131], we have chosen triplet carbenes as a representative example given the recent reemergence of this field [164, 131, 98, 145, 48] and the similarity between carbenes and existing hydrocarbon-based diradical colour centres [179, 46, 126, 181]. Indeed, the electronic structure is readily transferrable with added benefits not yet realised in conventional diradicals, such as widened ground singlet-triplet gaps, stronger SOC, better emissive properties, and the possibility for an extra ISC channel between the ground singlet and ground triplet states. This last advantage is crucial for returning the singlet population back into the triplet manifold, potentially

enhancing the ODMR signal of organic colour centres. As an illustrative example, we have designed carbene **2** to have this channel display the correct spin selectivity for spin purification and be relatively irreversible due to the broadened ground singlet-triplet gap. Further improvements in the emission properties are possible by alternancy-symmetry breaking, as exemplified by carbene **3**. To conclude, triplet carbenes promise to resolve many vital limitations of π -diradical spin-optical interfaces and recent developments at stabilising them are highly optimistic [164, 131, 98, 145, 48]. The synthesis of other types of electron sextets, such as stable nitrenes, is also being revived by the community with numerous influential reports being made in recent years [232, 244, 79, 109, 228]. Thus, we believe that expanding our scope into persistent, emissive electron sextets will reap us significant benefits in our quest towards novel quantum materials.

4.4 Methods

All DFT calculations of carbene **1** were performed with the Gaussian16 software [75]. The molecular geometry was first optimised as a triplet on UB3LYP/6–311+G(d,p) and a frequency analysis confirmed the presence of a local minimum. The electronic structure was then estimated using spin-unrestricted TDDFT within the Tamm–Dancoff approximation (TDA) and with the lowest-energy triplet and BS singlet states as references; these calculations were done with the same functional and basis set as before. Spin purification was performed on the singlet GS following Yamaguchi et al. [240] while spin contaminations in the excited singlets were assumed to be negligible due to the small excited singlet-triplet gaps (see Ref. [181] for a full discussion). The state irreps were then assigned by observing the transition dipole moments and the transitioning orbitals. Finally, a relaxed scan of the carbene bond angle was performed at the singlet restricted B3LYP/6–311+G(d,p) level of theory, which offers a computationally efficient way of capturing the GS and CT singlet energies in a single electronic calculation [165, 179] (see Supplementary Information S2). These relaxed geometries were used to construct the PESs found in Fig. 4.5b (the MC procedure will be presented later).

Henceforth, all ab initio calculations were conducted on the ORCA 5.0 code [166]. For our MC wavefunction-based investigations of carbene **1**, we utilised the complete active space self-consistent field (CASSCF) method with 10 electrons and 8 orbitals in the active space and with the def2-TZVPP basis set; the energy was state-averaged over the lowest five triplet and lowest seven singlet states (i.e. SA12). Also, the optimised wavefunctions and energies were corrected by the van Vleck quasi-degenerate (QD) extension to the strongly contracted second-order N-electron valence state perturbation theory (SC-NEVPT2) after requesting for the lowest nine triplet and lowest eleven singlet roots in a complete active space configuration interaction (CASCI) calculation. Starting from the DFT-optimised triplet geometry, which has a near-linear conformation, the zero-field splitting (ZFS) parameters for the lowest-energy triplet and the SOC matrix elements among the electronic states were calculated. Here, the electron spin states are reported in the principal axes frame of the ground triplet ZFS tensor. According to a benchmark done with carbon-based diatomics [78], the error associated with these SOC matrix elements is expected to be $< 10\%$. Then, to obtain the PESs plotted in Fig. 4.5b, the same procedure was repeated for all carbene bond angles using the molecular orbitals converged for larger angles as the initial guess. At the 120-degrees geometry, the ZFS parameters and SOC matrix elements were analogously found. In these calculations, the RI-JK approximation (RI-JK = resolution of identity approximation for both Coulomb and exchange terms) was applied with the def2/JK auxiliary basis set.

As for carbene **2**, its geometry was optimised as a triplet on UB3LYP-D3BJ/def2-SVP [86, 87] and the relevant frequency analysis was performed. Subsequent TDDFT/TDA calculations on the lowest-energy triplet and BS singlet solutions yielded estimates of the electronic structure after applying the same spin purification protocol as before; here, the level of theory was UB3LYP/def2-SVPD. To assign the state irreps, we examined the transition dipole moments and the transitioning orbitals. The ZFS parameters were also computed for the lowest-energy triplet on UB3LYP/IGLO-II; only the spin-spin contributions were considered since the spin-orbit contributions are expected to be insignificant

[126].

Next, the SOC matrix elements were calculated for carbene **2** at the MC level of theory, also with the def2-SVPD basis set. The method used was SA12-CASSCF(10,10)/CASCI/QD-SC-NEVPT2 (as described for carbene **1**) and again the electron spin states are expressed in the principal axes frame of the ground triplet ZFS tensor found earlier. In these calculations, the RIJCOSX approximation (RIJCOSX = resolution of identity approximation for the Coulomb term and chain-of-spheres approximation for the exchange term) was utilised with the def2/JK auxiliary basis set.

Finally, to estimate the lowest singlet conformation, we optimised the molecular geometry of carbene **2** as a spin-restricted singlet on B3LYP-D3BJ/def2-SVP [86, 87] and followed up with the appropriate frequency analysis. While the true minimum of the lowest singlet PES is likely to be slightly different due to mixings with other closed-shell singlet configurations (see Supplementary Information S2), we found this approach to be a compromise between accuracy and computational costs. At this geometry, the lowest triplet and lowest singlet energies were estimated via UB3LYP/def2-SVPD and BS-B3LYP/def2-SVPD respectively. The results were reported after performing the relevant spin purifications.

We note that the energies reported by TDDFT have a typical error of around 0.3 eV [134]. Meanwhile, the energies given by MC wavefunction-based methods are highly sensitive to the active space choice, with deviations as high as 0.4 eV being reported in π -diradicals [210]. Therefore, within these errors, we find the discrepancies between the energies computed by these two methods to be acceptable, given our aim of setting the semi-empirical solutions in the correct parameter range. Importantly, both methods predict the same energy ordering as the semi-empirical analysis, thus supporting the key result of this work. Further improvements may also be achieved by employing advanced DFT methods designed to capture the multiconfigurational nature of diradicals, such as the mixed-reference spin-flip TDDFT (MRSF-TDDFT) [100] and multiconfigurational pair-DFT (MCPDFT) [207] techniques.

With carbene **3**, following optimisation of its geometry on UB3LYP-D3BJ/def2-SVP [86, 87] (with the appropriate frequency analysis done), its triplet excitations were estimated using TDDFT/TDA at the UB3LYP/def2-SVPD level of theory.

4.5 Additional note

During the revision process, we became aware of an independent preprint [192] that experimentally demonstrated ODMR contrasts of >40% in triplet 2,2'-dinaphthylcarbene embedded in a 2,2'-dinaphthylketone molecular crystal. Their quantum chemical calculations proposed an ODMR pathway similar to our work, which we exemplified using carbene **2**. To elaborate, the authors found the ground-state ISC to be selective for the $\Delta M_S = 0$ transition, which we attribute to the on-site SOC's aforesaid. Their calculations also revealed a 13.5% CT contribution to the lowest singlet state in the bent conformation, which we ascribe to the vibronic effect needed for the ground-state ISC to be El-Sayed-allowed. Similarly, the authors found the excited-state ISC to be selective for the $\Delta M_S = \pm 1$ transitions. As mentioned earlier, this is a signature of beyond-nearest-neighbour SOC's [181], which might have dominated their excited-state ISC because their HOMOs and LUMOs have larger densities at the naphthyl 3-position (i.e. beyond-nearest-neighbour SOC) than at the carbene centre (i.e. on-site SOC); however, a more quantitative approach is required to strengthen our analysis. Interestingly, the authors used the structural similarity between the carbene dopant and the ketone matrix to stabilise the carbene without significantly modifying its structure, thereby retaining the proposed ODMR mechanism. Their photoluminescence quantum yield is relatively low at around 0.02, which is a well-understood consequence of alternancy symmetry [1, 95, 84], and breaking this symmetry should improve the emissive properties, as we have illustrated using carbene **3**.

Acknowledgments

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Chapter 5

Photoredox Catalysis with Spin Magnetic Field Effects: A Scheme for Chiral Resolution

5.1 Introduction

Most photochemical reactions generate pairs of radical intermediates [7, 160, 23, 113, 245, 185, 250], a phenomenon known as chemically induced dynamic electron polarisation (CIDEP) [14]. These spin-correlated radical pairs (RPs) can then evolve coherently among the singlet and triplet basis states, often influenced by an applied magnetic field through the spin Zeeman effect. Because the singlet states react differently from the triplet states, their average populations can be detected by the ensuing chemical kinetics, leading to techniques such as reaction yield-detected magnetic resonance [14]. Such magnetic field effects (MFEs) have been proposed as explanations for magnetoreception [191, 253, 101, 69] with potential applications ranging from light harvesting to quantum sensing [92, 91, 139].

Adjacent to this field is the study of chirality-induced spin selectivity (CISS), a more-recently discovered effect that also polarises electron spins [187]. This is achieved by passing an electron current through a chiral molecule or material, thereby relating the electron's magnetisation with the (geometric) chirality [64, 9, 44, 34, 125]. The CISS effect has been observed in various forms including photoemission [83, 5, 154], electron transport [231, 24, 13, 60], and transient charge polarisation [59, 129, 29]. Its theoretical

foundations are still being investigated [64], most of which point towards the role of chiral vibrations or phonons that couple to the electron spins through non-Born-Oppenheimer effects [238, 252, 49, 112, 25, 122, 225, 66, 42, 43, 224, 74, 202, 257].

Beyond observations of CISS, the same effect has also been harnessed to discriminate enantiomers using polarised electron spins [33, 163, 146], uncovering new prospects for chiral resolution [20, 215, 31, 143, 171, 144] and possibly new understanding of life’s homochirality [172, 171, 111]. While remarkable, this direction has so far been limited to the enantioselective adsorption of amino acids and small peptides onto magnetised surfaces [20, 143, 144]. To attain bulk separation, amplification processes such as flow reactions and crystallisation are required [20, 215, 31, 171], implying some restrictions in its synthetic applicability, although there is much potential for theoretical developments to guide the rational design of CISS-based separation systems [54, 227, 73, 144]. From there, benchmarks can be made against other spin-based techniques; for instance, photon spins are also known to discriminate enantiomers, albeit with a small enantiomeric excess (e.e.) of $< 1\%$ [37, 105, 116, 93, 188].

In this work, we offer a novel spin-based enantioseparation technology by utilising the MFE of radical pairs to invoke chiral resolution. The connection is achieved via the electron orbital angular momentum (OAM; labelled $\hat{\mathbf{L}}$). Being odd under both time-reversal symmetry (TRS) and mirror reflection [47], the OAM is time-reversed in opposite enantiomers [Fig. 5.1]. Hence, a process that breaks TRS, such as the introduction of a magnetic field $\mathbf{B}$, will also separate the two enantiomers. For instance, the *orbital* Zeeman coupling ($\sim \mathbf{B} \cdot \hat{\mathbf{L}}$) flips sign under mirror reflection, causing one enantiomer to absorb *linearly* polarised light more strongly than the other; this phenomenon is termed magneto-chiral dichroism [21, 226, 24, 189, 190, 239, 16, 17, 108, 15]. Unfortunately, the effect is weak resulting in an experimental e.e. of $< 0.1\%$ [190], mainly because the *orbital* Zeeman term in molecules is small relative to the typical orbital (i.e. electronic) energy separation [16, 108, 15]. By converting the OAM into spin angular momentum (SAM; labelled $\hat{\mathbf{S}}$) through a spin-orbit coupling (SOC), we propose the use of the *spin* Zeeman

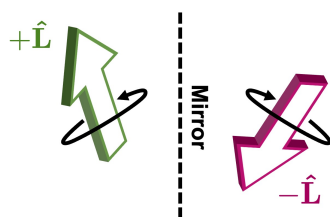


Figure 5.1. The OAM $\hat{L}$, being an axial vector, changes direction in the mirror image, connecting it with its time-reversed counterpart.

effect, the energy of which can be larger than the spin-intrinsic zero-field splitting (ZFS). This way, the time-reversed pair of SAM acts as a proxy for the two enantiomers through the OAM.

While the total orbital-spin angular momentum is known to link mirror symmetry to TRS [47, 67, 68], its application towards enantioselective photoredox catalysis through the *spin* Zeeman effect is, to our best knowledge, unprecedented. In our proposal, we shall distinguish the time-reversed SAMs by coherently evolving one of the photoinjected triplet M_S sublevels with the singlet state using a magnetic field, an implementation of the MFE [Fig. 5.2]. The subsequent collective singlet-triplet decay of the RP to the ground state will be faster in one enantiomer due to constructive interference between the electronic and spin-orbit channels. Therefore, at steady state, chiral resolution can be achieved in molecules that racemise faster in an oxidised or reduced state. Importantly, our analytical solutions show regimes of perfect enantioselectivity (i.e. an e.e. of 100%) to be accessible by chemical fine-tuning. For instance, the RP formed between an axially chiral binaphthyl derivative and a borane photosensitiser [Fig. 5.2] displayed an e.e. of 90% at steady state, a significant improvement from the $< 1\%$ e.e. obtained via other magnetochiral methods [33, 163, 146, 190]. Further, enantiopurification is achieved with a timescale of hundreds of milliseconds under a laser light source, which is experimentally feasible. Techniques for further improvement will also be discussed.

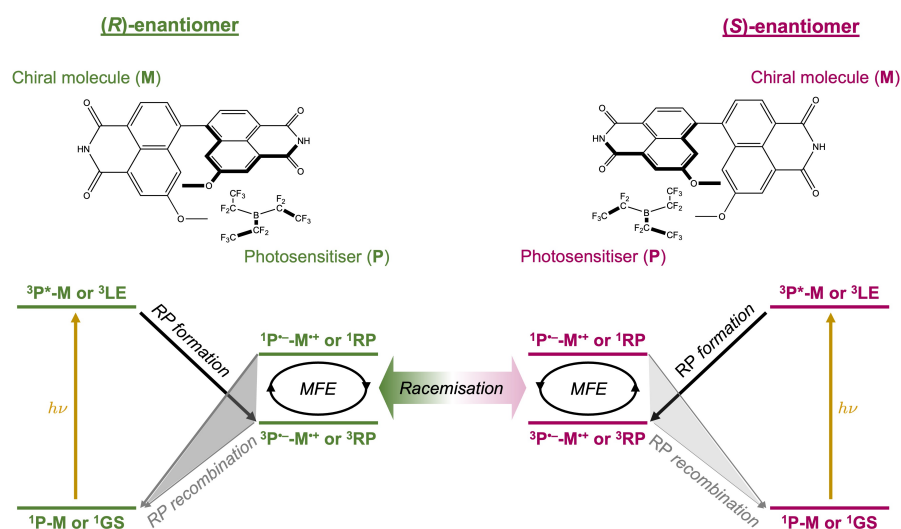


Figure 5.2. An overview of the spin-based enantioseparation scheme. In general, chiral molecules are destabilised and racemise faster in their oxidised/reduced ionic states. In this scheme, we first form a triplet RP between a photosensitiser and the chiral molecule by optical spin injection. This triplet RP then picks up a small amount of singlet character due to the MFE. The ensuing singlet-triplet coherence sets up a constructive interference between the singlet and triplet decay channels in one enantiomer, causing its RP to recombine more quickly. The other enantiomer, having spent more time in the (ionic) RP state, has a higher chance of inverting its chirality, leading to chiral resolution at steady state.

5.2 Results and Discussions

5.2.1 The chiral resolution protocol

Our photoredox catalysis set-up for enantiopurification comprises a photosensitiser (i.e. a photocatalyst) and a racemic mixture of chiral molecules [Fig. 5.2]. The photosensitiser is first excited from its singlet ground state, $|^1\text{GS}\rangle$ (GS = ground state), to a *triplet* excited state, $|^3\text{LE}\rangle$ (LE = local excitation), made possible by strong SOC in the photosensitiser (more to follow). The photoexcited state then undergoes a sub-nanosecond electron transfer to the chiral molecule to form a RP in the *triplet* state, $|^3\text{RP}\rangle$. Subsequently, this triplet RP state mixes with the singlet RP state, $|^1\text{RP}\rangle$, through a weak external magnetic field. All four RP states (one singlet and three triplets) can decay independently to the $|^1\text{GS}\rangle$ state, and we shall denote their rates by

$$w_T = \frac{1}{\hbar^2 \Omega} \left| V_{\text{SOC}, M_S}^{\text{RP-GS}} \right|^2 \quad (5.1)$$

for the triplet M_S sublevel $|^3\text{RP}; M_S\rangle$, and

$$w_S = \frac{1}{\hbar^2 \Omega} \left| V_{e,S}^{\text{RP-GS}} \right|^2 \quad (5.2)$$

for the singlet state $|^1\text{RP}\rangle$ [Fig. 5.3]. Here, $V_{e,S}^{\text{RP-GS}}$ and $V_{\text{SOC}, M_S}^{\text{RP-GS}}$ are, respectively, the real-valued electronic and complex-valued spin-orbit couplings responsible for the singlet and triplet RP recombination, while the prefactor $(\hbar^2 \Omega)^{-1}$ is a proportionality constant that encapsulates the bath interactions (see footnote ¹). Eqs. (5.1) and (5.2) require the RP states to be the lowest-lying excitations of the system (otherwise the triplet RP can decay into other lower-energy triplet states [91]). To satisfy that, we can use photosensitisers with HOMOs (or LUMOs) that are close in energy to the chiral molecule's LUMO (or HOMO), thereby minimising the energy for electron transfer (HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital).

¹Examples include the Franck-Condon overlaps in the Marcus-Levich-Jortner models [62, 180, 186] and the bath component of the system-bath interaction in most quantum master equations [36, 170].

If one of the triplet M_S RP sublevels is now brought into near-degeneracy with the singlet RP state, then their quantum coherence allows the two states to decay collectively. For instance, if the singlet RP state were to be higher in energy than its triplet counterpart, then a magnetic field can bring the $|^3\text{RP}; +1\rangle$ state into near-degeneracy with the $|^1\text{RP}\rangle$ state, yielding the following perturbed state (Supplementary Information S1):

$$|\overline{^3\text{RP}; +1}\rangle \approx |^3\text{RP}; +1\rangle + |^1\text{RP}\rangle \left[\frac{\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle}{\Delta E_{T_{+1}-S}} \right], \quad (5.3)$$

where $\Delta E_{T_{+1}-S} \equiv E(^3\text{RP}; +1) - E(^1\text{RP})$ is the energy difference between the near-degenerate states and $\hat{V}_s$ is the spin Hamiltonian for a RP. The collective decay rate $w_+^{(R)}$ between these two states will be approximately

$$w_+^{(R)} \approx \frac{1}{\hbar^2 \Omega} \left| V_{\text{SOC},+1}^{\text{RP-GS}} + V_{\text{e},S}^{\text{RP-GS}} \left[\frac{\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle}{\Delta E_{T_{+1}-S}} \right] \right|^2. \quad (5.4)$$

To understand the origin of the chiral resolution, let us denote Eq. (D.12) as the rate for the (R)-enantiomer. Its mirror image – the (S)-enantiomer – will experience a similar rate but with an opposite sign on $V_{\text{SOC},+1}^{\text{RP-GS}}$:

$$w_+^{(S)} \approx \frac{1}{\hbar^2 \Omega} \left| -V_{\text{SOC},+1}^{\text{RP-GS}} + V_{\text{e},S}^{\text{RP-GS}} \left[\frac{\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle}{\Delta E_{T_{+1}-S}} \right] \right|^2. \quad (5.5)$$

This is because $V_{\text{SOC},+1}^{\text{RP-GS}}$ is a matrix element of the SOC operator $\sim \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, and $\hat{\mathbf{L}}$, being an axial vector [Fig. 5.1], picks up a negative sign under mirror reflection. (Note that, in this work, $\hat{\mathbf{S}}$ stays aligned with $\hat{\mathbf{B}}$, while $\hat{\mathbf{B}}$ follows the symmetry of the electron transfer vector, which is a polar vector; this is consistent with Refs. [47, 67, 68].) Notice that where the two terms add up in Eq. (D.12), the same elements are subtracted in Eq. (5.5), and vice versa. This is a manifestation of the interference effect during collective singlet-triplet decay. The enantiomer experiencing a destructive interference will be funnelled into its mirror-reflected counterpart because the barrier to chirality inversion is lower in the

RP, which represents a less-stable oxidised/reduced state of the enantiomers. In other words, dynamic kinetic resolution is achieved, which is more valuable than traditional chiral resolution protocols because all molecules of a racemic mixture may, in principle, be converted into an enantiopure compound. Since the steady-state e.e. depends on the differential decay rates $w_+^{(R)}/w_+^{(S)}$, it does not vary much with the rate of chirality inversion.

Note that the triplet RP state decays more slowly than the singlet RP state (i.e. $|V_{\text{SOC},+1}^{\text{RP-GS}}| \ll |V_{\text{e},S}^{\text{RP-GS}}|$), thus the amplitude of the triplet component in Eq. (5.3) must be larger than the singlet component for the interference in Eqs. (D.12) and (5.5) to be appreciable. Put differently, there must be a small, yet appreciable, energy separation between the $|^3\text{RP}; +1\rangle$ and $|^1\text{RP}\rangle$ states, such that the $|^3\text{RP}; +1\rangle$ state contains only a perturbative admixture of $|^1\text{RP}\rangle$ character. This justifies the use of perturbation theory in Eq. (5.3), and also explains our choice for a spin-forbidden triplet photoexcitation, which would require a sufficiently strong SOC to occur [26, 249]. For our photosensitiser prototype, this transition occurs within one day under a mercury lamp and can be down to a microsecond using a regular laser [251] – see Supplementary Information S2.

While we have used the $|^3\text{RP}; +1\rangle$ state as an example, the $|^3\text{RP}; -1\rangle$ state can also be in near-degeneracy with the $|^1\text{RP}\rangle$ state by reversing the magnetic field direction, yielding analogous expressions $w_-^{(R/S)}$ for the collective decay rate. Other than that, no collective decay occurs because the interfering states must be separated by an energy (in frequency units) smaller than the overall decay rate, a consequence of the energy uncertainty due to lifetime broadening [36, 170, 223] (Supplementary Information S1). The chiral resolution χ , defined as the ratio of (R)-enantiomers to (S)-enantiomers at steady state, is characterised by the differential decay rates to be

$$\chi \approx \frac{w_+^{(R)}}{w_+^{(S)}} \times \frac{w_-^{(R)}}{w_-^{(S)}}, \quad (5.6)$$

where the multiplication arises because the factors $w_+^{(R)}/w_+^{(S)}$ and $w_-^{(R)}/w_-^{(S)}$ deviate most significantly from one in the positive and negative magnetic field regimes, respectively

(Supplementary Information S1). To further illustrate the enantioseparation, we consider only the spin Zeeman terms $\mu_B \mathbf{B} \cdot \mathbf{g}_j \cdot \hat{\mathbf{S}}_j$ and a singlet-triplet exchange coupling $2J \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$ in the spin Hamiltonian ($j = A, B$ labels the radicals in the RP and the remaining terms have their usual meanings). We shall also assume $\mathbf{B} = B_0 \mathbf{z}$ ($\mathbf{z}$ is the unit vector along the z -direction) to be aligned with $\mathbf{g}_A$'s principal axis. Denoting $\Delta \mathbf{g} \equiv \mathbf{g}_B - \mathbf{g}_A$ as the difference in g -tensors, we find that (Supplementary Information S1)

$$\Delta E_{T_{+1}-S} = 2\hbar^2 J + \hbar \mu_B g_{\text{eff}} B_0, \quad (5.7)$$

$$\langle {}^1\text{RP} | \hat{V}_s | {}^3\text{RP}; +1 \rangle = \hbar \mu_B \Delta g_{\text{eff}} B_0, \quad (5.8)$$

where $g_{\text{eff}} \equiv g_{A,zz} + \Delta g_{zz}/2 \approx 2$ represents an effective electron spin g -factor and $\Delta g_{\text{eff}} \equiv (\Delta g_{zx} + i\Delta g_{zy})/2\sqrt{2}$ denotes an effective difference in the g -tensors (i.e. the MFE). These expressions can be substituted into Eqs. (D.12), (5.5), and (5.6) to obtain an analytical expression for the chiral resolution χ (Supplementary Information S1). For instance, the enantioenrichment can be controlled by the magnetic field strength B_0 , as shown in Fig. 5.4a. For both $B_0 > 0$ and $B_0 < 0$, two extrema are obtained at

$$\chi_{\text{max}}^{(\pm)} = \frac{|\Delta g_{\text{eff}}| \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right| \pm \text{Re} \left(\Delta g_{\text{eff}}^* V_{\text{SOC},+1}^{\text{RP-GS}} \right)}{|\Delta g_{\text{eff}}| \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right| \mp \text{Re} \left(\Delta g_{\text{eff}}^* V_{\text{SOC},+1}^{\text{RP-GS}} \right)}, \quad (5.9)$$

$$B_{\text{max}}^{(\pm)} = \frac{2(\hbar J / \mu_B) \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right|}{\pm |\Delta g_{\text{eff}}| V_{\text{e},S}^{\text{RP-GS}} - g_{\text{eff}} \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right|}, \quad (5.10)$$

each corresponding to a *near*-perfect constructive interference in a specific enantiomer. (Note that in Eqs. (5.9) and (5.10), “ $\pm$ ” labels the two extrema rather than the sign of B_0 .) Notice how $\chi_{\text{max}}^{(\pm)}$ approaches either zero or infinity (i.e. perfect enantioseparation is achieved with 100% e.e.) when both Δg_{eff} and $V_{\text{SOC},+1}^{\text{RP-GS}}$ are purely real or purely imaginary. Indeed, this implies that the terms in either Eq. (D.12) or Eq. (5.5) *perfectly* cancel out at some magnetic field strength B_0 . Importantly, Δg_{eff} and $V_{\text{SOC},+1}^{\text{RP-GS}}$ both depend on some SOC

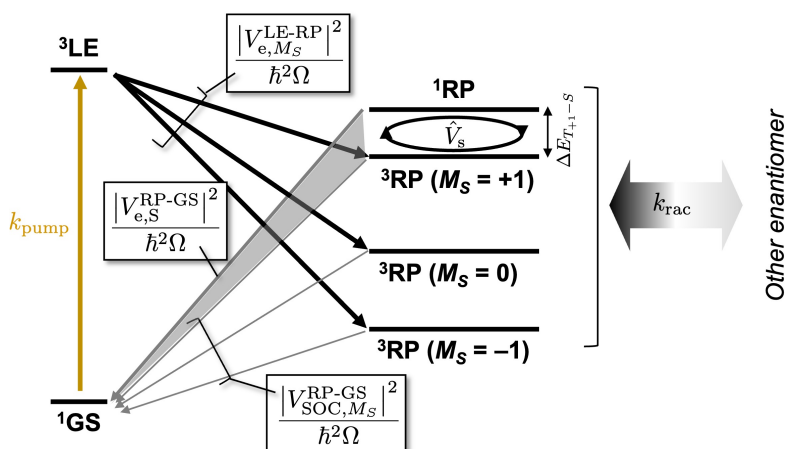


Figure 5.3. Summary of the excited-state kinetics and their associated rates or operators.

matrix elements [14] (see footnote ²). Therefore, the interference effect can be chemically tuned by considering the symmetry of the photosensitiser [181].

Other chemical knobs include the RP singlet-triplet gap, characterised by J , and the triplet RP decay, characterised by $V_{\text{SOC},+1}^{\text{RP-GS}}$. Their effects on χ are sketched in Fig. 5.4b-c. In particular, as the RP singlet-triplet gap changes, the same maximum chiral resolution can be obtained at a different B_0 value. Also, perfect enantioseparation (i.e. 100% e.e.) can be achieved when $\pm V_{\text{SOC},+1}^{\text{RP-GS}}$ exactly equals $V_{\text{e,S}}^{\text{RP-GS}} \times [\langle {}^1\text{RP} | \hat{V}_s | {}^3\text{RP}; +1 \rangle / \Delta E_{T+1-S}]$, which corresponds to either Eq. (D.12) or Eq. (5.5) being zero. These observations will be crucial for future optimisations of the photosensitiser.

5.2.2 A molecular prototype

As a molecular prototype, we consider an axially chiral binaphthyl derivative NMI₂ adsorbed onto a B(C₂F₅)₃ photosensitiser [Fig. 5.5a] and compute their properties using DFT and time-dependent DFT (TDDFT) (see Supplementary Information S7, which cites

²For instance, the elements of the g -tensor may be approximated by second-order perturbation theory in the SOC to be [14]

$$g_{ab} = g_e \delta_{ab} + 2\lambda \sum_{\Psi'} \frac{\langle \Psi | \hat{L}_a | \Psi' \rangle \langle \Psi' | \hat{L}_b | \Psi \rangle}{E_{\Psi} - E_{\Psi'}}, \quad (5.11)$$

where g_e is the electron g -factor, λ is an effective SOC constant, $|\Psi\rangle$ is the orbital eigenstate under consideration with energy E_{Ψ} , $\{|\Psi'\rangle\}$ is the set of orbital eigenstates that is orthogonal to $|\Psi\rangle$ and has the energy spectrum $\{E_{\Psi'}\}$, and $\hat{L}_a$ is the a -th component of $\hat{\mathbf{L}}$, with the indices a and b running over all three-dimensional coordinates.

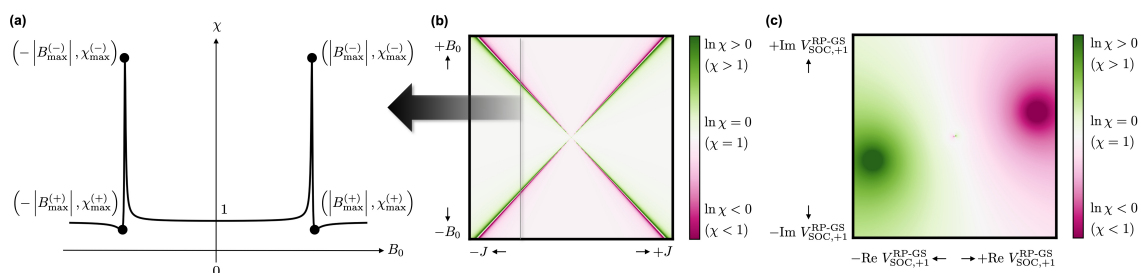


Figure 5.4. Schematic diagrams of the analytical solution to the chiral resolution χ [Eq. (5.6)] as a function of (a) the magnetic field strength, B_0 , (b) the RP singlet-triplet gap, parameterised by J , and (c) the real and imaginary parts of the SOC matrix element $V_{\text{SOC},+1}^{\text{RP-GS}}$ responsible for the triplet RP decay. In (c), the quantity $\ln \chi$ diverges (i.e. the e.e. reaches 100%) when $\pm V_{\text{SOC},+1}^{\text{RP-GS}} = V_{\text{e,S}}^{\text{RP-GS}} [\langle {}^1\text{RP} | \hat{V}_s | {}^3\text{RP}; +1 \rangle / \Delta E_{T+1-S}]$. This is represented by the two large dots.

Refs. [86, 87, 166]). By choosing an organic system, we may expect the singlet-triplet RP coherence to live longer than its recombination to the GS [91]. An analogue, $\text{B}(\text{C}_2\text{H}_5)_3$, was previously proposed as a triplet photosensitiser [214] and we introduced fluorine substituents to bring its LUMO energy closer to the HOMO energy of NMI_2 [Fig. 5.5b]. Indeed, the RP states form the lowest-lying singlet and triplet excited states [Fig. 5.5c]. As for the photosensitiser’s triplet LE, it appeared as the 33rd excited triplet state above other lower-lying triplet transitions [Fig. 5.5c]. We expect these additional transitions to provide a ladder of triplet intermediate states for the rapid relaxation of the triplet LE following Kasha’s rule [62, 180, 186].

After forming the RP, the NMI_2 radical cation has a lower activation barrier to racemisation (0.72 eV) than the neutral molecule (1.10 eV). Their racemisation timescales are, respectively, in the order of 10 ms and 1 day at room temperature, estimated using transition state theory at a mode frequency of 1000 cm^{-1} [169]. Chemically, the RP racemises faster because an electron has been removed from the NMI_2 HOMO, which has a nodal plane around the dimer linkage [Fig. 5.5d]. This creates a π -bond between the two aromatic subunits, thereby reducing the barrier to coplanarity in the transition state. For the same reason, the radical anion also has a lowered activation barrier of 0.64 eV – see Supplementary Information S7.

All other parameters fall within our expectations: We find $|V_{\text{SOC},M_S}^{\text{RP-GS}}|$ to be around

0.5 cm^{-1} [Fig. 5.5c], the ZFS parameters to be $D = -380\text{ MHz}$ and $E = -96\text{ MHz}$, and the radical g -anisotropy to be around 10^{-4} (Supplementary Information S7). If we approximate $J \approx -0.06\text{ cm}^{-1}$, $V_{e,S}^{\text{RP-GS}} \approx 100\text{ cm}^{-1}$, and $\Omega \approx 10^4\text{ cm}^{-1}$, values typical to organic systems [91, 68], then our analytical solution [Eq. (5.6)] predicts maximum chiral resolutions χ of 19 and 0.054 at magnetic field strengths $|B_0|$ of 0.126 T and 0.131 T respectively [Fig. 5.5e]; both values correspond to an e.e. of 90%. As mentioned earlier, a perfect enantioselectivity of 100% e.e. can be engineered by using a different photosensitiser, which would modify Δg_{eff} and $V_{\text{SOC},M_S}^{\text{RP-GS}}$.

For simplicity, we have not considered ZFS or hyperfine coupling effects yet. None of these are expected to impact the chiral resolution significantly – see the next section and Supplementary Information S3. We have also assumed a static molecular conformation and aligned the magnetic field perpendicularly to the $\text{B}(\text{C}_2\text{F}_5)_3$ plane. Nonetheless, we expect the chiral resolution to survive isotropic averaging given how the MFE is driven by g -anisotropy [Eq. (D.12)]. Future works will also include the diffusive motion of the two subsystems, which is known to create CIDEP in RP chemistry [7, 160, 23, 113, 245, 185, 250]. Under such conditions, effects due to g -anisotropy might be weakened due to rotational diffusion [14], an issue that can be tackled by trapping the photosensitiser on a surface or accelerating the RP decay through stronger SOC.

5.2.3 Further support using the Lindblad master equation

To investigate the full photoexcitation-decay kinetics, we consider the time evolution of the system density operator $\hat{\rho}(t)$, modelled by a Lindblad master equation:

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \sum_k \left(\hat{L}_k \hat{\rho} \hat{L}_k^\dagger - \frac{1}{2} \{ \hat{L}_k^\dagger \hat{L}_k, \hat{\rho} \} \right). \quad (5.12)$$

The first term describes the coherent oscillations under a Hamiltonian $\hat{H}$ that comprises the state energies and the spin Hamiltonian, while the second term describes the bath-mediated processes through the jump operators $\hat{L}_k$. These bath-mediated processes include the

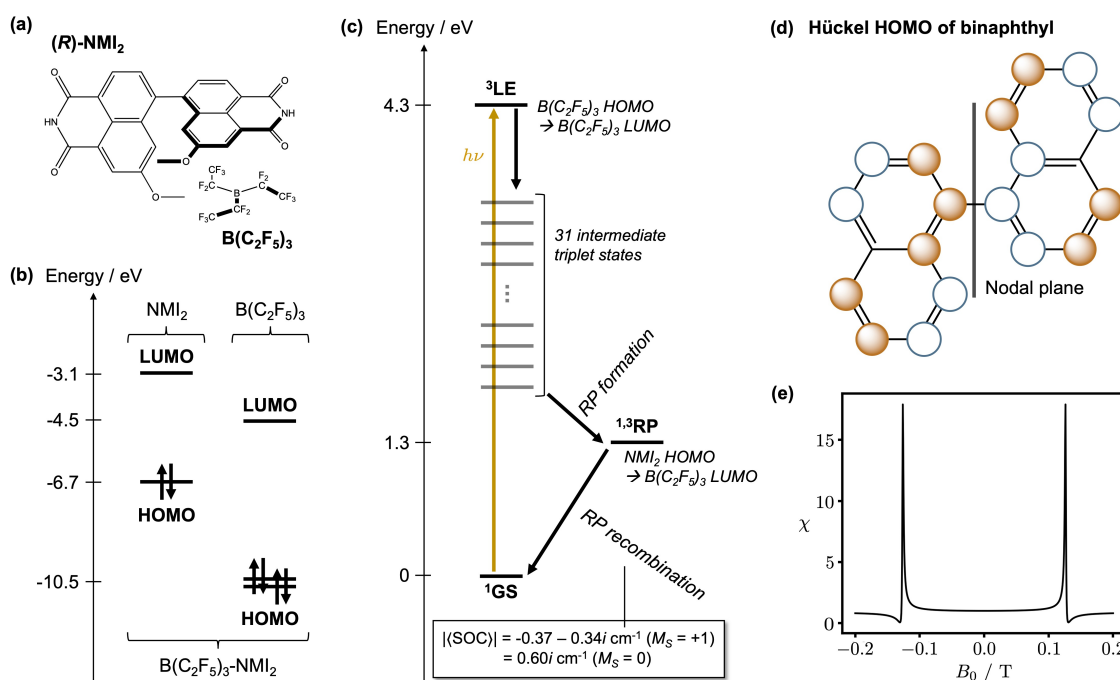


Figure 5.5. (a) Molecular structures of the model photosensitiser B(C₂F₅)₃ and the chiral molecule NMI₂. (b) Energies of the frontier MOs of B(C₂F₅)₃ and NMI₂, obtained using two separate DFT calculations (one for each fragment). (c) Excited-state electronic structure, calculated using TDDFT, along with our proposed excited-state relaxation pathway. Also indicated are $V_{\text{SOC},M_S}^{\text{RP-GS}}$, the SOC matrix elements between the lowest triplet state (i.e. the triplet RP state) and the ground singlet state. (d) Diagrammatic representation of the Hückel HOMO of binaphthyl, which mimicks the chiral molecule NMI₂. (e) Plot of the chiral resolution χ against the magnetic field strength B_0 , obtained using the analytical solution presented in Eq. (5.6).

triplet photoexcitation via $\hat{L}_{\text{pump}} = \sqrt{k_{\text{pump}}} \sum_{M_S=\pm 1} |^3\text{LE}; M_S\rangle \langle ^1\text{GS}|$ (see footnote ³), the RP formation via $\hat{L}_{\text{LE} \rightarrow \text{RP}, M_S} = V_{e, M_S}^{\text{LE-RP}} / \sqrt{\hbar^2 \Omega} \times |^3\text{RP}; M_S\rangle \langle ^3\text{LE}; M_S|$, and the collective RP decay via

$$\begin{aligned} \hat{L}_{\text{RP} \rightarrow \text{GS}} = & \frac{V_{e, S}^{\text{RP-GS}}}{\sqrt{\hbar^2 \Omega}} |^1\text{GS}\rangle \langle ^1\text{RP}| \\ & + \sum_{M_S=0, \pm 1} \frac{V_{\text{SOC}, M_S}^{\text{RP-GS}}}{\sqrt{\hbar^2 \Omega}} |^1\text{GS}\rangle \langle ^3\text{RP}; M_S|. \end{aligned} \quad (5.13)$$

Also, every state is duplicated to describe the two enantiomers, which are linked through the RP states via the jump operator $\hat{L}_{\text{rac}, m(X) \rightarrow m(X')} = \sqrt{k_{\text{rac}}} |m\rangle_{(X')} \langle m|_{(X)}$, where X and X' denote opposite enantiomers, and m is a RP state [Fig. 5.3]. As mentioned, metal-free RPs decay faster (at a timescale of microseconds) than their spins relax (milliseconds) [91]. Hence, for simplicity, there are no spin relaxation pathways in our model.

We simulated the steady-state outcome numerically using $V_{e, M_S}^{\text{LE-RP}} \approx 100 \text{ cm}^{-1}$, $k_{\text{pump}} \approx (1 \text{ s})^{-1}$ (i.e. a laser source), $k_{\text{rac}} \approx (10^{-2} \text{ s})^{-1}$, and other parameters as described before (Supplementary Information S4, which cites Ref. [110]). Table 5.1 summarises the actual parameters used in our QuTiP script [110]. Strikingly, without ZFS, the chiral resolution χ matches the analytical predictions made earlier (Fig. 5.6 versus Fig. 5.4), supporting our foregoing analysis. The enantioselectivity can also be perfected (i.e. the e.e. can also approach 100%) by tuning the photosensitiser structure, which would modify $V_{\text{SOC}, +1}^{\text{RP-GS}}$ [Fig. 5.6c]. No major difference was observed when k_{pump} was set as $(1 \text{ day})^{-1}$, corresponding to a mercury lamp source. We further develop a minimal three-level model comprising only the $|^1\text{GS}\rangle$, $|^1\text{RP}\rangle$, and $|^3\text{RP}; +1\rangle$ states (Supplementary Information S5), which led to consistent results [Fig. 5.6a]. Finally, even though the ZFS term introduces additional mixings among the triplet RP sublevels [14], these sublevels decay independently from one another under the magnetic field. Therefore, the impact of ZFS on the chiral resolution is small, as confirmed by our numerical simulations [Fig. 5.7].

³We have omitted the triplet $M_S = 0$ transition because it is symmetry-forbidden in our photosensitiser [214]. However, the general conclusion does not change even after including the $M_S = 0$ triplet photoexcitation.

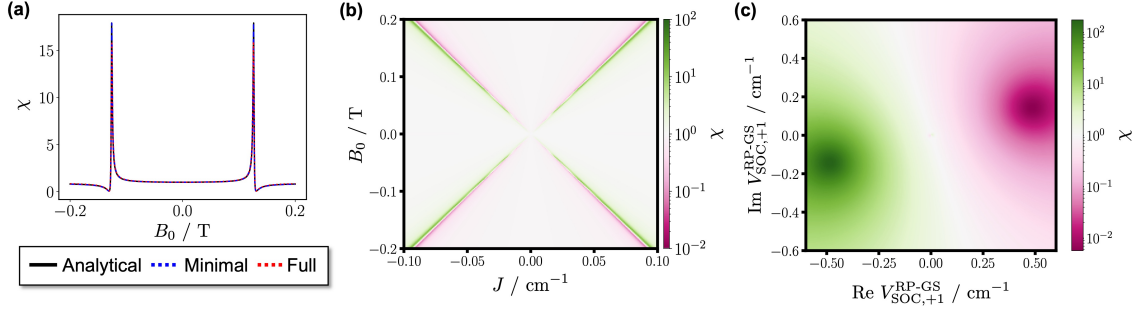


Figure 5.6. Numerical solution to the chiral resolution χ using the full Lindblad master equation, *neglecting* effects due to ZFS. The results are plotted across (a) the magnetic field strength, B_0 , (b) the RP singlet-triplet gap, parameterised by J , and (c) the SOC matrix element $V_{\text{SOC},+1}^{\text{RP-GS}}$ responsible for the triplet RP decay ($B_0 = 0.126$ T). In (c), the quantity χ approaches 187 (i.e. the e.e. reaches 99%) at the two large dots. Also presented in (a) are the results from the analytical [Eq. (5.6)] and minimal three-level models.

Table 5.1. Simulation parameters in units of cm^{-1} . The $\mathbf{g}$ and $\mathbf{D}$ tensors are available in Supplementary Information S7. The value of $V_{e,M_S}^{\text{LE-RP}}$ is the same for all three triplet M_S sublevels.

J	k_{pump}	$V_{e,M_S}^{\text{LE-RP}}$	$V_{\text{SOC},\pm 1}^{\text{RP-GS}}$	$V_{\text{SOC},0}^{\text{RP-GS}}$	$V_{e,S}^{\text{RP-GS}}$	Ω	k_{rac}
-0.06	10^{-11}	10^2	$-0.37 \mp 0.34i$	$0.60i$	10^2	10^4	10^{-9}

Note that the collective form of $\hat{L}_{\text{RP} \rightarrow \text{GS}}$ [Eq. (D.47)] is only fully justified if the four RP states have smaller energy separations (in frequency units) than their decay rates [26, 214, 249] (see footnote ⁴). When any two RP states become non-degenerate (relative to the decay rate), the collective effect is partly penalised by the large energy gap [36], although spurious interactions can still occur. This is particularly so in the $|B_0| \approx 0.01$ T regime of Fig. 5.7, where we find small additional peaks that vanish when the decay channels involving non-degenerate RP states are more properly modelled by different jump operators (Supplementary Information S4). To fully resolve this unphysical effect, we are currently working on a more systematic approach starting from a microscopic system-bath Hamiltonian.

⁴The justification stems from the Bloch-Redfield equation, which can be rigorously derived from a microscopic system-bath Hamiltonian. To obtain the Lindblad jump operator in Eq. (D.47), the non-secular Redfield terms responsible for the RP decay must be kept with their transition energies approximated to be equal – see Supplementary Information S4 and Ref. [36].

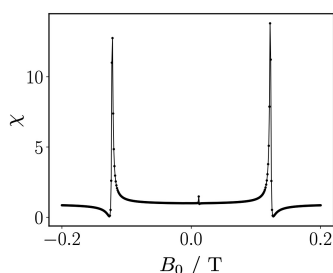


Figure 5.7. Chiral resolution χ at different magnetic field strengths B_0 as predicted by the full Lindblad master equation, *including* effects due to ZFS.

5.2.4 Estimated time to steady state

While this work focuses on the steady-state outcome, the time needed to achieve it is equally important. Under $k_{\text{pump}} \approx (1 \text{ s})^{-1}$ for a teaching laboratory laser source [251], enantioseparation occurs with a characteristic timescale of hundreds of milliseconds [Fig. 5.8] and is experimentally achievable. Unfortunately, the time evolution of the density operator $\hat{\rho}(t)$ could not be solved for a lower k_{pump} of $(1 \text{ day})^{-1}$, characteristic of a much lower intensity source such as a mercury lamp; this would be a more standard instrument in a synthetic chemistry laboratory. The underlying reason for this difficulty is the orders-of-magnitude differences in transition rates, resulting in an ill-conditioned rate constant matrix. As a preliminary solution, we consider a simplified kinetic scheme that assumes the stationary RP state in Eq. (5.3) to be formed prior to its recombination, which occurs within microseconds (Supplementary Information S6). This yields a timescale towards steady state of around 10^4 days. Despite being experimentally unfeasible, this timescale is most likely overestimated because, in reality, the singlet and triplet RP states are evolving over time as they decay to the GS, and the former decays faster with a sub-nanosecond timescale. In Supplementary Information S6, we explain how the time to steady state could potentially fall below one day once the full quantum master equations are considered, underscoring the limitation of our simple kinetic analysis. Work towards a more accurate quantum dynamics simulation is ongoing. Finally, we note that hyperfine coupling effects could prolong the time to steady state, although the new timescale remains experimentally

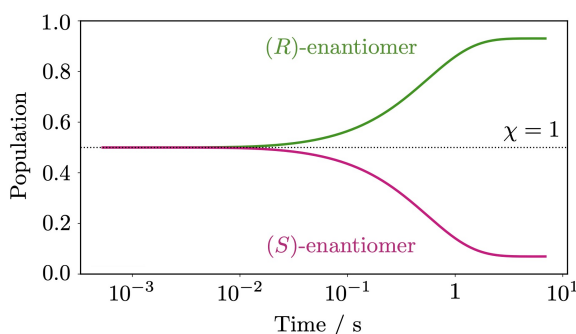


Figure 5.8. Time evolution of the enantiomer populations, defined as the trace of the density operator $\hat{\rho}(t)$ over the corresponding enantiomer subspace. These results are evaluated at $B_0 = 0.126$ T and $k_{\text{pump}} \approx (1 \text{ s})^{-1}$ (i.e. a laser source).

realistic; see Supplementary Information S6 for a full discussion.

5.2.5 Protocol requirements

To summarise the requirements for our enantiopurification scheme, the criteria strictly necessary are as follows: (1) The RP states must be the lowest-lying excited states of the system, achieved by keeping the electron donor's HOMO at an energy close to the electron acceptor's LUMO. In experimental terms, this means that the donor's reduction potential should be close to the acceptor's reduction potential. (2) Chirality inversion in the RP states should occur with an appreciable rate relative to triplet excitation of the photosensitiser. In particular, relative to the present rates of around $(10 \text{ ms})^{-1}$ and 1 s^{-1} , respectively, used in Fig. 5.8 and Table 5.1, any decrease in the former will require a proportionate increase in the latter to sustain the same enantiopurification timescale. Next, the following features are not necessary but would improve the chiral resolution: (3) A photosensitiser embedded on a surface, which would minimise deleterious effects due to rotational averaging and RP diffusion while allowing for targeted excitation of the photosensitiser over the chiral molecule. (4) A non-metallic photosensitiser, which would minimise loss of spin coherence, although this could be countered by a faster RP recombination rate achieved via stronger SOC from the metal.

5.3 Conclusion

Decades after establishing the link between mirror symmetry and TRS [21, 226, 24, 189], the magnetic field remains underutilised as a tool for chiral discrimination [33, 163, 146, 190]. Our proposal offers a key step in this direction by leveraging on the well-established MFE in photogenerated RPs, which induces a collective decay to the ground state. Because the enantioselectivity relies on the SOC matrix elements, it can be chemically controlled through symmetry considerations of the photosensitiser [181]. In essence, our work exploits underexplored spin chemistry concepts to tackle the enantioselectivity problem critical in photoredox catalysis [193, 80, 39]. Given its generality and tunability, we expect this photoredox catalysis protocol to offer a novel concept for enantioseparation technology. Concurrently, we hope that this work will inspire other powerful ideas involving the use of spin dynamics to achieve unprecedented synthetic goals. In our future works, we will explore the consequence of isotropic averaging and the enantioseparation kinetics, such as the role of RP diffusion in enhancing the spin polarisation [7, 160, 23, 113, 245, 185, 250]. We will also devote much effort towards designing catalysts that can achieve the desired enantiopurification using the aforesaid low-intensity light sources, but within much shorter illumination times.

5.4 Author contributions

Y.R.P. conceptualised the project, developed the analytical solutions, and performed the ab initio calculations. A.K. and Y.R.P. developed the full Lindblad master equation model. M.R. developed the minimal three-level Lindblad model. J.Y.-Z. supervised the project and checked for consistency throughout the calculations. All authors contributed to the experimental implications of the model and the writing and editing of this manuscript.

Acknowledgments

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Field Effects: A Scheme for Chiral Resolution" published in *J. Am. Chem. Soc.* 2025, 147, 40, 36579–36588. Copyright 2025 American Chemical Society. The dissertation author was the primary investigator, co-first author, and corresponding author of this paper. He conceptualised the project, developed the analytical solutions and full Lindblad master equation model, performed the ab initio calculations, and co-wrote the manuscript.

Chapter 6

Concluding Remarks

I started this Dissertation with the motivation of first contributing to *Physics* through my *Chemistry* background, and then giving back to *Chemistry* using my newfound *Physics* knowledge. The first goal was achieved through the design of organic high-spin molecular qubits, which promise to have the versatility of molecules through the vastness of chemical space, yet retain the robustness of electron spins for applications in quantum information science. This was accompanied by many experimental studies that validated the key components of my proposal [126, 127, 192]. The second goal was set in the context of dynamic kinetic resolution, a form of chemical transformation that funnels a racemic mixture of molecules into a particular enantiomeric form. There, chirality was successfully imprinted by the magnetic field with the help of photogenerated radical pairs – the first of its kind – and experimental studies are currently ongoing.

I emphasise that both avenues of using organic diradicals for quantum technological applications have much room for improvements. In the first, better designs can be proposed through large-scale molecular screening, potentially assisted by machine learning. An improved kinetic model, derived first-principles and complete with *ab initio* transition rates, will also offer new design principles. Finally, further optimisation of other qubit properties, such as the spin coherence times, may be accomplished through accurate models of the environment's influence on the electron spins. In the second, future developments of the quantum dynamical model will shed light on other dynamic kinetic resolution schemes suitable for a broader class of electronic structures. This, coupled with further

structural optimisation, could bring the proposal closer to experimental implementations. The influence of spin magnetic field effects on other aspects of chemical reactivity may also be explored.

It is with this foresight that I have decided to name this chapter "Concluding Remarks", rather than "Conclusion": It is my hope, and my ambition, that this Dissertation will be a continuation, rather than the end, of the electron spin's influence in *Physical Chemistry*.

Appendix A

Supporting Information of Chapter 2: Alternant Hydrocarbon Diradicals as Optically Addressable Molecular Qubits

A.1 Definitions of particle-hole transformation

We find Pariser’s “+” and “−” labels [174, 95] to be identical to symmetries of an operator $\hat{P}_C$ with the following action on “ordered” determinants $|\cdots\rangle_O$:

$$\hat{P}_C |\cdots (j+1) \overline{(j+1)} j\rangle_O = - |\cdots 0\bar{0} \cdots (j-1)' \overline{(j-1)'} j'\rangle_O, \quad (\text{A.1})$$

where “ordered” determinants are those written with increasing spin orbital indices¹. As an example,

$$\hat{P}_C |\Psi_{\bar{j}}^{\bar{0}}; +1/2\rangle = -\hat{P}_C |\cdots j \cdots 0\bar{0}\rangle = |\cdots 1\bar{1} j'\rangle = |\Psi_0^{j'}; +1/2\rangle, \quad (\text{A.2})$$

and indeed $\hat{P}_C |\Psi_{0j}^{\pm}; +1/2\rangle = \pm |\Psi_{0j}^{\pm}; +1/2\rangle$. Meanwhile, the PHT $\hat{a}_{\mu\sigma}^{\dagger} \rightarrow f_{\mu} \hat{a}_{\mu\bar{\sigma}}$ is equivalent to $\hat{b}_{j,\sigma}^{\dagger} \rightarrow \hat{b}_{j',\bar{\sigma}}$ in the MO basis because $c_{\mu j_r} = f_{\mu} c_{\mu j'_r}$ from the pairing theorem. Therefore, the two transformations achieve the same effect of converting occupied MOs into virtual ones. We note that the two definitions may sometimes return opposite symmetry

¹I.e. with ascending MO indices and, for doubly-occupied MOs, placing α -spin before β -spin. For instance, $|\cdots 100\rangle$ and $|\cdots 100\rangle$ are “ordered”, but not $|\cdots 010\rangle$ and $|\cdots 100\rangle$.

labels; for instance, $|\Psi_{0j}^+; +1/2\rangle$ is even (“+”) in the first and odd in the second. However, because both definitions assign unique symmetries to each electronic state, they make the same predictions and are equivalent for our purposes, differing only in the notation.

A.2 Expressions for the ground and lowest-lying excited electronic states

Here, we list the expressions for the ground and lowest-lying singly-excited electronic states.

A.2.1 Ground states

$$|{}^1\text{GS}; 0\rangle \equiv \frac{1}{\sqrt{2}} (|\Psi; +1/2\rangle_A \otimes |\Psi; -1/2\rangle_B - |\Psi; -1/2\rangle_A \otimes |\Psi; +1/2\rangle_B), \quad (\text{A.3})$$

$$|{}^3\text{GS}; -1\rangle \equiv |\Psi; -1/2\rangle_A \otimes |\Psi; -1/2\rangle_B, \quad (\text{A.4})$$

$$|{}^3\text{GS}; 0\rangle \equiv \frac{1}{\sqrt{2}} (|\Psi; +1/2\rangle_A \otimes |\Psi; -1/2\rangle_B + |\Psi; -1/2\rangle_A \otimes |\Psi; +1/2\rangle_B), \quad (\text{A.5})$$

$$|{}^3\text{GS}; +1\rangle \equiv |\Psi; +1/2\rangle_A \otimes |\Psi; +1/2\rangle_B, \quad (\text{A.6})$$

where subscripts label the monomer index $r \in \{A, B\}$ and $|\cdots j\bar{j}\rangle_A \otimes |\cdots k\bar{k}\rangle_B$ is to be interpreted as $|\cdots j_A \bar{j}_A \cdots k_B \bar{k}_B\rangle$.

A.2.2 Local excitations

$$S = 1, M_S = +1:$$

$$|{}^3\text{LE}_A^{10, \pm}; +1\rangle \equiv \frac{1}{\sqrt{2}} (|\Psi_{01}^{\pm}; +1/2\rangle_A \otimes |\Psi; +1/2\rangle_B - |\Psi; +1/2\rangle_A \otimes |\Psi_{01}^{\pm}; +1/2\rangle_B), \quad (\text{A.7})$$

$$|{}^3\text{LE}_B^{10, \pm}; +1\rangle \equiv \frac{1}{\sqrt{2}} (|\Psi_{01}^{\pm}; +1/2\rangle_A \otimes |\Psi; +1/2\rangle_B + |\Psi; +1/2\rangle_A \otimes |\Psi_{01}^{\pm}; +1/2\rangle_B). \quad (\text{A.8})$$

$S = 1, M_S = -1$:

$$\left| {}^3\text{LE}_A^{10,\pm}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| \Psi_{01}^{\pm}; -1/2 \right\rangle_A \otimes \left| \Psi; -1/2 \right\rangle_B - \left| \Psi; -1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_B \right), \quad (\text{A.9})$$

$$\left| {}^3\text{LE}_B^{10,\pm}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| \Psi_{01}^{\pm}; -1/2 \right\rangle_A \otimes \left| \Psi; -1/2 \right\rangle_B + \left| \Psi; -1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_B \right). \quad (\text{A.10})$$

$S = 1, M_S = 0$:

$$\left| {}^3\text{LE}_A^{10,\pm}; 0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\frac{\left| \Psi_{01}^{\pm}; +1/2 \right\rangle_A \otimes \left| \Psi; -1/2 \right\rangle_B + \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_A \otimes \left| \Psi; +1/2 \right\rangle_B}{\sqrt{2}} - \frac{\left| \Psi; +1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_B + \left| \Psi; -1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; +1/2 \right\rangle_B}{\sqrt{2}} \right), \quad (\text{A.11})$$

$$\left| {}^3\text{LE}_B^{10,\pm}; 0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\frac{\left| \Psi_{01}^{\pm}; +1/2 \right\rangle_A \otimes \left| \Psi; -1/2 \right\rangle_B + \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_A \otimes \left| \Psi; +1/2 \right\rangle_B}{\sqrt{2}} + \frac{\left| \Psi; +1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_B + \left| \Psi; -1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; +1/2 \right\rangle_B}{\sqrt{2}} \right). \quad (\text{A.12})$$

$S = 0, M_S = 0$:

$$\left| {}^1\text{LE}_A^{10,\pm}; 0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\frac{\left| \Psi_{01}^{\pm}; +1/2 \right\rangle_A \otimes \left| \Psi; -1/2 \right\rangle_B - \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_A \otimes \left| \Psi; +1/2 \right\rangle_B}{\sqrt{2}} + \frac{\left| \Psi; +1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_B - \left| \Psi; -1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; +1/2 \right\rangle_B}{\sqrt{2}} \right), \quad (\text{A.13})$$

$$\left| {}^1\text{LE}_B^{10,\pm}; 0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\frac{\left| \Psi_{01}^{\pm}; +1/2 \right\rangle_A \otimes \left| \Psi; -1/2 \right\rangle_B - \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_A \otimes \left| \Psi; +1/2 \right\rangle_B}{\sqrt{2}} - \frac{\left| \Psi; +1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; -1/2 \right\rangle_B - \left| \Psi; -1/2 \right\rangle_A \otimes \left| \Psi_{01}^{\pm}; +1/2 \right\rangle_B}{\sqrt{2}} \right). \quad (\text{A.14})$$

A.2.3 Charge transfer states

$S = 1, M_S = 1$:

$$\left| {}^3\text{CT}_A^{10,\pm}; +1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{CT}_A^{10}; +1 \right\rangle \pm \left| {}^3\text{CT}_A^{01'}; +1 \right\rangle \right), \quad (\text{A.15})$$

$$\left| {}^3\text{CT}_B^{10,\pm}; +1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{CT}_B^{10}; +1 \right\rangle \mp \left| {}^3\text{CT}_B^{01'}; +1 \right\rangle \right), \quad (\text{A.16})$$

where

$$\left| {}^3\text{CT}_A^{10}; +1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{1A}^{\overline{0B}}; +1 \right\rangle - \left| {}^3\text{GS}_{1B}^{\overline{0A}}; +1 \right\rangle \right), \quad (\text{A.17})$$

$$\left| {}^3\text{CT}_B^{10}; +1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{1A}^{\overline{0B}}; +1 \right\rangle + \left| {}^3\text{GS}_{1B}^{\overline{0A}}; +1 \right\rangle \right), \quad (\text{A.18})$$

$$\left| {}^3\text{CT}_A^{01'}; +1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{0A}^{1'B}; +1 \right\rangle - \left| {}^3\text{GS}_{0B}^{1'A}; +1 \right\rangle \right), \quad (\text{A.19})$$

$$\left| {}^3\text{CT}_B^{01'}; +1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{0A}^{1'B}; +1 \right\rangle + \left| {}^3\text{GS}_{0B}^{1'A}; +1 \right\rangle \right). \quad (\text{A.20})$$

$S = 1, M_S = -1$:

$$\left| {}^3\text{CT}_A^{10,\pm}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{CT}_A^{10}; -1 \right\rangle \pm \left| {}^3\text{CT}_A^{01'}; -1 \right\rangle \right), \quad (\text{A.21})$$

$$\left| {}^3\text{CT}_B^{10,\pm}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{CT}_B^{10}; -1 \right\rangle \mp \left| {}^3\text{CT}_B^{01'}; -1 \right\rangle \right), \quad (\text{A.22})$$

where

$$\left| {}^3\text{CT}_A^{10}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{1A}^{0B}; -1 \right\rangle - \left| {}^3\text{GS}_{1B}^{0A}; -1 \right\rangle \right), \quad (\text{A.23})$$

$$\left| {}^3\text{CT}_B^{10}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{1A}^{0B}; -1 \right\rangle + \left| {}^3\text{GS}_{1B}^{0A}; -1 \right\rangle \right), \quad (\text{A.24})$$

$$\left| {}^3\text{CT}_A^{01'}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{0A}^{\overline{1'B}}; -1 \right\rangle - \left| {}^3\text{GS}_{0B}^{\overline{1'A}}; -1 \right\rangle \right), \quad (\text{A.25})$$

$$\left| {}^3\text{CT}_B^{01'}; -1 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{0A}^{\overline{1'B}}; -1 \right\rangle + \left| {}^3\text{GS}_{0B}^{\overline{1'A}}; -1 \right\rangle \right). \quad (\text{A.26})$$

$S = 1, M_S = 0$:

$$\left| {}^3\text{CT}_A^{10,\pm};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{CT}_A^{10};0 \right\rangle \pm \left| {}^3\text{CT}_A^{01'};0 \right\rangle \right), \quad (\text{A.27})$$

$$\left| {}^3\text{CT}_B^{10,\pm};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{CT}_B^{10};0 \right\rangle \mp \left| {}^3\text{CT}_B^{01'};0 \right\rangle \right), \quad (\text{A.28})$$

where

$$\left| {}^3\text{CT}_A^{10};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{1_A}^{0_B};0 \right\rangle - \left| {}^3\text{GS}_{1_B}^{\overline{0}_A};0 \right\rangle \right), \quad (\text{A.29})$$

$$\left| {}^3\text{CT}_B^{10};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{1_A}^{0_B};0 \right\rangle + \left| {}^3\text{GS}_{1_B}^{\overline{0}_A};0 \right\rangle \right), \quad (\text{A.30})$$

$$\left| {}^3\text{CT}_A^{01'};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{0_A}^{1'_B};0 \right\rangle - \left| {}^3\text{GS}_{0_B}^{\overline{1}'_A};0 \right\rangle \right), \quad (\text{A.31})$$

$$\left| {}^3\text{CT}_B^{01'};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^3\text{GS}_{0_A}^{1'_B};0 \right\rangle + \left| {}^3\text{GS}_{0_B}^{\overline{1}'_A};0 \right\rangle \right), \quad (\text{A.32})$$

and $\left| {}^3\text{GS}_{1_A}^{0_B};0 \right\rangle$ is to be interpreted as $1_A \rightarrow 0_B$ of the first term and $\overline{1}_A \rightarrow \overline{0}_B$ of the second term in $\left| {}^3\text{GS};0 \right\rangle$, i.e. the label corresponds to the excitation of the first term in $\left| {}^3\text{GS};0 \right\rangle$.

$S = 0, M_S = 0$:

$$\left| {}^1\text{CT}_A^{10,\pm};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^1\text{CT}_A^{10};0 \right\rangle \mp \left| {}^1\text{CT}_A^{01'};0 \right\rangle \right), \quad (\text{A.33})$$

$$\left| {}^1\text{CT}_B^{10,\pm};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^1\text{CT}_B^{10};0 \right\rangle \pm \left| {}^1\text{CT}_B^{01'};0 \right\rangle \right), \quad (\text{A.34})$$

$$\left| {}^1\text{CT}_A^{00,-};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^1\text{GS}_{0_A}^{0_B};0 \right\rangle + \left| {}^1\text{GS}_{0_B}^{\overline{0}_A};0 \right\rangle \right), \quad (\text{A.35})$$

$$\left| {}^1\text{CT}_B^{00,+};0 \right\rangle \equiv \frac{1}{\sqrt{2}} \left(\left| {}^1\text{GS}_{0_A}^{0_B};0 \right\rangle - \left| {}^1\text{GS}_{0_B}^{\overline{0}_A};0 \right\rangle \right), \quad (\text{A.36})$$

where

$$|{}^1\text{CT}_A^{10}; 0\rangle \equiv \frac{1}{\sqrt{2}} \left(|{}^1\text{GS}_{1_A}^{0_B}; 0\rangle + |{}^1\text{GS}_{1_B}^{\overline{0}_A}; 0\rangle \right), \quad (\text{A.37})$$

$$|{}^1\text{CT}_B^{10}; 0\rangle \equiv \frac{1}{\sqrt{2}} \left(|{}^1\text{GS}_{1_A}^{0_B}; 0\rangle - |{}^1\text{GS}_{1_B}^{\overline{0}_A}; 0\rangle \right), \quad (\text{A.38})$$

$$|{}^1\text{CT}_A^{01'}; 0\rangle \equiv \frac{1}{\sqrt{2}} \left(|{}^1\text{GS}_{0_A}^{1'_B}; 0\rangle + |{}^1\text{GS}_{0_B}^{\overline{1}'_A}; 0\rangle \right), \quad (\text{A.39})$$

$$|{}^1\text{CT}_B^{01'}; 0\rangle \equiv \frac{1}{\sqrt{2}} \left(|{}^1\text{GS}_{0_A}^{1'_B}; 0\rangle - |{}^1\text{GS}_{0_B}^{\overline{1}'_A}; 0\rangle \right), \quad (\text{A.40})$$

and $|{}^1\text{GS}_{1_A}^{0_B}; 0\rangle$ is to be interpreted as $1_A \rightarrow 0_B$ of the first term and $\overline{1}_A \rightarrow \overline{0}_B$ of the second term in $|{}^1\text{GS}; 0\rangle$, i.e. the label corresponds to the excitation of the first term in $|{}^1\text{GS}; 0\rangle$.

A.3 Perturbation theory results

Table A.1. Properties of ground and low-lying excited electronic states of AHR m -dimers, presented approximately in increasing order of zeroth-order energies. Definitions: ε_j = energy of monoradical's j -th MO; $J_{jk} = (jj|kk)$ and $K_{jk} = (jk|kj)$ in chemists' notation [213]; $c_{\mathcal{A}1} = (c_{\mathcal{B}1} =)$ coefficient of the AO at the dimer linkage to the HOMO–1 of monomer A (B), assumed to be real-valued; $\{|\Phi_j\rangle|j\}$ = set containing states $|\Phi_j\rangle$ of all possible values j .

State	Energy
$\{ ^{2S+1}\text{GS}; M_S \rangle S, M_S \}$	0
$ ^1\text{CT}_{\text{A}}^{00,-}; 0\rangle; ^1\text{CT}_{\text{B}}^{00,+}; 0\rangle$	J_{00}
$\{ ^{2S+1}\text{LE}_{\Gamma}^{10,-}; M_S \rangle S, M_S, \Gamma \}$	$E(\text{LE}^-) \equiv (\varepsilon_0 - \varepsilon_1)$ $-J_{10} + \frac{1}{2}J_{00} - \frac{1}{2}K_{10}$
$\{ ^3\text{CT}_{\Gamma}^{10,P}; M_S \rangle M_S, P, \Gamma \}$	$E(\text{LE}^-) + J_{10}$
$\{ ^{2S+1}\text{LE}_{\Gamma}^{10,+}; M_S \rangle S, M_S, \Gamma \}$	$E(\text{LE}^-) + 2K_{10}$
$\{ ^1\text{CT}_{\Gamma}^{10,P}; 0 \rangle P, \Gamma \}$	$E(\text{LE}^-) + J_{10} + 2K_{10}$

Table A.1. Properties of ground and low-lying excited electronic states of AHR m -dimers, presented approximately in increasing order of zeroth-order energies, Continued.

Corrected state to $\mathcal{O}(V_{\text{NN}})$
$\{ ^{2S+1}\text{GS}; M_S\rangle S, M_S\rangle\}$
$ ^1\text{CT}_\text{A}^{00,-}; 0\rangle; ^1\text{CT}_\text{B}^{00,+}; 0\rangle$
$\left\{ ^3\text{LE}_\text{A}^{10,-}; M_S\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^3\text{CT}_\text{A}^{10,-}; M_S\rangle \right\}$
$\left\{ ^3\text{LE}_\text{B}^{10,-}; M_S\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^3\text{CT}_\text{B}^{10,-}; M_S\rangle \right\}$
$ ^1\text{LE}_\text{A}^{10,-}; 0\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}+2K_{10}} ^1\text{CT}_\text{A}^{10,-}; 0\rangle$
$ ^1\text{LE}_\text{B}^{10,-}; 0\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}+2K_{10}} ^1\text{CT}_\text{B}^{10,-}; 0\rangle$
$\left\{ ^3\text{CT}_\text{A}^{10,+}; M_S\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}-2K_{10}} ^3\text{LE}_\text{A}^{10,+}; M_S\rangle M_S\rangle \right\}$
$\left\{ ^3\text{CT}_\text{B}^{10,+}; M_S\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}-2K_{10}} ^3\text{LE}_\text{B}^{10,+}; M_S\rangle M_S\rangle \right\}$
$\left\{ ^3\text{CT}_\text{A}^{10,-}; M_S\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^3\text{LE}_\text{A}^{10,-}; M_S\rangle M_S\rangle \right\}$
$\left\{ ^3\text{CT}_\text{B}^{10,-}; M_S\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^3\text{LE}_\text{B}^{10,-}; M_S\rangle M_S\rangle \right\}$
$\left\{ ^3\text{LE}_\text{A}^{10,+}; M_S\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}-2K_{10}} ^3\text{CT}_\text{A}^{10,+}; M_S\rangle M_S\rangle \right\}$
$\left\{ ^3\text{LE}_\text{B}^{10,+}; M_S\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}-2K_{10}} ^3\text{CT}_\text{B}^{10,+}; M_S\rangle M_S\rangle \right\}$
$ ^1\text{LE}_\text{A}^{10,+}; 0\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^1\text{CT}_\text{A}^{10,+}; 0\rangle$
$ ^1\text{LE}_\text{B}^{10,+}; 0\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^1\text{CT}_\text{B}^{10,+}; 0\rangle$
$ ^1\text{CT}_\text{A}^{10,-}; 0\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}+2K_{10}} ^1\text{LE}_\text{A}^{10,-}; 0\rangle$
$ ^1\text{CT}_\text{B}^{10,-}; 0\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}+2K_{10}} ^1\text{LE}_\text{B}^{10,-}; 0\rangle$
$ ^1\text{CT}_\text{A}^{10,+}; 0\rangle + \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^1\text{LE}_\text{A}^{10,+}; 0\rangle$
$ ^1\text{CT}_\text{B}^{10,+}; 0\rangle - \frac{c_{\mathcal{A}}c_{\mathcal{B}}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} ^1\text{LE}_\text{B}^{10,+}; 0\rangle$

Table A.1. Properties of ground and low-lying excited electronic states of AHR m -dimers, presented approximately in increasing order of zeroth-order energies, Continued.

Corrected energy to $\mathcal{O}(V_{\text{NN}}^2)$	Transition dipole moment
$\gamma_{\mathcal{A}\mathcal{B}}$	–
$J_{00} + \gamma_{\mathcal{A}\mathcal{B}}$	0
$(1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} - \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}}$	0
$(1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} - \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}+2K_{10}}$	
$E(\text{LE}^-) + J_{10} + (1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} + \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}-2K_{10}}$	$\left\{ \langle {}^3\text{GS}; M_S \boldsymbol{\mu} {}^3\text{LE}_A^{10,+}; M_S \rangle \times \left(-\frac{c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}-2K_{10}} \right) M_S \rangle \right\}$
	$\left\{ \langle {}^3\text{GS}; M_S \boldsymbol{\mu} {}^3\text{LE}_B^{10,+}; M_S \rangle \times \left(\frac{c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}-2K_{10}} \right) M_S \rangle \right\}$
$E(\text{LE}^-) + J_{10} + (1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} + \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}}$	0
$E(\text{LE}^-) + 2K_{10} + (1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} - \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}-2K_{10}}$	$\left\{ \langle {}^{2S+1}\text{GS}; M_S \boldsymbol{\mu} {}^{2S+1}\text{LE}_\Gamma^{10,+}; M_S \rangle \right\}$
$E(\text{LE}^-) + 2K_{10} + (1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} - \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}}$	$ S, M_S, \Gamma\rangle$
$E(\text{LE}^-) + J_{10} + 2K_{10} + (1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} + \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}+2K_{10}}$	0
$E(\text{LE}^-) + J_{10} + 2K_{10} + (1 + c_{\mathcal{A}1}c_{\mathcal{A}1})\gamma_{\mathcal{A}\mathcal{B}} + \frac{(c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}})^2}{J_{10}}$	$\frac{c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} \langle {}^1\text{GS}; 0 \boldsymbol{\mu} {}^1\text{LE}_A^{10,+}; 0 \rangle$
	$-\frac{c_{\mathcal{A}1}c_{\mathcal{B}1}\beta_{\mathcal{A}\mathcal{B}}}{J_{10}} \langle {}^1\text{GS}; 0 \boldsymbol{\mu} {}^1\text{LE}_B^{10,+}; 0 \rangle$

A.4 Deriving the SOC operator for AHR m -dimers

Our derivation of the SOC operator for the PPP model closely follows that of Barford et al. [22]. We begin with the following effective one-electron Breit-Pauli Hamiltonian (in atomic units):

$$\hat{V}_{\text{SOC}} = \frac{1}{2c^2} \sum_j \sum_{\mu} \frac{Z_{\mu}^{\text{eff}}}{\hat{r}_{j\mu}^3} \hat{\mathbf{l}}_j^{(\mu)} \cdot \hat{\mathbf{s}}_j, \quad (\text{A.41})$$

where the indices j and μ are summed over all electrons and nuclei respectively. Here, $\hat{\mathbf{l}}_j^{(\mu)}$ is the orbital angular momentum of electron j with respect to nucleus μ , separated by a distance $\hat{r}_{j\mu}$, and $\hat{\mathbf{s}}_j$ is the corresponding spin angular momentum. Also, Z_{μ}^{eff} is the effective nuclear charge of atom μ including screening effects by the two-electron Breit-Pauli terms and c is the speed of light in vacuum. Within the minimal basis of $2p$ AOs being considered by the PPP formalism, we may restrict ourselves to the computation of the following matrix elements:

$$\left\langle 2p_{z'}^{(\mu')}; \sigma' \right| \frac{1}{2c^2} \sum_{\mu''} \frac{Z_{\mu''}^{\text{eff}}}{\hat{r}_{\mu''}^3} \hat{\mathbf{l}}^{(\mu'')} \cdot \hat{\mathbf{s}} \left| 2p_z^{(\mu)}; \sigma \right\rangle, \quad (\text{A.42})$$

where, in considering a specific electron j , we have omitted the electron index. The state $\left| 2p_z^{(\mu)}; \sigma \right\rangle$ denotes a spin- σ electron occupying the $2p_z$ AO of atom μ , with z representing the orbital quantisation axis local to atom μ . Due to the $1/r^3$ scaling, we assume the above integral to be zero unless μ and μ' represent the same or nearest-neighbour atom(s) and also assume the sum over μ'' to be dominated by terms of $\mu'' \in \{\mu, \mu'\}$. Thus, the above integral vanishes when $\mu = \mu'$ (by evaluating its value explicitly) and the only matrix element we require is

$$A_{\mu\mu'} \equiv \left\langle 2p_{z'}^{(\mu')}; \sigma' \right| \frac{1}{c^2} \frac{Z_{\mu}^{\text{eff}}}{\hat{r}_{\mu}^3} \hat{\mathbf{l}}^{(\mu)} \cdot \hat{\mathbf{s}} \left| 2p_z^{(\mu)}; \sigma \right\rangle, \quad (\text{A.43})$$

with atoms μ and μ' being nearest-neighbours, such that

$$\left\langle 2p_{z'}^{(\mu')}; \sigma' \right| \frac{1}{2c^2} \sum_{\mu''} \frac{Z_{\mu''}^{\text{eff}}}{\hat{r}_{\mu''}^3} \hat{\mathbf{I}}^{(\mu'')} \cdot \hat{\mathbf{s}} \left| 2p_z^{(\mu)}; \sigma \right\rangle \approx \frac{A_{\mu\mu'}}{2} + \frac{A_{\mu'\mu}^*}{2}, \quad (\text{A.44})$$

where we have noted that $\hat{\mathbf{I}}^{(\mu)} \cdot \hat{\mathbf{s}} / \hat{r}_{\mu}^3$ is Hermitian. In general, the z -axis of atom μ may not coincide with the z' -axis of atom μ' , instead having a component parallel to the y' -axis of atom μ' (if we align both x - and x' -axes to the vector connecting atom μ to atom μ'). Therefore, for convenience, we rotate the coordinate system of atom μ so that the two atoms have parallel Cartesian axes. This is done by observing elements of the 3D rotation matrix for the x -axis and substituting

$$\left| 2p_z^{(\mu)}; \sigma \right\rangle = -\sin \theta_{\mu\mu'} \left| 2p_{y'}^{(\mu)}; \sigma \right\rangle + \cos \theta_{\mu\mu'} \left| 2p_{z'}^{(\mu)}; \sigma \right\rangle, \quad (\text{A.45})$$

where $\theta_{\mu\mu'}$ is the clockwise angle that the z' -axis makes relative to the z -axis. We also align the z' -axis to the spin axis so that we may easily evaluate the action of the components of $\hat{\mathbf{s}}$ on the spin orbitals. Because we expect the spin quantisation axis to be perpendicular to the x -axis (parallel to the dimer C_2 axis), we again use elements of the 3D rotation matrix for the x -axis and make the following substitutions:

$$\left| 2p_{y'}^{(\mu)}; \sigma \right\rangle = \cos \varphi \left| 2p_{y''}^{(\mu)}; \sigma \right\rangle + \sin \varphi \left| 2p_{z''}^{(\mu)}; \sigma \right\rangle, \quad (\text{A.46})$$

$$\left| 2p_{z'}^{(\mu)}; \sigma \right\rangle = -\sin \varphi \left| 2p_{y''}^{(\mu)}; \sigma \right\rangle + \cos \varphi \left| 2p_{z''}^{(\mu)}; \sigma \right\rangle, \quad (\text{A.47})$$

$$\left| 2p_{z'}^{(\mu')}; \sigma' \right\rangle = -\sin \varphi \left| 2p_{y''}^{(\mu')}; \sigma' \right\rangle + \cos \varphi \left| 2p_{z''}^{(\mu')}; \sigma' \right\rangle, \quad (\text{A.48})$$

with z'' representing the spin quantisation axis and φ being the clockwise angle that the z'' -axis makes relative to the z' -axis. From here, Eq. (A.43) is easily evaluated by observing the matrix elements of $\hat{\mathbf{I}} \cdot \hat{\mathbf{s}}$ in the $2p$ AO basis (see, for instance, Ref. [22]). Because the

following spatial integrals are equal:

$$\left(2p_{y''}^{(\mu')} \middle| \frac{Z_{\mu}^{\text{eff}}}{\hat{r}_{\mu}^3} \middle| 2p_{y''}^{(\mu)}\right) = \left(2p_{z''}^{(\mu')} \middle| \frac{Z_{\mu}^{\text{eff}}}{\hat{r}_{\mu}^3} \middle| 2p_{z''}^{(\mu)}\right) = \left(2p_z^{(\mu')} \middle| \frac{Z_{\mu}^{\text{eff}}}{\hat{r}_{\mu}^3} \middle| 2p_z^{(\mu)}\right) \quad (\text{A.49})$$

due to invariance of $1/\hat{r}_{\mu}^3$ under rotation about the x -axis, we find $A_{\mu\mu'}$ to have the following result:

$$A_{\mu\mu'} = B_{\mu\mu'} \sin(\theta_{\mu\mu'}) \delta_{\sigma'\bar{\sigma}}, \quad (\text{A.50})$$

$$B_{\mu\mu'} \equiv -\frac{i}{2c^2} \left(2p_z^{(\mu')} \middle| \frac{Z_{\mu}^{\text{eff}}}{\hat{r}_{\mu}^3} \middle| 2p_z^{(\mu)}\right), \quad (\text{A.51})$$

with no dependence on φ ($\bar{\sigma}$ is the spin complementary to σ). Also, $A_{\mu'\mu}^* = A_{\mu\mu'}$ because (1) $\theta_{\mu\mu'} = -\theta_{\mu'\mu}$ and (2) $B_{\mu\mu'}$, being a purely imaginary number, equals $-B_{\mu'\mu}^*$. Therefore, overall, we find the SOC operator for the PPP model to be

$$\hat{V}_{\text{SOC}} = \sum_{\langle\mu,\mu'\rangle} B_{\mu\mu'} \sin(\theta_{\mu\mu'}) \left(\hat{a}_{\mu\alpha}^{\dagger} \hat{a}_{\mu'\beta} - \hat{a}_{\mu'\beta}^{\dagger} \hat{a}_{\mu\alpha} \right). \quad (\text{A.52})$$

Assuming AHRs to be planar, the only surviving terms in $\hat{V}_{\text{SOC}}$ for AHR m -dimer systems will be for $\mu, \mu' \in \{\mathcal{A}, \mathcal{B}\}$. This yields the following expression from the main text:

$$\hat{V}_{\text{SOC}} = \sum_{\sigma} B \sin(\theta) \left(\hat{a}_{\mathcal{A}\sigma}^{\dagger} \hat{a}_{\mathcal{B}\bar{\sigma}} - \hat{a}_{\mathcal{B}\bar{\sigma}}^{\dagger} \hat{a}_{\mathcal{A}\sigma} \right), \quad (\text{A.53})$$

where $\theta \equiv \theta_{\mathcal{A}\mathcal{B}}$ is the torsional angle between the two AHRs and $B \equiv B_{\mathcal{A}\mathcal{B}}$.

A.5 Results from configuration interaction between

$\left|{}^3\text{LE}_{\Gamma}^{10,+}\right\rangle$ and $\left|{}^3\text{CT}_{\Gamma}^{10,+}\right\rangle$ states

When the $\left|{}^3\text{LE}_{\Gamma}^{10,+}; M_S\right\rangle$ and $\left|{}^3\text{CT}_{\Gamma}^{10,+}; M_S\right\rangle$ excitations are near-degenerate, off-diagonal matrix elements of the Hamiltonian $\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}_{AB}$ between these states

cannot be ignored. Instead, we diagonalise the following configuration interaction matrix:

$$\mathbf{H}_{M_S, \Gamma} = \begin{pmatrix} \langle {}^3\text{LE}_{\Gamma}^{10,+}; M_S | \hat{H} | {}^3\text{LE}_{\Gamma}^{10,+}; M_S \rangle & \langle {}^3\text{LE}_{\Gamma}^{10,+}; M_S | \hat{H} | {}^3\text{CT}_{\Gamma}^{10,+}; M_S \rangle \\ \langle {}^3\text{CT}_{\Gamma}^{10,+}; M_S | \hat{H} | {}^3\text{LE}_{\Gamma}^{10,+}; M_S \rangle & \langle {}^3\text{CT}_{\Gamma}^{10,+}; M_S | \hat{H} | {}^3\text{CT}_{\Gamma}^{10,+}; M_S \rangle \end{pmatrix}, \quad (\text{A.54})$$

where we have noted that the full Hamiltonian matrix is block-diagonal in M_S and Γ .

Approximating $\hat{V}_{AB} \approx \hat{V}_{\text{NN}}$ and using values from Table A.1, we obtain the following eigenfunctions:

$$|{}^3[\text{CT} + \text{LE}]_{\Gamma}^{10,+}; M_S\rangle = \cos\left(\frac{\phi}{2}\right) |{}^3\text{LE}_{\Gamma}^{10,+}; M_S\rangle + \sin\left(\frac{\phi}{2}\right) |{}^3\text{CT}_{\Gamma}^{10,+}; M_S\rangle, \quad (\text{A.55})$$

$$|{}^3[\text{CT} - \text{LE}]_{\Gamma}^{10,+}; M_S\rangle = -\sin\left(\frac{\phi}{2}\right) |{}^3\text{LE}_{\Gamma}^{10,+}; M_S\rangle + \cos\left(\frac{\phi}{2}\right) |{}^3\text{CT}_{\Gamma}^{10,+}; M_S\rangle, \quad (\text{A.56})$$

and energies

$$E\left({}^3[\text{CT} + \text{LE}]_{\Gamma}^{10,+}\right) = E(\text{LE}^-) + (1 + c_{\mathcal{A}1}^* c_{\mathcal{A}1}) \gamma_{\mathcal{A}\mathcal{B}} + J_{10} + \frac{\Delta}{2} + \sqrt{\frac{\Delta^2}{4} + (c_{\mathcal{A}1} c_{\mathcal{B}1} \beta_{\mathcal{A}\mathcal{B}})^2}, \quad (\text{A.57})$$

$$E\left({}^3[\text{CT} - \text{LE}]_{\Gamma}^{10,+}\right) = E(\text{LE}^-) + (1 + c_{\mathcal{A}1}^* c_{\mathcal{A}1}) \gamma_{\mathcal{A}\mathcal{B}} + J_{10} + \frac{\Delta}{2} - \sqrt{\frac{\Delta^2}{4} + (c_{\mathcal{A}1} c_{\mathcal{B}1} \beta_{\mathcal{A}\mathcal{B}})^2}, \quad (\text{A.58})$$

with detuning Δ and mixing angle ϕ defined as

$$\Delta \equiv 2K_{10} - J_{10}, \quad \phi \equiv \tan^{-1} \left[\frac{-\chi_{\Gamma}(C_2) c_{\mathcal{A}1} c_{\mathcal{B}1} \beta_{\mathcal{A}\mathcal{B}}}{\Delta/2} \right] \in (-\pi, \pi]. \quad (\text{A.59})$$

Here, $\chi_{\Gamma}(C_2)$ is the character of irrep Γ for the C_2 operator, with

$$\chi_{\Gamma}(C_2) = \begin{cases} +1 & \Gamma = \text{A}, \\ -1 & \Gamma = \text{B}. \end{cases}$$

A.6 Deriving the energy expression for CS states

We find the energy expression for a CS state by expanding its determinant using $j_{\pm} \approx 2^{-1/2}(j_A \pm j_B)$:

$$|\text{CS}\rangle \equiv |\cdots 1_+ \overline{1_+} 1_- \overline{1_-} 0_+ \overline{0_+}\rangle = \frac{1}{2} \sum_{r,r'=A,B} |\cdots 1_A \overline{1_A} \cdots 1_B \overline{1_B} 0_r \overline{0_{r'}}\rangle. \quad (\text{A.60})$$

For AHR m -dimers, the approximate Hamiltonian $\hat{H} \approx \hat{H}_A + \hat{H}_B + \hat{V}_{\text{NN}}$ does not facilitate intermonomer excitations involving the SOMOs due to their nodal structures. Hence, when evaluating the energy expectation of $|\text{CS}\rangle$, the cross terms vanish and we obtain

$$\langle \text{CS} | \hat{H} | \text{CS} \rangle \approx \frac{1}{2} (\langle \cdots 0_A \overline{0_A} | \hat{H} | \cdots 0_A \overline{0_A} \rangle + \langle \cdots 0_A \overline{0_B} | \hat{H} | \cdots 0_A \overline{0_B} \rangle), \quad (\text{A.61})$$

where we have noted that $\hat{H}$ is invariant under the C_2 unitary operation. Using standard electronic structure theory algebra [213], we find that

$$\langle \cdots 0_A \overline{0_A} | \hat{H} | \cdots 0_A \overline{0_A} \rangle - \langle \cdots 0_A \overline{0_B} | \hat{H} | \cdots 0_A \overline{0_B} \rangle = J_{00}, \quad (\text{A.62})$$

$$\langle {}^1\text{GS}; 0 | \hat{H} | {}^1\text{GS}; 0 \rangle \approx \langle \cdots 0_A \overline{0_B} | \hat{H} | \cdots 0_A \overline{0_B} \rangle, \quad (\text{A.63})$$

and noting $\langle {}^3\text{GS}; 0 | \hat{H} | {}^3\text{GS}; 0 \rangle \approx \langle {}^1\text{GS}; 0 | \hat{H} | {}^1\text{GS}; 0 \rangle$ from Table A.1 yields

$$\langle \text{CS} | \hat{H} | \text{CS} \rangle \approx \langle {}^3\text{GS}; 0 | \hat{H} | {}^3\text{GS}; 0 \rangle + \frac{J_{00}}{2}, \quad (\text{A.64})$$

which is the expression in the main text.

A.7 Results from ab initio calculations of AHR *m*-dimers

A.7.1 Methylated benzylic radical *m*-dimer

DFT results

Table A.2. Ground-state properties of the methylated benzylic radical *m*-dimer, calculated using DFT at the UB3LYP/6–31G(d,p) level.

Geometry	Optimised ($\theta = 92.347^\circ$)	$\theta = 90.000^\circ$	$\theta = 110.000^\circ$
Triplet			
Energy / Hartree	−776.5671117	−776.5670704	−776.5651492
$\langle S^2 \rangle$	2.069167388	2.069193399	2.068885009
BS			
Energy / Hartree		−776.5671568	−776.5653157
$\langle S^2 \rangle$		1.071306721	1.071552230
CS			
Energy / Hartree		−776.5295652	−776.5293547
$\langle S^2 \rangle$		0.000000000	0.000000000

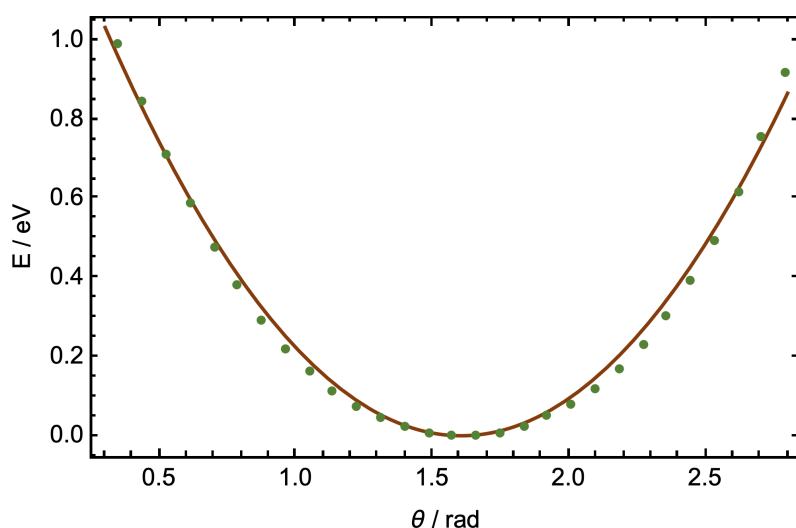


Figure A.1. Ground-state PES of the methylated benzylic radical *m*-dimer over different torsional angles θ . (Green) Relative energies from a PES scan of the triplet configuration using DFT at the UB3LYP/6-31G(d,p) level. (Brown) Plot of $V_{\text{steric}}(\theta) = E_{\text{steric}}(\theta - \theta_{\text{eq}})^2$ using the fitted parameters of $E_{\text{steric}} = 0.606 \text{ eV rad}^{-1}$ and $\theta_{\text{eq}} = 1.605 \text{ rad}$.

Optimised geometry ($\theta = 92.347^\circ$)

```

C
C 1 1.409368
C 1 1.441059 2 116.340956
C 3 1.401527 1 120.070634 2 15.202939 0
H 4 1.087988 3 118.341091 1 175.683527 0
C 4 1.382896 3 122.997361 1 -9.117845 0
C 6 1.433807 4 118.274331 3 -0.726817 0
C 7 1.401193 6 120.026492 4 -176.084995 0
H 8 1.080866 7 122.456139 6 178.933076 0
H 8 1.082035 7 121.072888 6 0.063847 0
C 6 1.506883 4 120.175026 3 -178.597849 0
H 11 1.092955 6 110.715186 4 -2.994127 0
H 11 1.096680 6 111.774410 4 -123.236227 0
H 11 1.096908 6 111.713183 4 117.134509 0
C 1 1.511803 2 124.774624 3 -153.713020 0

```

C 15 1.409346 1 124.777118 2 19.999997 0
 C 15 1.441080 1 114.006582 2 -134.241430 0
 C 17 1.401508 15 120.070820 1 171.734601 0
 H 18 1.087986 17 118.342080 15 175.685206 0
 C 18 1.382915 17 122.996491 15 -9.115603 0
 C 20 1.433796 18 118.274351 17 -0.733019 0
 C 21 1.401196 20 120.026201 18 -176.076942 0
 H 22 1.080866 21 122.455975 20 178.929019 0
 H 22 1.082035 21 121.072902 20 0.060727 0
 C 20 1.506883 18 120.174930 17 -178.599386 0
 H 25 1.092955 20 110.715266 18 -2.999552 0
 H 25 1.096680 20 111.774380 18 -123.241474 0
 H 25 1.096909 20 111.713426 18 117.129123 0
 C 17 1.516466 15 123.125798 1 1.968581 0
 H 29 1.089739 17 115.467470 15 -51.719423 0
 H 29 1.093907 17 110.425507 15 -174.558522 0
 H 29 1.097909 17 109.273136 15 67.763138 0
 C 3 1.516474 1 123.135737 2 -154.546153 0
 H 33 1.089702 3 115.472708 1 -51.480275 0
 H 33 1.093917 3 110.430699 1 -174.337781 0
 H 33 1.097933 3 109.262519 1 67.998117 0
 C 16 1.517329 15 120.487495 1 29.233221 0
 H 37 1.089055 16 111.663034 15 -2.551472 0
 H 37 1.095417 16 112.722561 15 -124.139845 0
 H 37 1.095950 16 109.749322 15 117.043730 0
 C 2 1.517329 1 120.487316 3 -177.051349 0
 H 41 1.089051 2 111.663928 1 -2.563660 0
 H 41 1.095415 2 112.722805 1 -124.153865 0

H 41 1.095953 2 109.747978 1 117.030713 0

Geometry at $\theta = 90.000^\circ$

C

C 1 1.399552

C 1 1.418419 2 120.253895

C 3 1.402188 1 118.900634 2 0.164518 0

H 4 1.088026 3 118.440872 1 -179.909128 0

C 4 1.385963 3 122.796421 1 -0.067502 0

C 6 1.437187 4 119.111578 3 0.032632 0

C 7 1.402242 6 120.476927 4 -180.000000 0

H 8 1.081467 7 121.983110 6 179.984734 0

H 8 1.082068 7 121.397085 6 0.060852 0

C 1 1.506072 2 121.038541 3 -179.857867 0

C 11 1.399553 1 121.038670 2 90.000001 0

C 11 1.418420 1 118.707332 2 -89.860545 0

C 13 1.402188 11 118.900646 1 -179.976053 0

H 14 1.088026 13 118.440862 11 -179.907273 0

C 14 1.385963 13 122.796447 11 -0.065992 0

C 16 1.437187 14 119.111573 13 0.032888 0

C 17 1.402242 16 120.476842 14 179.998723 0

H 18 1.081467 17 121.983225 16 179.984860 0

H 18 1.082068 17 121.397007 16 0.060756 0

C 6 1.508194 4 119.889099 3 -179.938509 0

H 21 1.092897 6 110.826282 4 0.009973 0

H 21 1.096838 6 111.741943 4 -120.150420 0

H 21 1.096885 6 111.801511 4 120.191184 0

C 16 1.508194 14 119.889099 13 -179.938123 0

H 25 1.092897 16 110.826298 14 0.013292 0
 H 25 1.096838 16 111.741962 14 -120.147137 0
 H 25 1.096884 16 111.801379 14 120.194496 0
 C 3 1.509316 1 121.444807 2 -178.917156 0
 H 29 1.093360 3 110.799597 1 -177.225860 0
 H 29 1.095928 3 112.118801 1 -56.517698 0
 H 29 1.096637 3 111.692286 1 62.544234 0
 C 13 1.509317 11 121.444868 1 0.941061 0
 H 33 1.093360 13 110.799465 11 -177.229045 0
 H 33 1.095929 13 112.118187 11 -56.521644 0
 H 33 1.096636 13 111.692779 11 62.540325 0
 C 2 1.510815 1 120.956022 3 -179.978450 0
 H 37 1.089506 2 111.588571 1 -0.997702 0
 H 37 1.096564 2 111.284282 1 -121.544604 0
 H 37 1.096873 2 111.215588 1 119.628989 0
 C 12 1.510815 11 120.956186 1 0.164869 0
 H 41 1.089507 12 111.588891 11 -1.000241 0
 H 41 1.096563 12 111.284382 11 -121.547634 0
 H 41 1.096873 12 111.215335 11 119.626152 0

Geometry at $\theta = 110.000^\circ$

C
 C 1 1.400611
 C 1 1.420229 2 119.944080
 C 3 1.403111 1 118.869523 2 -1.925929 0
 H 4 1.087964 3 118.350547 1 -179.877467 0
 C 4 1.385002 3 122.978926 1 0.857552 0
 C 6 1.437137 4 119.018082 3 0.099275 0

C 7 1.402315 6 120.503771 4 -179.958207 0
 H 8 1.081357 7 122.003550 6 -179.944770 0
 H 8 1.082081 7 121.400903 6 0.010622 0
 C 1 1.506656 2 121.061967 3 173.919544 0
 C 11 1.400612 1 121.060588 2 110.000002 0
 C 11 1.420228 1 118.721760 2 -76.009871 0
 C 13 1.403112 11 118.869420 1 -175.984045 0
 H 14 1.087964 13 118.350711 11 -179.878235 0
 C 14 1.385002 13 122.978879 11 0.857583 0
 C 16 1.437137 14 119.018232 13 0.098808 0
 C 17 1.402315 16 120.503677 14 -179.959065 0
 H 18 1.081356 17 122.003377 16 -179.943542 0
 H 18 1.082081 17 121.400899 16 0.011457 0
 C 6 1.508012 4 119.932375 3 179.800301 0
 H 21 1.092994 6 110.794216 4 -0.356820 0
 H 21 1.096629 6 111.747082 4 -120.535327 0
 H 21 1.096974 6 111.788535 4 119.790702 0
 C 16 1.508012 14 119.932439 13 179.799081 0
 H 25 1.092993 16 110.794314 14 -0.359195 0
 H 25 1.096629 16 111.746989 14 -120.537687 0
 H 25 1.096974 16 111.788594 14 119.788492 0
 C 3 1.509711 1 122.015181 2 177.751454 0
 H 29 1.093649 3 110.637404 1 -164.724957 0
 H 29 1.093873 3 111.954366 1 -43.794978 0
 H 29 1.097182 3 111.764383 1 75.774881 0
 C 13 1.509713 11 122.015499 1 3.692891 0
 H 33 1.093648 13 110.637081 11 -164.723187 0
 H 33 1.093872 13 111.954262 11 -43.793214 0


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H 33 1.097181 13 111.764472 11 75.776579 0
C 12 1.511105 11 120.778261 1 -6.759416 0
H 37 1.089670 12 111.555612 11 1.313032 0
H 37 1.096699 12 111.618461 11 122.346732 0
H 37 1.096805 12 110.970783 11 -118.836401 0
C 2 1.511107 1 120.778625 3 179.322947 0
H 41 1.089670 2 111.556325 1 1.321094 0
H 41 1.096698 2 111.618416 1 122.355288 0
H 41 1.096806 2 110.970469 1 -118.828184 0

```

MCSCF/CI results

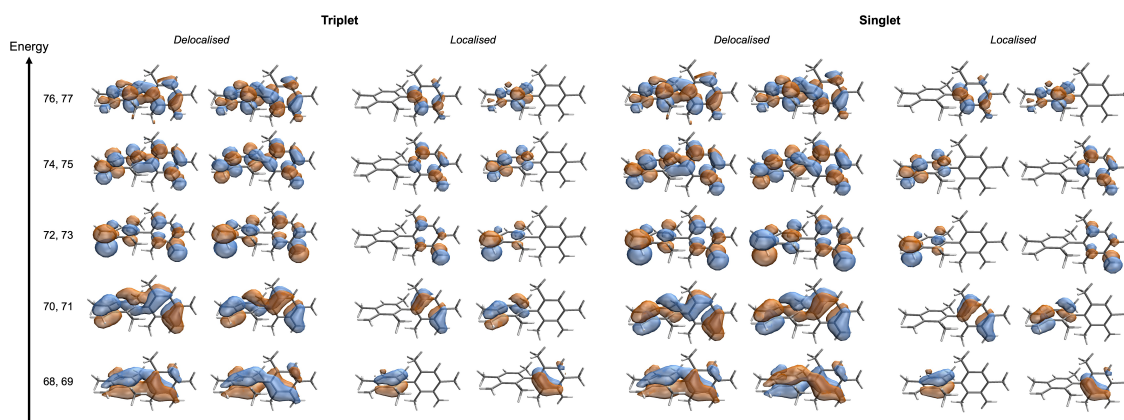


Figure A.2. Active space MOs of the methylated benzylic radical *m*-dimer from a state-specific CASSCF(10,10)/6–31G(d,p) calculation of the triplet and singlet ground states using the UB3LYP-optimised triplet ground-state geometry ($\theta = 92.347^\circ$). Delocalised MOs are MOs obtained directly from a CASSCF(10,10) calculation (isovalue = 0.030). Mixing each consecutive pair of MOs equally yields spatially localised MOs (isovalue = 0.060). MOs are arranged in increasing order of energy.

Table A.3. Excited-state properties of the methylated benzylic radical *m*-dimer, calculated at the state-specific CASSCF(10,10)/CASCI/QD-SC-NEVPT2/6–31G(d,p) level using the UB3LYP-optimised triplet ground-state geometry ($\theta = 92.347^\circ$). Each excitation was assigned a state $\Phi_{\Gamma}^{j0,P}$. The class $\Phi \in \{\text{GS}, \text{LE}, \text{CT}\}$ and orbital $j = 1, 2, \dots$ were found by observing the dominant contributions to the CI vector in the spatially localised orbital basis [Fig. A.2]. The particle-hole symmetry $P \in \{+, -\}$ was labelled based on the oscillator strengths, with $P = +$ states being significantly brighter than $P = -$ states; see Table A.1. Because the triplet states at around 4.2 eV were dominated by both $1 \rightarrow 0$ and $2 \rightarrow 0$ CT transitions with little contributions from $0 \rightarrow 1'$ and $0 \rightarrow 2'$ CT transitions, no particle-hole symmetry was assigned. These results are not surprising since the $\text{CT}^{j0,+}$ and $\text{CT}^{j0,-}$ excitations are near-degenerate when $\theta \approx 90^\circ$ [Fig. 2c].

Triplets			Singlets		
Energy / eV	Oscillator strength	Assignment	Energy / eV	Oscillator strength	Assignment
0	–	GS	–0.005	–	GS
3.164	0.0153	$\text{LE}^{10,-}$	2.223	0.0000	CT^{00}
3.168	0.0097	$\text{LE}^{10,-}$	2.226	0.0016	CT^{00}
3.779	0.0185	$\text{LE}^{20,-}$	3.164	0.0096	$\text{LE}^{10,-}$
3.789	0.0039	$\text{LE}^{20,-}$	3.167	0.0170	$\text{LE}^{10,-}$
4.180	0.0058	$\text{CT}^{1 \rightarrow 0}$ & $\text{CT}^{2 \rightarrow 0}$	3.788	0.0048	$\text{LE}^{20,-}$
4.191	0.0007	$\text{CT}^{1 \rightarrow 0}$ & $\text{CT}^{2 \rightarrow 0}$	3.793	0.0185	$\text{LE}^{20,-}$
4.317	0.1369	$\text{LE}^{10,+}$ & $\text{LE}^{20,+}$	4.326	0.1404	$\text{LE}^{10,+}$ & $\text{LE}^{20,+}$
4.347	0.1413	$\text{LE}^{10,+}$ & $\text{LE}^{20,+}$	4.343	0.1486	$\text{LE}^{10,+}$ & $\text{LE}^{20,+}$

SOC matrix elements

Table A.4. SOC matrix elements between close-lying (within 0.4 eV) electronic states of the methylated benzylic radical *m*-dimer. These calculations were performed at the CASCI/QD-SC-NEVPT2/6–31G(d,p) level using the UB3LYP-optimised triplet ground-state geometry ($\theta = 92.347^\circ$) and orbitals from CASSCF(10,10) state-specific to the triplet ground state. Excitations were assigned in the same way as Table A.3 and the labels “(1)” and “(2)” indicate the lower and higher energy state of a particular excitation type. Note that the triplet magnetic sublevels are presented in the eigenbasis of $\hat{S}_z$, with the *z*-axis coinciding with the molecular C_2 axis. Matrix elements larger than 0.1 cm^{-1} in magnitude are presented in bold.

Triplet	Singlet	SOC magnitude / cm^{-1}	
		$M_S = \pm 1$	$M_S = 0$
GS	GS	0.001	0.000
LE ^{10,-} (1)	LE ^{10,-} (1)	0.001	0.001
LE ^{10,-} (1)	LE ^{10,-} (2)	0.011	0.000
LE ^{20,-} (1)	LE ^{20,-} (1)	0.001	0.005
LE ^{20,-} (1)	LE ^{20,-} (2)	0.043	0.000
CT ^{1→0} & CT ^{2→0} (1)	LE ^{20,-} (1)	0.005	0.099
CT ^{1→0} & CT ^{2→0} (1)	LE ^{20,-} (2)	0.236	0.002
CT ^{1→0} & CT ^{2→0} (1)	LE ^{10,+} & LE ^{20,+} (1)	0.001	0.007
CT ^{1→0} & CT ^{2→0} (1)	LE ^{10,+} & LE ^{20,+} (2)	0.126	0.000
LE ^{10,+} & LE ^{20,+} (1)	LE ^{10,+} & LE ^{20,+} (1)	0.062	0.003
LE ^{10,+} & LE ^{20,+} (1)	LE ^{10,+} & LE ^{20,+} (2)	0.021	0.015

Table A.4. SOC matrix elements between close-lying (within 0.4 eV) electronic states of the methylated benzylic radical *m*-dimer, Continued.

Triplet	Singlet	SOC magnitude / cm ⁻¹	
		$M_S = \pm 1$	$M_S = 0$
LE ^{10,-} (2)	LE ^{10,-} (1)	0.004	0.000
LE ^{10,-} (2)	LE ^{10,-} (2)	0.000	0.014
LE ^{20,-} (2)	LE ^{20,-} (1)	0.016	0.000
LE ^{20,-} (2)	LE ^{20,-} (2)	0.000	0.002
CT ^{1→0} & CT ^{2→0} (2)	LE ^{20,-} (1)	0.234	0.004
CT ^{1→0} & CT ^{2→0} (2)	LE ^{20,-} (2)	0.007	0.059
CT ^{1→0} & CT ^{2→0} (2)	LE ^{10,+} & LE ^{20,+} (1)	0.159	0.001
CT ^{1→0} & CT ^{2→0} (2)	LE ^{10,+} & LE ^{20,+} (2)	0.010	0.009
LE ^{10,+} & LE ^{20,+} (2)	LE ^{10,+} & LE ^{20,+} (1)	0.032	0.014
LE ^{10,+} & LE ^{20,+} (2)	LE ^{10,+} & LE ^{20,+} (2)	0.007	0.006

Table A.5. Selected SOC matrix elements involving the GSs and $^1\text{CT}^{00}$ states of the methylated benzylic radical *m*-dimer. See Table A.4 for computational details.

Triplet	Singlet	SOC magnitude / cm^{-1}	
		$M_S = \pm 1$	$M_S = 0$
GS	$\text{CT}^{00} (1)$	0.016	0.002
$\text{CT}^{1 \rightarrow 0}$ & $\text{CT}^{2 \rightarrow 0} (1)$	GS	0.008	0.409
$\text{LE}^{10,-} (1)$	$\text{CT}^{00} (1)$	0.012	0.018
$\text{LE}^{10,-} (1)$	$\text{CT}^{00} (2)$	0.339	0.001

Triplet	Singlet	SOC magnitude / cm^{-1}	
		$M_S = \pm 1$	$M_S = 0$
GS	$\text{CT}^{00} (2)$	0.001	0.061
$\text{CT}^{1 \rightarrow 0}$ & $\text{CT}^{2 \rightarrow 0} (2)$	GS	0.297	0.013
$\text{LE}^{10,-} (2)$	$\text{CT}^{00} (1)$	0.025	0.016
$\text{LE}^{10,-} (2)$	$\text{CT}^{00} (2)$	0.001	0.437

Table A.6. SOC matrix elements between the ${}^1\text{LE}^{10,-}$ states and $\text{CT}^{1\rightarrow 0}$ & $\text{CT}^{2\rightarrow 0}$ states of the methylated benzylic radical m -dimer. See Table A.4 for computational details.

Triplet	Singlet	SOC magnitude / cm^{-1}	
		$M_S = \pm 1$	$M_S = 0$
$\text{CT}^{1\rightarrow 0}$ & $\text{CT}^{2\rightarrow 0}$ (1)	$\text{LE}^{10,-}$ (1)	0.005	0.071
$\text{CT}^{1\rightarrow 0}$ & $\text{CT}^{2\rightarrow 0}$ (1)	$\text{LE}^{10,-}$ (2)	0.163	0.001

Triplet	Singlet	SOC magnitude / cm^{-1}	
		$M_S = \pm 1$	$M_S = 0$
$\text{CT}^{1\rightarrow 0}$ & $\text{CT}^{2\rightarrow 0}$ (2)	$\text{LE}^{10,-}$ (1)	0.165	0.003
$\text{CT}^{1\rightarrow 0}$ & $\text{CT}^{2\rightarrow 0}$ (2)	$\text{LE}^{10,-}$ (2)	0.008	0.064

We first analysed the SOC matrix elements between states separated in energy by < 0.4 eV (approximately one vibrational quantum) [Table A.4]. These are also states among which ISC processes are most probable [62]. Indeed, CT-type transitions involving the triplet $M_S = \pm 1$ sublevels experienced the largest SOC matrix elements, dominating others by at least an order of magnitude. Furthermore, for each excitation containing two near-degenerate states of opposite irreps (labelled “(1)” and “(2)”), SOC matrix elements were selective for one of the two irreps. All these observations are consistent with the predictions made by the PPP model. Unfortunately, because the CT^{10} and CT^{20} excitations were not computed with definite particle-hole symmetry, selection rules for this property could not be verified.

Next, we tabulated the SOC matrix elements for CT-type transitions of the GSs and ${}^1\text{CT}^{00}$ states [Table A.5]. Interestingly, significant couplings were observed to some higher-lying states despite the SOMO having a node at the dimer linkage. In two cases,

spin selectivity was even reversed to become $\Delta M_S = 0$. One explanation could be the presence of through-space spin-orbit interactions between electrons in $2p$ AOs that are spatially close but not adjacent to each other on the nuclear framework. Such effects can mix triplet $M_S = 0$ sublevels [248] and are not captured by the PPP model, which assumes nearest-neighbour coupling (i.e. only through-bond effects). Fortunately for us, the GSs and $^1\text{CT}^{00}$ states are energetically separated from other excitations by at least 0.8 eV (around two vibrational quanta), so ISC processes of these states are likely to be slow [62]. As such, their impact on the accumulation of ground-state spin polarisation is likely to be small.

Pertaining to the spin polarisation mechanisms described in the main text, three sets of SOC matrix elements are particularly relevant:

1. For case 1 of ODMR in AHR m -dimers [Fig. 2d], the $|^3\text{CT}^{10,+}\rangle \rightarrow |^1\text{LE}^{10,+}\rangle$ ISC causes accumulation of spin polarisation. Their SOC matrix elements are presented in green in Table A.4 and indeed, we find nearly 100% selectivity for the $M_S = \pm 1$ components of the $^3\text{CT}^{10}$ excited states, in agreement with the PPP model.
2. As for case 2 of ODMR in AHR m -dimers [Fig. 2e], the $|^3\text{CT}^{10,-}\rangle \rightarrow |^1\text{LE}^{10,-}\rangle$ ISC causes accumulation of spin polarisation. These matrix elements are presented in Table A.6 and also display close to 100% spin selectivity for the $M_S = \pm 1$ components of the $^3\text{CT}^{10}$ excited state, in line with the PPP model.
3. Specific to the methylated benzylic radical m -dimer [Fig. 5b], MCSCF/CI calculations place this system in case 2. However, the $^1\text{LE}^{10,-}$ states are > 1 eV lower in energy than the $^3\text{CT}^{10}$ states, suggesting that ISC through this pathway is energetically disfavoured [62]. Instead, ISC is likely to occur to the closer-lying (0.39 eV) $^1\text{LE}^{20,-}$ state, which is not an issue because the selection rules derived from the PPP model are generalisable to higher-lying LE and CT excitations. The $|^3\text{CT}^{10,-}\rangle \rightarrow |^1\text{LE}^{20,-}\rangle$ matrix elements are tabulated in red in Table A.4. Again, we find these ISC processes to also be almost 100% selective for the $M_S = \pm 1$

components of the $^3\text{CT}^{10}$ excited state, as predicted by the PPP framework.

A.7.2 TTM *m*-dimer

Table A.7. Ground-state properties of the TTM *m*-dimer, calculated using DFT at the UB3LYP/6–31G(d,p) level.

Geometry	Optimised ($\theta = 94.022^\circ$)	$\theta = 90.000^\circ$	$\theta = 110.000^\circ$
Triplet			
Energy / Hartree	−9737.4945065	−9737.4945443	−9737.4932289
$\langle \mathbf{S}^2 \rangle$	2.040030882	2.039735356	2.039988794
BS			
Energy / Hartree		−9737.4960016	−9737.49409
$\langle \mathbf{S}^2 \rangle$		1.034521264	1.0312
CS			
Energy / Hartree		−9737.4566476	−9737.4557726
$\langle \mathbf{S}^2 \rangle$		−0.000000000	−0.000000000

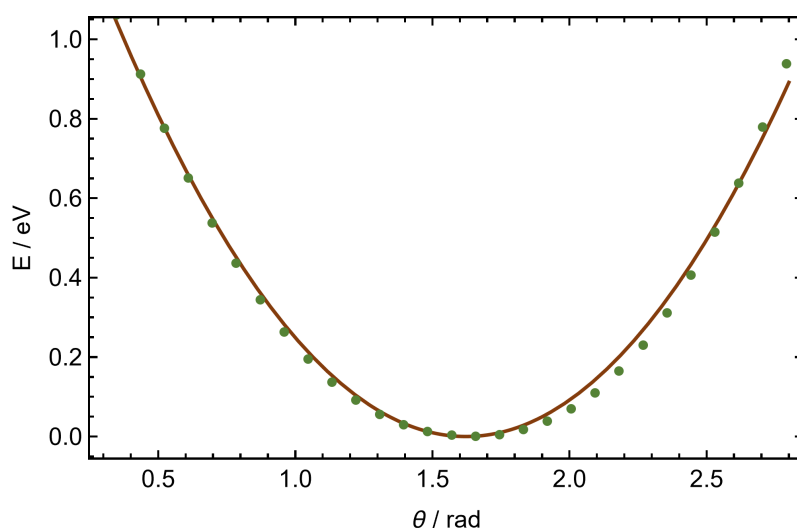


Figure A.3. Ground-state PES of the TTM *m*-dimer over different torsional angles θ . (Green) Relative energies from a PES scan of the triplet configuration using DFT at the UB3LYP/6–31G(d,p) level. (Brown) Plot of $V_{\text{steric}}(\theta) = E_{\text{steric}}(\theta - \theta_{\text{eq}})^2$ using the fitted parameters of $E_{\text{steric}} = 0.643 \text{ eV rad}^{-1}$ and $\theta_{\text{eq}} = 1.622 \text{ rad}$.

Optimised geometry ($\theta = 94.022^\circ$)

```

Cl
C 1 1.751799
C 2 1.402938 1 116.601767
C 3 1.401602 2 117.373233 1 -175.977144 0
C 4 1.389046 3 121.497716 2 0.146928 0
H 5 1.082109 4 120.359912 3 -179.125979 0
C 5 1.388134 4 119.435924 3 -0.487427 0
C 7 1.416077 5 122.756338 4 0.196756 0
C 8 1.476804 7 122.254762 5 -179.575975 0
C 9 1.473664 8 119.954750 7 -49.701863 0
C 10 1.419428 9 122.587078 8 131.180403 0
C 11 1.390522 10 123.263292 9 179.713317 0
H 12 1.082217 11 120.139706 10 178.956896 0
C 12 1.390762 11 118.962200 10 0.306325 0
C 14 1.390683 12 120.866310 11 -0.077919 0

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H 15 1.082316 14 120.924838 12 -178.931241 0
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 C 18 1.419160 9 122.633366 8 131.368734 0
 C 19 1.390816 18 123.269670 9 -179.332712 0
 H 20 1.082238 19 120.115031 18 178.756533 0
 C 20 1.390556 19 118.977700 18 0.197707 0
 C 22 1.390489 20 120.838307 19 -0.426246 0
 H 23 1.082238 22 120.887786 20 -178.753937 0
 C 23 1.390874 22 118.978963 20 0.052299 0
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 C 27 1.389046 26 121.497716 3 -179.542036 0
 H 28 1.082109 27 120.359912 26 -179.125979 0
 C 28 1.388134 27 119.435924 26 -0.487427 0
 C 26 1.402938 3 121.712421 2 -94.021634 0
 C 30 1.416077 28 122.756338 27 0.196756 0
 C 32 1.476804 30 122.254762 28 -179.575975 0
 C 33 1.473664 32 119.954750 30 -49.701863 0
 C 34 1.419428 33 122.587078 32 131.180403 0
 C 35 1.390522 34 123.263292 33 179.713317 0
 H 36 1.082217 35 120.139706 34 178.956896 0
 C 36 1.390762 35 118.962200 34 0.306325 0
 C 38 1.390683 36 120.866310 35 -0.077919 0
 H 39 1.082316 38 120.924838 36 -178.931241 0
 C 39 1.390861 38 118.979806 36 -0.206287 0
 C 33 1.474298 32 119.952019 30 129.893971 0
 C 42 1.419160 33 122.633366 32 131.368734 0

C 43 1.390816 42 123.269670 33 -179.332712 0
 H 44 1.082238 43 120.115031 42 178.756533 0
 C 44 1.390556 43 118.977700 42 0.197707 0
 C 46 1.390489 44 120.838307 43 -0.426246 0
 H 47 1.082238 46 120.887786 44 -178.753937 0
 C 47 1.390874 46 118.978963 44 0.052299 0
 Cl 27 1.748625 26 120.416165 3 0.504861 0
 Cl 4 1.748625 3 120.416165 2 -179.806175 0
 Cl 38 1.749533 36 119.527040 35 179.814910 0
 Cl 14 1.749533 12 119.527040 11 179.814910 0
 Cl 46 1.750108 44 119.579778 43 179.428546 0
 Cl 22 1.750108 20 119.579778 19 179.428546 0
 Cl 31 1.751799 26 116.601767 3 3.709171 0
 Cl 30 1.752882 28 115.706988 27 -176.366242 0
 Cl 7 1.752882 5 115.706988 4 -176.366242 0
 Cl 41 1.753764 39 115.582866 38 -176.333728 0
 Cl 17 1.753764 15 115.582866 14 -176.333728 0
 Cl 49 1.754031 47 115.506561 46 -176.120010 0
 Cl 25 1.754031 23 115.506561 22 -176.120010 0
 Cl 43 1.754332 42 121.158698 33 -3.202799 0
 Cl 19 1.754332 18 121.158698 9 -3.202799 0
 Cl 35 1.754804 34 121.157263 33 -4.092130 0
 Cl 11 1.754804 10 121.157263 9 -4.092130 0

Geometry at $\theta = 90.000^\circ$

Cl
 C 1 1.751771
 C 2 1.403211 1 116.633814

C 3 1.401377 2 117.319593 1 -176.273522 0
 C 4 1.388983 3 121.533456 2 0.007214 0
 H 5 1.082160 4 120.346860 3 -179.164590 0
 C 5 1.388212 4 119.436003 3 -0.324343 0
 C 7 1.415901 5 122.728780 4 0.003478 0
 C 8 1.477314 7 122.223695 5 -179.460654 0
 C 9 1.474226 8 119.873546 7 -49.920770 0
 C 10 1.419135 9 122.695318 8 -49.282987 0
 C 11 1.390926 10 123.190200 9 -179.982110 0
 H 12 1.082347 11 120.102480 10 178.962500 0
 C 12 1.390647 11 118.987133 10 0.211249 0
 C 14 1.390785 12 120.893495 11 -0.199114 0
 H 15 1.082215 14 120.905253 12 -178.735772 0
 C 15 1.390531 14 118.913074 12 -0.022696 0
 C 9 1.474285 8 120.053381 7 129.678484 0
 C 18 1.419140 9 122.712252 8 -48.137716 0
 C 19 1.390823 18 123.292027 9 178.914751 0
 H 20 1.082182 19 120.129393 18 179.342068 0
 C 20 1.390386 19 118.958691 18 0.552351 0
 C 22 1.390551 20 120.839712 19 0.063836 0
 H 23 1.082241 22 120.856549 20 -179.102304 0
 C 23 1.390794 22 118.999400 20 -0.418080 0
 C 3 1.493689 2 121.712442 1 2.280919 0
 C 26 1.401377 3 120.951894 2 88.502409 0
 C 27 1.388983 26 121.533456 3 -178.558864 0
 H 28 1.082160 27 120.346860 26 -179.164590 0
 C 28 1.388212 27 119.436003 26 -0.324343 0
 C 26 1.403211 3 121.712442 2 -90.000002 0

C 30 1.415901 28 122.728780 27 0.003478 0
 C 32 1.477314 30 122.223695 28 -179.460654 0
 C 33 1.474226 32 119.873546 30 -49.920770 0
 C 34 1.419135 33 122.695318 32 -49.282987 0
 C 35 1.390926 34 123.190200 33 -179.982110 0
 H 36 1.082347 35 120.102480 34 178.962500 0
 C 36 1.390647 35 118.987133 34 0.211249 0
 C 38 1.390785 36 120.893495 35 -0.199114 0
 H 39 1.082215 38 120.905253 36 -178.735772 0
 C 39 1.390531 38 118.913074 36 -0.022696 0
 C 33 1.474285 32 120.053381 30 129.678484 0
 C 42 1.419140 33 122.712252 32 -48.137716 0
 C 43 1.390823 42 123.292027 33 178.914751 0
 H 44 1.082182 43 120.129393 42 179.342068 0
 C 44 1.390386 43 118.958691 42 0.552351 0
 C 46 1.390551 44 120.839712 43 0.063836 0
 H 47 1.082241 46 120.856549 44 -179.102304 0
 C 47 1.390794 46 118.999400 44 -0.418080 0
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Cl 11 1.753375 10 121.092191 9 -3.759172 0
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 Cl 19 1.754121 18 121.132939 9 -4.718598 0
 Cl 49 1.754381 47 115.452125 46 -176.224378 0
 Cl 25 1.754381 23 115.452125 22 -176.224378 0
 Cl 41 1.755145 39 115.528237 38 -176.221696 0
 Cl 17 1.755145 15 115.528237 14 -176.221696 0

Geometry at $\theta = 110.000^\circ$

Cl
 C 1 1.753122
 C 2 1.404165 1 116.489222
 C 3 1.403236 2 117.104344 1 -175.716474 0
 C 4 1.389390 3 121.512421 2 1.784679 0
 H 5 1.082136 4 120.249438 3 -179.142203 0
 C 5 1.387828 4 119.558360 3 -1.191336 0
 C 7 1.415679 5 122.665889 4 0.319790 0
 C 8 1.476859 7 122.242202 5 179.593250 0
 C 9 1.473868 8 120.133607 7 130.121698 0
 C 10 1.418996 9 122.723367 8 -48.165459 0
 C 11 1.390845 10 123.252193 9 179.312014 0
 H 12 1.082391 11 120.149000 10 179.155858 0
 C 12 1.390707 11 118.978846 10 0.388694 0
 C 14 1.390514 12 120.857290 11 -0.012209 0
 H 15 1.082153 14 120.918205 12 -178.875173 0
 C 15 1.390599 14 118.948318 12 -0.251061 0
 C 9 1.474321 8 119.676476 7 -49.645608 0
 C 18 1.419454 9 122.639677 8 131.072841 0

C 19 1.390759 18 123.297409 9 -179.788923 0
 H 20 1.082213 19 120.169105 18 178.889036 0
 C 20 1.390576 19 118.913218 18 0.230435 0
 C 22 1.390551 20 120.886379 19 -0.231310 0
 H 23 1.082333 22 120.871921 20 -178.792700 0
 C 23 1.390746 22 119.005728 20 -0.012640 0
 C 3 1.492927 2 121.615188 1 9.333902 0
 C 26 1.403236 3 121.083368 2 75.250015 0
 C 27 1.389390 26 121.512421 3 176.762854 0
 H 28 1.082136 27 120.249438 26 -179.142203 0
 C 28 1.387828 27 119.558360 26 -1.191336 0
 C 26 1.404165 3 121.615188 2 -110.000003 0
 C 30 1.415679 28 122.665889 27 0.319790 0
 C 32 1.476859 30 122.242202 28 179.593250 0
 C 33 1.473868 32 120.133607 30 130.121698 0
 C 34 1.418996 33 122.723367 32 -48.165459 0
 C 35 1.390845 34 123.252193 33 179.312014 0
 H 36 1.082391 35 120.149000 34 179.155858 0
 C 36 1.390707 35 118.978846 34 0.388694 0
 C 38 1.390514 36 120.857290 35 -0.012209 0
 H 39 1.082153 38 120.918205 36 -178.875173 0
 C 39 1.390599 38 118.948318 36 -0.251061 0
 C 33 1.474321 32 119.676476 30 -49.645608 0
 C 42 1.419454 33 122.639677 32 131.072841 0
 C 43 1.390759 42 123.297409 33 -179.788923 0
 H 44 1.082213 43 120.169105 42 178.889036 0
 C 44 1.390576 43 118.913218 42 0.230435 0
 C 46 1.390551 44 120.886379 43 -0.231310 0

H 47 1.082333 46 120.871921 44 -178.792700 0
C 47 1.390746 46 119.005728 44 -0.012640 0
Cl 27 1.748529 26 120.773911 3 -2.011653 0
Cl 4 1.748529 3 120.773911 2 -176.989828 0
Cl 38 1.749702 36 119.619410 35 -179.980240 0
Cl 14 1.749702 12 119.619410 11 -179.980240 0
Cl 46 1.749929 44 119.576230 43 179.661839 0
Cl 22 1.749929 20 119.576230 19 179.661839 0
Cl 30 1.753015 28 115.801830 27 -176.031475 0
Cl 7 1.753015 5 115.801830 4 -176.031475 0
Cl 31 1.753122 26 116.489222 3 9.333902 0
Cl 49 1.753650 47 115.512744 46 -176.314223 0
Cl 25 1.753650 23 115.512744 22 -176.314223 0
Cl 41 1.754523 39 115.457443 38 -176.239871 0
Cl 17 1.754523 15 115.457443 14 -176.239871 0
Cl 35 1.754574 34 121.126473 33 -4.386325 0
Cl 11 1.754574 10 121.126473 9 -4.386325 0
Cl 43 1.754663 42 121.133346 33 -3.557135 0
Cl 19 1.754663 18 121.133346 9 -3.557135 0

A.7.3 Removing two methyl substituents from the methylated benzylic radical *m*-dimer

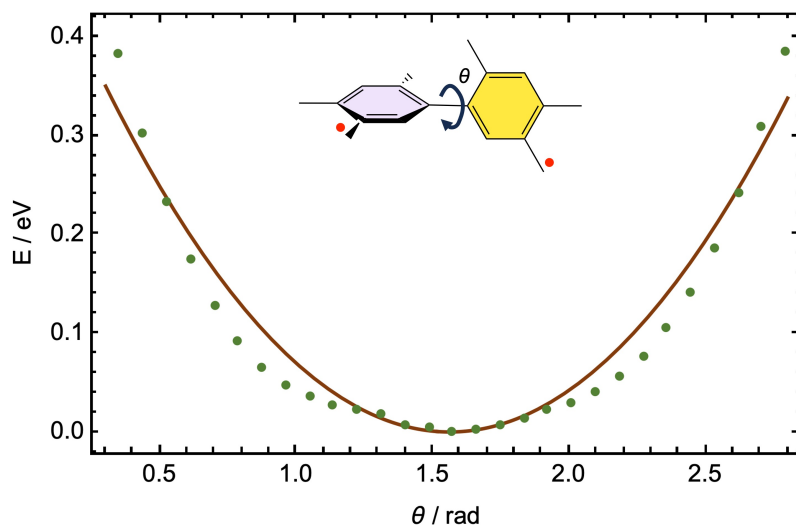


Figure A.4. Ground-state PES of the methylated benzylic radical *m*-dimer over different torsional angles θ after removing the *ortho*-methyl substituents facing the dimer linkage. (Green) Relative energies from a PES scan of the triplet configuration using DFT at the UB3LYP/6-31G(d,p) level. (Brown) Plot of $V_{\text{steric}}(\theta) = E_{\text{steric}}(\theta - \theta_{\text{eq}})^2$ using the fitted parameters of $E_{\text{steric}} = 0.220 \text{ eV rad}^{-1}$ and $\theta_{\text{eq}} = 1.561 \text{ rad}$.

A.8 Results from *ab initio* calculations of AHRs

A.8.1 Methylated benzylic radical

The SCF calculation converged to an energy of -388.8867831125 Hartree and an $\langle S^2 \rangle$ value of 0.784892232.

Table A.8. Key electronic transitions of the methylated benzylic radical, calculated using TDDFT/TDA at the UB3LYP/6–31G(d,p) level.

Energy / eV	$\langle S^2 \rangle$	Oscillator strength	Main contributions (sign)	Assignment
3.0802	0.8435	0.0044487822	$36\beta \rightarrow 37\beta (+)$ $37\alpha \rightarrow 38\alpha (+)$	$ \Psi_{01}^-; +1/2\rangle$
3.4101	0.8425	0.0103001979	$35\beta \rightarrow 37\beta (+)$ $37\alpha \rightarrow 39\alpha (+)$	$ \Psi_{02}^-; +1/2\rangle$
4.0035	0.9006	0.0695851770	$37\alpha \rightarrow 38\alpha (+)$ $36\beta \rightarrow 37\beta (-)$	$ \Psi_{01}^+; +1/2\rangle$
5.2016	0.8524	0.3740902854	$37\alpha \rightarrow 39\alpha (+)$ $35\beta \rightarrow 37\beta (-)$	$ \Psi_{02}^+; +1/2\rangle$

Optimised geometry

C

C 1 1.401417

H 2 1.082238 1 121.754082

H 2 1.082253 1 121.794892 3 -179.970652 0

C 1 1.440113 2 121.034980 3 0.057816 0

C 5 1.388984 1 119.661480 2 179.957364 0

H 6 1.088027 5 118.775280 1 -179.973799 0

C 6 1.402451 5 122.396270 1 -0.017491 0

C 8 1.406359 6 117.909635 5 -0.012993 0

H 9 1.088405 8 118.871406 6 -179.876368 0

C 9 1.385794 8 122.348414 6 0.038432 0
 C 8 1.508017 6 121.341711 5 179.683170 0
 H 12 1.093289 8 111.390407 6 3.192378 0
 H 12 1.096604 8 111.479725 6 123.681384 0
 H 12 1.097126 8 111.451286 6 -117.120122 0
 C 5 1.508241 1 120.592261 2 -0.013536 0
 H 16 1.092956 5 110.894195 1 179.882668 0
 H 16 1.096787 5 111.723058 1 59.677967 0
 H 16 1.096815 5 111.721412 1 -59.912630 0
 C 11 1.508312 9 119.840576 8 179.993808 0
 H 20 1.092964 11 110.898636 9 -0.550835 0
 H 20 1.096669 11 111.706966 9 -120.765074 0
 H 20 1.096810 11 111.701013 9 119.666405 0

Orbital energies in Hartrees

Alpha MOs

– Occupied –

-10.1926 -10.1923 -10.1920 -10.1866 -10.1811 -10.1807 -10.1785 -10.1784
 -10.1749 -10.1746 -0.8559 -0.7867 -0.7770 -0.7169 -0.6953 -0.6726
 -0.6303 -0.5673 -0.5531 -0.4848 -0.4775 -0.4281 -0.4252 -0.4107
 -0.4087 -0.4048 -0.3986 -0.3971 -0.3921 -0.3780 -0.3587 -0.3346
 -0.3315 -0.3203 -0.2735 -0.2367 -0.1669

– Virtual –

0.0093 0.0298 0.1008 0.1119 0.1209 0.1322 0.1392 0.1424
 0.1640 0.1738 0.1781 0.1824 0.1884 0.1894 0.2107 0.2129
 0.2454 0.2515 0.2645 0.3015 0.3514 0.3606 0.3716 0.3893
 0.4484 0.4844 0.5101 0.5157 0.5393 0.5440 0.5490 0.5634
 0.5753 0.5848 0.5901 0.5980 0.6144 0.6167 0.6582 0.6745

0.6868 0.7135 0.7194 0.7264 0.7279 0.7414 0.7544 0.7675
 0.7839 0.8195 0.8257 0.8259 0.8349 0.8536 0.8659 0.8716
 0.8944 0.8993 0.9129 0.9287 0.9411 0.9533 0.9989 1.0087
 1.0160 1.0605 1.0933 1.1176 1.1416 1.1921 1.2050 1.2259
 1.2575 1.2705 1.3130 1.3157 1.3519 1.3662 1.3722 1.4102
 1.4197 1.4598 1.4745 1.5693 1.5845 1.7001 1.7197 1.7338
 1.7406 1.7612 1.7652 1.7912 1.8377 1.8427 1.8575 1.8591
 1.8811 1.8981 1.9610 1.9649 1.9732 1.9984 2.0141 2.0183
 2.0469 2.0487 2.0529 2.0872 2.0893 2.0935 2.1068 2.1380
 2.1535 2.1633 2.1838 2.1927 2.2070 2.2181 2.2192 2.2410
 2.3114 2.3279 2.3765 2.4115 2.4202 2.4428 2.4479 2.4607
 2.4772 2.5385 2.5421 2.5517 2.5587 2.5928 2.6322 2.6484
 2.6550 2.6667 2.6805 2.7276 2.7393 2.7924 2.7982 2.8477
 2.8541 2.8554 2.8644 2.8769 2.8778 2.8829 3.0369 3.0616
 3.0838 3.1822 3.1965 3.2073 3.2130 3.2572 3.3802 3.4151
 3.4279 3.4315 3.4326 3.4530 3.4727 3.4855 3.6146 3.7059
 4.1101 4.1486 4.1626 4.2530 4.3634 4.4123 4.4444 4.5645
 4.5835 4.8592

Beta MOs

– Occupied –

-10.1894 -10.1890 -10.1886 -10.1880 -10.1810 -10.1788 -10.1787 -10.1766
 -10.1763 -10.1720 -0.8517 -0.7806 -0.7733 -0.7080 -0.6950 -0.6738
 -0.6188 -0.5639 -0.5482 -0.4826 -0.4755 -0.4250 -0.4194 -0.4065
 -0.4057 -0.4024 -0.3974 -0.3957 -0.3901 -0.3755 -0.3581 -0.3293
 -0.3272 -0.3191 -0.2492 -0.2300

– Virtual –

-0.0735 0.0195 0.0515 0.1017 0.1136 0.1217 0.1334 0.1425
 0.1467 0.1646 0.1762 0.1799 0.1847 0.1912 0.1937 0.2117

0.2189 0.2490 0.2553 0.2678 0.3044 0.3529 0.3624 0.3730
 0.3904 0.4493 0.4863 0.5129 0.5190 0.5423 0.5463 0.5648
 0.5677 0.5772 0.5903 0.5921 0.6153 0.6181 0.6192 0.6702
 0.6751 0.6873 0.7167 0.7203 0.7282 0.7374 0.7435 0.7569
 0.7763 0.7872 0.8234 0.8254 0.8290 0.8342 0.8560 0.8684
 0.8734 0.8953 0.9022 0.9130 0.9302 0.9426 0.9547 1.0039
 1.0127 1.0215 1.0671 1.0952 1.1201 1.1443 1.1933 1.2070
 1.2286 1.2629 1.2760 1.3184 1.3200 1.3517 1.3696 1.3828
 1.4128 1.4257 1.4620 1.4988 1.5720 1.5884 1.7018 1.7214
 1.7384 1.7436 1.7621 1.7663 1.7933 1.8408 1.8473 1.8590
 1.8656 1.8974 1.8999 1.9645 1.9736 1.9789 2.0030 2.0135
 2.0223 2.0482 2.0499 2.0547 2.0898 2.0943 2.0954 2.1090
 2.1450 2.1556 2.1639 2.1914 2.2015 2.2067 2.2175 2.2221
 2.2457 2.3159 2.3306 2.3779 2.4127 2.4221 2.4446 2.4551
 2.4681 2.4785 2.5455 2.5474 2.5556 2.5704 2.5949 2.6353
 2.6545 2.6572 2.6739 2.6817 2.7293 2.7409 2.7935 2.7993
 2.8495 2.8551 2.8568 2.8659 2.8791 2.8798 2.8839 3.0398
 3.0627 3.0852 3.1834 3.1973 3.2086 3.2154 3.2588 3.3840
 3.4148 3.4295 3.4326 3.4339 3.4535 3.4731 3.4862 3.6190
 3.7063 4.1133 4.1528 4.1659 4.2681 4.3631 4.4151 4.4464
 4.5661 4.5866 4.8624

Excited states from TDDFT/TDA

Excited state 1: excitation energy (eV) = 3.0802

Total energy for state 1: -388.77359883 au

$\langle S^2 \rangle$: 0.8435

Trans. Mom.: -0.0022 X 0.2428 Y -0.0001 Z

Strength : 0.0044487822

S(1) → V(1) amplitude = 0.4617 alpha
 D(36) → S(1) amplitude = 0.8787 beta
 Excited state 2: excitation energy (eV) = 3.4101
 Total energy for state 2: -388.76147426 au
 <S**2> : 0.8425
 Trans. Mom.: -0.3473 X 0.0520 Y 0.0001 Z
 Strength : 0.0103001979
 S(1) → V(2) amplitude = 0.5888 alpha
 D(35) → S(1) amplitude = 0.7901 beta
 Excited state 3: excitation energy (eV) = 4.0035
 Total energy for state 3: -388.73966630 au
 <S**2> : 0.9006
 Trans. Mom.: -0.0926 X -0.8372 Y 0.0005 Z
 Strength : 0.0695851770
 S(1) → V(1) amplitude = 0.8539 alpha
 D(35) → V(1) amplitude = 0.1676 beta
 D(36) → S(1) amplitude = -0.4395 beta
 Excited state 4: excitation energy (eV) = 4.5314
 Total energy for state 4: -388.72026636 au
 <S**2> : 2.6575
 Trans. Mom.: -0.1837 X -0.0051 Y 0.0004 Z
 Strength : 0.0037511235
 D(36) → V(1) amplitude = 0.7120 alpha
 D(33) → S(1) amplitude = 0.1509 beta
 D(36) → V(1) amplitude = -0.6463 beta
 Excited state 5: excitation energy (eV) = 5.2016
 Total energy for state 5: -388.69563862 au
 <S**2> : 0.8524

Trans. Mom.: 1.7132 X -0.0171 Y -0.0027 Z

Strength : 0.3740902854

S(1) $\rightarrow$ V(2) amplitude = 0.7467 alpha

D(35) $\rightarrow$ S(1) amplitude = -0.5379 beta

D(36) $\rightarrow$ V(1) amplitude = -0.2777 beta

Excited state 6: excitation energy (eV) = 5.3993

Total energy for state 6: -388.68837232 au

$\langle S^2 \rangle$: 0.8165

Trans. Mom.: -0.0056 X -0.0017 Y 0.0112 Z

Strength : 0.0000213317

D(34) $\rightarrow$ S(1) amplitude = 0.9893 beta

A.8.2 TTM

The SCF calculation converged to an energy of -4869.3523950252 Hartree and an $\langle S^2 \rangle$ value of 0.770122243.

Table A.9. Key electronic transitions of TTM, calculated using TDDFT/TDA at the UB3LYP/6–31G(d,p) level.

Energy / eV	$\langle S^2 \rangle$	Oscillator strength	Main contribution	Assignment
2.7281	0.8880	0.0313359	$136\beta \rightarrow 137\beta$	
2.7285	0.8881	0.0309486	$135\beta \rightarrow 137\beta$	
2.9581	0.8504	0.0089905	$134\beta \rightarrow 137\beta$	$\left\{ \left \Psi_{0j}^{-}; +1/2 \right\rangle \mid 1 \leq j \leq 5 \right\}$
2.9622	0.8651	0.0077979	$133\beta \rightarrow 137\beta$	
2.9626	0.8655	0.0077561	$132\beta \rightarrow 137\beta$	
3.2083	0.9633	0.0000022	$131\beta \rightarrow 137\beta$	$\left \Psi_{06}^{-}; +1/2 \right\rangle$
3.4542	0.9972	0.2236567	$137\alpha \rightarrow 138\alpha$	
3.4586	0.9994	0.2251558	$137\alpha \rightarrow 139\alpha$	
3.6154	0.9600	0.0134796	$137\alpha \rightarrow 140\alpha$	$\left\{ \left \Psi_{0j}^{+}; +1/2 \right\rangle \mid 1 \leq j \leq 5 \right\}$
3.8078	1.0358	0.0025513	$137\alpha \rightarrow 141\alpha$	
3.8103	1.0372	0.0024961	$137\alpha \rightarrow 142\alpha$	

Optimised geometry

Cl

C 1 1.754165

C 2 1.390734 1 115.565389

H 3 1.082225 2 120.152346 1 -2.689353 0

C 3 1.390703 2 118.957480 1 176.161590 0

C 5 1.390687 3 120.892833 2 0.166266 0

H 6 1.082301 5 120.896230 3 178.792063 0

C 6 1.390814 5 118.929301 3 0.127814 0

C 8 1.419121 6 123.269660 5 -0.348016 0
 C 9 1.474603 8 122.633894 6 -179.656507 0
 C 10 1.474150 9 119.996029 8 49.113020 0
 C 11 1.418896 10 122.674453 9 48.902969 0
 C 12 1.390747 11 123.261458 10 -179.902948 0
 H 13 1.082287 12 120.084967 11 -179.042116 0
 C 13 1.390622 12 118.974203 11 -0.254731 0
 C 15 1.390651 13 120.850369 12 0.039889 0
 H 16 1.082310 15 120.926798 13 178.911948 0
 C 16 1.390907 15 118.960721 13 0.235135 0
 C 10 1.474505 9 119.943789 8 -131.186218 0
 C 19 1.418865 10 122.632103 9 49.017468 0
 C 20 1.390958 19 123.284184 10 -179.435463 0
 H 21 1.082326 20 120.083080 19 -179.202059 0
 C 21 1.390423 20 118.936828 19 -0.458268 0
 C 23 1.390815 21 120.870440 20 0.062223 0
 H 24 1.082316 23 120.856463 21 178.954611 0
 C 24 1.390725 23 118.978413 21 0.248260 0
 Cl 5 1.749706 3 119.526945 2 -179.992049 0
 Cl 23 1.749780 21 119.546308 20 179.975256 0
 Cl 15 1.749973 13 119.528692 12 179.885688 0
 Cl 26 1.753908 24 115.539302 23 176.161861 0
 Cl 8 1.754325 6 115.555971 5 176.182597 0
 Cl 18 1.754437 16 115.516781 15 176.292285 0
 Cl 12 1.754566 11 121.130407 10 3.892930 0
 Cl 20 1.755086 19 121.131852 10 4.281575 0

Orbital energies in Hartrees

Alpha MOs

– Occupied –

*****-101.5689-101.5688-101.5658-101.5657-101.5657-101.5657-101.5657

***** -10.2840 -10.2840 -10.2840 -10.2840 -10.2839 -10.2839 -10.2817

-10.2817 -10.2817 -10.2564 -10.2479 -10.2479 -10.2479 -10.2290 -10.2290

-10.2290 -10.2290 -10.2290 -10.2290 -9.4851 -9.4851 -9.4850 -9.4819

-9.4819 -9.4819 -9.4818 -9.4818 -9.4818 -7.2492 -7.2491 -7.2489

-7.2461 -7.2461 -7.2460 -7.2460 -7.2460 -7.2460 -7.2395 -7.2395

-7.2394 -7.2389 -7.2389 -7.2389 -7.2362 -7.2361 -7.2361 -7.2361

-7.2360 -7.2360 -7.2357 -7.2357 -7.2356 -7.2356 -7.2356 -7.2356

-0.9456 -0.9314 -0.9314 -0.8984 -0.8916 -0.8916 -0.8915 -0.8882

-0.8882 -0.8358 -0.8259 -0.8259 -0.8180 -0.7618 -0.7617 -0.7566

-0.7563 -0.7562 -0.6899 -0.6339 -0.6338 -0.6274 -0.6232 -0.6231

-0.5983 -0.5474 -0.5473 -0.5289 -0.5169 -0.5168 -0.5075 -0.4859

-0.4859 -0.4762 -0.4617 -0.4616 -0.4567 -0.4567 -0.4563 -0.4391

-0.4390 -0.4356 -0.4224 -0.4100 -0.4100 -0.4073 -0.3968 -0.3968

-0.3865 -0.3840 -0.3839 -0.3781 -0.3728 -0.3728 -0.3407 -0.3367

-0.3359 -0.3358 -0.3337 -0.3336 -0.3314 -0.3232 -0.3219 -0.3219

-0.3148 -0.3148 -0.2962 -0.2680 -0.2680 -0.2670 -0.2615 -0.2615

-0.2114

– Virtual –

-0.0542 -0.0540 -0.0476 -0.0394 -0.0393 -0.0203 -0.0153 -0.0153

-0.0035 0.0354 0.0373 0.0374 0.0392 0.0393 0.0397 0.1029

0.1029 0.1295 0.1355 0.1375 0.1375 0.1498 0.1498 0.1568

0.1802 0.2045 0.2047 0.2376 0.2377 0.2495 0.2501 0.2501

0.2549 0.2659 0.2660 0.2675 0.2676 0.2751 0.3050 0.3051

0.3120 0.3347 0.3348 0.3615 0.3615 0.3617 0.3701 0.3702

0.3776 0.3810 0.3812 0.3833 0.3837 0.3837 0.3974 0.4011
0.4012 0.4058 0.4164 0.4165 0.4166 0.4261 0.4262 0.4265
0.4348 0.4364 0.4364 0.4428 0.4428 0.4562 0.4585 0.4591
0.4592 0.4743 0.5053 0.5056 0.5165 0.5209 0.5212 0.5354
0.5355 0.5508 0.5549 0.5559 0.5560 0.5677 0.5678 0.5720
0.5735 0.5735 0.5797 0.5855 0.5928 0.5929 0.5988 0.5990
0.6147 0.6284 0.6297 0.6354 0.6354 0.6438 0.6440 0.6714
0.6715 0.6846 0.6957 0.6958 0.7079 0.7082 0.7148 0.7235
0.7360 0.7360 0.7483 0.7485 0.7549 0.7549 0.7581 0.7760
0.7929 0.8010 0.8011 0.8073 0.8140 0.8141 0.8204 0.8207
0.8269 0.8418 0.8421 0.8456 0.8474 0.8485 0.8485 0.8535
0.8536 0.8537 0.8659 0.8661 0.8692 0.8711 0.8894 0.8894
0.8937 0.8995 0.8996 0.9036 0.9092 0.9093 0.9173 0.9259
0.9261 0.9491 0.9492 0.9510 0.9566 0.9761 0.9764 0.9798
0.9841 0.9843 1.0134 1.0137 1.0139 1.0199 1.0247 1.0250
1.0494 1.0496 1.0543 1.0929 1.0930 1.0998 1.1117 1.1136
1.1137 1.1189 1.1342 1.1344 1.1470 1.1488 1.1489 1.1502
1.1806 1.1809 1.2050 1.2100 1.2105 1.2446 1.2752 1.2894
1.2895 1.3015 1.3016 1.3469 1.3548 1.3549 1.3733 1.3734
1.3772 1.3931 1.3972 1.3977 1.4261 1.4263 1.4264 1.4332
1.4357 1.4358 1.4852 1.5202 1.5247 1.5253 1.5277 1.5277
1.5465 1.5466 1.5698 1.5714 1.6057 1.6435 1.6440 1.7107
1.7164 1.7166 1.7516 1.7517 1.7931 1.8091 1.8095 1.8101
1.8306 1.8571 1.8572 1.8815 1.8816 1.8861 1.8921 1.9275
1.9277 1.9391 1.9392 1.9995 2.0063 2.0064 2.0115 2.0141
2.0141 2.0394 2.0496 2.0497 2.0677 2.0698 2.0718 2.0718
2.1075 2.1077 2.1543 2.1544 2.1596 2.1779 2.2220 2.2221
2.2420 2.2581 2.2584 2.2675 2.2680 2.2944 2.2944 2.4018

2.4032 2.4034 2.4266 2.4268 2.4688 2.4896 2.4896 2.4967
2.5276 2.5277 2.5490 2.5491 2.5677 2.5768 2.5798 2.5801
2.5841 2.5926 2.5927 2.5965 2.5968 2.6052 2.6583 2.6762
2.6764 2.7085 2.7261 2.7261 2.8316 2.8493 2.8494 2.8711
2.9030 2.9062 2.9062 2.9724 2.9728 3.0982 3.1488 3.1519
3.1521 3.1705 3.1707 3.3510 3.3526 3.3527 3.5651 3.5725
3.5726 4.0501 4.0525 4.0526 4.0584 4.0589 4.0590 4.0859
4.1107 4.1108 4.2300 4.2398 4.2400 4.2485 4.2716 4.2717
4.3063 4.3064 4.3275 4.3616 4.3727 4.3731 4.4013 4.4287
4.4289 4.4718 4.6889 4.6891 4.7339

Beta MOs

– Occupied –

*****-101.5688-101.5688-101.5658-101.5657-101.5657-101.5657-101.5657
***** -10.2824 -10.2824 -10.2824 -10.2824 -10.2824 -10.2824 -10.2804
-10.2804 -10.2804 -10.2495 -10.2494 -10.2494 -10.2456 -10.2296 -10.2296
-10.2296 -10.2296 -10.2296 -10.2295 -9.4850 -9.4850 -9.4850 -9.4819
-9.4818 -9.4818 -9.4818 -9.4818 -9.4818 -7.2492 -7.2491 -7.2490
-7.2461 -7.2461 -7.2461 -7.2461 -7.2461 -7.2461 -7.2392 -7.2392
-7.2392 -7.2389 -7.2389 -7.2388 -7.2361 -7.2360 -7.2360 -7.2360
-7.2359 -7.2359 -7.2356 -7.2356 -7.2356 -7.2356 -7.2356 -7.2356
-0.9425 -0.9301 -0.9301 -0.8962 -0.8905 -0.8905 -0.8904 -0.8872
-0.8871 -0.8303 -0.8256 -0.8256 -0.8135 -0.7615 -0.7614 -0.7566
-0.7562 -0.7562 -0.6805 -0.6319 -0.6318 -0.6244 -0.6215 -0.6215
-0.5948 -0.5461 -0.5460 -0.5242 -0.5161 -0.5161 -0.5053 -0.4847
-0.4846 -0.4755 -0.4597 -0.4596 -0.4563 -0.4563 -0.4558 -0.4365
-0.4364 -0.4317 -0.4211 -0.4086 -0.4086 -0.4044 -0.3956 -0.3955
-0.3842 -0.3814 -0.3813 -0.3751 -0.3703 -0.3703 -0.3391 -0.3364
-0.3357 -0.3357 -0.3336 -0.3335 -0.3299 -0.3224 -0.3218 -0.3218

-0.3138 -0.3138 -0.2780 -0.2667 -0.2666 -0.2656 -0.2605 -0.2605

– Virtual –

-0.1264 -0.0505 -0.0503 -0.0446 -0.0364 -0.0363 -0.0178 -0.0133

-0.0132 0.0112 0.0373 0.0389 0.0390 0.0406 0.0406 0.0413

0.1051 0.1052 0.1335 0.1360 0.1375 0.1375 0.1501 0.1502

0.1584 0.1875 0.2065 0.2067 0.2391 0.2392 0.2501 0.2502

0.2556 0.2564 0.2660 0.2661 0.2676 0.2755 0.2809 0.3071

0.3072 0.3126 0.3351 0.3352 0.3623 0.3623 0.3632 0.3706

0.3707 0.3796 0.3817 0.3820 0.3852 0.3852 0.3855 0.3980

0.4026 0.4027 0.4062 0.4171 0.4171 0.4184 0.4267 0.4268

0.4270 0.4358 0.4372 0.4372 0.4431 0.4432 0.4573 0.4594

0.4597 0.4598 0.4822 0.5062 0.5065 0.5212 0.5215 0.5222

0.5363 0.5364 0.5521 0.5561 0.5565 0.5566 0.5683 0.5685

0.5734 0.5736 0.5736 0.5818 0.5842 0.5932 0.5933 0.6009

0.6012 0.6183 0.6306 0.6315 0.6363 0.6363 0.6458 0.6460

0.6732 0.6733 0.6873 0.6971 0.6972 0.7082 0.7084 0.7155

0.7320 0.7370 0.7370 0.7506 0.7507 0.7560 0.7561 0.7591

0.7826 0.7929 0.8009 0.8010 0.8077 0.8143 0.8144 0.8214

0.8217 0.8284 0.8424 0.8426 0.8468 0.8482 0.8492 0.8493

0.8541 0.8542 0.8544 0.8667 0.8669 0.8707 0.8717 0.8900

0.8901 0.8958 0.9004 0.9005 0.9052 0.9103 0.9104 0.9188

0.9266 0.9268 0.9499 0.9500 0.9561 0.9617 0.9773 0.9777

0.9804 0.9853 0.9855 1.0150 1.0152 1.0192 1.0219 1.0252

1.0255 1.0502 1.0503 1.0534 1.0941 1.0942 1.1039 1.1128

1.1148 1.1150 1.1220 1.1355 1.1356 1.1488 1.1501 1.1502

1.1506 1.1819 1.1821 1.2069 1.2111 1.2116 1.2483 1.2791

1.2913 1.2914 1.3020 1.3022 1.3483 1.3551 1.3551 1.3735

1.3737 1.3788 1.3940 1.3988 1.3993 1.4277 1.4280 1.4283

1.4342 1.4366 1.4368 1.4897 1.5220 1.5267 1.5274 1.5301
 1.5302 1.5494 1.5494 1.5726 1.5736 1.6082 1.6479 1.6485
 1.7111 1.7174 1.7175 1.7529 1.7531 1.8056 1.8109 1.8117
 1.8120 1.8371 1.8611 1.8611 1.8838 1.8839 1.8861 1.8922
 1.9366 1.9368 1.9438 1.9439 2.0020 2.0088 2.0088 2.0149
 2.0173 2.0173 2.0416 2.0520 2.0521 2.0678 2.0722 2.0723
 2.0736 2.1087 2.1089 2.1576 2.1577 2.1611 2.1773 2.2239
 2.2240 2.2437 2.2610 2.2613 2.2694 2.2827 2.2976 2.2976
 2.4031 2.4061 2.4063 2.4336 2.4338 2.4806 2.4891 2.4892
 2.5056 2.5284 2.5285 2.5497 2.5499 2.5674 2.5772 2.5808
 2.5811 2.5845 2.5936 2.5937 2.5981 2.5984 2.6090 2.6590
 2.6769 2.6770 2.7101 2.7290 2.7291 2.8371 2.8507 2.8508
 2.8720 2.9036 2.9070 2.9070 2.9744 2.9748 3.0988 3.1497
 3.1538 3.1540 3.1715 3.1716 3.3509 3.3526 3.3527 3.5653
 3.5727 3.5727 4.0526 4.0543 4.0544 4.0601 4.0604 4.0605
 4.0875 4.1125 4.1126 4.2330 4.2394 4.2395 4.2482 4.2716
 4.2717 4.3064 4.3066 4.3313 4.3648 4.3734 4.3738 4.4022
 4.4283 4.4285 4.4817 4.6892 4.6894 4.7384

Excited states from TDDFT/TDA

Excited state 1: excitation energy (eV) = 2.7281

Total energy for state 1: -4869.25209542 au

$\langle S^2 \rangle$: 0.8880

Trans. Mom.: -0.6714 X 0.1344 Y 0.0007 Z

Strength : 0.0313358686

S(1) $\rightarrow$ V(2) amplitude = 0.2669 alpha

D(133) $\rightarrow$ S(1) amplitude = -0.1747 beta

D(136) $\rightarrow$ S(1) amplitude = 0.9191 beta

Excited state 2: excitation energy (eV) = 2.7285

Total energy for state 2: -4869.25208239 au

$\langle S^2 \rangle$: 0.8881

Trans. Mom.: -0.1337 X -0.6672 Y 0.0007 Z

Strength : 0.0309485674

S(1) $\rightarrow$ V(1) amplitude = 0.2678 alpha

D(132) $\rightarrow$ S(1) amplitude = -0.1745 beta

D(135) $\rightarrow$ S(1) amplitude = 0.9188 beta

Excited state 3: excitation energy (eV) = 2.9581

Total energy for state 3: -4869.24364404 au

$\langle S^2 \rangle$: 0.8504

Trans. Mom.: 0.0534 X -0.0076 Y 0.3481 Z

Strength : 0.0089904967

S(1) $\rightarrow$ V(3) amplitude = 0.1703 alpha

D(134) $\rightarrow$ S(1) amplitude = 0.9607 beta

Excited state 4: excitation energy (eV) = 2.9622

Total energy for state 4: -4869.24349239 au

$\langle S^2 \rangle$: 0.8651

Trans. Mom.: 0.2421 X -0.2160 Y -0.0469 Z

Strength : 0.0077979747

S(1) $\rightarrow$ V(2) amplitude = -0.1661 alpha

D(132) $\rightarrow$ S(1) amplitude = -0.1961 beta

D(133) $\rightarrow$ S(1) amplitude = 0.8961 beta

D(136) $\rightarrow$ S(1) amplitude = 0.1997 beta

Excited state 5: excitation energy (eV) = 2.9626

Total energy for state 5: -4869.24348018 au

$\langle S^2 \rangle$: 0.8655

Trans. Mom.: 0.2156 X 0.2439 Y -0.0294 Z

Strength : 0.0077560765

S(1) → V(1) amplitude = -0.1698 alpha

D(132) → S(1) amplitude = 0.9018 beta

D(133) → S(1) amplitude = 0.1878 beta

D(135) → S(1) amplitude = 0.2031 beta

Excited state 6: excitation energy (eV) = 3.2083

Total energy for state 6: -4869.23444938 au

$\langle S^2 \rangle$: 0.9633

Trans. Mom.: -0.0002 X -0.0049 Y 0.0019 Z

Strength : 0.0000022116

S(1) → V(9) amplitude = -0.2535 alpha

D(131) → S(1) amplitude = 0.9118 beta

Excited state 7: excitation energy (eV) = 3.4542

Total energy for state 7: -4869.22541154 au

$\langle S^2 \rangle$: 0.9972

Trans. Mom.: 0.2293 X 1.6094 Y -0.0018 Z

Strength : 0.2236567315

S(1) → V(1) amplitude = 0.8772 alpha

D(132) → S(1) amplitude = 0.2496 beta

D(135) → S(1) amplitude = -0.2399 beta

Excited state 8: excitation energy (eV) = 3.4586

Total energy for state 8: -4869.22525163 au

$\langle S^2 \rangle$: 0.9994

Trans. Mom.: 1.6137 X -0.2305 Y 0.0041 Z

Strength : 0.2251558495

S(1) → V(2) amplitude = 0.8770 alpha

D(133) → S(1) amplitude = 0.2485 beta

D(136) → S(1) amplitude = -0.2393 beta

Excited state 9: excitation energy (eV) = 3.6154

Total energy for state 9: -4869.21948916 au

$\langle S^2 \rangle$: 0.9600

Trans. Mom.: 0.0072 X -0.0073 Y -0.3900 Z

Strength : 0.0134795990

S(1) $\rightarrow$ V(3) amplitude = 0.9529 alpha

D(134) $\rightarrow$ S(1) amplitude = -0.1777 beta

Excited state 10: excitation energy (eV) = 3.8078

Total energy for state 10: -4869.21241806 au

$\langle S^2 \rangle$: 1.0358

Trans. Mom.: -0.0566 X -0.1554 Y 0.0021 Z

Strength : 0.0025512786

S(1) $\rightarrow$ V(4) amplitude = 0.9382 alpha

Excited state 11: excitation energy (eV) = 3.8103

Total energy for state 11: -4869.21232661 au

$\langle S^2 \rangle$: 1.0372

Trans. Mom.: -0.1542 X 0.0543 Y -0.0018 Z

Strength : 0.0024961320

S(1) $\rightarrow$ V(5) amplitude = 0.9378 alpha

Excited state 12: excitation energy (eV) = 3.9515

Total energy for state 12: -4869.20713792 au

$\langle S^2 \rangle$: 2.5780

Trans. Mom.: 0.0002 X -0.0007 Y -0.0002 Z

Strength : 0.0000000596

D(132) $\rightarrow$ V(1) amplitude = 0.1630 alpha

D(132) $\rightarrow$ V(4) amplitude = -0.2163 alpha

D(133) $\rightarrow$ V(2) amplitude = 0.1625 alpha

D(133) $\rightarrow$ V(5) amplitude = -0.2157 alpha

D(134) -> V(3) amplitude = -0.3314 alpha
 D(135) -> V(1) amplitude = -0.1913 alpha
 D(135) -> V(4) amplitude = -0.1854 alpha
 D(136) -> V(2) amplitude = -0.1884 alpha
 D(136) -> V(5) amplitude = -0.1863 alpha
 D(131) -> S(1) amplitude = -0.2687 beta
 D(132) -> V(1) amplitude = 0.1736 beta
 D(132) -> V(4) amplitude = -0.2004 beta
 D(133) -> V(2) amplitude = -0.1731 beta
 D(133) -> V(5) amplitude = -0.2000 beta
 D(134) -> V(3) amplitude = -0.3009 beta
 D(135) -> V(1) amplitude = -0.2429 beta
 D(135) -> V(4) amplitude = -0.1688 beta
 D(136) -> V(2) amplitude = 0.2405 beta
 D(136) -> V(5) amplitude = -0.1695 beta
 Excited state 13: excitation energy (eV) = 4.0679
 Total energy for state 13: -4869.20285902 au
 $\langle S^2 \rangle$: 2.5489
 Trans. Mom.: 0.0324 X -0.1957 Y -0.0003 Z
 Strength : 0.0039214477
 D(132) -> V(3) amplitude = 0.2029 alpha
 D(132) -> V(4) amplitude = 0.1957 alpha
 D(133) -> V(3) amplitude = 0.2318 alpha
 D(133) -> V(5) amplitude = -0.1948 alpha
 D(134) -> V(5) amplitude = 0.2945 alpha
 D(135) -> V(1) amplitude = -0.1608 alpha
 D(136) -> V(2) amplitude = 0.1574 alpha
 D(136) -> V(3) amplitude = 0.2296 alpha

S(1) → V(1) amplitude = -0.2323 alpha
 D(132) → V(3) amplitude = 0.1982 beta
 D(132) → V(4) amplitude = 0.1950 beta
 D(133) → V(3) amplitude = 0.2424 beta
 D(133) → V(5) amplitude = -0.1954 beta
 D(134) → V(5) amplitude = 0.2915 beta
 D(136) → V(3) amplitude = 0.2128 beta
 Excited state 14: excitation energy (eV) = 4.0684
 Total energy for state 14: -4869.20284124 au
 $\langle S^2 \rangle$: 2.5477
 Trans. Mom.: -0.1983 X -0.0317 Y 0.0002 Z
 Strength : 0.0040192136
 D(132) → V(3) amplitude = -0.2315 alpha
 D(132) → V(5) amplitude = -0.1953 alpha
 D(133) → V(3) amplitude = 0.2009 alpha
 D(133) → V(4) amplitude = -0.1945 alpha
 D(134) → V(4) amplitude = -0.2957 alpha
 D(135) → V(2) amplitude = 0.1601 alpha
 D(135) → V(3) amplitude = -0.2254 alpha
 D(136) → V(1) amplitude = 0.1607 alpha
 S(1) → V(2) amplitude = -0.2333 alpha
 D(132) → V(3) amplitude = -0.2413 beta
 D(132) → V(5) amplitude = -0.1952 beta
 D(133) → V(3) amplitude = 0.1963 beta
 D(133) → V(4) amplitude = -0.1929 beta
 D(134) → V(4) amplitude = -0.2946 beta
 D(135) → V(3) amplitude = -0.2090 beta
 Excited state 15: excitation energy (eV) = 4.3434

Total energy for state 15: -4869.19273364 au

$\langle S^2 \rangle$: 1.2222

Appendix B

Supporting Information of Chapter 3: Enhancing the ODMR Signal of Organic Molecular Qubits

B.1 Rate equations for the microkinetic model

The rate equations are

$$\frac{d}{dt}\mathbf{N} = \mathbf{K}\mathbf{N}, \quad (\text{B.1})$$

where

$$\mathbf{N} \equiv \left(n_{\text{GS}} \quad n_{\text{GT0}} \quad n_{\text{GT1}} \quad n_{\text{CT}} \quad n_{\text{ES}} \quad n_{\text{ES}^*} \quad n_{\text{ET0}} \quad n_{\text{ET1}} \quad n_{\text{ET}^*0} \quad n_{\text{ET}^*1} \right)^{\text{T}} \quad (\text{B.2})$$

is a column vector containing the eigenstate populations, and

$$\begin{aligned}
\mathbf{K} \equiv \text{diag} & \begin{pmatrix} -2k_{\text{abs}} - 3k_{\text{decoh}} \\ -2k_{\text{abs}} - k_{\text{decoh}} - 2\kappa_{\text{decoh}} \\ -4k_{\text{abs}} - k_{\text{decoh}} - \kappa_{\text{decoh}} \\ -k_{\text{CT-GS}} - 4k_{\text{CT-ET}} - k_{\text{CT-GT}}/2 \\ -2k_{\text{ES-CT}} - 2k_{\text{ES-GT}} - 6k_{\text{decoh}} \\ -2k_{\text{VR}} - k_{\text{abs}} \\ -k_{\text{ET-GT}} - 2k_{\text{decoh}} - 4\kappa_{\text{decoh}} \\ -2k_{\text{ET-CT}} - k_{\text{ET-GS}} - 2k_{\text{ET-GT}} - 2k_{\text{decoh}} - 2\kappa_{\text{decoh}} \\ -2k_{\text{VR}} - k_{\text{abs}} \\ -4k_{\text{VR}} - 2k_{\text{abs}} \end{pmatrix} \\
+ & \begin{pmatrix} 0 & k_{\text{decoh}} & k_{\text{decoh}} & k_{\text{CT-GS}} & 0 & k_{\text{abs}} & 0 & k_{\text{ET-GS}} & 0 & 0 \\ k_{\text{decoh}} & 0 & \kappa_{\text{decoh}} & k_{\text{CT-GT}}/2 & 0 & 0 & k_{\text{ET-GT}} & 0 & k_{\text{abs}} & 0 \\ 2k_{\text{decoh}} & 2\kappa_{\text{decoh}} & 0 & 0 & 2k_{\text{ES-GT}} & 0 & 0 & 2k_{\text{ET-GT}} & 0 & 2k_{\text{abs}} \\ 0 & 0 & 0 & 0 & 2k_{\text{ES-CT}} & 0 & 0 & 2k_{\text{ET-CT}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2k_{\text{VR}} & 2k_{\text{decoh}} & 2k_{\text{decoh}} & 0 & 0 \\ 2k_{\text{abs}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2k_{\text{decoh}} & 0 & 0 & 2\kappa_{\text{decoh}} & 2k_{\text{VR}} & 0 \\ 0 & 0 & 0 & 4k_{\text{CT-ET}} & 4k_{\text{decoh}} & 0 & 4\kappa_{\text{decoh}} & 0 & 0 & 4k_{\text{VR}} \\ 0 & 2k_{\text{abs}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 4k_{\text{abs}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}
\end{aligned} \tag{B.3}$$

is a matrix containing the rate constants. Note the factor of 1/2 accompanying $k_{\text{CT-GT}}$, which is needed because this ISC occurs only from the $^1\text{CT}_A$ state. Also, we have defined

the diag operator by

$$\text{diag } (a_1, a_2, \dots, a_j, \dots)^T \equiv \begin{pmatrix} a_1 & & & \\ & a_2 & & \\ & & \ddots & \\ & & & a_j \\ & & & & \ddots \end{pmatrix}. \quad (\text{B.4})$$

B.2 Estimate of the maximum optical pump rate

We estimate the pump rate k_{abs} using the Einstein B coefficient to be

$$k_{\text{abs}} = \frac{e^2 \rho(\nu)}{4\epsilon_0 m_e h \nu} f_{\text{osc}}, \quad (\text{B.5})$$

where ν and f_{osc} are the frequency and oscillator strength of the transition in question, and $\rho(\nu)$ is the spectral energy density of the radiation field at frequency ν . The remaining symbols are constants with e for the elementary charge, ϵ_0 for the vacuum permittivity, m_e for the electron mass, and h for the Planck constant. To obtain $\rho(\nu)$, we considered a teaching lab set-up [251], which focused a 532 nm Thorlabs DJ532-40 laser with a power P of 40 mW onto a diameter $2r$ of $10\mu\text{m}$. We further assumed the lineshape to be flat around the peak frequency and zero elsewhere; the linewidth $\delta\nu$ was estimated from the user manual to be around 30 MHz. Then, a crude estimate of $\rho(\nu)$ would be

$$\rho(\nu) \approx \frac{P}{c\pi r^2 \delta\nu} = 5.67 \times 10^{-8} \text{ J m}^{-3} \text{ Hz}^{-1}, \quad (\text{B.6})$$

where c is the speed of light. Taking ν to be the frequency corresponding to 532 nm wavelength light, we obtain the following upper bound to the pump rate:

$$k_{\text{abs}} \lesssim (1.21 \times 10^{14} \text{ s}^{-1}) f_{\text{osc}}. \quad (\text{B.7})$$

f_{osc} for the lowest-lying excitation of trityl-based radicals is typically around 0.01 [179], hence

$$k_{\text{abs}} \lesssim 10^{12} \text{ s}^{-1}. \quad (\text{B.8})$$

B.3 Results from ab initio calculations

B.3.1 Benzyl-*p*-benzyl diradical

The triplet SCF calculation converged to an energy of -14692.84714 eV and an $\langle \mathbf{S}^2 \rangle$ value of 2.066128. The level of theory was UB3LYP-D3BJ/def2-SVP.

Relaxed geometry

```

C 0.00000 -0.00000 0.74467
C 0.85600 0.85600 1.46798
C 0.86047 0.86047 2.85451
C 0.00000 -0.00000 3.60202
C -0.86047 -0.86047 2.85451
C -0.85600 -0.85600 1.46798
C 0.00000 -0.00000 5.00984
C 0.00000 0.00000 -0.74467
C -0.85600 0.85600 -1.46798
C -0.86047 0.86047 -2.85451
C 0.00000 0.00000 -3.60202
C 0.86047 -0.86047 -2.85451
C 0.85600 -0.85600 -1.46798
C 0.00000 0.00000 -5.00984
H 1.53268 1.53268 3.39476
H -1.53268 -1.53268 3.39476
H 1.52419 1.52419 0.91856

```


H -1.52419 -1.52419 0.91856
 H 0.66239 0.66239 5.57165
 H -0.66239 -0.66239 5.57165
 H -1.52419 1.52419 -0.91856
 H -1.53268 1.53268 -3.39476
 H 1.53268 -1.53268 -3.39476
 H 1.52419 -1.52419 -0.91856
 H 0.66239 -0.66239 -5.57165
 H -0.66239 0.66239 -5.57165

B.3.2 PT₂TM-*p*-PT₂TM diradical

At the UB3LYP-D3BJ/def2-SVP level, the triplet SCF calculation converged to an energy of -289833.13523 eV and an $\langle S^2 \rangle$ value of 2.042099. At the UB3LYP/def2-SVPD level, the triplet SCF calculation converged to an energy of -289830.85584 eV and an $\langle S^2 \rangle$ value of 2.042475, while the BS SCF calculation converged to an energy of -289830.85637 eV and an $\langle S^2 \rangle$ value of 1.043240.

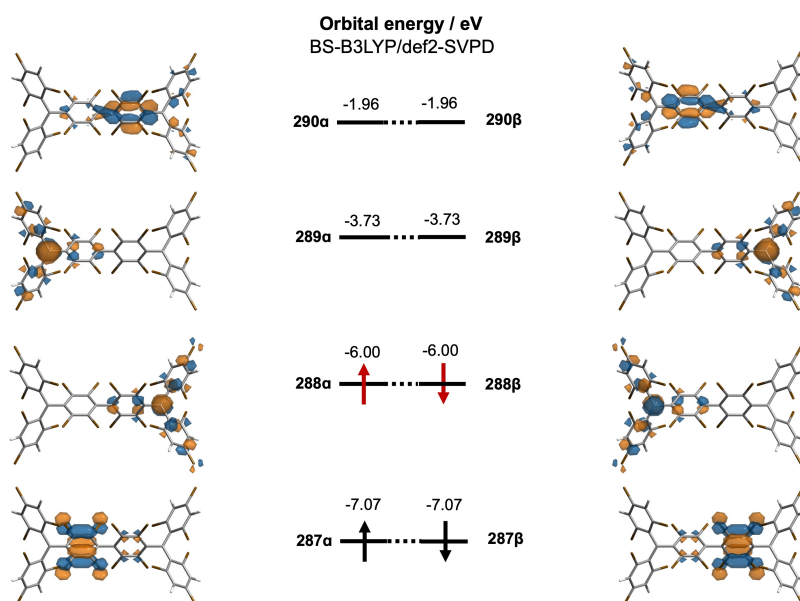


Figure B.1. Frontier MOs (isovalue = 0.040) of PT₂TM-*p*-PT₂TM in the open-shell BS ground state, calculated at the BS-B3LYP/def2-SVPD level.

Optimised geometry

C -0.00000574198939 0.00001886283277 -0.74318861439021
C -0.82678095278225 -0.88014609927434 -1.45536400066426
Cl -1.86258482682735 -1.95194106627830 -0.56444113784991
C -0.83158350247726 -0.88052339029383 -2.85590319631644
Cl -1.95524855748238 -1.91142816496441 -3.68705975754690
C -0.00000581608866 0.00001070235900 -3.58709128147569
C -0.00000299485762 0.00000270365669 -5.06000657824186
C 0.83157078934871 0.88055023033315 -2.85590840237393
Cl 1.95523778087506 1.91144805135712 -3.68707097425392
C 0.82676835945782 0.88018086804408 -1.45536905544954
Cl 1.86257456143681 1.95197859168642 -0.56445230199539
C -0.00000217001731 0.00001886023804 0.74318883337673
C -0.82677472934388 0.88018224539217 1.45536943291133
Cl -1.86258005949903 1.95198119702163 0.56445301708662
C -0.83157635775357 0.88055200382982 2.85590876820934
Cl -1.95524159458849 1.91145152361032 3.68707165578374
C -0.00000037868010 0.00001166522908 3.58709138684470
C -0.00000217031194 0.00000400182907 5.06000668839507
C 0.83157573883127 -0.88052373037234 2.85590315107515
Cl 1.95523992781849 -1.91142956821651 3.68705956373061
C 0.82677228466328 -0.88014698607087 1.45536398549090
Cl 1.86257439566614 -1.95194342327608 0.56444084701128
C 0.17900551702102 1.26105603892104 5.78366664773472
C 1.18654999229765 2.19790973989786 5.43741456569588
Cl 2.34674782212454 1.83644445241497 4.18400725246410
C 1.35578328747814 3.40684333867228 6.10821255653891
C 0.50637407962282 3.71770775388578 7.17018267287389

CI 0.70601325535163 5.22457207778832 8.01770385285598
C -0.50173341875719 2.83484933278354 7.55989016889500
C -0.65389520593741 1.63504372449640 6.86985291974398
CI -1.99962191524371 0.62889321298102 7.34263264520852
C -0.17900731381876 -1.26105719724744 5.78365132901835
C 0.65389603742513 -1.63505770789699 6.86983115658126
CI 1.99962002055447 -0.62890949357922 7.34262357276859
C 0.50173985908195 -2.83487427268144 7.55985059808921
C -0.50636443216016 -3.71773102480600 7.17013096038665
CI -0.70599589518047 -5.22460914677200 8.01762938869358
C -1.35577635243562 -3.40685394272176 6.10816672444608
C -1.18654882214552 -2.19790949292590 5.43738678478131
CI -2.34674901230920 -1.83643049144512 4.18398555581708
C -0.17900758247265 1.26105489983025 -5.78366697668087
C 0.65389622129251 1.63504114729646 -6.86985133538927
CI 1.99962136494639 0.62888751881681 -7.34262894868841
C 0.50173892567358 2.83484762634097 -7.55988803632161
C -0.50636691203772 3.71770851048111 -7.17018180219864
CI -0.70599985874512 5.22457422381186 -8.01770195128842
C -1.35577896714643 3.40684562968217 -6.10821351254259
C -1.18655038448497 2.19791090446352 -5.43741629119332
CI -2.34675149392943 1.83644779362864 -4.18401136732756
C 0.17900538028328 -1.26105804288897 -5.78365098915979
C 1.18655104625317 -2.19790638119409 -5.43738774456401
CI 2.34675168860653 -1.83642266135838 -4.18398831465705
C 1.35578318435328 -3.40684960143919 -6.10816867440069
C 0.50637160709494 -3.71772954726441 -7.17013232856319
CI 0.70600875240596 -5.22460635065789 -8.01763178908284

C -0.50173704243424 -2.83487703443063 -7.55985028577585
 C -0.65389753780493 -1.63506141783068 -6.86983015992414
 Cl -1.99962641341773 -0.62891874914231 -7.34262045883576
 H 2.15383251571159 4.08730443443524 5.81464959278671
 H -1.17756531411163 3.08516224915109 8.37639864788383
 H 1.17757398010457 -3.08519688520980 8.37635426492385
 H -2.15382312551000 -4.08731387719391 5.81459441988635
 H 1.17757314063382 3.08515940411222 -8.37639495110400
 H -2.15382680646866 4.08730873330317 -5.81465144967596
 H 2.15383311378736 -4.08730637419219 -5.81459757501016
 H -1.17757097095111 -3.08520213298905 -8.37635336504712

Triplet excited states from UB3LYP/TDDFT/TDA/def2-SVPD

STATE 1: E= 0.093149 au

282b -> 288b : 0.057155 (c= 0.23907088)
 283b -> 287b : 0.083378 (c= 0.28875206)
 285b -> 288b : 0.348725 (c= -0.59052963)
 286b -> 287b : 0.457583 (c= 0.67644853)

STATE 2: E= 0.093205 au

282b -> 287b : 0.063197 (c= -0.25138950)
 283b -> 288b : 0.083895 (c= -0.28964616)
 285b -> 287b : 0.397785 (c= 0.63070190)
 286b -> 288b : 0.400775 (c= -0.63306814)

STATE 3: E= 0.096181 au

287a -> 290a : 0.021460 (c= -0.14649167)
 288a -> 289a : 0.028774 (c= 0.16962792)
 277b -> 288b : 0.037751 (c= 0.19429633)
 281b -> 288b : 0.335959 (c= 0.57961952)

284b -> 287b : 0.520854 (c= -0.72170183)

STATE 4: E= 0.096859 au

287a -> 289a : 0.038217 (c= 0.19549194)

288a -> 290a : 0.035136 (c= -0.18744546)

277b -> 287b : 0.033009 (c= -0.18168410)

281b -> 287b : 0.373787 (c= -0.61138117)

284b -> 288b : 0.465990 (c= 0.68263493)

STATE 5: E= 0.096945 au

287a -> 292a : 0.028892 (c= 0.16997656)

288a -> 291a : 0.024328 (c= -0.15597515)

282b -> 288b : 0.351610 (c= -0.59296688)

283b -> 287b : 0.375825 (c= -0.61304560)

285b -> 288b : 0.035408 (c= -0.18816884)

286b -> 287b : 0.133565 (c= 0.36546515)

STATE 6: E= 0.097079 au

287a -> 291a : 0.024191 (c= -0.15553573)

288a -> 292a : 0.030420 (c= 0.17441401)

282b -> 287b : 0.378789 (c= 0.61545844)

283b -> 288b : 0.344036 (c= 0.58654606)

285b -> 287b : 0.054106 (c= 0.23260648)

286b -> 288b : 0.119298 (c= -0.34539516)

STATE 7: E= 0.104197 au

287a -> 291a : 0.012208 (c= 0.11049073)

288a -> 293a : 0.012435 (c= -0.11151433)

279b -> 287b : 0.471603 (c= -0.68673332)

280b -> 288b : 0.437931 (c= -0.66176332)

282b -> 287b : 0.012287 (c= 0.11084545)

STATE 8: E= 0.104205 au

287a -> 293a : 0.012500 (c= -0.11180518)

288a -> 291a : 0.012225 (c= 0.11056768)

279b -> 288b : 0.434934 (c= 0.65949515)

280b -> 287b : 0.474013 (c= 0.68848638)

282b -> 288b : 0.011371 (c= -0.10663722)

283b -> 287b : 0.011275 (c= -0.10618423)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State Energy Wavelength fosc T2 TX TY TZ
(cm-1) (nm) (au**2) (au) (au)

1 20443.8 489.1 0.003282776 0.05286 0.22991 -0.00163 -0.00000

2 20456.0 488.9 0.019409525 0.31237 -0.00069 -0.55890 0.00005

3 21109.3 473.7 0.060043138 0.93641 -0.00003 0.00005 -0.96768

4 21258.1 470.4 0.000000020 0.00000 0.00016 -0.00052 -0.00009

5 21276.9 470.0 0.000801065 0.01239 0.11133 0.00083 -0.00019

6 21306.4 469.3 0.061450615 0.94949 -0.00010 0.97442 0.00010

7 22868.6 437.3 0.005164043 0.07434 -0.00696 -0.27257 0.00004

8 22870.3 437.2 0.011462876 0.16501 0.40618 -0.00466 0.00004

Singlet excited states from BS-B3LYP/TDDFT/TDA/def2-SVPD

STATE 1: E= 0.072498 au

287a -> 288a : 0.440292 (c= 0.66354522)

287b -> 288b : 0.555762 (c= -0.74549461)

STATE 2: E= 0.072512 au

287a -> 288a : 0.555944 (c= -0.74561668)

287b -> 288b : 0.440475 (c= -0.66368284)

STATE 3: E= 0.093217 au

284a -> 288a : 0.074182 (c= 0.27236462)

285a -> 288a : 0.059299 (c= 0.24351293)

286a -> 288a : 0.349276 (c= 0.59099606)

284b -> 288b : 0.071064 (c= -0.26657893)

285b -> 288b : 0.056877 (c= 0.23848921)

286b -> 288b : 0.334941 (c= -0.57874068)

STATE 4: E= 0.093249 au

284a -> 288a : 0.073716 (c= 0.27150602)

285a -> 288a : 0.057721 (c= 0.24025234)

286a -> 288a : 0.331261 (c= 0.57555284)

284b -> 288b : 0.076815 (c= 0.27715504)

285b -> 288b : 0.060221 (c= -0.24540067)

286b -> 288b : 0.345538 (c= 0.58782483)

STATE 5: E= 0.096325 au

278a -> 288a : 0.012457 (c= 0.11160882)

281a -> 288a : 0.078066 (c= 0.27940275)

283a -> 288a : 0.352531 (c= -0.59374329)

287a -> 289a : 0.020073 (c= -0.14168042)

278b -> 288b : 0.012411 (c= 0.11140512)

281b -> 288b : 0.078090 (c= 0.27944607)

283b -> 288b : 0.351778 (c= -0.59310870)

287b -> 289b : 0.020113 (c= -0.14182153)

STATE 6: E= 0.096800 au

281a -> 288a : 0.076101 (c= 0.27586331)

283a -> 288a : 0.343482 (c= -0.58607367)

287a -> 289a : 0.031310 (c= 0.17694758)

281b -> 288b : 0.076389 (c= -0.27638594)

283b -> 288b : 0.343945 (c= 0.58646847)

287b -> 289b : 0.031262 (c= -0.17681019)

STATE 7: E= 0.097041 au

284a -> 288a : 0.359091 (c= -0.59924219)

286a -> 288a : 0.087502 (c= 0.29580779)

287a -> 291a : 0.024935 (c= 0.15790760)

284b -> 288b : 0.353061 (c= -0.59418932)

286b -> 288b : 0.086024 (c= 0.29329775)

287b -> 291b : 0.025363 (c= -0.15925665)

STATE 8: E= 0.097082 au

284a -> 288a : 0.354277 (c= 0.59521151)

286a -> 288a : 0.084660 (c= -0.29096448)

287a -> 291a : 0.026324 (c= 0.16224807)

284b -> 288b : 0.360305 (c= -0.60025406)

286b -> 288b : 0.086093 (c= 0.29341546)

287b -> 291b : 0.025886 (c= 0.16089062)

STATE 9: E= 0.104217 au

280a -> 288a : 0.511958 (c= 0.71551211)

284a -> 288a : 0.012066 (c= 0.10984483)

280b -> 288b : 0.397747 (c= -0.63067226)

287b -> 291b : 0.011606 (c= -0.10773213)

STATE 10: E= 0.104226 au

280a -> 288a : 0.397434 (c= -0.63042366)

287a -> 291a : 0.011375 (c= -0.10665240)

280b -> 288b : 0.511638 (c= -0.71528872)

284b -> 288b : 0.012492 (c= -0.11176961)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm ⁻¹)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ (au)
1	15911.4	628.5	0.000009813	0.00020	-0.00000	0.00000	0.01425
2	15914.6	628.4	0.002904789	0.06009	-0.00000	-0.00000	0.24513
3	20458.7	488.8	0.019443057	0.31287	0.00239	-0.55934	0.00004
4	20465.8	488.6	0.003239369	0.05211	0.22820	0.00583	0.00000
5	21140.9	473.0	0.059563393	0.92754	0.00002	0.00005	0.96309
6	21245.1	470.7	0.000000015	0.00000	-0.00002	0.00028	-0.00040
7	21298.0	469.5	0.000872328	0.01348	0.11605	0.00413	-0.00012
8	21307.0	469.3	0.061700546	0.95333	0.00049	-0.97638	-0.00000
9	22872.9	437.2	0.005190136	0.07470	-0.02564	0.27211	-0.00002
10	22875.0	437.2	0.011509315	0.16564	0.40663	0.01714	0.00004

B.3.3 Cl₄M-*p*-Cl₄M diradical

The triplet SCF calculation converged to an energy of -114701.41640 eV and an $\langle \mathbf{S}^2 \rangle$ value of 2.075353. The level of theory was UB3LYP-D3BJ/def2-SVP.

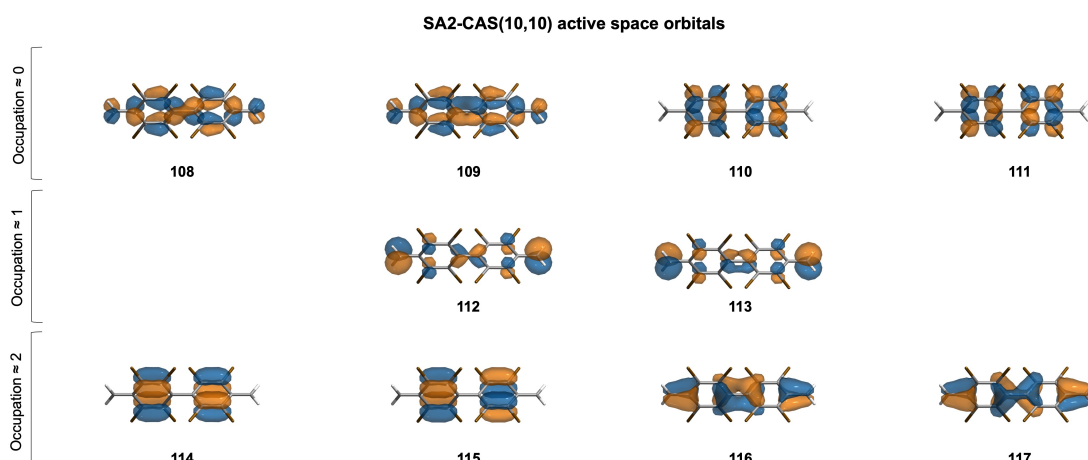


Figure B.2. Active space MOs (isovalue = 0.040) of $\text{Cl}_4\text{M-}p\text{-Cl}_4\text{M}$ from a CASSCF(10,10)/def2-SVPD calculation state-averaged over the triplet and singlet ground states (i.e. SA2).

Table B.1. Excited-state properties of $\text{Cl}_4\text{M-}p\text{-Cl}_4\text{M}$, calculated at the SA2-CASSCF(10,10)/CASCI/SC-NEVPT2/def2-SVPD level. The triplet and singlet LE_{B_2} states are dominated by the following transitions: $114 \rightarrow 113$, $115 \rightarrow 112$, $113 \rightarrow 111$, $112 \rightarrow 110$. The triplet and singlet LE_{B_3} states are dominated by the following transitions: $114 \rightarrow 112$, $115 \rightarrow 113$, $112 \rightarrow 111$, $113 \rightarrow 110$.

Triplets		Singlets	
Energy / eV	Assignment	Energy / eV	Assignment
0.006	$^3\text{GS}_{B_1}$	0.000	$^1\text{GS}_A$
		1.617	$^1\text{CT}_A$
		1.622	$^1\text{CT}_{B_1}$
2.604	$^3\text{LE}_{B_2}$	2.612	$^1\text{LE}_{B_2}$
2.604	$^3\text{LE}_{B_3}$	2.612	$^1\text{LE}_{B_3}$

Optimised geometry

C 0.00000041285253 0.00000029555640 0.74297677529495
C 0.85732573641907 0.85732631288620 1.46036723377016
C 0.86449831678849 0.86449897249083 2.85373875414654
Cl 1.93779307205256 1.93779488416541 3.69549743130807

C -0.00000014382067 -0.00000005359037 3.61203276227255
 C -0.00000040175185 -0.00000028309773 5.01220248078794
 C -0.86449833501065 -0.86449887424287 2.85373817543095
 Cl -1.93779341609317 -1.93779493750990 3.69549621346067
 C -0.85732522342353 -0.85732588248186 1.46036665514901
 Cl 1.90872191143777 1.90872327279931 0.56204835859350
 Cl -1.90872102502467 -1.90872254490025 0.56204699493039
 H 0.66403776579042 0.66403836065583 5.56214484145260
 H -0.66403867943697 -0.66403921249331 5.56214434734771
 C 0.00000059154361 0.00000047708230 -0.74297680842324
 C -0.85732498072283 0.85732650236958 -1.46036693763725
 Cl -1.90872068612633 1.90872347952667 -0.56204752525952
 C -0.86449821272356 0.86449900828024 -2.85373843687065
 Cl -1.93779350464977 1.93779467711227 -3.69549669018358
 C -0.00000016226542 -0.00000015609920 -3.61203278430882
 C -0.00000070594291 -0.00000065316442 -5.01220250752925
 C 0.86449845299473 -0.86449884127681 -2.85373851575171
 Cl 1.93779309206189 -1.93779501603972 -3.69549697710167
 C 0.85732597981825 -0.85732568976200 -1.46036699911219
 Cl 1.90872202824070 -1.90872234501100 -0.56204762706680
 H 0.66403725680076 -0.66403966557926 -5.56214462005595
 H -0.66403913980843 0.66403791232367 -5.56214459464441

B.3.4 PT₂TM-H monoradical

The doublet SCF calculation converged to an energy of -144932.58265 eV and an $\langle S^2 \rangle$ value of 0.770696. The level of theory was UB3LYP-D3BJ/def2-SVP.

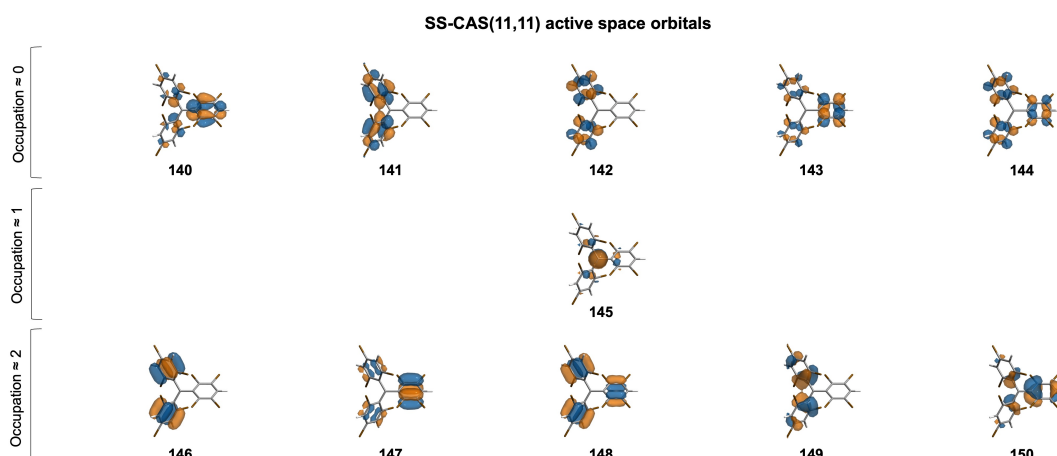


Figure B.3. Active space MOs (isovalue = 0.040) of PT₂TM-H from a CASSCF(11,11)/def2-SVPD calculation state-specific to the ground doublet.

Table B.2. Excited-state properties of PT₂TM-H, calculated at the SS-CASSCF(11,11)/CASCI/SC-NEVPT2/def2-SVPD level.

Energy / eV	Main contribution	Assignment
0.000	—	² GS _B
2.780	147 → 145	² LE _A
2.988	146 → 145	² LE _B
3.078	149 → 145	² LE _A
3.296	150 → 145	² LE _B

Optimised geometry

C -0.00000100878170 0.00000169583685 4.12761634902078
 C -0.85851151864839 -0.84825523996764 3.42970609427926
 Cl -1.92674366505162 -1.87460275292160 4.33649252936941
 C -0.86593552020095 -0.85043019279702 2.02751198441216
 Cl -2.02880823448355 -1.83842286789924 1.19812103091070
 C 0.00000078223341 -0.00000051292764 1.29728867140791
 C 0.00000068858206 -0.00000072793933 -0.17626186450116
 C 0.86593621128483 0.85043028720999 2.02751182881201

CI 2.02880918443113 1.83842267932249 1.19812093592387
 C 0.85851038281088 0.84825754834784 3.42970593743530
 CI 1.92674044220314 1.87460731220680 4.33649225374461
 H -0.00000190376054 0.00000268662313 5.21685381496298
 C -0.12598996386433 1.26578433548672 -0.90410738379568
 C 0.72838903626060 1.60545985538092 -1.98454582181853
 CI 2.04360888115442 0.55206219939831 -2.43980438625745
 C 0.62212380120034 2.80591663776188 -2.68244689972772
 C -0.35989860412666 3.72341732904067 -2.30653883135869
 CI -0.50466198860348 5.23000087113262 -3.16590016424509
 C -1.22733044492931 3.44765896661459 -1.24944541387940
 C -1.10390077055072 2.23733510764173 -0.57129516226888
 CI -2.28661969547178 1.91766442755174 0.67187747918888
 C 0.12599048854006 -1.26578580916702 -0.90410764623741
 C 1.10390190812176 -2.23733651837442 -0.57129696102111
 CI 2.28662214563588 -1.91766617759692 0.67187451667678
 C 1.22733129011585 -3.44765996512256 -1.24944800338326
 C 0.35989862743596 -3.72341798012113 -2.30654085170079
 CI 0.50466181794816 -5.23000100911267 -3.16590313167695
 C -0.62212426204596 -2.80591724030012 -2.68244763865872
 C -0.72838916842485 -1.60546084978066 -1.98454578265692
 CI -2.04360934075232 -0.55206304737579 -2.43980314450043
 H 1.31251887555110 3.02906092760722 -3.49460860037946
 H -2.00486979890244 4.15580546212846 -0.96671010777986
 H 2.00487110610469 -4.15580639100197 -0.96671381080138
 H -1.31251978101571 -3.02906104688623 -3.49460909226058

Appendix C

Supporting Information of Chapter 4: Electron Sextets as Optically Addressable Molecular Qubits: Triplet Carbenes

C.1 Semi-empirical analysis of linear carbenes

In this section, we will describe how the Pariser-Parr-Pople (PPP) framework [175, 182, 138] offers a semi-empirical perspective into the electronic structure of carbenes. We shall begin by adapting this framework towards linear carbenes with an emphasis on the low-lying electronic states and energies. The implications of non-linear carbenes will be explored in a later section.

C.1.1 Derivation

The PPP theory [175, 182, 138] is an extension of the Hückel method to include two-electron interactions and offers a minimal description of the ground and excited states of planar π -conjugated systems. Because a linear carbene may be interpreted as a pair of fused planar π -systems, we expect each π -system to admit a PPP description as well. The focus of this section is to derive the interaction Hamiltonian between these two π -systems which, due to the π -systems being spatially orthogonal to each other, cannot be described by the canonical PPP framework. Because our procedure follows that of Linderberg and öhrn [138] for the standard PPP model, we will refer some steps to Linderberg and öhrn

[138] without further explanation.

We consider the dimeric carbene as a framework of $2N + 1$ atoms. The central carbene atom is labelled by $\mu = 0$, the N atoms on one monomer by $\mu \in \{1_A, 2_A, \dots, N_A\}$, and the remaining N atoms on the other monomer by $\mu \in \{1_B, 2_B, \dots, N_B\}$. Assuming a linear carbene, we may, without loss of generality, pick the carbene axis to be the z -axis. Because we are only interested in the π electronic structure, we shall consider a minimal basis of π -orbitals, where the first set of atoms each contribute a $2p_x$ spatial atomic orbital (AO) $\phi_\mu(\pi_x)$ and a single π_x -electron while the second set of atoms each contribute a $2p_y$ spatial AO $\phi_\mu(\pi_y)$ and a single π_y -electron. As for the central carbene atom $\mu = 0$, it bridges the two sets of π -orbitals and hence contributes both a $2p_x$ spatial AO $\phi_{0_A}(\pi_x)$ and a $2p_y$ spatial AO $\phi_{0_B}(\pi_y)$, each with a single electron. Collectively, the AOs under consideration are grouped into two sets, $\mathcal{A} \equiv \{0_A, 1_A, 2_A, \dots, N_A\}$ and $\mathcal{B} \equiv \{0_B, 1_B, 2_B, \dots, N_B\}$.

The many-electron molecular Hamiltonian is partitioned into a sum over three terms:

$$H = H_0 + H_1 + H_2. \quad (\text{C.1})$$

The first term denotes the internuclear repulsion:

$$H_0 = \frac{1}{2} \sum_{g \neq h} \frac{e^2 Z_g Z_h}{|\mathbf{R}_g - \mathbf{R}_h|}, \quad (\text{C.2})$$

where e is the elementary charge, $\mathbf{R}_g$ is the position of nucleus g , and Z_g is its effective nuclear charge. The second term describes the electron kinetic and potential energy:

$$H_1 = \int d\mathbf{x} \psi^\dagger(\mathbf{x}) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \sum_g \frac{e^2 Z_g}{|\mathbf{r} - \mathbf{R}_g|} \right) \psi(\mathbf{x}), \quad (\text{C.3})$$

where we have chosen to represent the electrons in second quantisation notation with $\psi(\mathbf{x})$ being the electron field operator of spatial coordinate $\mathbf{r}$ and spin coordinate ω ,

denoted collectively by $\mathbf{x}$ (i.e. $\mathbf{x} \equiv \{\mathbf{r}, \omega\}$) [213]. The remaining symbols adopt their usual meanings: $\hbar$ is the reduced Planck constant and m is the electron mass. Finally, the last term signifies the electron-electron repulsion and reads, also in second quantisation notation,

$$H_2 = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \psi^\dagger(\mathbf{x}) \psi^\dagger(\mathbf{x}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi(\mathbf{x}') \psi(\mathbf{x}). \quad (\text{C.4})$$

To begin, we decompose the electron field operator $\psi(\mathbf{x})$ into its σ and π components:

$$\psi(\mathbf{x}) = \psi_\sigma(\mathbf{x}) + \psi_\pi(\mathbf{x}), \quad (\text{C.5})$$

and use this to simplify the expressions for H_1 [Eq. (C.3)] and H_2 [Eq. (C.4)]. The former becomes

$$H_1 = H_1(\sigma) + H_1(\pi) + \text{cross terms}, \quad (\text{C.6})$$

where

$$H_1(\sigma) \equiv \int d\mathbf{x} \psi_\sigma^\dagger(\mathbf{x}) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \sum_g \frac{e^2 Z_g}{|\mathbf{r} - \mathbf{R}_g|} \right) \psi_\sigma(\mathbf{x}), \quad (\text{C.7})$$

$$H_1(\pi) \equiv \int d\mathbf{x} \psi_\pi^\dagger(\mathbf{x}) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \sum_g \frac{e^2 Z_g}{|\mathbf{r} - \mathbf{R}_g|} \right) \psi_\pi(\mathbf{x}). \quad (\text{C.8})$$

In Linderberg and öhrn [138], the σ and π wavefunctions are orthogonal to each other (assuming planarity) and so the cross terms of Eq. (C.6) vanish by symmetry. In linear carbenes, this is still true if the two wavefunctions are localised on the same monomer, but is otherwise an approximation that we shall make. **Chemically, this is equivalent to neglecting σ - π hyperconjugation** and we expect further improvements to this model to

begin from here. As for H_2 , it adopts the following structure:

$$\begin{aligned} H_2 = & H_2(\sigma, \sigma, \sigma, \sigma) + 2H_2(\pi, \sigma, \sigma, \pi) + 2H_2(\pi, \sigma, \pi, \sigma) \\ & + H_2(\sigma, \sigma, \pi, \pi) + H_2(\pi, \pi, \sigma, \sigma) + H_2(\pi, \pi, \pi, \pi), \end{aligned} \quad (\text{C.9})$$

where

$$H_2(a, b, c, d) \equiv \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \psi_a^\dagger(\mathbf{x}) \psi_b^\dagger(\mathbf{x}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_c(\mathbf{x}') \psi_d(\mathbf{x}). \quad (\text{C.10})$$

The terms in Eq. (C.9) represent, in order of appearance, the self-interaction of the σ field, the Coulomb and exchange interactions between the σ and π fields, the energy of electron transfer from π to σ and its reverse, and the self-interaction of the π -field. Notice that the electron transfer terms $H_2(\sigma, \sigma, \pi, \pi)$ and $H_2(\pi, \pi, \sigma, \sigma)$ do not conserve the number of σ and π excitations. To obtain a minimal model comprising only the π electrons, we need to omit them and consider only

$$H_2 \approx H_2(\sigma, \sigma, \sigma, \sigma) + 2H_2(\pi, \sigma, \sigma, \pi) + 2H_2(\pi, \sigma, \pi, \sigma) + H_2(\pi, \pi, \pi, \pi). \quad (\text{C.11})$$

Indeed, the deleted terms are small as justified in Linderberg and öhrn [138] and expected from our chemical intuition of σ - π hyperconjugation being perturbative. Along the same direction, we shall neglect the operator nature of the σ field operators $\psi_\sigma(\mathbf{x})$ and replace products of two σ field operators with some empirically determined expectation values, denoted by $\langle \cdot \rangle$ (e.g. $\psi_\sigma^\dagger(\mathbf{x}) \psi_\sigma(\mathbf{x}') \approx \langle \psi_\sigma^\dagger(\mathbf{x}) \psi_\sigma(\mathbf{x}') \rangle$). This assumption is standard to the derivation of the PPP Hamiltonian and thoroughly justified by Linderberg and öhrn [138]. Applying these two approximations to Eqs. (C.2), (C.6), and (C.9) allows us to reorganise the total Hamiltonian [Eq. (C.1)] into

$$H \approx H'_0 + H_{\text{core}}(\pi) + H_2(\pi, \pi, \pi, \pi), \quad (\text{C.12})$$

where H'_0 represents the internuclear repulsion and electronic effects due to the σ field:

$$H'_0 \equiv H_0 + H_1(\sigma) + H_2(\sigma, \sigma, \sigma, \sigma), \quad (\text{C.13})$$

$H_{\text{core}}(\pi)$ represents the kinetic and potential energy of the π field:

$$\begin{aligned} H_{\text{core}}(\pi) = & \int d\mathbf{x} \psi_{\pi}^{\dagger}(\mathbf{x}) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V_{\text{core}}(\mathbf{r}) \right) \psi_{\pi}(\mathbf{x}) \\ & - \int d\mathbf{x} d\mathbf{x}' \psi_{\pi}^{\dagger}(\mathbf{x}) \left\langle \psi_{\sigma}^{\dagger}(\mathbf{x}') \psi_{\sigma}(\mathbf{x}) \right\rangle \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{\pi}(\mathbf{x}'), \end{aligned} \quad (\text{C.14})$$

and $H_2(\pi, \pi, \pi, \pi)$ represents the two-electron self-interaction of the π field, reproduced below for convenience:

$$H_2(\pi, \pi, \pi, \pi) = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \psi_{\pi}^{\dagger}(\mathbf{x}) \psi_{\pi}^{\dagger}(\mathbf{x}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{\pi}(\mathbf{x}') \psi_{\pi}(\mathbf{x}). \quad (\text{C.15})$$

In writing Eq. (C.14), we have defined an effective core potential for the π field due to the nuclei and σ skeleton:

$$V_{\text{core}}(\mathbf{r}) \equiv -\sum_g \frac{e^2 Z_g}{|\mathbf{r} - \mathbf{R}_g|} + \int d\mathbf{x}' \left\langle \psi_{\sigma}^{\dagger}(\mathbf{x}') \psi_{\sigma}(\mathbf{x}') \right\rangle \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{C.16})$$

We are now ready to introduce the minimal π -orbital basis described at the start of this section. By invoking the linear combination of atomic orbitals (LCAO) approximation, we expand

$$\psi_{\pi}(\mathbf{x}) \approx \sum_{\mu\sigma} \phi_{\mu\sigma}(\mathbf{x}) a_{\mu\sigma}, \quad (\text{C.17})$$

where $a_{\mu\sigma}$ is the fermionic annihilation operator for a spin- σ electron in the π AO of index μ , and $\phi_{\mu\sigma}(\mathbf{x}) \equiv \langle \mathbf{x} | \phi_{\mu\sigma} \rangle$ is the coordinate representation (i.e. wavefunction) of the corresponding π AO. Furthermore, we shall adopt the complete neglect of differential overlap (CNDO) approximation, which sets products of wavefunctions localised on different atoms

to zero:

$$\phi_\mu^*(\mathbf{r}) \phi_{\mu'}(\mathbf{r}) \approx |\phi_\mu(\mathbf{r})|^2 \delta_{\mu\mu'} + \phi_{0_A}^*(\mathbf{r}) \phi_{0_B}(\mathbf{r}) \delta_{\mu 0_A} \delta_{\mu' 0_B} + \phi_{0_B}^*(\mathbf{r}) \phi_{0_A}(\mathbf{r}) \delta_{\mu 0_B} \delta_{\mu' 0_A},$$

with δ_{jk} being the Kronecker delta. Note that the last two terms arise because the central carbene atom contributes two π -orbitals, i.e. they are absent in the regular PPP Hamiltonian discussed by Linderberg and öhrn [138]. Together, we find that the single-electron terms read

$$\begin{aligned} & \int d\omega \psi_\pi^\dagger(\mathbf{x}) \psi_\pi(\mathbf{x}) \\ & \approx \sum_\sigma \left[\sum_\mu |\phi_\mu^*(\mathbf{r})|^2 a_{\mu\sigma}^\dagger a_{\mu\sigma} + \phi_{0_A}^*(\mathbf{r}) \phi_{0_B}(\mathbf{r}) a_{0_A\sigma}^\dagger a_{0_B\sigma} + \phi_{0_B}^*(\mathbf{r}) \phi_{0_A}(\mathbf{r}) a_{0_B\sigma}^\dagger a_{0_A\sigma} \right], \end{aligned} \quad (\text{C.18})$$

where $\phi_\mu(\mathbf{r}) \equiv \int d\omega \phi_{\mu\sigma}(\mathbf{x})$, while the two-electron terms read

$$\begin{aligned} & \int d\omega d\omega' \psi_\pi^\dagger(\mathbf{x}) \psi_\pi^\dagger(\mathbf{x}') \psi_\pi(\mathbf{x}') \psi_\pi(\mathbf{x}) \\ & \approx \sum_{\mu\nu} \sum_{\sigma\tau} |\phi_\mu^*(\mathbf{r})|^2 |\phi_\nu^*(\mathbf{r}')|^2 a_{\mu\sigma}^\dagger a_{\mu\sigma} a_{\nu\tau}^\dagger a_{\nu\tau} \\ & \quad + \sum_{\mu \neq \nu \in \{0_A, 0_B\}} \sum_{\sigma\tau} \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) \phi_\mu^*(\mathbf{r}') \phi_\nu(\mathbf{r}') a_{\mu\sigma}^\dagger a_{\nu\sigma} a_{\mu\tau}^\dagger a_{\nu\tau} \\ & \quad + \sum_{\mu \neq \nu \in \{0_A, 0_B\}} \sum_{\sigma\tau} \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) \phi_\nu^*(\mathbf{r}') \phi_\mu(\mathbf{r}') a_{\mu\sigma}^\dagger a_{\nu\sigma} a_{\nu\tau}^\dagger a_{\mu\tau}, \end{aligned} \quad (\text{C.19})$$

where we have noted that coefficients of the form $\phi_{0_A}^*(\mathbf{r}) \phi_{0_B}(\mathbf{r}) |\phi_\nu(\mathbf{r}')|^2$ vanish upon spatial integration with $|\mathbf{r} - \mathbf{r}'|^{-1}$ [Eq. (C.15)] because either orbitals ϕ_{0_A} or ϕ_{0_B} will have an opposite parity under reflection as compared to the other orbital on $\mu = 0$ and also orbital ϕ_ν . Substituting these two results into Eqs. (C.14) and (C.15) and noting Eq. (C.12)

yields the carbene PPP Hamiltonian:

$$\begin{aligned}
H \approx & H'_0 + \sum_{\mu} \sum_{\sigma} \alpha_{\mu} a_{\mu\sigma}^{\dagger} a_{\mu\sigma} - \sum_{\mu \neq \nu} \sum_{\sigma} \beta_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu} \sum_{\sigma\tau}' \gamma_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\mu\sigma} a_{\nu\tau}^{\dagger} a_{\nu\tau} \\
& + \frac{1}{2} \sum_{\mu \neq \nu \in \{0_A, 0_B\}} \sum_{\sigma\tau} \left[\kappa_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} a_{\mu\tau}^{\dagger} a_{\nu\tau} + \kappa'_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} a_{\nu\tau}^{\dagger} a_{\mu\tau} \right], \quad (C.20)
\end{aligned}$$

where we have defined the on-site energy of AO μ as

$$\begin{aligned}
\alpha_{\mu} \equiv & \int d\mathbf{r} |\phi_{\mu}(\mathbf{r})|^2 \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V_{\text{core}}(\mathbf{r}) \right) \\
& - \int d\mathbf{r} d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \left\langle \psi_{\sigma}^{\dagger}(\mathbf{r}') \psi_{\sigma}(\mathbf{r}) \right\rangle \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_{\mu}(\mathbf{r}'), \quad (C.21)
\end{aligned}$$

the hopping amplitude between AOs μ and ν as

$$\begin{aligned}
\beta_{\mu\nu} \equiv & \int d\mathbf{r} d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \left\langle \psi_{\sigma}^{\dagger}(\mathbf{r}') \psi_{\sigma}(\mathbf{r}) \right\rangle \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_{\nu}(\mathbf{r}') \\
& - \delta_{\mu 0_A} \delta_{\nu 0_B} \int d\mathbf{r} \phi_{0_A}^*(\mathbf{r}) \phi_{0_B}(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V_{\text{core}}(\mathbf{r}) \right) \\
& - \delta_{\mu 0_B} \delta_{\nu 0_A} \int d\mathbf{r} \phi_{0_B}^*(\mathbf{r}) \phi_{0_A}(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V_{\text{core}}(\mathbf{r}) \right), \quad (C.22)
\end{aligned}$$

the effective repulsion between an electron on AO μ and another electron on AO ν as

$$\gamma_{\mu\nu} \equiv \int d\mathbf{r} d\mathbf{r}' |\phi_{\mu}(\mathbf{r})|^2 |\phi_{\nu}(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (C.23)$$

and the analogous effective exchange interactions as

$$\kappa_{\mu\nu} \equiv \int d\mathbf{r} d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) \phi_{\mu}^*(\mathbf{r}') \phi_{\nu}(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (C.24)$$

$$\kappa'_{\mu\nu} \equiv \int d\mathbf{r} d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) \phi_{\nu}^*(\mathbf{r}') \phi_{\mu}(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (C.25)$$

Note that the primed sum indicates the omission of $a_{\mu\sigma}^{\dagger} a_{\mu\sigma} a_{\mu\sigma}^{\dagger} a_{\mu\sigma}$ terms. Finally, to

reflect the diradical nature of a triplet carbene, we re-divide the Hamiltonian as such:

$$H \approx H'_0 + \sum_{M=A,B} H_M + H_{\text{int}}, \quad (\text{C.26})$$

$$\begin{aligned} H_M \equiv & \sum_{\mu \in \mathcal{M}} \sum_{\sigma} \alpha_{\mu} a_{\mu\sigma}^{\dagger} a_{\mu\sigma} - \sum_{\mu \neq \nu \in \mathcal{M}} \sum_{\sigma} \beta_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} \\ & + \frac{1}{2} \sum_{\mu\nu \in \mathcal{M}} \sum_{\sigma\tau} ' \gamma_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\mu\sigma} a_{\nu\tau}^{\dagger} a_{\nu\tau}, \end{aligned} \quad M = A, B, \quad (\text{C.27})$$

$$\begin{aligned} H_{\text{int}} \equiv & - \sum_{\mu \in \mathcal{A}} \sum_{\nu \in \mathcal{B}} \sum_{\sigma} \beta_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} \\ & + \frac{1}{2} \sum_{\mu \in \mathcal{A}} \sum_{\nu \in \mathcal{B}} \sum_{\sigma\tau} \gamma_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\mu\sigma} a_{\nu\tau}^{\dagger} a_{\nu\tau} + \text{H.c.} \\ & + \frac{1}{2} \sum_{\mu \neq \nu \in \{0_A, 0_B\}} \sum_{\sigma\tau} \left[\kappa_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} a_{\mu\tau}^{\dagger} a_{\nu\tau} + \kappa'_{\mu\nu} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} a_{\nu\tau}^{\dagger} a_{\mu\tau} \right], \end{aligned} \quad (\text{C.28})$$

where H_M is the Hamiltonian for monomer M and H_{int} is the interaction between monomers. The PPP model usually assumes $\alpha_{\mu} \approx \alpha$ for all AOs μ and nearest neighbour (n.n.) hopping which, in the present context, reads

$$\beta_{\mu\nu} \approx \begin{cases} \beta & \text{if } (\mu, \nu) \in \text{n.n.} \cap \mathcal{A} \text{ or } \mathcal{B}, \\ 0 & \text{otherwise.} \end{cases} \quad (\text{C.29})$$

Note that the values of $\beta_{\mu\nu}$ [Eq. (C.22)] with μ and ν being in opposite π -systems will vanish by symmetry. We shall further assume the Coulomb repulsion $\gamma_{\mu\nu}$ [Eq. (C.23)] to be small unless μ and ν are localised on the same atoms, which is consistent with the derivation of the PPP model [198]. Specifically,

$$\gamma_{\mu\nu} \approx \begin{cases} U & \text{if } \mu = \nu, \\ \gamma_{AB} & \text{if } (\mu, \nu) \in \{(0_A, 0_B), (0_B, 0_A)\}, \\ 0 & \text{otherwise,} \end{cases} \quad (\text{C.30})$$

Finally, we shall assume the spatial AOs ϕ_{0_A} and ϕ_{0_B} to be real-valued such that [Eqs. (C.24) and (C.25)]

$$\kappa_{\mu\nu} = \kappa'_{\mu\nu} \equiv \kappa_{AB} \quad \text{for all } \mu \neq \nu \in \{0_A, 0_B\}. \quad (\text{C.31})$$

Then, the Hamiltonian becomes

$$H \approx H'_0 + \sum_{M=A,B} H_M + H_{\text{int}}, \quad (\text{C.32})$$

$$H_M \approx \alpha \sum_{\mu \in \mathcal{M}} n_{\mu} - \beta \sum_{\langle \mu, \nu \in \mathcal{M} \rangle} \sum_{\sigma} a_{\mu\sigma}^{\dagger} a_{\nu\sigma} + U \sum_{\mu \in \mathcal{M}} n_{\mu\uparrow} n_{\mu\downarrow}, \quad M = A, B, \quad (\text{C.33})$$

$$H_{\text{int}} \approx \gamma_{AB} n_{0_A} n_{0_B} + \frac{\kappa_{AB}}{2} \sum_{\mu \neq \nu \in \{0_A, 0_B\}} \sum_{\sigma\tau} \left(a_{\mu\sigma}^{\dagger} a_{\nu\sigma} a_{\mu\tau}^{\dagger} a_{\nu\tau} + a_{\mu\sigma}^{\dagger} a_{\nu\sigma} a_{\nu\tau}^{\dagger} a_{\mu\tau} \right), \quad (\text{C.34})$$

where we have introduced the number operator

$$n_{\mu} \equiv \sum_{\sigma=\uparrow, \downarrow} n_{\mu\sigma} = \sum_{\sigma=\uparrow, \downarrow} a_{\mu\sigma}^{\dagger} a_{\mu\sigma}. \quad (\text{C.35})$$

This concludes our derivation of the minimal model for linear carbenes, summarised by Eqs. (C.32), (C.33), and (C.34). The results are consistent with existing semi-empirical analyses of carbenes [32, 53, 124, 10, 107] except for the additional on-site Coulomb term necessary to describe the excited-state structure (more to follow).

C.1.2 Properties of the low-lying electronic states

Because H_M resembles the diradical Hamiltonian discussed in our previous study [179], the approximate electronic wavefunctions and energies in the $H_{\text{int}} = 0$ limit remain the same as that study and will not be further discussed. Instead, we shall focus on the corrections to these electronic energies and their associated wavefunctions due to H_{int} .

Energies

One may easily verify using time-independent perturbation theory and the Slater-Condon rules [213] that, to first-order in H_{int} , the state energies (labelled $E(\cdot)$) relative to their zeroth-order counterparts (labelled $E^{(0)}(\cdot)$) read

$$E(^3\text{GS}) \approx E^{(0)}(\text{GS}) + \Delta E_{\text{int}}^{\text{GS}} - \kappa_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}0}|^2, \quad (\text{C.36})$$

$$E(^1\text{GS}) \approx E^{(0)}(\text{GS}) + \Delta E_{\text{int}}^{\text{GS}} + \kappa_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}0}|^2, \quad (\text{C.37})$$

$$E(^3\text{LE}_A) \approx E^{(0)}(\text{LE}) + \Delta E_{\text{int}}^{\text{GS}} + \Delta E_{\text{int}}^{\text{LE}} - \gamma_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}1'}|^2, \quad (\text{C.38})$$

$$E(^3\text{LE}_B) \approx E^{(0)}(\text{LE}) + \Delta E_{\text{int}}^{\text{GS}} + \Delta E_{\text{int}}^{\text{LE}} - (2\kappa_{AB} - \gamma_{AB}) |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}1'}|^2, \quad (\text{C.39})$$

$$E(^1\text{LE}_A) \approx E^{(0)}(\text{LE}) + \Delta E_{\text{int}}^{\text{GS}} + \Delta E_{\text{int}}^{\text{LE}} + (2\kappa_{AB} + \gamma_{AB}) |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}1'}|^2, \quad (\text{C.40})$$

$$E(^1\text{LE}_B) \approx E^{(0)}(\text{LE}) + \Delta E_{\text{int}}^{\text{GS}} + \Delta E_{\text{int}}^{\text{LE}} - \gamma_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}1'}|^2, \quad (\text{C.41})$$

$$E(^1\text{CT}_A) \approx E^{(0)}(\text{CT}) + \Delta E_{\text{int}}^{\text{GS}} + \Delta E_{\text{int}}^{\text{CT}} + \kappa_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}0}|^2, \quad (\text{C.42})$$

$$E(^1\text{CT}_B) \approx E^{(0)}(\text{CT}) + \Delta E_{\text{int}}^{\text{GS}} + \Delta E_{\text{int}}^{\text{CT}} - \kappa_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}0}|^2. \quad (\text{C.43})$$

Here, $c_{\mathcal{A}0}$ and $c_{\mathcal{A}1'}$ are, respectively, the coefficients of the central carbene atom (i.e. $\mu = 0$) in the singly occupied molecular orbital (SOMO) and lowest unoccupied molecular orbital (LUMO) of the A π -system. Meanwhile, $c_{\mathcal{B}0}$ and $c_{\mathcal{B}1'}$ are assumed to be equal to their A counterparts due to the carbene's dimeric structure. To be consistent with Ref. [179], we have assigned the state irreps in typewriter font and according to their parities under permutation between the two monomeric subsystems. For completeness, the shift terms (which are inconsequential to the conclusions made by this section) are defined as

such:

$$\Delta E_{\text{int}}^{\text{GS}} \equiv (4\gamma_{AB} - 2\kappa_{AB}) \left(\sum_{j,k=1}^{(N-1)/2} |c_{\mathcal{A}j}|^2 |c_{\mathcal{B}k}|^2 + \sum_{j=1}^{(N-1)/2} |c_{\mathcal{A}j}|^2 |c_{\mathcal{B}0}|^2 \right) + \gamma_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}0}|^2, \quad (\text{C.44})$$

$$\Delta E_{\text{int}}^{\text{LE}} \equiv \left(|c_{\mathcal{B}1'}|^2 - |c_{\mathcal{B}0}|^2 \right) \left[\left(\gamma_{AB} - \frac{1}{2} \kappa_{AB} \right) \sum_{j=1}^{(N-1)/2} |c_{\mathcal{A}j}|^2 + \gamma_{AB} |c_{\mathcal{A}0}|^2 \right], \quad (\text{C.45})$$

$$\Delta E_{\text{int}}^{\text{CT}} \equiv -\gamma_{AB} |c_{\mathcal{A}0}|^2 |c_{\mathcal{B}0}|^2. \quad (\text{C.46})$$

Again, $c_{\mathcal{A}j}$ ($c_{\mathcal{B}j}$) denotes the j -th molecular orbital (MO) of the A (B) π -system (see Ref. [179] for more details). Importantly, the energetic splittings of the electronic states relative to the diradical solutions, summarised in Fig. C.1, are consistent with the ab initio results. For instance, in both carbenes **1** and **2**, the ground singlet-triplet gaps are similar to the energy gaps between the two singlet CTs. Also, the energy difference between the two triplet LEs is relatively small in carbene **2** because this value depends mostly on the on-site couplings at the central carbene atom, at which the LUMO has a node (i.e. $c_{\mathcal{B}1'} \approx 0$).

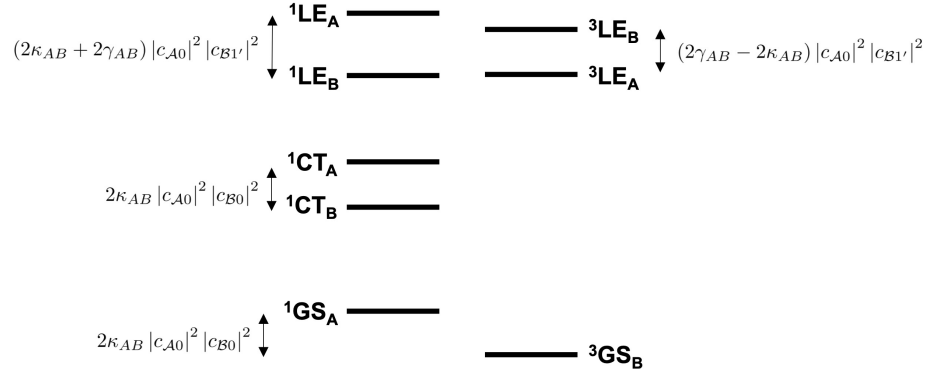


Figure C.1. Schematic diagram of the carbene electronic structure based on the semi-empirical analysis. The state irreps are assigned based on their characters under permutation between the two identical π -systems.

States

We also consider the possibility of configuration interaction between the close-lying states, namely, among the singlet GS and CTs and among the singlet CTs and LEs. One

may again verify with the Slater-Condon rules [213] that

$$\langle {}^1\text{GS}_\text{A} | H_\text{int} | {}^1\text{CT}_\text{B} \rangle \approx \langle {}^1\text{GS}_\text{B} | H_\text{int} | {}^1\text{CT}_\text{A} \rangle \approx 0, \quad (\text{C.47})$$

and

$$\begin{aligned} \langle {}^1\text{CT}_\text{A} | H_\text{int} | {}^1\text{LE}_\text{A} \rangle &\approx \langle {}^1\text{CT}_\text{A} | H_\text{int} | {}^1\text{LE}_\text{B} \rangle \approx \langle {}^1\text{CT}_\text{B} | H_\text{int} | {}^1\text{LE}_\text{A} \rangle \\ &\approx \langle {}^1\text{CT}_\text{B} | H_\text{int} | {}^1\text{LE}_\text{B} \rangle \approx 0. \end{aligned} \quad (\text{C.48})$$

Therefore, any changes to the state wavefunctions due to H_int must arise from couplings with states of larger energy separations, such as the LEs and higher-lying CTs. (Note that H_int only connects between states of the same spin multiplicity and parity under interchange of the two monomeric subsystems.)

C.2 Changes to the low-lying electronic states upon bending

In this section, we will investigate how the low-lying electronic states are modified when the bond angle around the carbene atom deviates from linearity.

As explored in our previous work [179], in the limit of weak radical-radical interactions, the two SOMOs become near-degenerate, hence the unpaired electron of each π -system resides in its own SOMO in the lowest-energy state. This leads to the wavefunctions being considered by the preceding section. When the carbene is bent, one of the carbene $2p$ orbitals is swapped out for the $(sp)^j p^k$ hybrid that, upon forming MOs with the π -orbitals of the carbene substituents, results in a new $(sp)^j p^k$ -like SOMO. Depending on the extent of π and σ stabilisations being imparted by the substituents, this $(sp)^j p^k$ -like SOMO may have a different energy from the analogous $2p$ -like SOMO, resulting in an inclination for one of the unpaired electrons to hop over and pair up with the other. **Note that this is only a rough picture of the true electronic structure** – a proper examination should consider this process to be smooth and continuous over the geometrical distortion,

that is, the open-shell state should gradually pick up the character of a paired configuration as the carbene adiabatically bends. However, this also necessitates a multiconfigurational framework, which is contradictory because the concept of orbital energies formally breaks down in this picture [213]. **A more rigorous translation into the basis of multiconfigurational wavefunctions** would be to introduce couplings between the GSs, which host unpaired configurations, and CTs, which host paired configurations (and these couplings intensify as the bond angle decreases). Moreover, there are restrictions on these couplings: Because the total electronic Hamiltonian must remain invariant under the molecular symmetry operations, at any one geometry only states of the same spatial symmetry and spin multiplicity can mix. The bent molecule remains C_2 -symmetric; hence, within the minimal basis of GSs and CTs, **the only off-diagonal matrix elements that can survive are those between $|^1\text{GS}_A\rangle$ and $|^1\text{CT}_A\rangle$.**

To make things concrete, we recall that the GS and CT wavefunctions have the following expressions in the linear conformation [179]:

$$|^3\text{GS}_B\rangle = |\cdots 0_A 0_B\rangle, \quad (\text{C.49})$$

$$|^1\text{GS}_A\rangle = \frac{|\cdots 0_A \overline{0}_B\rangle - |\cdots \overline{0}_A 0_B\rangle}{\sqrt{2}}, \quad (\text{C.50})$$

$$|^1\text{CT}_A\rangle = \frac{|\cdots 0_A \overline{0}_A\rangle + |\cdots 0_B \overline{0}_B\rangle}{\sqrt{2}}, \quad (\text{C.51})$$

$$|^1\text{CT}_B\rangle = \frac{|\cdots 0_A \overline{0}_A\rangle - |\cdots 0_B \overline{0}_B\rangle}{\sqrt{2}}. \quad (\text{C.52})$$

Note that, in this section, 0_A and 0_B will refer to the SOMOs localised on π -system A and B respectively. Also, we shall consider only the $M_S = +1$ sublevel of the triplet GS since the two other M_S sublevels may be found by constructing the appropriate spin-adapted linear combinations. To smoothly interpolate between the linear and bent conformations, we recall our earlier conclusion of the bent molecule having C_2 symmetry due to its dimeric structure. In other words, the electronic states and their constituent MOs in the bent geometry can be characterised by the same irreps, A and B , as those introduced in

the previous section. Thus, the electronic basis that smoothly connects between the two geometries will be the C_2 -symmetry-adapted basis, which is found by first rewriting the SOMOs as their symmetry-adapted linear combinations:

$$0_A \equiv \frac{0_A + 0_B}{\sqrt{2}}, \quad 0_B \equiv \frac{0_A - 0_B}{\sqrt{2}}, \quad (\text{C.53})$$

and then reexpressing the electronic states at the linear geometry in this MO basis:

$$|^3\text{GS}_B\rangle = |\cdots 0_A 0_B\rangle, \quad (\text{C.54})$$

$$|^1\text{GS}_A\rangle = \frac{|\cdots 0_A \overline{0_A}\rangle - |\cdots 0_B \overline{0_B}\rangle}{\sqrt{2}}, \quad (\text{C.55})$$

$$|^1\text{CT}_A\rangle = \frac{|\cdots 0_A \overline{0_A}\rangle + |\cdots 0_B \overline{0_B}\rangle}{\sqrt{2}}, \quad (\text{C.56})$$

$$|^1\text{CT}_B\rangle = \frac{|\cdots 0_A \overline{0_B}\rangle - |\cdots \overline{0_A} 0_B\rangle}{\sqrt{2}}. \quad (\text{C.57})$$

(As a reminder, state irreps are presented in typewriter fonts.) Next, notice that the molecular C_2 axis passes through the carbene atom, hence the $(sp)^j p^k$ hybrid and remaining $2p$ orbitals must have well-defined parities under the molecular C_2 operation. Starting with the $(sp)^j p^k$ hybrid orbital, its s -character prevents it from possessing an equatorial mirror plane, that is, its only symmetry element is the axial C_2 axis and the orbital is symmetric under such an operation. Consequently, the $(sp)^j p^k$ hybrid orbital must point along the molecular C_2 axis and thereby transform as A. Meanwhile, the remaining $2p$ orbital, being perpendicular in spatial orientation to the $(sp)^j p^k$ hybrid orbital, must transform as B. Upon conjugation with the substituent π -orbitals, the new $(sp)^j p^k$ - and $2p$ -like MOs must retain the same symmetries of A and B respectively, else no π -conjugation would have occurred. Therefore, for the $^3\text{GS}_B$ and $^1\text{CT}_B$ states, we may directly substitute $0_A \rightarrow 0_{(sp)^j p^k}$ as the $(sp)^j p^k$ -like MO of irrep A and $0_B \rightarrow 0_{2p}$ as the $2p$ -like MO of irrep B

to obtain

$$|{}^3\text{GS}_\text{B}\rangle = |\cdots 0_{(sp)^j p^k} 0_{2p}\rangle, \quad (\text{C.58})$$

$$|{}^1\text{CT}_\text{B}\rangle = \frac{|\cdots 0_{(sp)^j p^k} \overline{0_{2p}}\rangle - |\cdots \overline{0_{(sp)^j p^k}} 0_{2p}\rangle}{\sqrt{2}}. \quad (\text{C.59})$$

We reiterate that this is possible because the state symmetries must be conserved in the bent conformation and no further configuration interaction occurs between the $|{}^3\text{GS}_\text{B}\rangle$ and $|{}^1\text{CT}_\text{B}\rangle$ states within our minimal electronic basis. As for the remaining two states, they mix; if we retain the same definition of

$$|{}^1\text{GS}_\text{A}\rangle = \frac{|\cdots 0_{(sp)^j p^k} \overline{0_{(sp)^j p^k}}\rangle - |\cdots 0_{2p} \overline{0_{2p}}\rangle}{\sqrt{2}}, \quad (\text{C.60})$$

$$|{}^1\text{CT}_\text{A}\rangle = \frac{|\cdots 0_{(sp)^j p^k} \overline{0_{(sp)^j p^k}}\rangle + |\cdots 0_{2p} \overline{0_{2p}}\rangle}{\sqrt{2}}, \quad (\text{C.61})$$

then we have the two new singlets as

$$\left\{ \frac{|{}^1\text{GS}_\text{A}\rangle + C |{}^1\text{CT}_\text{A}\rangle}{\sqrt{1+C^2}}, \frac{-C |{}^1\text{GS}_\text{A}\rangle + |{}^1\text{CT}_\text{A}\rangle}{\sqrt{1+C^2}} \right\}. \quad (\text{C.62})$$

Here, we have noted that the expansion coefficients must be real-valued [213] and the two resulting states must be orthogonal to each other. As such, one real-valued parameter C is sufficient to describe both states.

Eqs. (C.58), (C.59), and (C.62) sums up the new carbene electronic states at the bent geometry. They suggest that, for bent carbenes, the ground singlet state will contain some CT character, which facilitates ISC between the ground singlet and triplet states [179]. This extra CT character, which scales with the extent of bending, also stabilises the singlet state relative to the triplet state due to level repulsion, causing the singlet's geometry to bend more than the triplet's. Finally, notice that, when $C = 1$, we obtain $\left\{ |\cdots 0_{(sp)^j p^k} \overline{0_{(sp)^j p^k}}\rangle, |\cdots 0_{2p} \overline{0_{2p}}\rangle \right\}$ as two of our singlet electronic states. This corresponds to the limit of the two frontier orbitals ($2p$ and $(sp)^j p^k$) being so separated in

energy that the ground singlet state corresponds to a lone pair in the lower-energy orbital. Such a scenario is commonly encountered in singlet carbenes (see, for instance, Ref. [102]). Therefore, overall, we find consistency between the formal analysis discussed here and the approximate picture being presented in the main text.

To extract the contributions of $^1\text{GS}_\text{A}$ and $^1\text{CT}_\text{A}$ to the singlet states computed ab initio, we note that most quantum chemical packages will print the singlet A states as

$$|S\rangle = c_{(sp)^j p^k} |\cdots 0_{(sp)^j p^k} \overline{0_{(sp)^j p^k}}\rangle + c_{2p} |\cdots 0_{2p} \overline{0_{2p}}\rangle + \cdots, \quad (\text{C.63})$$

where $c_{(sp)^j p^k}^2$ and c_{2p}^2 may not sum to one due to further dynamical correlations. Hence, by recasting the above expression as

$$|S\rangle = \frac{c_{(sp)^j p^k} + c_{2p}}{\sqrt{2}} |^1\text{CT}_\text{A}\rangle + \frac{c_{(sp)^j p^k} - c_{2p}}{\sqrt{2}} |^1\text{GS}_\text{A}\rangle + \cdots, \quad (\text{C.64})$$

we obtain our desired quantities as

$$c_{\text{CT}}^2 = \frac{[c_{(sp)^j p^k} + c_{2p}]^2}{2}, \quad (\text{C.65})$$

$$c_{\text{GS}}^2 = \frac{[c_{(sp)^j p^k} - c_{2p}]^2}{2}. \quad (\text{C.66})$$

C.3 Results from ab initio calculations

C.3.1 Carbene 1

The triplet SCF calculation converged to an energy of -3372.69258002 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 2.0758. The BS SCF calculation converged to an energy of -3372.68560285 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 1.0551. In both cases, the level of theory was UB3LYP/6-311+G(d,p).

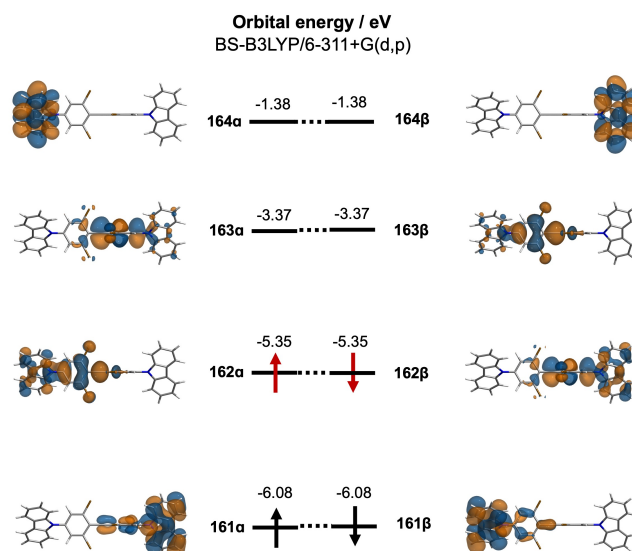


Figure C.2. Frontier MOs (isovalue = 0.020) of carbene **1** in the open-shell BS ground state, calculated at the BS-B3LYP/6-311+G(d,p) level and using the triplet geometry.

Optimised triplet geometry

```

C -0.00000 -0.00048 0.00186
C -1.35910 -0.00036 0.00131
C -2.13689 -0.85474 0.86085
Cl -1.28815 -1.91951 1.95626
C -3.51360 -0.85014 0.86782
H -4.05099 -1.48844 1.55600
C -4.21901 -0.00006 0.00028
N -5.62928 0.00009 -0.00024
C -3.51280 0.84988 -0.86676
H -4.04957 1.48829 -1.55533
C -2.13612 0.85417 -0.85878
Cl -1.28633 1.91890 -1.95364
C 1.35909 -0.00028 0.00127
C 2.13674 0.85425 0.86080
Cl 1.28779 1.91890 1.95623

```

C 3.51344 0.84990 0.86778
H 4.05071 1.48831 1.55594
C 4.21901 -0.00006 0.00025
N 5.62928 0.00005 -0.00027
C 3.51295 -0.85015 -0.86678
H 4.04984 -1.48846 -1.55534
C 2.13627 -0.85469 -0.85879
Cl 1.28667 -1.91961 -1.95365
C -6.45115 -1.12933 -0.13813
C -7.80448 -0.71839 -0.08910
C -7.80438 0.71909 0.08687
C -6.45099 1.12971 0.13698
C -6.09969 -2.46351 -0.34589
C -7.12892 -3.39119 -0.47874
C -8.47557 -3.00331 -0.41499
C -8.81911 -1.66947 -0.22641
C -6.09937 2.46379 0.34506
C -7.12849 3.39171 0.47712
C -8.47519 3.00416 0.41230
C -8.81889 1.67040 0.22340
C 6.45120 -1.12942 0.13699
C 7.80451 -0.71855 0.08692
C 6.45095 1.12962 -0.13814
C 7.80435 0.71893 -0.08907
C 6.09983 -2.46357 0.34506
C 7.12911 -3.39130 0.47715
C 8.47574 -3.00350 0.41237
C 8.81919 -1.66967 0.22348

C 6.09924 2.46373 -0.34592
 C 7.12830 3.39160 -0.47873
 C 8.47503 3.00397 -0.41495
 C 8.81880 1.67019 -0.22634
 H -5.06501 -2.77453 -0.41196
 H -6.88084 -4.43417 -0.63890
 H -9.25273 -3.75096 -0.52140
 H -9.86078 -1.37051 -0.19198
 H -5.06468 2.77456 0.41197
 H -9.25225 3.75199 0.51809
 H -9.86060 1.37170 0.18814
 H 5.06519 -2.77453 0.41195
 H 6.88111 -4.43426 0.63755
 H 9.25294 -3.75117 0.51818
 H 9.86085 -1.37077 0.18824
 H 5.06451 2.77456 -0.41202
 H 6.88004 4.43454 -0.63891
 H 9.25206 3.75176 -0.52133
 H 9.86053 1.37143 -0.19188
 H -6.88029 4.43463 0.63751

Triplet excited states from UB3LYP/TDDFT/TDA/6-311+G(d,p)

Excited State 1: 3.087-A 2.2439 eV 552.55 nm f=0.3660 <S**2>=2.132

160B -> 163B 0.67013

161B -> 162B 0.72914

Excited State 2: 3.092-A 2.3299 eV 532.14 nm f=0.0000 <S**2>=2.139

162A -> 168A -0.12379

163A -> 169A 0.12070

160B -> 162B 0.66396

161B -> 163B 0.71632

Excited State 3: 3.061-A 2.4639 eV 503.21 nm f=0.0000 <S**2>=2.093

160B -> 162B 0.72854

161B -> 163B -0.67658

Excited State 4: 3.062-A 2.4734 eV 501.28 nm f=0.0001 <S**2>=2.094

160B -> 163B 0.73296

161B -> 162B -0.67407

Ground to excited state transition electric dipole moments (Au):

state X Y Z Dip. S. Osc.

1 -2.5803 0.0000 0.0000 6.6582 0.3660

2 0.0013 0.0002 -0.0007 0.0000 0.0000

3 0.0002 -0.0000 -0.0001 0.0000 0.0000

4 -0.0406 -0.0000 0.0000 0.0016 0.0001

NOTE: These calculations were run with the x-axis pointing along the two carbene substituents.

Singlet excited states from BS-B3LYP/TDDFT/TDA/6-311+G(d,p)

Excited State 1: 1.140-?Sym 0.7244 eV 1711.60 nm f=0.0000 <S**2>=0.075

160A -> 163A 0.19465

162A -> 163A 0.66338

160B -> 163B -0.19465

162B -> 163B -0.66332

Excited State 2: 1.132-?Sym 1.0635 eV 1165.77 nm f=0.0000 <S**2>=0.070

160A -> 163A 0.15168

162A -> 163A 0.68553

160B -> 163B 0.15171

162B -> 163B 0.68558

Excited State 3: 2.303-?Sym 2.0796 eV 596.20 nm f=0.3730 $\langle S^{*2} \rangle = 1.076$

161A -> 163A 0.69851

161B -> 163B -0.69796

Excited State 4: 2.308-?Sym 2.1970 eV 564.34 nm f=0.0000 $\langle S^{*2} \rangle = 1.082$

161A -> 163A 0.69083

162A -> 168A 0.12205

161B -> 163B 0.69138

162B -> 168B -0.12199

Excited State 5: 2.288-?Sym 2.3918 eV 518.38 nm f=0.0000 $\langle S^{*2} \rangle = 1.059$

160A -> 163A -0.66643

162A -> 163A 0.21544

160B -> 163B 0.66721

162B -> 163B -0.21563

Excited State 6: 2.309-?Sym 2.4121 eV 514.00 nm f=0.0000 $\langle S^{*2} \rangle = 1.083$

159B -> 163B 0.99569

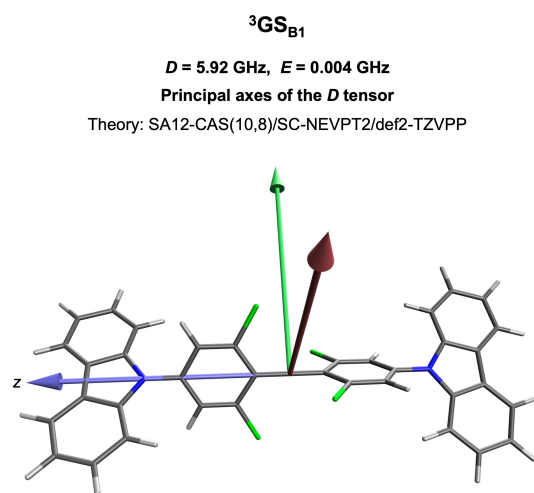


Figure C.3. Properties related to carbene **1**'s ground-triplet ZFS tensor, including the principal axes frame and the axial (D) and rhombic (E) ZFS parameters. These results were calculated at the SA12-CASSCF(10,8)/SC-NEVPT2/def2-TZVPP level and using the triplet geometry.

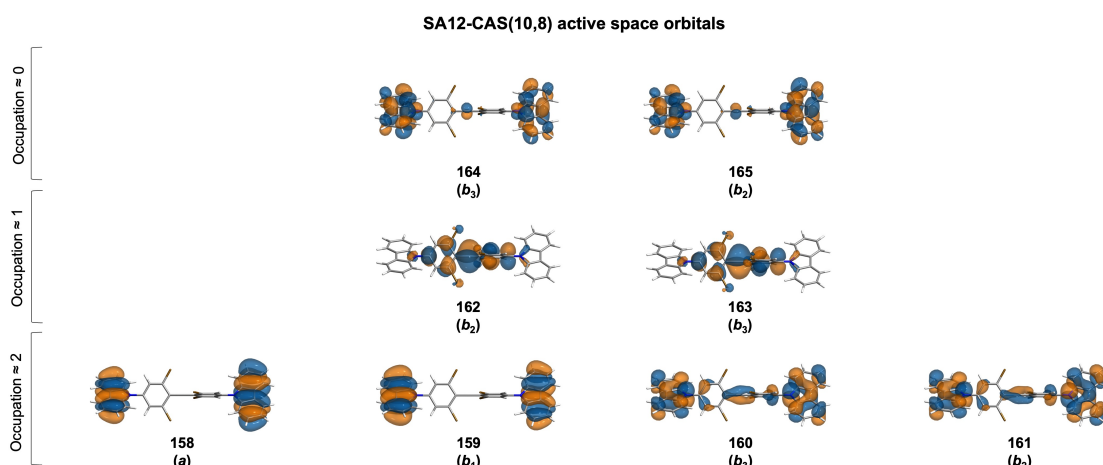


Figure C.4. Active space MOs (isovalue = 0.020) of carbene **1** from an SA12-CASSCF(10,8)/def2-TZVPP calculation of the triplet geometry. Also assigned in parenthesis are the orbital irreps based on the molecule's approximate D_2 point group symmetry (where the z -axis lies along the two carbene substituents).

Table C.1. Excited-state properties of carbene **1**, calculated at the SA12-CASSCF(10,8)/CASCI/QD-SC-NEVPT2/def2-TZVPP level and with the triplet geometry. The first triplet and singlet LEs are dominated by the following transitions: $161 \rightarrow 162$, $160 \rightarrow 163$. The second triplet and singlet LEs are dominated by the following transitions: $161 \rightarrow 163$, $160 \rightarrow 162$. The excitation characters are defined by Fig. 3d and are assigned by observing the CI vectors. As an example, one may localise the active space MOs on a monomer subunit for ease of comparison, during which the NEVPT2 energies will remain invariant.

Triplets		Singlets	
Energy / eV	Assignment	Energy / eV	Assignment
0.000	$^3\text{GS}_{B_1}$	0.422	$^1\text{GS}_A$
		0.493	$^1\text{CT}_{B_1}$
		0.952	$^1\text{CT}_A$
2.618	$^3\text{LE}_{B_1}$	2.663	$^1\text{LE}_{B_1}$
2.666	$^3\text{LE}_A$	2.668	$^1\text{LE}_A$

120°-geometry following relaxation on B3LYP/6–311+G(d,p) as a spin-restricted singlet

C 0.0001 -2.0270 -0.0037

C -1.2299 -1.3160 0.0467
C -1.6111 -0.2329 -0.8055
Cl -0.4707 0.4721 -1.9391
C -2.9030 0.2538 -0.8659
H -3.1533 1.0228 -1.5832
C -3.8900 -0.2543 -0.0115
N -5.1930 0.2729 -0.0422
C -3.5673 -1.2964 0.8692
H -4.3057 -1.6757 1.5615
C -2.2955 -1.8278 0.8537
Cl -1.9387 -3.1218 1.9704
C 1.2300 -1.3164 -0.0517
C 2.2982 -1.8312 -0.8540
Cl 1.9455 -3.1291 -1.9671
C 3.5699 -1.2997 -0.8679
H 4.3101 -1.6814 -1.5569
C 3.8900 -0.2539 0.0095
N 5.1925 0.2736 0.0414
C 2.9005 0.2574 0.8592
H 3.1488 1.0290 1.5745
C 1.6089 -0.2299 0.7975
Cl 0.4663 0.4787 1.9263
C -5.5305 1.6374 -0.0076
C -6.9392 1.7595 -0.0499
C -7.4806 0.4177 -0.1162
C -6.3826 -0.4740 -0.1077
C -4.7052 2.7559 0.1126
C -5.3126 4.0078 0.1589

C -6.7066 4.1469 0.0964
C -7.5246 3.0270 -0.0009
C -6.5626 -1.8533 -0.2158
C -7.8671 -2.3319 -0.3010
C -8.9672 -1.4624 -0.2892
C -8.7802 -0.0874 -0.2042
C 5.5299 1.6383 0.0074
C 6.9384 1.7606 0.0538
C 6.3823 -0.4731 0.1107
C 7.4799 0.4189 0.1223
C 4.7049 2.7566 -0.1165
C 5.3123 4.0085 -0.1619
C 6.7060 4.1478 -0.0953
C 7.5239 3.0280 0.0054
C 6.5624 -1.8522 0.2204
C 7.8668 -2.3303 0.3099
C 8.9667 -1.4604 0.3008
C 8.7794 -0.0855 0.2145
H -3.6291 2.6646 0.1797
H -4.6912 4.8913 0.2494
H -7.1476 5.1360 0.1336
H -8.6030 3.1356 -0.0315
H -5.7241 -2.5366 -0.2447
H -9.9699 -1.8677 -0.3562
H -9.6312 0.5843 -0.2129
H 3.6290 2.6653 -0.1870
H 4.6911 4.8919 -0.2553
H 7.1471 5.1369 -0.1320

H 8.6021 3.1367 0.0390
H 5.7242 -2.5360 0.2475
H 8.0311 -3.3985 0.3931
H 9.9694 -1.8653 0.3711
H 9.6301 0.5865 0.2256
H -8.0313 -3.4002 -0.3829

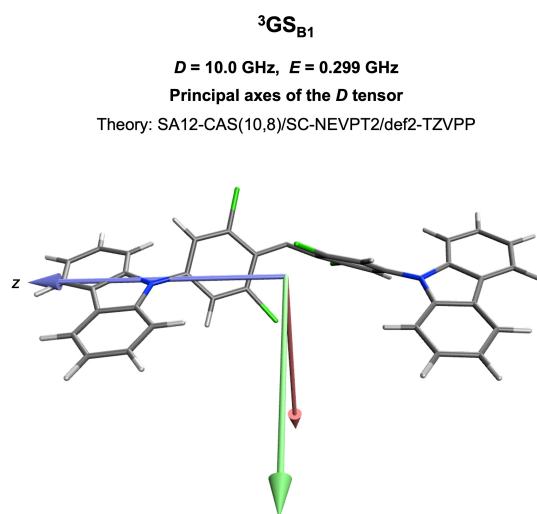


Figure C.5. Properties related to carbene **1**'s ground-triplet ZFS tensor, including the principal axes frame and the axial (D) and rhombic (E) ZFS parameters. These results were calculated at the SA12-CASSCF(10,8)/SC-NEVPT2/def2-TZVPP level and using the 120°-geometry.

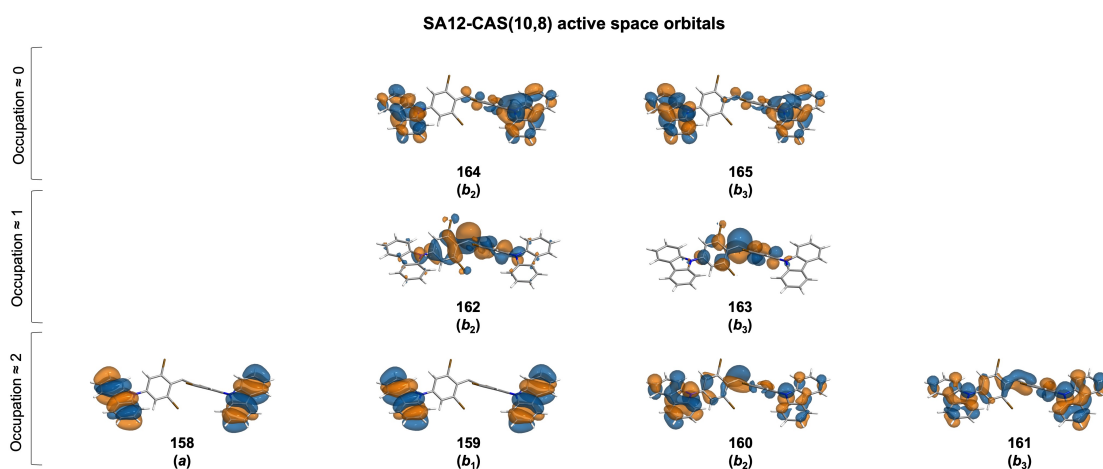


Figure C.6. Active space MOs (isovalue = 0.020) of carbene **1** from an SA12-CASSCF(10,8)/def2-TZVPP calculation of the 120°-geometry. Also assigned in parenthesis are the orbital irreps based on the molecule's approximate D_2 point group symmetry (where the z -axis lies along the two carbene substituents).

Table C.2. Excited-state properties of carbene **1**, calculated at the SA12-CASSCF(10,8)/CASCI/QD-SC-NEVPT2/def2-TZVPP level and with the 120°-geometry. The triplet and singlet excitations of energies between 2.672 eV and 2.918 eV are dominated by the following transitions: 160 → 162, 161 → 162. The excitation characters are defined by Fig. 3d and are assigned by observing the CI vectors. The degrees of CT and GS contributions to the first singlet state are quantified by Eqs. (C.65) and (C.66) to be, respectively, 45% and 45%, and the same is true for the third singlet state as well.

Triplets	
Energy / eV	Assignment
0.000	$^3\text{GS}_{B_1}$
2.672	$^3\text{LE}_{B_1}$ & $^3\text{LE}_A$ & $^3\text{CT}_{B_1}$ & $^3\text{CT}_A$
2.875	$^3\text{LE}_A$ & $^3\text{LE}_{B_1}$ & $^3\text{CT}_A$ & $^3\text{CT}_{B_1}$
Singlets	
Energy / eV	Assignment
0.083	$^1\text{GS}_A$ & $^1\text{CT}_A$
0.936	$^1\text{CT}_{B_1}$
2.076	$^1\text{CT}_A$ & $^1\text{GS}_A$
2.739	$^1\text{LE}_{B_1}$ & $^1\text{LE}_A$ & $^1\text{CT}_{B_1}$ & $^1\text{CT}_A$
2.918	$^1\text{LE}_A$ & $^1\text{LE}_{B_1}$ & $^1\text{CT}_A$ & $^1\text{CT}_{B_1}$

Further confirmation of a linear carbene

To further ascertain the presence of a linear carbene, a relaxed scan of the carbene bond angle was performed for the ground triplet state of carbene **1** at the UB3LYP/6-311+G(d,p) level of theory. This calculation was performed using the Gaussian16 code [75] and the results are presented in Fig. C.7.

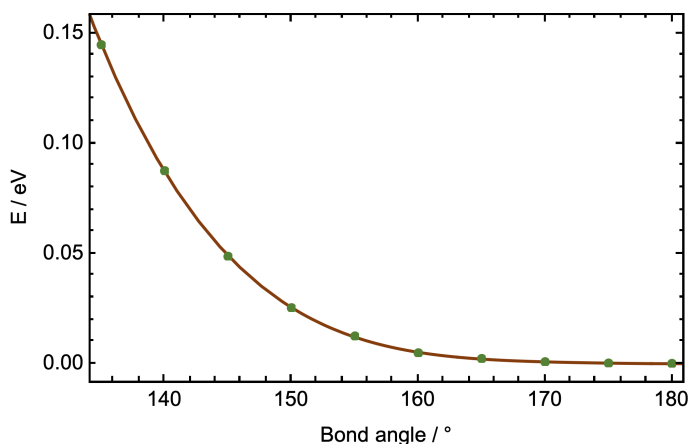


Figure C.7. PES of the ground triplet state of carbene **1**, calculated using UB3LYP/6–311+G(d,p). The DFT-computed energies are shown in green and a quartic fit is presented in brown to guide the eye.

We acknowledge the discussion of DFT biasing the culumene-like linear structure as compared to wavefunction-based methods [236, 222]. Indeed, a state-specific CASSCF(10,8)/def2-SVP calculation performed with the ORCA 5.0 package [166] optimised the triplet geometry to a bond angle of 137.17° , in agreement with the existing literature [222]. However, in the same reference and also in a more recent work [155], such a dramatic deviation from linearity is heavily weakened to only a few degrees away from 180° when dynamical correlations are included. Hence, we find it unlikely that a MC wavefunction-based method encompassing dynamical correlations will show a huge difference from the DFT-predicted bond angle of near 180° .

C.3.2 Carbene 2

C.3.3 Triplet geometry:

At the UB3LYP-D3BJ/def2-SVP level, the triplet SCF calculation converged to an energy of -7855.44381669 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 2.074123. At the UB3LYP/def2-SVPD level, the triplet SCF calculation converged to an energy of -7855.39513917 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 2.075060, while the BS SCF calculation converged to an energy of -7855.38074134 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 1.007342.

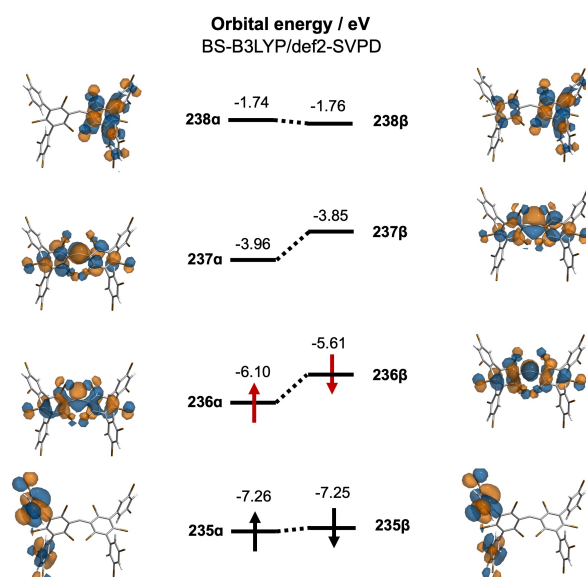


Figure C.8. Frontier MOs (isovalue = 0.020) of carbene **2** in the open-shell BS ground state, calculated at the BS-B3LYP/def2-SVPD level and using the triplet geometry.

Optimised triplet geometry

```

C 1.02173207379810 -0.08981847478325 -0.00860315303199
C 0.66933406471544 0.00452194269773 -1.34356281184384
C -0.45103077651271 -0.69349010644284 -1.90131210591443
Cl -1.42105181518168 -1.66915224694712 -0.83818980853697
C -0.78754961600810 -0.61197500075218 -3.25253443816162
C 0.02167283395063 0.18570924872773 -4.08981626672495
Cl -0.36946689181028 0.28163772498387 -5.78337876144928
C 1.14195778144157 0.89807662237343 -3.60963991987985
C 1.44364728039555 0.79273579758562 -2.25276306349040
Cl 2.79736940786067 1.66302538470728 -1.59511131512138
C 0.68075001723186 -0.13243282757374 1.33007758250342
C -0.42781060160045 0.59736298146606 1.87357767876570
Cl -1.38871702807643 1.56018302986701 0.79010594846417
C -0.75177912518442 0.56811852202601 3.22993883718925
C 0.05856459442923 -0.20504749983179 4.08885519621257

```

CI -0.32594280809135 -0.25153749199186 5.78593069554439
C 1.16991255257839 -0.94136748554896 3.62466307182073
C 1.45766618693714 -0.89252761141285 2.26224585936222
CI 2.80303535290992 -1.79301332382692 1.62892837519153
C -1.96766544942855 -1.34418691754202 -3.79690887192909
C -1.84222197498906 -2.68299686410146 -4.18510984594681
H -0.88713323427379 -3.20055895565613 -4.09320083847397
C -2.95662827336063 -3.35442889594046 -4.69202739597466
CI -2.80455288175367 -5.02386539775444 -5.17626222431838
C -4.19358922147709 -2.71855353162735 -4.82048212552275
H -5.05674930996325 -3.25176788011062 -5.21755720122167
C -4.29639095292324 -1.38214971165381 -4.42734808413940
CI -5.83106286313448 -0.56602473794629 -4.58057372714890
C -3.19824103878765 -0.68786370563157 -3.91600575539117
H -3.30242668759605 0.35489296538635 -3.61542130108065
C 1.97153855167638 1.73966243672627 -4.51898971757142
C 3.18447588336676 1.24566103139313 -5.01301927519054
H 3.53057713102818 0.24886241048307 -4.73888593900598
C 3.95467919467121 2.04628184207213 -5.85854452948119
CI 5.46763830089770 1.43357266464779 -6.47496364211969
C 3.54113077652206 3.33001166578594 -6.22165192239494
H 4.15004618219128 3.94702112769145 -6.88168157434326
C 2.32844857079544 3.80411066487791 -5.71586220595916
CI 1.79348047800617 5.40668133516810 -6.15216735699883
C 1.53837457720966 3.02375687792947 -4.86961092728650
H 0.59463998587622 3.41449297736430 -4.48835541298539
C 2.00717479136181 -1.74727827756154 4.55930992605811
C 3.17845645804078 -1.19746804423367 5.09312743729697

H 3.48565433494757 -0.18467876379211 4.83126428875996
 C 3.95678709568359 -1.96244064918799 5.96401197243601
 Cl 5.41873977708950 -1.28094612628670 6.62987923742165
 C 3.59088503595451 -3.26404383325386 6.31443035562876
 H 4.20530268637825 -3.85235316256354 6.99523047446106
 C 2.41910534356050 -3.79368598433950 5.76872428555520
 Cl 1.94425195940468 -5.41934156291367 6.18908679622166
 C 1.62239327261020 -3.05019447540112 4.89571062993346
 H 0.71135759793542 -3.48378450243808 4.48256241415441
 C -1.91900194912987 1.33274397463637 3.75683551806630
 C -1.73027972553952 2.60862918300476 4.30045394341322
 H -0.73464999551651 3.05006894982672 4.34777956057789
 C -2.83332476733413 3.31497593783259 4.78397886796813
 Cl -2.60213605980293 4.90658609780436 5.46066063176298
 C -4.12084306538337 2.77529447605373 4.73736605040911
 H -4.97506744005838 3.33517775591469 5.11665781285439
 C -4.28612580347068 1.50011117191472 4.19172850570044
 Cl -5.88499118169565 0.80494487634127 4.12246449955746
 C -3.20047610917302 0.77286063924993 3.70001311722033
 H -3.35424548419949 -0.21879626749236 3.27394594812764

Triplet excited states from UB3LYP/TDDFT/TDA/def2-SVPD

STATE 1: E= 0.107467 au 2.924 eV 23586.2 cm⁻¹ <S²> = 2.174562
 235a -> 237a : 0.058892 (c= 0.24267604)
 236a -> 237a : 0.217242 (c= -0.46609279)
 225b -> 235b : 0.018304 (c= -0.13529245)
 225b -> 236b : 0.011304 (c= 0.10632061)
 226b -> 235b : 0.145062 (c= 0.38086976)

226b -> 236b : 0.043384 (c= -0.20828862)

227b -> 235b : 0.053618 (c= 0.23155594)

227b -> 236b : 0.016571 (c= -0.12872656)

230b -> 235b : 0.287577 (c= 0.53626175)

230b -> 236b : 0.081458 (c= -0.28540859)

231b -> 235b : 0.014839 (c= 0.12181686)

STATE 2: E= 0.107949 au 2.937 eV 23692.1 cm⁻¹ <S²> = 2.169988

235a -> 238a : 0.047540 (c= -0.21803697)

236a -> 238a : 0.259238 (c= -0.50915434)

225b -> 235b : 0.068813 (c= -0.26232157)

225b -> 236b : 0.046619 (c= -0.21591345)

226b -> 236b : 0.010500 (c= -0.10246714)

228b -> 235b : 0.283149 (c= -0.53211710)

228b -> 236b : 0.211194 (c= -0.45955868)

232b -> 235b : 0.013044 (c= -0.11421126)

STATE 3: E= 0.114666 au 3.120 eV 25166.3 cm⁻¹ <S²> = 2.183074

235a -> 250a : 0.013120 (c= -0.11454354)

236a -> 239a : 0.273074 (c= -0.52256458)

236a -> 240a : 0.024881 (c= 0.15773782)

236a -> 247a : 0.030506 (c= -0.17466039)

223b -> 236b : 0.063474 (c= -0.25193962)

224b -> 235b : 0.236242 (c= 0.48604732)

226b -> 235b : 0.025798 (c= -0.16061843)

229b -> 235b : 0.060244 (c= -0.24544647)

230b -> 235b : 0.027213 (c= 0.16496325)

231b -> 235b : 0.011284 (c= 0.10622431)

233b -> 235b : 0.092627 (c= 0.30434680)

233b -> 236b : 0.012796 (c= -0.11311933)

234b -> 235b : 0.052732 (c= 0.22963360)

234b -> 236b : 0.015689 (c= 0.12525544)

STATE 4: E= 0.117153 au 3.188 eV 25712.0 cm⁻¹ <S²> = 2.148126

235a -> 239a : 0.023430 (c= 0.15306971)

236a -> 250a : 0.011997 (c= 0.10953011)

223b -> 235b : 0.020158 (c= 0.14197921)

224b -> 236b : 0.037663 (c= -0.19406979)

233b -> 235b : 0.435630 (c= 0.66002297)

233b -> 236b : 0.070636 (c= -0.26577436)

234b -> 235b : 0.240511 (c= -0.49041939)

234b -> 236b : 0.084453 (c= -0.29060821)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State Energy Wavelength fosc T2 TX TY TZ

(cm⁻¹) (nm) (au²) (au) (au) (au)

1 23586.2 424.0 0.002393762 0.03341 -0.15075 -0.10257 -0.01292

2 23692.1 422.1 0.001521319 0.02114 0.10005 -0.09910 0.03617

3 25166.3 397.4 0.003570289 0.04670 -0.00461 -0.00665 -0.21596

4 25712.0 388.9 0.000004563 0.00006 -0.00682 -0.00211 0.00274

Singlet excited states from BS-B3LYP/TDDFT/TDA/def2-SVPD

STATE 1: E= 0.011495 au 0.313 eV 2522.9 cm⁻¹ <S²> = 0.073089

235a -> 236a : 0.279197 (c= 0.52839106)

235b -> 236b : 0.675199 (c= 0.82170523)

STATE 2: E= 0.046708 au 1.271 eV 10251.2 cm⁻¹ <S²> = 0.057773

223a -> 236a : 0.019000 (c= 0.13783949)
 235a -> 236a : 0.660018 (c= -0.81241495)
 235b -> 236b : 0.262668 (c= 0.51251129)
 STATE 3: E= 0.096836 au 2.635 eV 21253.1 cm⁻¹ <S²> = 1.052785
 226a -> 236a : 0.217181 (c= 0.46602657)
 227a -> 236a : 0.064152 (c= 0.25328274)
 230a -> 236a : 0.373437 (c= -0.61109505)
 233a -> 236a : 0.025727 (c= -0.16039528)
 226b -> 236b : 0.055891 (c= 0.23641235)
 230b -> 236b : 0.044575 (c= -0.21112681)
 235b -> 237b : 0.029730 (c= 0.17242289)
 235b -> 238b : 0.122562 (c= 0.35008871)
 STATE 4: E= 0.099121 au 2.697 eV 21754.6 cm⁻¹ <S²> = 1.172348
 225a -> 236a : 0.179597 (c= -0.42378902)
 228a -> 236a : 0.351183 (c= 0.59260710)
 231a -> 236a : 0.027452 (c= 0.16568577)
 235a -> 237a : 0.014789 (c= -0.12161142)
 225b -> 236b : 0.103538 (c= 0.32177261)
 228b -> 236b : 0.175344 (c= 0.41874133)
 235b -> 237b : 0.068944 (c= -0.26257282)
 235b -> 238b : 0.020189 (c= 0.14208685)
 STATE 5: E= 0.104023 au 2.831 eV 22830.4 cm⁻¹ <S²> = 1.034643
 224a -> 236a : 0.024474 (c= -0.15644194)
 233a -> 236a : 0.057396 (c= -0.23957499)
 234a -> 236a : 0.843253 (c= 0.91828816)
 224b -> 236b : 0.021651 (c= -0.14714167)
 STATE 6: E= 0.104924 au 2.855 eV 23028.1 cm⁻¹ <S²> = 1.036054
 230a -> 236a : 0.014455 (c= -0.12022983)

233a -> 236a : 0.905936 (c= 0.95180670)

234a -> 236a : 0.060916 (c= 0.24681211)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MO-
MENTS

State Energy Wavelength fosc T2 TX TY TZ

(cm-1) (nm) (au**2) (au) (au) (au)

1 2522.9 3963.7 0.001991251 0.25984 0.01667 -0.00020 -0.50947

2 10251.2 975.5 0.161004743 5.17058 0.02754 -0.00788 -2.27371

3 21253.1 470.5 0.001400236 0.02169 0.07902 0.05359 0.11213

4 21754.6 459.7 0.000053719 0.00081 0.02574 -0.01223 -0.00090

5 22830.4 438.0 0.000039647 0.00057 0.00708 0.00168 0.02278

6 23028.1 434.3 0.000279398 0.00399 0.05764 0.02531 -0.00554

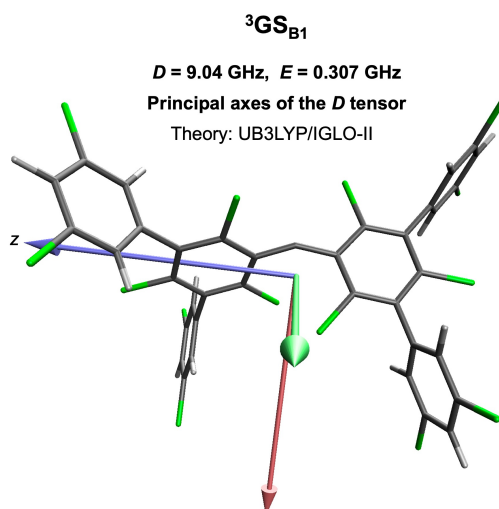


Figure C.9. Properties related to carbene **2**'s ground-triplet ZFS tensor, including the principal axes frame and the axial (D) and rhombic (E) ZFS parameters. These results were calculated at the UB3LYP/IGLO-II level and using the triplet geometry.

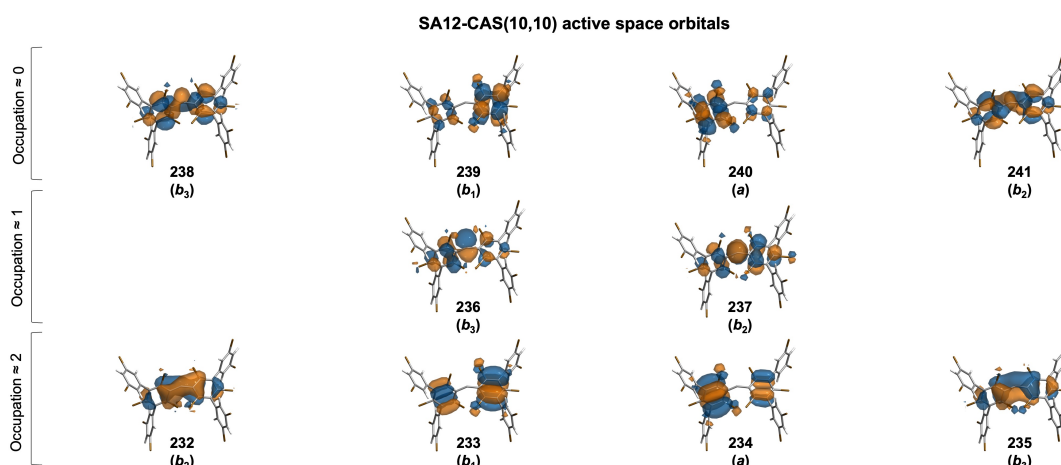


Figure C.10. Active space MOs (isovalue = 0.020) of carbene **2** from an SA12-CASSCF(10,10)/def2-SVPD calculation of the triplet geometry. Also assigned in parenthesis are the orbital irreps based on the molecule’s approximate D_2 point group symmetry (where the z -axis lies along the two carbene substituents).

Table C.3. Excited-state properties of carbene **2**, calculated at the SA12-CASSCF(10,10)/CASCI/QD-SC-NEVPT2/def2-SVPD level and with the triplet geometry. The first triplet and singlet LEs are dominated by the following transitions: $233 \rightarrow 237$, $237 \rightarrow 239$. The second triplet and singlet LEs are dominated by the following transitions: $234 \rightarrow 236$, $234 \rightarrow 237$, $237 \rightarrow 240$, $236 \rightarrow 240$. The excitation characters are defined by Fig. 3d and are assigned by observing the CI vectors. The degree of CT contribution to the first singlet state is quantified by Eq. (C.65) to be 4.6%. Meanwhile, the degree of GS contribution to the third singlet state is quantified by Eq. (C.66) to be 4.3%.

Triplets		Singlets	
Energy / eV	Assignment	Energy / eV	Assignment
0.000	$^3\text{GS}_{B_1}$	0.607	$^1\text{GS}_A$
		0.978	$^1\text{CT}_{B_1}$
		1.567	$^1\text{CT}_A$
3.108	$^3\text{LE}_{B_2}$ & $^3\text{LE}_{B_3}$	3.112	$^1\text{LE}_{B_2}$ & $^1\text{LE}_{B_3}$
3.121	$^3\text{LE}_{B_2}$ & $^3\text{LE}_{B_3}$	3.125	$^1\text{LE}_{B_2}$ & $^1\text{LE}_{B_3}$

C.3.4 Singlet geometry:

At the B3LYP-D3BJ/def2-SVP level, the spin-restricted singlet SCF calculation converged to an energy of -7855.42441709 Hartree. At the UB3LYP/def2-SVPD level,

the triplet SCF calculation converged to an energy of -7855.38314827 Hartree and an $\langle S^2 \rangle$ value of 2.067361, while the BS SCF calculation converged to an energy of -7855.37328142 Hartree and an $\langle S^2 \rangle$ value of 0.000012.

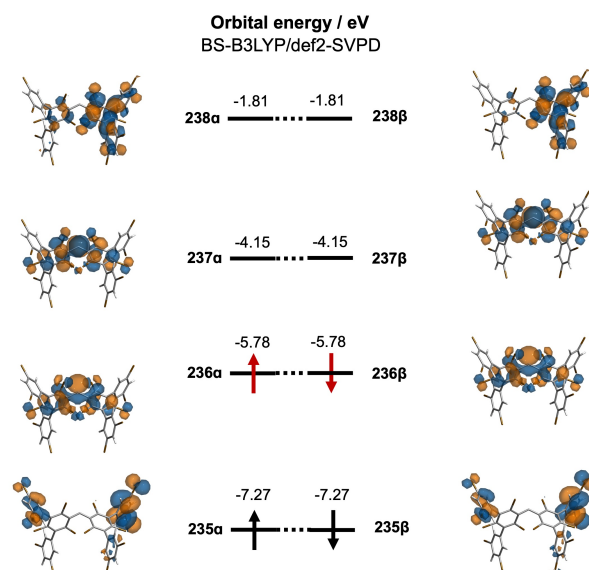


Figure C.11. Frontier MOs (isovalue = 0.020) of carbene **2** in the BS ground state, calculated at the BS-B3LYP/def2-SVPD level and using the singlet geometry.

Optimised singlet geometry

```

C 1.69653023325689 -0.01606372282361 -0.00234905902818
C 1.07230359562566 0.13098402817900 -1.25472822397553
C -0.02071356258007 -0.67471407120989 -1.70901837507512
Cl -0.76998104882087 -1.80120022548909 -0.60886709586523
C -0.49107976818726 -0.63292164937385 -3.02378636752719
C 0.09400959573903 0.29989821072482 -3.90519458869142
Cl -0.50296827294697 0.39581891172782 -5.53541615264576
C 1.13807794083034 1.16340464488975 -3.51443160895669
C 1.62276682349164 1.03974801222511 -2.21259709050034
Cl 2.89025249166223 2.09425416471849 -1.67279217225395
C 1.07355853532666 -0.15047585753256 1.25215879375943
C 0.00149219359438 0.67999767273023 1.71131271621639

```

CI -0.72226846454733 1.82726219861837 0.61555757079856
C -0.46703004375144 0.64552040009093 3.02688590606154
C 0.09802898594371 -0.30292836908114 3.90471732072462
CI -0.49741836520224 -0.38927234180113 5.53609415778554
C 1.12118191963315 -1.18897615704643 3.50940107929928
C 1.60523935235744 -1.07362407089099 2.20654689377713
CI 2.84605511869691 -2.15636937469111 1.66047272029181
C -1.61965168651992 -1.50315183239371 -3.46531512185995
C -1.36396233550784 -2.69845047134121 -4.14660420961063
H -0.34126103606589 -3.00360149358313 -4.36890319505231
C -2.43612077404141 -3.50246108865673 -4.53980153719454
CI -2.12290150489197 -4.99585006816213 -5.38584555666850
C -3.75720624436913 -3.13868948638821 -4.26846412875470
H -4.58591101760518 -3.77438032947432 -4.57857180311981
C -3.98947259044326 -1.94154596800604 -3.58722967378687
CI -5.63075537607615 -1.46929605232678 -3.22983173231796
C -2.93626744504693 -1.11899780198416 -3.18379008380322
H -3.13959863767597 -0.19222374233185 -2.64686530298371
C 1.70813529456779 2.16864156231503 -4.45710093054858
C 2.90411295717626 1.89793147383201 -5.13190227119170
H 3.42637158953890 0.95331465179012 -4.97894101920223
C 3.43086646605983 2.85672541285886 -5.99981398075209
CI 4.92409542482172 2.52538199643456 -6.83915669042927
C 2.78957236314750 4.07975659791177 -6.20934603325047
H 3.20985328323977 4.82120749127296 -6.88805588533593
C 1.59768117067032 4.32977539224236 -5.52529891456170
CI 0.78077784676224 5.85266370893683 -5.76722082361366
C 1.04921848668693 3.38833901903073 -4.65231467656504

H 0.11759400228778 3.60647716911600 -4.12976986603869
 C 1.67177692068702 -2.20834583084802 4.44840811086707
 C 2.87919523460097 -1.96758218053748 5.11414631361020
 H 3.42349642105281 -1.03629342706524 4.95655300470775
 C 3.38845221507193 -2.93903997317913 5.97837024900968
 Cl 4.89573738379929 -2.64467627080943 6.80634184564158
 C 2.71829189146248 -4.14563484339403 6.19290170811766
 H 3.12473208141639 -4.89747518514024 6.86860342628154
 C 1.51544813874528 -4.36580856006958 5.51783235514557
 Cl 0.66286126584179 -5.86792973341550 5.76606935935108
 C 0.98392663533434 -3.41107271218648 4.64883825502022
 H 0.04313759270857 -3.60583873868498 4.13348105848130
 C -1.57382857772820 1.54074987744755 3.47333942214604
 C -1.28884753915979 2.72589792542762 4.16074741131299
 H -0.25890784917995 3.00499169394798 4.38388010948103
 C -2.34101612635728 3.55313056320805 4.55953538128258
 Cl -1.99152147909390 5.03348159762226 5.41417497508206
 C -3.67071076596949 3.22275910937580 4.28753023827785
 H -4.48349231124838 3.87654768078045 4.60209915506317
 C -3.93229961793410 2.03520409108043 3.60017883596483
 Cl -5.58483218320450 1.60407226635451 3.24258174034658
 C -2.89953918825438 1.18984809041223 3.19108360798618
 H -3.12563963942822 0.27110801461556 2.64948444926961

Analysis of the results from the BS calculations

Generally speaking, a BS calculation involving a pair of paramagnetic centres optimises for a linear combination of the triplet wavefunction, the singlet ionic wavefunction, and the singlet neutral wavefunction (see Ref. [165] for the definitions; note that

the magnetic orbitals are also being variationally optimised, thus the ionic and neutral wavefunctions may not correspond to the charge-recombined and diradical wavefunctions respectively). This optimisation is, however, done with unequal weights – the neutral wavefunction always takes up 50% of the solution and the variational procedure partitions the remaining weight of 50% between the two other wavefunctions [165]. Throughout this work, the triplet wavefunction is lower in energy than the singlet wavefunctions, verified by separate triplet spin-unrestricted DFT calculations. Hence, we expect the contribution from the ionic wavefunction to be underestimated in favour of mixing with a lower-energy triplet.

Results for the ground triplet geometry: At this geometry, the BS calculation converged to $\langle S^2 \rangle \approx 1$, which implies that no ionic contribution is present. In this case, the BS formalism does not guarantee the neutral wavefunction to be an electronic eigenstate because the true eigenstate could have some ionic singlet character that was not captured by the dramatically lower triplet energy. However, the orbitals suggest that the singlet contribution to the BS solution is actually ${}^1CT_{B_1}$, which we expect from the semiempirical analysis to be an electronic eigenstate. Hence, the BS solution, once spin-purified, is a valid solution for an excited singlet state.

Results for the ground singlet geometry: At this geometry, the BS calculation converged to $\langle S^2 \rangle \approx 0$, which implies that no triplet contribution is present. In this case, the BS solution, which is essentially the closed-shell spin-pure solution, must be the singlet ground state since we expect the triplet contribution to be overestimated. Thus, we may directly take the difference in energy between the BS and triplet solutions to obtain the ground singlet-triplet gap as 0.268 eV (with the singlet being higher in energy).

C.3.5 Carbene 3

C.3.6 Triplet geometry:

At the UB3LYP-D3BJ/def2-SVP level, the triplet SCF calculation converged to an energy of -3674.55975397 Hartree and an $\langle S^2 \rangle$ value of 2.075389. At the UB3LYP/def2-

SVPD level, the triplet SCF calculation converged to an energy of -3674.53207678 Hartree and an $\langle S^2 \rangle$ value of 2.076452.

Optimised triplet geometry

C -0.00000439934011 -2.51943919370125 0.00000102571214
C 0.52850832880930 -2.18069680939706 1.23342679578647
C 0.04870877695217 -1.07230691950306 2.01215262262356
Cl -1.25581393431134 -0.14486582370336 1.31872531838592
C 0.55553809002387 -0.73400141922536 3.27716332704319
C 1.59207810482306 -1.56127166688678 3.77915673305629
Cl 2.33241633999971 -1.21642062782338 5.32020254065850
C 2.09084838241976 -2.66038324903276 3.06894618854528
C 1.56989045508120 -2.96261240139311 1.82407284378418
Cl 2.19898695356598 -4.31732451882595 0.93333317074508
C -0.52851505435240 -2.18069761125384 -1.23342570364933
C -1.56989407197126 -2.96261445002815 -1.82407570932438
Cl -2.19899222165224 -4.31732758360225 -0.93333862964502
C -2.09084711824675 -2.66038637821357 -3.06895135051424
C -1.59207511188317 -1.56127476818102 -3.77916057352587
C -0.55553827044779 -0.73400298788128 -3.27716345860417
C -0.04871400521821 -1.07230718557077 -2.01215035333569
Cl 1.25580290302252 -0.14486192724525 -1.31871794196352
C 0.03637466508903 0.40698565266480 4.05619265596436
C -0.03493423059770 1.72781851137371 3.63496183889599
N -0.58193222102122 2.46537772906827 4.64913670261961
C -0.87329313580083 1.65239217421587 5.72046108656540
C -0.49716080380980 0.36823954564556 5.38673594277380
C -0.03637301660693 0.40698434547522 -4.05619140909366

C 0.49717086000799 0.36823754228975 -5.38673125088873
 C 0.87330082658001 1.65239084021391 -5.72045644263336
 N 0.58192908332222 2.46537770894718 -4.64913595797225
 C 0.03492903541722 1.72781817041921 -3.63496242672198
 Cl -2.33240749471715 -1.21642473901138 -5.32020932356453
 H 2.89369260234646 -3.26329635485032 3.49122423764136
 H -2.89368915877337 -3.26330033610689 -3.49123234553133
 H 0.25630643030045 2.17853709624206 2.69004647446404
 H -0.74748172116139 3.46223302559326 4.61347833736066
 H -1.32131054958452 2.04954362680726 6.62830559508138
 H -0.58969177205210 -0.51231819121338 6.01749846306896
 H 0.58970833648726 -0.51232095846471 -6.01749178618860
 H 1.32132286100637 2.04954196135403 -6.62829881175506
 H 0.74747407107375 3.46223377635050 -4.61347886451088
 H -0.25631881478005 2.17853739445429 -2.69004956135357

Triplet excited states from UB3LYP/TDDFT/TDA/def2-SVPD

STATE 1: E= 0.089736 au 2.442 eV 19694.7 cm⁻¹ <S²> = 2.145979
 126a -> 128a : 0.029652 (c= -0.17219732)
 121b -> 126b : 0.012813 (c= 0.11319551)
 122b -> 125b : 0.027816 (c= -0.16678202)
 123b -> 126b : 0.180940 (c= 0.42537022)
 124b -> 125b : 0.716406 (c= -0.84640765)
 STATE 2: E= 0.090334 au 2.458 eV 19825.9 cm⁻¹ <S²> = 2.150198
 125a -> 128a : 0.011628 (c= -0.10783186)
 126a -> 127a : 0.029313 (c= -0.17121179)
 121b -> 125b : 0.029133 (c= -0.17068359)
 122b -> 126b : 0.012550 (c= 0.11202566)

123b -> 125b : 0.643836 (c= -0.80239406)

124b -> 126b : 0.252907 (c= 0.50289841)

STATE 3: E= 0.098562 au 2.682 eV 21631.8 cm⁻¹ <S²> = 2.123581

122b -> 126b : 0.021977 (c= 0.14824653)

123b -> 125b : 0.291860 (c= 0.54024036)

124b -> 126b : 0.669024 (c= 0.81793900)

STATE 4: E= 0.099360 au 2.704 eV 21807.0 cm⁻¹ <S²> = 2.125730

121b -> 126b : 0.025592 (c= -0.15997363)

123b -> 126b : 0.739196 (c= -0.85976499)

124b -> 125b : 0.218016 (c= -0.46692207)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy	Wavelength	fosc	T2	TX	TY	TZ
	(cm ⁻¹)	(nm)	(au ²)	(au)	(au)	(au)	(au)

1	19694.7	507.8	0.015450630	0.25827	-0.35391	-0.00001	-0.36472
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2	19825.9	504.4	0.002904466	0.04823	-0.00002	0.21961	-0.00002
---	---------	-------	-------------	---------	----------	---------	----------

3	21631.8	462.3	0.002069751	0.03150	0.00001	0.17748	-0.00009
---	---------	-------	-------------	---------	---------	---------	----------

4	21807.0	458.6	0.008190698	0.12365	0.04018	-0.00005	-0.34934
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C.3.7 Monoradical analogues

The geometries of the monoradical analogues to the carbenes were optimised as doublets on UB3LYP-D3BJ/def2-SVP [86, 87], followed by the appropriate harmonic frequency analysis. The open ends of the monoradicals were capped with hydrogen atoms. These calculations were performed on the ORCA 5.0 code [166].

Optimised geometry of carbene 1's monoradical analogue

C -0.04529674533207 -0.00045675530592 0.00179482611630
C 1.35182212612997 -0.00032887308409 0.00130237341751
C 2.13379423518766 0.89083929907069 0.81844891631253
Cl 1.31557082661754 2.02047914937467 1.86930762087917
C 3.51771123427047 0.88797302195634 0.82919016431974
H 4.05487009410498 1.56358701148494 1.49364767120710
C 4.22784806540714 -0.00006174175257 0.00028638530387
N 5.63412801451828 0.00004967573701 -0.00021452937613
C 3.51728723959689 -0.88822627573904 -0.82811529082121
H 4.05410979311949 -1.56374096087978 -1.49294474496189
C 2.13338108818338 -0.89135546012051 -0.81639277141679
Cl 1.31462878862704 -2.02116505556784 -1.86665724253884
C 6.45325523008099 -1.13175829729277 0.12758081223484
C 7.81285785942761 -0.72079947548441 0.08065349455077
C 6.45300396214041 1.13196663044385 -0.12865181516466
C 7.81269754090368 0.72118561528870 -0.08279628444042
C 6.10151240854034 -2.47174695069900 0.32365334809613
C 7.13408220455604 -3.40375591704685 0.44539222916261
C 8.48467618399120 -3.01532631849537 0.38204902425302
C 8.83002494379871 -1.67562591530696 0.20563116231403
C 6.10093284195708 2.47191123753020 -0.32443562583458
C 7.13328653696373 3.40405440482638 -0.44698315600978
C 8.48398013807026 3.01580086857688 -0.38470863094782
C 8.82964217976527 1.67614458193815 -0.20856862863841
H 5.05848087275965 -2.78318009526554 0.38904900661639
H 6.88358358055918 -4.45658184186226 0.59687509641706
H 9.26789283844258 -3.77059283414095 0.47957325671042

H 9.87902487774695 -1.37159044485714 0.17043996638325
H 5.05780972570382 2.78321099682733 -0.38900103828030
H 6.88253255862499 4.45684873450591 -0.59826349737243
H 9.26702078961170 3.77116998020225 -0.48284999241012
H 9.87870885513868 1.37224519413754 -0.17420238382850
H -0.59595441729218 -0.69531920194331 -0.63000235376152
H -0.59563637192153 0.69430411294350 0.63398063150864

Optimised geometry of carbene 2's monoradical analogue

C 0.93641310860044 0.02685970321370 0.05860705044083
C 0.63727027002181 0.08430483624904 -1.30710818347640
C -0.47205344858841 -0.62573783864524 -1.88394596977427
Cl -1.48211837954089 -1.58878127834394 -0.83715120424751
C -0.78690214892442 -0.58224829220358 -3.24102970180402
C 0.03024058210508 0.19864572441494 -4.08548923006301
Cl -0.33416158132916 0.25774178435757 -5.78704673364423
C 1.13570176082019 0.92827008173393 -3.59886048823637
C 1.41487977554836 0.86055255365478 -2.23475381378267
Cl 2.77389715302643 1.77096035510119 -1.62726884447573
C -1.95399784871647 -1.33138546969277 -3.79166142169967
C -1.80586987321979 -2.66507281093949 -4.18933314080536
H -0.84247890770436 -3.16734529504267 -4.09940535294731
C -2.90777220451295 -3.35134873377583 -4.70340604848439
Cl -2.72656525870767 -5.01488864000326 -5.19936376029970
C -4.15524150813440 -2.73598009979090 -4.82990631620725
H -5.00869010318984 -3.28102971965227 -5.23183503084490
C -4.28053115823238 -1.40410931736120 -4.42829601279853
Cl -5.82890125187959 -0.61259792627897 -4.57828559119182

C -3.19495757599069 -0.69501147844293 -3.91068213164984
 H -3.31695685511421 0.34412941069404 -3.60439454183530
 C 1.97381295037980 1.74617489858665 -4.52334180359203
 C 3.14425245656568 1.20495016821590 -5.06756571941523
 H 3.45441613115395 0.19004560849161 -4.81778262094661
 C 3.91760053156548 1.98063940693277 -5.93330192157293
 Cl 5.37935346673530 1.30949131502868 -6.61120407271218
 C 3.54744600459035 3.28463457480568 -6.27005567891773
 H 4.15762400958283 3.88108801558728 -6.94755505652185
 C 2.37603919964130 3.80527620131501 -5.71521891583706
 Cl 1.89399957806319 5.43329726878904 -6.11963097624543
 C 1.58473792545567 3.05121335323741 -4.84652429480221
 H 0.67337878130386 3.47804446299423 -4.42714468688813
 H 1.78421660393529 0.57863161407008 0.46014387482339
 H 0.32465821469023 -0.57092283730053 0.73160674045550

Appendix D

Supporting Information of Chapter 5: Photoredox Catalysis with Spin Magnetic Field Effects: A Scheme for Chiral Resolution

D.1 Derivation of the analytical results

In this section, we will derive the analytical solution to the collective decay rates $w_{\pm}^{(R/S)}$ and, hence, the chiral resolution χ using perturbation theory. We begin with the photoexcited triplet state of the photosensitiser, $|^3\text{LE}\rangle$. As mentioned in the main text, its dominant relaxation process is the spin-preserving charge separation that forms the triplet RP state $|^3\text{RP}\rangle$, mediated by a real-valued electronic coupling $V_{\text{e},M_S}^{\text{LE-RP}}$. Schematically,

$$|^3\text{LE}; M_S\rangle \rightarrow |^3\text{RP}; M_S\rangle, \quad \text{rate} = \frac{1}{\hbar^2 \Omega} |V_{\text{e},M_S}^{\text{LE-RP}}|^2. \quad (\text{D.1})$$

At this step, two other minor decay channels are possible: First, the SOC also connects the $|^3\text{LE}\rangle$ state to the $|^1\text{RP}\rangle$ state. Second, because the $|^3\text{LE}\rangle$ state is, strictly speaking, not a spin-pure state (due to the singlet admixtures necessary for the spin-forbidden triplet excitation [214]), any singlet spin contaminant can also decay in a spin-preserving manner, populating the $|^1\text{RP}\rangle$ state. These decay avenues are minor because the associated transition matrix elements are perturbative relative to $V_{\text{e},M_S}^{\text{LE-RP}}$. In the first case, a TDDFT calculation estimates the relevant SOC matrix element to be around

1 cm^{-1} , which is small when compared to $V_{e,M_S}^{\text{LE-RP}} \approx 100 \text{ cm}^{-1}$. Further, since the rates are proportional to the square of the matrix elements, the probability of populating the $|^1\text{RP}\rangle$ state is four orders of magnitude smaller and can be ignored. In the second case, the singlet perturbation has an amplitude of $\sim \langle \hat{V}_{\text{SOC}} \rangle / \Delta E_{\text{ST}}$ with $\langle \hat{V}_{\text{SOC}} \rangle$ and ΔE_{ST} being the SOC matrix element and the energy gap between the $|^3\text{LE}\rangle$ state and the singlet contaminant. The same TDDFT calculation also reveals $\langle \hat{V}_{\text{SOC}} \rangle \approx 1 \text{ cm}^{-1}$ and $\Delta E_{\text{ST}} \gtrsim 21000 \text{ cm}^{-1}$, making the second case an *even smaller* perturbation. Note that transitions from a single state into multiple degenerate final states generally do not experience any collective effects across the decay channels. Therefore, these additional minor channels only lead to a tiny subensemble of molecules in the $|^1\text{RP}\rangle$ state that evolves *independently* from the dominant $|^3\text{RP}\rangle$ subensemble. In that sense, these additional $|^1\text{RP}\rangle$ molecules have little bearing on the MFE-induced enantioselectivity and can thus be omitted from our discussion.

Next, the $|^3\text{RP}; M_S\rangle$ states will, due to the applied magnetic field, pick up a small $|^1\text{RP}\rangle$ contribution. For a spin Hamiltonian of

$$\begin{aligned} \hat{H}_s + \hat{V}_s = & \mu_B \mathbf{B} \cdot \mathbf{g}_A \cdot \hat{\mathbf{S}}_A + \mu_B \mathbf{B} \cdot \mathbf{g}_B \cdot \hat{\mathbf{S}}_B \\ & + J (\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_A^2 - \hat{\mathbf{S}}_B^2) + \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}} \end{aligned} \quad (\text{D.2})$$

with $\mathbf{D}$ being the ZFS tensor, and for $\mathbf{B} \equiv B_0 \mathbf{z}$ that is aligned with $\mathbf{g}_A$'s principal axis (i.e. $g_{A,zx} = g_{A,zy} = 0$ [14]), the matrix representation of the spin Hamiltonian in the singlet-triplet basis reads

$$\hat{H}_s = \begin{pmatrix} E(^1\text{RP}) & 0 & 0 & 0 \\ 0 & E(^3\text{RP}; +1) & 0 & 0 \\ 0 & 0 & E(^3\text{RP}; 0) & 0 \\ 0 & 0 & 0 & E(^3\text{RP}; -1) \end{pmatrix}, \quad (\text{D.3})$$

and

$$\hat{V}_s = \frac{\hbar}{2\sqrt{2}} \begin{pmatrix} 0 & \mu_B B_0 \Delta g_{zx} + i\mu_B B_0 \Delta g_{zy} & & & & & & \\ \mu_B B_0 \Delta g_{zx} - i\mu_B B_0 \Delta g_{zy} & 0 & & & & & & \\ -\sqrt{2}\mu_B B_0 \Delta g_{zz} & \mu_B B_0 \Delta g_{zx} + i\mu_B B_0 \Delta g_{zy} & & & & & & \\ -\mu_B B_0 \Delta g_{zx} - i\mu_B B_0 \Delta g_{zy} & 0 & & & & & & \\ & -\sqrt{2}\mu_B B_0 \Delta g_{zz} & -\mu_B B_0 \Delta g_{zx} + i\mu_B B_0 \Delta g_{zy} & & & & & \\ \mu_B B_0 \Delta g_{zx} - i\mu_B B_0 \Delta g_{zy} & 0 & & & & & & \\ 0 & \mu_B B_0 \Delta g_{zx} - i\mu_B B_0 \Delta g_{zy} & & & & & & \\ \mu_B B_0 \Delta g_{zx} + i\mu_B B_0 \Delta g_{zy} & 0 & & & & & & \end{pmatrix} + \frac{\hbar^2}{2\sqrt{2}} \begin{pmatrix} 0 & 0 & & & & & & \\ 0 & 0 & & & & & & \\ 0 & 2D_{xz} + i2D_{yz} & & & & & & \\ 0 & \sqrt{2}(D_{xx} - D_{yy}) + i\sqrt{2}(D_{yx} + D_{xy}) & & & & & & \\ & 0 & 0 & & & & & \\ 2D_{zx} - i2D_{zy} & \sqrt{2}(D_{xx} - D_{yy}) - i\sqrt{2}(D_{yx} + D_{xy}) & & & & & & \\ 0 & -2D_{xz} + i2D_{yz} & & & & & & \\ -2D_{zx} - i2D_{zy} & 0 & & & & & & \end{pmatrix}, \quad (\text{D.4})$$

where the elements run over $\{|^1\text{RP}\rangle, |^3\text{RP}; +1\rangle, |^3\text{RP}; 0\rangle, |^3\text{RP}; -1\rangle\}$. Here, we have organised the off-diagonal elements into $\hat{V}_s$ and the on-diagonal elements into $\hat{H}_s$, which read

$$E(^1\text{RP}) = -\frac{3\hbar^2 J}{2}, \quad (\text{D.5})$$

$$E(^3\text{RP}; +1) = \frac{\hbar^2 J}{2} + \hbar\mu_B g_{A,zz} B_0 + \frac{\hbar\mu_B B_0 \Delta g_{zz}}{2} + \hbar^2 D_{zz} + \frac{\hbar^2 (D_{xx} + D_{yy})}{2}, \quad (\text{D.6})$$

$$E(^3\text{RP}; 0) = \frac{\hbar^2 J}{2} + \hbar^2 (D_{xx} + D_{yy}), \quad (\text{D.7})$$

$$E(^3\text{RP}; -1) = \frac{\hbar^2 J}{2} - \hbar\mu_B g_{A,zz} B_0 - \frac{\hbar\mu_B B_0 \Delta g_{zz}}{2} + \hbar^2 D_{zz} + \frac{\hbar^2 (D_{xx} + D_{yy})}{2}. \quad (\text{D.8})$$

We shall now make some arguments on the basis of perturbation theory, the validity of which we will quantify later. First, notice that $\hat{V}_s$ mixes the photoinitialised $|^3\text{RP}; M_S\rangle$ states with the other RP states for the duration of the ensemble's lifetime $\tau_{\text{RP-GS}}$. Further, $\hat{V}_s$, being proportional to $\Delta\mathbf{g}$, is small in organic systems, and so the ensemble will still have $|^3\text{RP}; M_S\rangle$ as its principal component even after the MFE. Therefore, $\tau_{\text{RP-GS}}$ is approximately the triplet RP's lifetime, which is around 10^{-7} s. We shall assume $\tau_{\text{RP-GS}}$ to be long enough such that all oscillating phases accumulated during the singlet-triplet dynamics are dampened and the final state corresponds to a stationary state. This damping timescale is most likely associated with the fastest possible decay process, being the singlet RP decay that occurs within 10^{-11} s $\ll \tau_{\text{RP-GS}}$. If we further assume $\hat{V}_s$ to be smaller than the energy gaps within the RP states, then these Rabi oscillations will occur at a timescale given by the inverse of the energy gaps (in frequency units), which we assume to be shorter than $\tau_{\text{RP-GS}}$ for sufficient oscillations to occur during the RP's lifetime. Also, this stationary (eigen)state may be approximated by first-order time-*independent* perturbation theory in $\hat{V}_s$, which amounts to acting the following operator on the $|^3\text{RP}; M_S\rangle$ states:

$$\hat{U}(\tau_{\text{RP-GS}}) \approx 1 + \sum_{m,n} \frac{\langle m | \hat{V}_s | n \rangle}{E_n - E_m} |m\rangle \langle n|, \quad (\text{D.9})$$

where $|m\rangle$ and $|n\rangle$ are the RP states. Considering the $|^3\text{RP}; +1\rangle$ sublevel for now, we find that

$$\begin{aligned} \hat{U}(\tau_{\text{RP-GS}}) |^3\text{RP}; +1\rangle &\equiv |\overline{^3\text{RP}; +1}\rangle \approx |^3\text{RP}; +1\rangle \\ &+ |^1\text{RP}\rangle \frac{\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1\rangle}{E(^3\text{RP}; +1) - E(^1\text{RP})} \\ &+ |^3\text{RP}; 0\rangle \frac{\langle ^3\text{RP}; 0 | \hat{V}_s | ^3\text{RP}; +1\rangle}{E(^3\text{RP}; +1) - E(^3\text{RP}; 0)} \\ &+ |^3\text{RP}; -1\rangle \frac{\langle ^3\text{RP}; -1 | \hat{V}_s | ^3\text{RP}; +1\rangle}{E(^3\text{RP}; +1) - E(^3\text{RP}; -1)}. \end{aligned} \quad (\text{D.10})$$

The operator responsible for the relaxation to the GS is

$$\hat{V}^{\text{RP-GS}} = |^1\text{GS}\rangle \left[\sum_{M_S=0,\pm 1} V_{\text{SOC},M_S}^{\text{RP-GS}} \langle ^3\text{RP}; M_S | + V_{e,S}^{\text{RP-GS}} \langle ^1\text{RP} | \right] + \text{H.c.}, \quad (\text{D.11})$$

and we propose that, for $J < 0$, an applied magnetic field in the positive z -direction (i.e. $B_0 > 0$) would bring the $|^3\text{RP}; +1\rangle$ state into near-degeneracy with the $|^1\text{RP}\rangle$ state. Hence, only the first two terms of Eq. (D.10) will decay collectively, leading to the relaxation rate presented in the main text:

$$w_+^{(R)} \approx \frac{1}{\hbar^2 \Omega} \left| V_{\text{SOC},+1}^{\text{RP-GS}} + V_{e,S}^{\text{RP-GS}} \left[\frac{\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle}{E(^3\text{RP}; +1) - E(^1\text{RP})} \right] \right|^2, \quad (\text{D.12})$$

where, in the no-ZFS limit (i.e. $\mathbf{D} = 0$),

$$\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle = \hbar \mu_B B_0 \left(\frac{\Delta g_{zx} + i \Delta g_{zy}}{2\sqrt{2}} \right) = \hbar \mu_B \Delta g_{\text{eff}} B_0, \quad (\text{D.13})$$

$$E(^3\text{RP}; +1) - E(^1\text{RP}) = 2\hbar^2 J + \hbar \mu_B B_0 \left(g_{A,zz} + \frac{\Delta g_{zz}}{2} \right) = 2\hbar^2 J + \hbar \mu_B g_{\text{eff}} B_0, \quad (\text{D.14})$$

found by reading off Eq. (D.4) directly. As for the $|^3\text{RP}; 0\rangle$ and $|^3\text{RP}; -1\rangle$ components, we argue that they are too far away in energy from each other and from the $|^1\text{RP}\rangle$ state to create any substantial collective effects. The validity of these assumptions will be quantified in the next few paragraphs.

Having presented the mathematical derivation for the $M_S = +1$ sublevel, let us set these parameters into their experimental ranges and justify the use of perturbation theory. As explored in the main text, the energy difference (in frequency units) between the $|^3\text{RP}; +1\rangle$ and $|^1\text{RP}\rangle$ states must be smaller than the RP decay rate, being $1/\tau_{\text{RP-GS}} \approx (10^{-7} \text{ s})^{-1}$, for collective decay to occur. Yet, the same value must be larger than the RP decay rate for sufficient Rabi oscillations to occur prior to the decay. Together, they constrain $|E(^3\text{RP}; +1) - E(^1\text{RP})|$ at around 10 MHz. Given that the typical RP singlet-triplet gap is between 100 MHz and 100 GHz [68], we expect a magnetic field strength B_0 of at least 0.01 to 1 T to be necessary to satisfy that constraint. In this regime, the

matrix elements of $\hat{V}_s$, i.e. the MFE, are between 0.01 MHz and 1 MHz if we note that $\Delta g \approx 10^{-4}$ for organic systems [14]. Also, we are likely to be in the high-field regime because the Zeeman energy of at least 100 MHz (needed to bridge the RP singlet-triplet gap) is similar to or higher than the typical ZFS parameter of $D \approx 100$ MHz (see DFT predictions). This leaves $|E(^3\text{RP}; +1) - E(^3\text{RP}; 0 \text{ or } -1)| \gtrsim 100$ MHz, which, indeed, makes the $|^3\text{RP}; 0\rangle$ and $|^3\text{RP}; -1\rangle$ components too far away from any other state for collective decay. From Eq. (D.10), we find the largest perturbative parameter to be $\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle / [E(^3\text{RP}; +1) - E(^1\text{RP})]$. This, at its maximum value, is around 10^{-1} , which is small enough for our purposes.

Going further, we note from Eq. (D.12) that the interference effect is only appreciable if $V_{\text{SOC},+1}^{\text{RP-GS}}$ has the same magnitude order (in amplitude) as $V_{e,S}^{\text{RP-GS}} \times \langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle / [E(^3\text{RP}; +1) - E(^1\text{RP})]$. Typical values for these parameters are $V_{\text{SOC},+1}^{\text{RP-GS}} \approx 1 \text{ cm}^{-1}$ and $V_{e,S}^{\text{RP-GS}} \approx 100 \text{ cm}^{-1}$. Therefore, the interference is optimised when the RP singlet-triplet gap is around 1000 MHz ($J \approx -500$ MHz), which would be narrowed to 10 MHz by a magnetic field of 0.1 T, which in turn leads to $\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle \approx 0.1$ MHz. Indeed, this is the parameter range observed in the main text and underscores the need for chemical fine-tuning.

A similar argument holds for the photogenerated RP sublevel $|^3\text{RP}; -1\rangle$, where this time the magnetic field should be applied in the negative z -direction (i.e. $B_0 < 0$) to bring the $|^3\text{RP}; -1\rangle$ state into near-degeneracy with the $|^1\text{RP}\rangle$ state. Eq. (D.12) becomes modified as

$$V_{\text{SOC},+1}^{\text{RP-GS}} \rightarrow V_{\text{SOC},-1}^{\text{RP-GS}} = \left(V_{\text{SOC},+1}^{\text{RP-GS}} \right)^*, \quad (\text{D.15})$$

$$\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle \rightarrow \langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; -1 \rangle = -\langle ^1\text{RP} | \hat{V}_s | ^3\text{RP}; +1 \rangle^*, \quad (\text{D.16})$$

$$E(^3\text{RP}; +1) - E(^1\text{RP}) \rightarrow E(^3\text{RP}; -1) - E(^1\text{RP}) = 2\hbar^2 J - \hbar \mu_B B_0 \left(g_{A,zz} + \frac{\Delta g_{zz}}{2} \right). \quad (\text{D.17})$$

The equality in the first line is a general feature of SOC matrix elements [67] while the

equalities in the other two lines may be found directly from Eq. (D.4). Applying these changes to Eq. (D.12) and removing the complex conjugate under the absolute operation yields

$$w_-^{(R)} \approx \frac{1}{\hbar^2 \Omega} \left| V_{\text{SOC},+1}^{\text{RP-GS}} - V_{\text{e},S}^{\text{RP-GS}} \left[\frac{\langle {}^1\text{RP} | \hat{V}_s | {}^3\text{RP}; +1 \rangle}{2\hbar^2 J - \hbar \mu_B g_{\text{eff}} B_0} \right] \right|^2, \quad (\text{D.18})$$

and, taking $V_{\text{SOC},+1}^{\text{RP-GS}} \rightarrow -V_{\text{SOC},+1}^{\text{RP-GS}}$ for the opposite enantiomer yields

$$w_-^{(S)} \approx \frac{1}{\hbar^2 \Omega} \left| -V_{\text{SOC},+1}^{\text{RP-GS}} - V_{\text{e},S}^{\text{RP-GS}} \left[\frac{\langle {}^1\text{RP} | \hat{V}_s | {}^3\text{RP}; +1 \rangle}{2\hbar^2 J - \hbar \mu_B g_{\text{eff}} B_0} \right] \right|^2. \quad (\text{D.19})$$

As for the $|{}^3\text{RP}; 0\rangle$ state, its energy, which does not change with the magnetic field strength, will always be far away from the other RP states, so no collective decay is expected. Also, no collective decay is present between multiple triplet RP states because the spin Zeeman energy of 100 MHz – 100 GHz exceeds the triplet RP decay rate of around 10 MHz. Thus, the magnetic field brings *only one* triplet M_S sublevel into near-degeneracy with the singlet RP state for collective effects.

Finally, recall from the main text that, when the magnetic field is applied in the positive z -direction (i.e. $B_0 > 0$), the chiral resolution is approximated by

$$\chi \approx \frac{w_+^{(R)}}{w_+^{(S)}}. \quad (\text{D.20})$$

Each of these terms reads

$$\begin{aligned} \hbar^2 \Omega w_+^{(R)} &= \left[\text{Re} \left(V_{\text{SOC},+1}^{\text{RP-GS}} \right) + V_{\text{e},S}^{\text{RP-GS}} \times \frac{B_0 \text{Re} (\hbar \mu_B \Delta g_{\text{eff}})}{2\hbar^2 J + \hbar \mu_B g_{\text{eff}} B_0} \right]^2 \\ &\quad + \left[\text{Im} \left(V_{\text{SOC},+1}^{\text{RP-GS}} \right) + V_{\text{e},S}^{\text{RP-GS}} \times \frac{B_0 \text{Im} (\hbar \mu_B \Delta g_{\text{eff}})}{2\hbar^2 J + \hbar \mu_B g_{\text{eff}} B_0} \right]^2, \end{aligned} \quad (\text{D.21})$$

$$\begin{aligned} \hbar^2 \Omega w_+^{(S)} &= \left[-\text{Re} \left(V_{\text{SOC},+1}^{\text{RP-GS}} \right) + V_{\text{e},S}^{\text{RP-GS}} \times \frac{B_0 \text{Re} (\hbar \mu_B \Delta g_{\text{eff}})}{2\hbar^2 J + \hbar \mu_B g_{\text{eff}} B_0} \right]^2 \\ &\quad + \left[-\text{Im} \left(V_{\text{SOC},+1}^{\text{RP-GS}} \right) + V_{\text{e},S}^{\text{RP-GS}} \times \frac{B_0 \text{Im} (\hbar \mu_B \Delta g_{\text{eff}})}{2\hbar^2 J + \hbar \mu_B g_{\text{eff}} B_0} \right]^2. \end{aligned} \quad (\text{D.22})$$

By computing

$$\frac{\partial \chi}{\partial B_0} = 0, \quad (\text{D.23})$$

we find, after some algebraic manipulation, that there exists two extrema, labelled “ $\pm$ ”, at magnetic field strengths B_0 of

$$B_{\max}^{(\pm)} = \frac{2 (\hbar J / \mu_B) \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right|}{\pm |\Delta g_{\text{eff}}| V_{\text{e,S}}^{\text{RP-GS}} - g_{\text{eff}} \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right|}, \quad (\text{D.24})$$

and with chiral resolutions χ of

$$\chi_{\max}^{(\pm)} = \frac{|\Delta g_{\text{eff}}| \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right| \pm \text{Re} \left(\Delta g_{\text{eff}}^* V_{\text{SOC},+1}^{\text{RP-GS}} \right)}{|\Delta g_{\text{eff}}| \left| V_{\text{SOC},+1}^{\text{RP-GS}} \right| \mp \text{Re} \left(\Delta g_{\text{eff}}^* V_{\text{SOC},+1}^{\text{RP-GS}} \right)}, \quad (\text{D.25})$$

where Δg_{eff}^* is the complex conjugate of Δg_{eff} . These are the expressions presented in the main text. The same calculation for the negative- z magnetic field (i.e. $B_0 < 0$) yields another two extrema at magnetic field strengths of $-B_{\max}^{(\pm)}$ with the same chiral resolution values of $\chi_{\max}^{(\pm)}$. This underscores the claim that the factors $w_+^{(R)}/w_+^{(S)}$ and $w_-^{(R)}/w_-^{(S)}$ deviate most significantly from one in the positive and negative magnetic field regimes, respectively, which allows us to approximate

$$\chi \approx \frac{w_+^{(R)}}{w_+^{(S)}} \times \frac{w_-^{(R)}}{w_-^{(S)}}. \quad (\text{D.26})$$

D.2 Estimates of the triplet photoexcitation rate

To estimate the pump rate to the $|^3\text{LE}\rangle$ state, we consider two light sources:

(a) A mercury lamp

For that, we consider a set-up used by a synthetic lab [188] to generate 436 nm light at a flux Φ of 34 mW cm^{-2} using a mercury lamp. We shall make a conservative estimate of

the full width at half maximum (FWHM) to be 4 nm, which translates into an approximate linewidth $\delta\nu$ of 6.31 THz. Then, the spectral energy density ρ is approximately

$$\rho \approx \frac{\Phi}{c\delta\nu} = 1.80 \times 10^{-19} \text{ J m}^{-3} \text{ Hz}^{-1} \quad (\text{D.27})$$

with c being the speed of light. The pump rate is estimated by the Einstein B coefficient to be

$$k_{\text{pump}} \approx \left[\frac{e^2 \rho}{4\epsilon_0 m_e h \nu} \right] f_{\text{osc}}, \quad (\text{D.28})$$

where e is the elementary charge, ϵ_0 is the vacuum permittivity, m_e is the electron mass, h is the Planck constant, ν is the light frequency, and f_{osc} is the oscillator strength, computed by Ref. [214] to be around 2×10^{-8} for our photosensitiser prototype. Substituting the parameters yields a pump rate of

$$k_{\text{pump}} \approx 10^{-5} \text{ s}^{-1}, \quad (\text{D.29})$$

which translates into an optical pumping timescale of around one day.

(b) A laser

To simulate a laser, we consider a teaching lab set-up [251] that focused a 532 nm Thorlabs DJ532-40 laser of power $P = 40$ mW onto a diameter $2r$ of $10 \mu\text{m}$. If we assume the lineshape to be flat around the peak frequency and zero elsewhere, then the linewidth $\delta\nu$ is around 30 MHz based on the user manual. Hence, the spectral energy density ρ is approximately

$$\rho \approx \frac{P}{c\pi r^2 \delta\nu} = 5.67 \times 10^{-8} \text{ J m}^{-3} \text{ Hz}^{-1}. \quad (\text{D.30})$$

Again, using the Einstein B coefficient and taking the frequency ν to be the value for 532 nm wavelength light, we obtain the following pump rate:

$$k_{\text{pump}} \approx 10^6 \text{ s}^{-1}, \quad (\text{D.31})$$

which corresponds to a photoexcitation timescale of microseconds.

D.3 Effects due to hyperfine couplings

An important limitation of this model is its absence of hyperfine couplings, which can also mix the singlet and triplet RP states. To exemplify this, consider an electron spin $S = 1/2$ coupled to a nuclear spin $I = 1/2$ via an isotropic hyperfine interaction:

$$\hat{V}_{\text{h.f.}} = a \hat{\mathbf{I}} \cdot \hat{\mathbf{S}}. \quad (\text{D.32})$$

The Hamiltonian has the following matrix representation in the basis of product states, labelled $|M_S : M_I\rangle$:

$$\hat{V}_{\text{h.f.}} = \hbar^2 \begin{pmatrix} a/4 & 0 & 0 & 0 \\ 0 & -a/4 & a/2 & 0 \\ 0 & a/2 & -a/4 & 0 \\ 0 & 0 & 0 & a/4 \end{pmatrix}, \quad (\text{D.33})$$

where the elements run over $\{|\alpha : \alpha\rangle, |\alpha : \beta\rangle, |\beta : \alpha\rangle, |\beta : \beta\rangle\}$. Hence, hyperfine interactions induce mixings between the $|\alpha : \beta\rangle$ and $|\beta : \alpha\rangle$ states, that is, the electron spin state can be flipped by interacting with the nuclear spin. In the context of the spin-correlated RP, singlet-triplet mixing ensues. The characteristic coupling constant a , which is around 10 MHz for organic radicals [14], is much larger than $\hat{V}_s$ (being at most 1 MHz). Hence, the singlet contribution to Eq. (D.12) can easily reach one with the inclusion of hyperfine effects, limiting the interference.

Nevertheless, we expect the chiral resolution scheme to remain robust under hyperfine effects because not all of the electron-nuclear spin states are coupled by $\hat{V}_{\text{h.f.}}$. In the above example, these are the $|\alpha : \alpha\rangle$ and $|\beta : \beta\rangle$ states, which then precess under $\hat{V}_s$ (i.e. the MFE) and result in chiral resolution like before. To extend this to the singlet-triplet manifold of RP states, we consider an electron-spin pair, labelled $S_A = 1/2$ and $S_B = 1/2$, and assume isotropic hyperfine couplings to their own nuclear spins, labelled $I_A = 1/2$ and $I_B = 1/2$ respectively. This leads to the following hyperfine Hamiltonian:

$$\hat{V}_{\text{h.f.}} = a_A \hat{\mathbf{I}}_A \cdot \hat{\mathbf{S}}_A + a_B \hat{\mathbf{I}}_B \cdot \hat{\mathbf{S}}_B.$$

Assuming an equal distribution of nuclear spin states (for context, $k_B T \approx 6 \times 10^6$ MHz at $T = 298$ K), the initial distribution within the $|^3\text{RP}; +1\rangle$ manifold after photoexcitation is

$$|^3\text{RP}; +1 : \alpha\alpha\rangle \equiv |\alpha\alpha : \alpha\alpha\rangle, \quad \text{probability} \approx 1/4, \quad (\text{D.34})$$

$$|^3\text{RP}; +1 : \alpha\beta\rangle \equiv |\alpha\alpha : \alpha\beta\rangle, \quad \text{probability} \approx 1/4, \quad (\text{D.35})$$

$$|^3\text{RP}; +1 : \beta\alpha\rangle \equiv |\alpha\alpha : \beta\alpha\rangle, \quad \text{probability} \approx 1/4, \quad (\text{D.36})$$

$$|^3\text{RP}; +1 : \beta\beta\rangle \equiv |\alpha\alpha : \beta\beta\rangle, \quad \text{probability} \approx 1/4. \quad (\text{D.37})$$

Here, states after the colon are the nuclear spin states. Thus, the labels on the left- and right-hand sides are, respectively, $|^3\text{RP}; +1 : M_{I_A} M_{I_B}\rangle$ and $|M_{S_A} M_{S_B} : M_{I_A} M_{I_B}\rangle$. Meanwhile, the near-degenerate $|^1\text{RP}\rangle$ manifold has the following representations:

$$|^1\text{RP} : \alpha\alpha\rangle \equiv \frac{|\alpha\beta : \alpha\alpha\rangle - |\beta\alpha : \alpha\alpha\rangle}{\sqrt{2}}, \quad (\text{D.38})$$

$$|^1\text{RP} : \alpha\beta\rangle \equiv \frac{|\alpha\beta : \alpha\beta\rangle - |\beta\alpha : \alpha\beta\rangle}{\sqrt{2}}, \quad (\text{D.39})$$

$$|^1\text{RP} : \beta\alpha\rangle \equiv \frac{|\alpha\beta : \beta\alpha\rangle - |\beta\alpha : \beta\alpha\rangle}{\sqrt{2}}, \quad (\text{D.40})$$

$$|^1\text{RP} : \beta\beta\rangle \equiv \frac{|\alpha\beta : \beta\beta\rangle - |\beta\alpha : \beta\beta\rangle}{\sqrt{2}}. \quad (\text{D.41})$$

Following the same analysis as before, we shall assume the time-evolved states to be

approximately stationary after $\tau_{\text{RP-GS}}$. By first-order perturbation theory in $\hat{V}_{\text{h.f.}}$ [Eq. (D.9)], we approximate

$$\hat{U}_{\text{h.f.}}(\tau_{\text{RP-GS}}) \approx 1 + \sum_{m,n} \frac{\langle m | \hat{V}_{\text{h.f.}} | n \rangle}{E_n - E_m} |m\rangle \langle n|, \quad (\text{D.42})$$

and so

$$\hat{U}_{\text{h.f.}}(\tau_{\text{RP-GS}}) |^3\text{RP}; +1 : \alpha\alpha\rangle = |^3\text{RP}; +1 : \alpha\alpha\rangle, \quad (\text{D.43})$$

$$\hat{U}_{\text{h.f.}}(\tau_{\text{RP-GS}}) |^3\text{RP}; +1 : \alpha\beta\rangle \approx |^3\text{RP}; +1 : \alpha\beta\rangle + |^1\text{RP} : \alpha\alpha\rangle \frac{\hbar^2 a_{\text{B}}/2\sqrt{2}}{E(^3\text{RP}; +1) - E(^1\text{RP})}, \quad (\text{D.44})$$

$$\hat{U}_{\text{h.f.}}(\tau_{\text{RP-GS}}) |^3\text{RP}; +1 : \beta\alpha\rangle \approx |^3\text{RP}; +1 : \beta\alpha\rangle - |^1\text{RP} : \alpha\alpha\rangle \frac{\hbar^2 a_{\text{A}}/2\sqrt{2}}{E(^3\text{RP}; +1) - E(^1\text{RP})}, \quad (\text{D.45})$$

$$\begin{aligned} \hat{U}_{\text{h.f.}}(\tau_{\text{RP-GS}}) |^3\text{RP}; +1 : \beta\beta\rangle &= |^3\text{RP}; +1 : \beta\beta\rangle - |^1\text{RP} : \alpha\beta\rangle \frac{\hbar^2 a_{\text{A}}/2\sqrt{2}}{E(^3\text{RP}; +1) - E(^1\text{RP})} \\ &\quad + |^1\text{RP} : \beta\alpha\rangle \frac{\hbar^2 a_{\text{B}}/2\sqrt{2}}{E(^3\text{RP}; +1) - E(^1\text{RP})}, \end{aligned} \quad (\text{D.46})$$

each with probability 1/4. Notice that the $|^3\text{RP}; +1 : \alpha\alpha\rangle$ state is completely unaffected by $\hat{V}_{\text{h.f.}}$ (hence the equal sign) and will undergo the same $\hat{V}_{\text{s}}$ effect as before, leading to the same chiral resolution. As for the remaining three states, they decay almost solely through their singlet component, which is now large at around 0.35 (computed for $a \approx 10$ MHz and $|E(^3\text{RP}; +1) - E(^1\text{RP})| \approx 10$ MHz) and which decays more than 10^4 times faster than the triplet component. Therefore, these *independent* decay channels are *not* enantioselective and do not affect the overall chiral resolution.

D.4 Details of the full Lindblad master equation model

D.4.1 Method

The solution to the full Lindblad master equation was solved numerically using version 5.0.3 of the QuTiP package [110].

D.4.2 Spurious interference effects due to the collective form of $\hat{L}_{\text{RP} \rightarrow \text{GS}}$

As mentioned in the main text, the collective form of the RP decay jump operator $\hat{L}_{\text{RP} \rightarrow \text{GS}}$, reproduced below:

$$\hat{L}_{\text{RP} \rightarrow \text{GS}} = \hat{L}_{1\text{RP} \rightarrow \text{GS}} + \sum_{M_S=0,\pm 1} \hat{L}_{3\text{RP},M_S \rightarrow \text{GS}}, \quad (\text{D.47})$$

$$\hat{L}_{1\text{RP} \rightarrow \text{GS}} \equiv \frac{V_{\text{e,S}}^{\text{RP-GS}}}{\sqrt{\hbar^2 \Omega}} |^1\text{GS}\rangle \langle ^1\text{RP}|, \quad (\text{D.48})$$

$$\hat{L}_{3\text{RP},M_S \rightarrow \text{GS}} \equiv \frac{V_{\text{SOC},M_S}^{\text{RP-GS}}}{\sqrt{\hbar^2 \Omega}} |^1\text{GS}\rangle \langle ^3\text{RP}; M_S|, \quad M_S = 0, \pm 1, \quad (\text{D.49})$$

is motivated by the derivation of the Lindblad equation from the Bloch-Redfield equation. In particular, Eq. (D.47) is obtained when the non-secular terms of the Bloch-Redfield equations responsible for the RP decay are retained, and after their transition energies are set to be equal [36]. Hence, it is rigorously true only if the four RP states are separated by energies (in frequency units) smaller than the characteristic system rate, being the triplet RP decay rate in this case. Note that in the opposite limit of the four RP states being non-degenerate, the secular approximation holds, yielding the four operators of Eqs. (D.48) and (D.49) as four *separate* jump operators of the Lindblad master equation. An outline of the derivation is described in the next section.

As a crude estimate of the errors induced by the collective form of $\hat{L}_{\text{RP} \rightarrow \text{GS}}$ [Eq. (D.47)], we shall now introduce an energy threshold Δ_{th} such that any pair of states separated by an energy gap above Δ_{th} will have their decay described by separate jump operators. For ambiguous cases whereby three states, $|a\rangle$, $|b\rangle$, and $|c\rangle$, have their energies E_j ($j = a, b, c$) satisfy $|E_a - E_b| < \Delta_{\text{th}}$, $|E_b - E_c| < \Delta_{\text{th}}$, and $|E_a - E_c| > \Delta_{\text{th}}$, we shall omit these data points. The results of various threshold values Δ_{th} are shown in Fig. D.1. We find that the additional peaks near $|B_0| \approx 0.01$ T, which are present only with ZFS, disappear as the threshold Δ_{th} is tightened. Interestingly, the larger features at $|B_0| \approx 0.1$ T are also diminished at tighter threshold values Δ_{th} . Without a rigorous framework to interpolate

between the secular and non-secular limits, many important data points are missing. Thus, a more systematic master equation framework is necessary to understand the effect of collective decay, and works in this direction are ongoing.

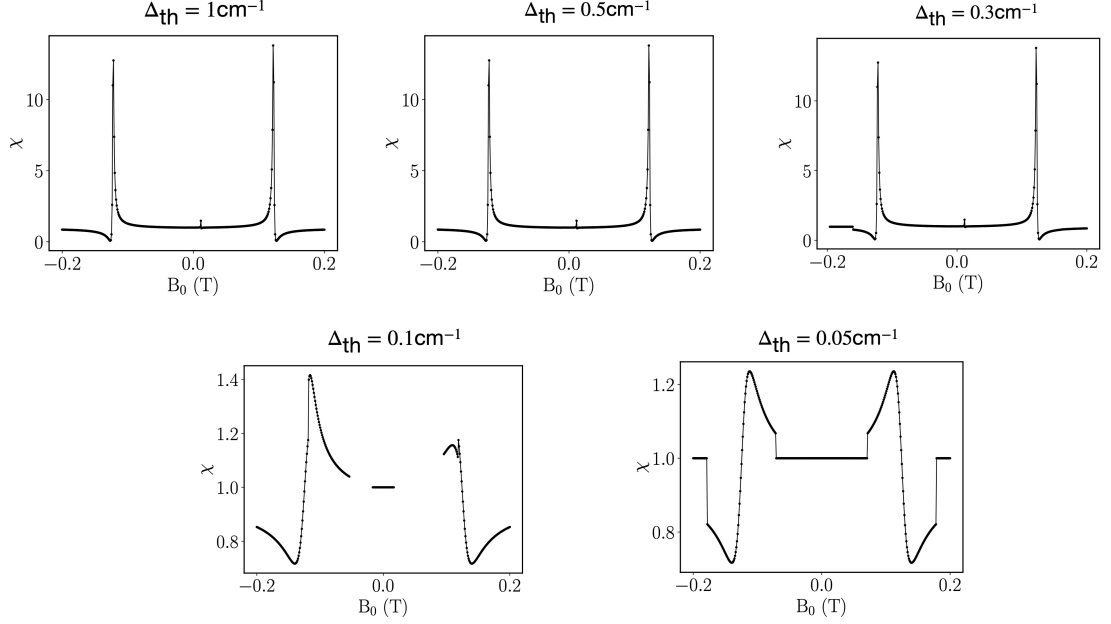


Figure D.1. Chiral resolution χ at different magnetic field strengths B_0 , computed using the full Lindblad master equation for different energy thresholds Δ_{th} . These results are evaluated at $k_{\text{pump}} \approx (1 \text{ s})^{-1}$ (i.e. a laser source).

D.4.3 Understanding the secular approximation

(In this section, we shall drop the hats on operators for brevity.)

We recall that, for a general system-bath interaction $V = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha}$ with A_{α} and B_{α} being the system and bath operators respectively, the Bloch-Redfield equation for the time evolution of the system density operator $\rho(t)$ reads [36, 170]

$$\begin{aligned}
 \dot{\rho}_I(t) = & - \sum_{\omega\omega'} \sum_{\alpha\beta} e^{i(\omega'-\omega)t} \Gamma_{\alpha\beta}(\omega) A_{\alpha I}^{\dagger}(\omega') A_{\beta I}(\omega) \rho_I \\
 & - \sum_{\omega\omega'} \sum_{\alpha\beta} e^{i(\omega-\omega')t} \Gamma_{\beta\alpha}^*(\omega) \rho_I A_{\alpha I}^{\dagger}(\omega) A_{\beta I}(\omega') \\
 & + \sum_{\omega\omega'} \sum_{\alpha\beta} e^{i(\omega'-\omega)t} \Gamma_{\alpha\beta}(\omega) A_{\beta I}(\omega) \rho_I A_{\alpha I}^{\dagger}(\omega') \\
 & + \sum_{\omega\omega'} \sum_{\alpha\beta} e^{i(\omega-\omega')t} \Gamma_{\beta\alpha}^*(\omega) A_{\beta I}(\omega') \rho_I A_{\alpha I}^{\dagger}(\omega). \tag{D.50}
 \end{aligned}$$

Here, the subscript “I” indicates the interaction picture of the system-bath coupling V , and

$$\Gamma_{\alpha\beta}(\omega) \equiv \frac{1}{\hbar^2} \int_0^\infty d\tau \langle \delta B_{\alpha I}(\tau) \delta B_{\beta I}(0) \rangle e^{i\omega\tau} \quad (\text{D.51})$$

is the one-sided Fourier transform of the bath correlation function. Meanwhile, $A_\alpha(\omega)$ denotes the component of the system operator A_α that mediates transitions of frequency ω , so defined:

$$A_\alpha(\omega) \equiv \sum_{\mathcal{E}} \sum_{\mathcal{E}' = \mathcal{E} + \omega} \Pi(\mathcal{E}) A_\alpha \Pi(\mathcal{E}'), \quad (\text{D.52})$$

where $\Pi(\mathcal{E})$ projects onto the eigenspace of energy $\mathcal{E}$. The secular approximation brings the Bloch-Redfield equation in Eq. (D.50) into Lindblad form by assuming terms of $e^{i(\omega' - \omega)t}$ to be zero if $\omega' \neq \omega$; these terms are hence called “non-secular”. However, the neglect of these terms is only rigorously justified if the oscillation frequency $|\omega' - \omega|$ is much larger than the maximum characteristic system rate ω_S . Otherwise, the secular approximation breaks down and one may first retain these non-secular terms to obtain

$$\begin{aligned} \dot{\rho}_I(t) \approx & - \sum_{\omega} \sum_{|\omega' - \omega| < \omega_S} \sum_{\alpha\beta} e^{i(\omega' - \omega)t} \Gamma_{\alpha\beta}(\omega) A_{\alpha I}^\dagger(\omega') A_{\beta I}(\omega) \rho_I \\ & - \sum_{\omega} \sum_{|\omega' - \omega| < \omega_S} \sum_{\alpha\beta} e^{i(\omega - \omega')t} \Gamma_{\beta\alpha}^*(\omega) \rho_I A_{\alpha I}^\dagger(\omega) A_{\beta I}(\omega') \\ & + \sum_{\omega} \sum_{|\omega' - \omega| < \omega_S} \sum_{\alpha\beta} e^{i(\omega' - \omega)t} \Gamma_{\alpha\beta}(\omega) A_{\beta I}(\omega) \rho_I A_{\alpha I}^\dagger(\omega') \\ & + \sum_{\omega} \sum_{|\omega' - \omega| < \omega_S} \sum_{\alpha\beta} e^{i(\omega - \omega')t} \Gamma_{\beta\alpha}^*(\omega) A_{\beta I}(\omega') \rho_I A_{\alpha I}^\dagger(\omega). \end{aligned} \quad (\text{D.53})$$

Moving back to the Schrödinger picture,

$$\begin{aligned}
\dot{\rho} \approx & -\frac{i}{\hbar} [H_S, \rho] \\
& - \sum_{\omega} \sum_{|\omega' - \omega| \lesssim \omega_S} \sum_{\alpha\beta} \Gamma_{\alpha\beta}(\omega) A_{\alpha}^{\dagger}(\omega') A_{\beta}(\omega) \rho \\
& - \sum_{\omega} \sum_{|\omega' - \omega| \lesssim \omega_S} \sum_{\alpha\beta} \Gamma_{\beta\alpha}^*(\omega) \rho A_{\alpha}^{\dagger}(\omega) A_{\beta}(\omega') \\
& + \sum_{\omega} \sum_{|\omega' - \omega| \lesssim \omega_S} \sum_{\alpha\beta} \Gamma_{\alpha\beta}(\omega) A_{\beta}(\omega) \rho A_{\alpha}^{\dagger}(\omega') \\
& + \sum_{\omega} \sum_{|\omega' - \omega| \lesssim \omega_S} \sum_{\alpha\beta} \Gamma_{\beta\alpha}^*(\omega) A_{\beta}(\omega') \rho A_{\alpha}^{\dagger}(\omega), \tag{D.54}
\end{aligned}$$

where H_S is the system Hamiltonian. As a crude estimate, we shall consider the case whereby the system operators $\{A_{\alpha}(\omega)\}$ mediate transitions that are well-separated in frequency space ω except for a set of near-degenerate transitions between $\omega_0 - \omega_S/2$ and $\omega_0 + \omega_S/2$. Then, the only scenarios whereby $\omega' \neq \omega$ are if the transitions fall within this near-degenerate window, in which case the ω -sum covers the same frequency values as the ω' -sum. This allows us to replace $A_{\alpha}(\omega)$ with $\tilde{A}_{\alpha}(\omega)$ as the transition operator of frequency range $\omega \in (\omega - \omega_S/2, \omega + \omega_S/2)$:

$$\tilde{A}_{\alpha}(\omega) \equiv \sum_{\tilde{\omega} \in (\omega - \omega_S/2, \omega + \omega_S/2)} A_{\alpha}(\tilde{\omega}), \tag{D.55}$$

and use it to remove the ω' -sum in Eq. (D.54). We shall also approximate $\Gamma_{\alpha\beta}(\omega \pm \omega_S/2) \approx \Gamma_{\alpha\beta}(\omega)$ on the basis of a rapidly relaxing bath (see Eq. (D.51)), which is consistent with the Markov approximation used to obtain the Bloch-Redfield

equation. The result is

$$\begin{aligned}\dot{\rho} \approx & -\frac{i}{\hbar} [H_S, \rho] \\ & - \sum_{\omega}' \sum_{\alpha\beta} \left[\Gamma_{\alpha\beta}(\omega) \tilde{A}_{\alpha}^{\dagger}(\omega) \tilde{A}_{\beta}(\omega) \rho + \Gamma_{\beta\alpha}^*(\omega) \rho \tilde{A}_{\alpha}^{\dagger}(\omega) \tilde{A}_{\beta}(\omega) \right] \\ & + \sum_{\omega}' \sum_{\alpha\beta} \left[\Gamma_{\alpha\beta}(\omega) \tilde{A}_{\beta}(\omega) \rho \tilde{A}_{\alpha}^{\dagger}(\omega) + \Gamma_{\beta\alpha}^*(\omega) \tilde{A}_{\beta}(\omega) \rho \tilde{A}_{\alpha}^{\dagger}(\omega) \right],\end{aligned}\quad (\text{D.56})$$

where the ω -sum is now restricted to all non-degenerate transitions and $\omega = \omega_0$, denoted by a prime. We now divide the Γ -matrix into a sum of two Hermitian matrices:

$$\Gamma_{\alpha\beta}(\omega) \equiv \frac{\gamma_{\alpha\beta}(\omega)}{2} + iS_{\alpha\beta}(\omega), \quad (\text{D.57})$$

$$\gamma_{\alpha\beta}(\omega) \equiv \Gamma_{\alpha\beta}(\omega) + \Gamma_{\beta\alpha}^*(\omega), \quad (\text{D.58})$$

$$S_{\alpha\beta}(\omega) \equiv \frac{\Gamma_{\alpha\beta}(\omega) - \Gamma_{\beta\alpha}^*(\omega)}{2i}. \quad (\text{D.59})$$

Also, by noting Eq. (D.51) and the relationship

$$\langle \delta B_{\alpha I}(\tau) \delta B_{\beta I}(0) \rangle = \langle \delta B_{\beta I}(-\tau) \delta B_{\alpha I}(0) \rangle^*, \quad (\text{D.60})$$

we obtain

$$\gamma_{\alpha\beta}(\omega) \equiv \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau \langle \delta B_{\alpha I}(\tau) \delta B_{\beta I}(0) \rangle e^{i\omega\tau}. \quad (\text{D.61})$$

This way, the master equation in Eq. (D.56) becomes

$$\begin{aligned}\dot{\rho} \approx & -\frac{i}{\hbar} [H_S, \rho] - i[H_{LS}, \rho] \\ & + \sum_{\omega}' \sum_{\alpha\beta} \gamma_{\alpha\beta}(\omega) \left[\tilde{A}_{\beta}(\omega) \rho \tilde{A}_{\alpha}^{\dagger}(\omega) - \frac{1}{2} \left\{ \tilde{A}_{\alpha}^{\dagger}(\omega) \tilde{A}_{\beta}(\omega), \rho \right\} \right],\end{aligned}\quad (\text{D.62})$$

where we have defined the Lamb shift Hamiltonian to be

$$H_{\text{LS}} \equiv \sum_{\omega} ' \sum_{\alpha\beta} S_{\alpha\beta}(\omega) \tilde{A}_{\alpha}^{\dagger}(\omega) \tilde{A}_{\beta}(\omega). \quad (\text{D.63})$$

The final step to bringing the master equation into Lindblad form is to diagonalise the γ -matrix. Introducing the unitary matrix $\mathbf{U}(\omega)$ that diagonalises $\boldsymbol{\gamma}(\omega)$, we obtain

$$\begin{aligned} \dot{\rho} \approx & -\frac{i}{\hbar} [H_{\text{S}}, \rho] - i [H_{\text{LS}}, \rho] \\ & + \sum_j \sum_{\omega} ' \gamma_j(\omega) \left[L_j(\omega) \rho L_j^{\dagger}(\omega) - \frac{1}{2} \left\{ L_j^{\dagger}(\omega) L_j(\omega), \rho \right\} \right], \end{aligned} \quad (\text{D.64})$$

where

$$L_j(\omega) \equiv \sum_{\alpha} \mathbf{U}_{\alpha j}^*(\omega) \tilde{A}_{\alpha}(\omega). \quad (\text{D.65})$$

Eq. (D.64) is of Lindblad form (i.e. $L_j(\omega)$, as defined by Eq. (D.65), is a Lindblad jump operator) if the $\gamma_j(\omega)$ values are real and non-negative, a criterion justified on pp. 136 of Ref. [36]. **The important message here is that, based on Eqs. (D.55) and (D.65), only transitions of the same frequency ω within an uncertainty of the maximum characteristic system rate ω_{S} can be grouped into the same jump operator $L_j(\omega)$. Otherwise, different jump operators are required to describe the non-collective decay dynamics.** The former corresponds to a retention of the non-secular terms, and the latter, a neglect.

D.5 A minimal three-level model

To further understand the essential spin dynamics driving chiral resolution, we introduce a reduced three-level system model comprising the ground state $|^1\text{GS}\rangle \equiv |G\rangle$, the singlet RP state $|^1\text{RP}\rangle \equiv |S\rangle$, and the triplet $M_{\text{S}} = +1$ RP state $|^3\text{RP}; +1\rangle \equiv |T\rangle$. This effective model captures the core features of the spin-dependent decay pathways and their interference in a minimal basis, allowing for a simplified numerical analysis and additional

analytical insight. Within the effective Hilbert space spanned by these three states, the coherent system dynamics is described by the simplified Hamiltonian:

$$\hat{H} = E_S |S\rangle \langle S| + E_T |T\rangle \langle T| + (V_s |S\rangle \langle T| + \text{H.c.}), \quad (\text{D.66})$$

where E_S and E_T are the energies of the singlet and triplet $M_S = +1$ RP states relative to the ground state, and $V_s \equiv \langle {}^1\text{RP} | \hat{V}_s | {}^3\text{RP}; +1 \rangle$ captures the spin Zeeman interaction.

Dissipative decay back to the ground state is included in the collective Lindblad decay term

$$\mathcal{L}_{\text{coll}}[\hat{\rho}] = \hat{L}_{\text{coll}} \hat{\rho} \hat{L}_{\text{coll}}^\dagger - \frac{1}{2} \left\{ \hat{L}_{\text{coll}}^\dagger \hat{L}_{\text{coll}}, \hat{\rho} \right\}, \quad (\text{D.67})$$

written in terms of the collapse operator

$$\hat{L}_{\text{coll}} = \frac{V_{\text{e,S}}^{\text{RP-GS}}}{\hbar\sqrt{\Omega}} |G\rangle \langle S| + \frac{V_{\text{SOC},+1}^{\text{RP-GS}}}{\hbar\sqrt{\Omega}} |G\rangle \langle T|, \quad (\text{D.68})$$

where $V_{\text{SOC},+1}^{\text{RP-GS}}$ flips signs for opposite enantiomers. In addition, we consider incoherent pumping at a rate k_{pump} into the triplet state $|T\rangle$ with the collapse operator $|T\rangle \langle G|$:

$$\mathcal{L}_{\text{pump}}[\hat{\rho}] = k_{\text{pump}} \left(|T\rangle \langle G| \hat{\rho} |G\rangle \langle T| - \frac{1}{2} \{ |G\rangle \langle G|, \hat{\rho} \} \right). \quad (\text{D.69})$$

This model arises naturally when adiabatically eliminating the photoexcited $|{}^3\text{LE}\rangle$ state, which decays quickly into the triplet state $|{}^3\text{RP}; +1\rangle \equiv |T\rangle$. The total system dynamics is then encompassed in the master equation

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \mathcal{L}_{\text{coll}}[\hat{\rho}] + \mathcal{L}_{\text{pump}}[\hat{\rho}]. \quad (\text{D.70})$$

From this, one can derive the equations of motion for the coherences between

ground and excited states to be

$$\frac{\partial \langle |G\rangle \langle S| \rangle}{\partial t} = - \left(\frac{iE_S}{\hbar} + \frac{w_S}{2} \right) \langle |G\rangle \langle S| \rangle - \left(\frac{iV_s}{\hbar} + \frac{w_{TS}}{2} \right) \langle |G\rangle \langle T| \rangle, \quad (\text{D.71})$$

$$\frac{\partial \langle |G\rangle \langle T| \rangle}{\partial t} = - \left(\frac{iE_T}{\hbar} + \frac{w_T + k_{\text{pump}}}{2} \right) \langle |G\rangle \langle T| \rangle - \left(\frac{iV_s^*}{\hbar} + \frac{w_{TS}^*}{2} \right) \langle |G\rangle \langle S| \rangle, \quad (\text{D.72})$$

where we have defined the decay rates for the singlet state, the triplet state, and the interference term as

$$w_S \equiv \frac{|V_{e,S}^{\text{RP-GS}}|^2}{\hbar^2 \Omega}, \quad w_T \equiv \frac{|V_{\text{SOC},+1}^{\text{RP-GS}}|^2}{\hbar^2 \Omega}, \quad w_{TS} \equiv \frac{(V_{e,S}^{\text{RP-GS}})^* V_{\text{SOC},+1}^{\text{RP-GS}}}{\hbar^2 \Omega}. \quad (\text{D.73})$$

Similarly, the equations of motion for the populations of the singlet and triplet states, $\langle \hat{p}_T \rangle$ and $\langle \hat{p}_S \rangle$, as well as for the coherence between $|S\rangle$ and $|T\rangle$, are given by (assuming a low excitation regime of $\langle \hat{p}_T \rangle, \langle \hat{p}_S \rangle \ll 1$):

$$\frac{\partial \langle \hat{p}_S \rangle}{\partial t} = \partial_t \langle |S\rangle \langle S| \rangle = -w_S \langle \hat{p}_S \rangle - 2\text{Im} \left[\frac{V_s^*}{\hbar} \langle |T\rangle \langle S| \rangle \right] - \text{Re} [w_{TS}^* \langle |T\rangle \langle S| \rangle], \quad (\text{D.74})$$

$$\frac{\partial \langle \hat{p}_T \rangle}{\partial t} = \partial_t \langle |T\rangle \langle T| \rangle = k_{\text{pump}} - w_T \langle \hat{p}_T \rangle + 2\text{Im} \left[\frac{V_s^*}{\hbar} \langle |T\rangle \langle S| \rangle \right] - \text{Re} [w_{TS}^* \langle |T\rangle \langle S| \rangle], \quad (\text{D.75})$$

$$\begin{aligned} \frac{\partial \langle |T\rangle \langle S| \rangle}{\partial t} = & - \left(\frac{w_T + w_S}{2} + \frac{i(E_S - E_T)}{\hbar} \right) \langle |T\rangle \langle S| \rangle \\ & + \frac{iV_s}{\hbar} (\langle \hat{p}_S \rangle - \langle \hat{p}_T \rangle) - \frac{w_{TS}}{2} (\langle \hat{p}_T \rangle + \langle \hat{p}_S \rangle). \end{aligned} \quad (\text{D.76})$$

With this, $\langle \hat{p}_S \rangle$ and $\langle \hat{p}_T \rangle$ are solved for their steady-state values by setting their time derivatives to zero. While the full dynamics have not been simulated, we expect the collective decay rate to be inversely proportional to the aforementioned steady-state values, that is, the chiral resolution χ_+ for the positive- z magnetic field (i.e. $B_0 > 0$) may be approximated by

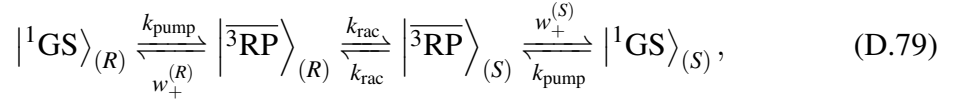
$$\chi_+ \approx \frac{[\langle \hat{p}_S \rangle + \langle \hat{p}_T \rangle]_{(S)\text{-enantiomer}}}{[\langle \hat{p}_S \rangle + \langle \hat{p}_T \rangle]_{(R)\text{-enantiomer}}} \bigg|_{\text{steady state}}. \quad (\text{D.77})$$

To obtain the chiral resolution χ_- for the negative- z magnetic field (i.e. $B_0 < 0$), the mappings described in Eqs. (D.15), (D.16), and (D.17) are made. The full chiral resolution is described by the main text to be

$$\chi \approx \chi_+ \times \chi_- . \quad (\text{D.78})$$

D.6 Estimates of the time to steady state

As a preliminary study of the time towards steady state under a mercury lamp, we solve the time evolution of a simplified kinetic scheme:



where the subscripts label the two enantiomers. This translates into the following rate equation:

$$\frac{d}{dt}\mathbf{N} = \mathbf{K}\mathbf{N}, \quad (\text{D.80})$$

where

$$\mathbf{N} \equiv \begin{pmatrix} n_{1\text{GS},(R)} & n_{\overline{3}\text{RP},(R)} & n_{\overline{3}\text{RP},(S)} & n_{1\text{GS},(S)} \end{pmatrix}^T \quad (\text{D.81})$$

is a column vector containing the populations, and

$$\mathbf{K} \equiv \begin{pmatrix} -k_{\text{pump}} & w_+^{(R)} & 0 & 0 \\ k_{\text{pump}} & -w_+^{(R)} - k_{\text{rac}} & k_{\text{rac}} & 0 \\ 0 & k_{\text{rac}} & -w_+^{(S)} - k_{\text{rac}} & k_{\text{pump}} \\ 0 & 0 & w_+^{(S)} & -k_{\text{pump}} \end{pmatrix} \quad (\text{D.82})$$

is a matrix containing the rate constants. The general solution to a set of D coupled linear first-order differential equations is

$$\mathbf{N}(t) = \sum_{j=1}^D c_j e^{\lambda_j t} \boldsymbol{\eta}_j, \quad (\text{D.83})$$

where $\boldsymbol{\eta}_j$ is the j -th eigenvector of $\mathbf{K}$ with eigenvalue λ_j , and c_j is the j -th expansion coefficient. Therefore, the steady-state solution can be found by diagonalising $\mathbf{K}$ and observing the eigenvector corresponding to an eigenvalue of zero. Also, the next highest eigenvalue represents the timescale towards this steady state outcome.

The parameters $w_+^{(R)}$ and $w_+^{(S)}$ are chosen to maximise the chiral resolution χ , being $9.58 \times 10^{-5} \text{ cm}^{-1}$ and $0.52 \times 10^{-5} \text{ cm}^{-1}$ respectively. The simulation results are shown in Fig. D.2. With a pump rate k_{pump} of $(1 \text{ day})^{-1}$ from a mercury lamp, a steady-state chiral resolution χ of 19 was obtained after around 10^4 days. This is despite having the slowest process, being the photoexcitation step, occur within a day, and we attribute this 10^4 -fold difference in timescale to the probability of a triplet RP molecule racemising relative to its decay, estimated as $k_{\text{rac}}/w_+^{(S)} \approx 10^{-4}$. Also, we find that, at higher pump rates k_{pump} , the chiral resolution χ suffers while the steady-state timescale decreases to the racemisation timescale of around 10^{-2} s . This happens because a larger fraction of the steady-state population accumulates in the excited state and thus does not see the differential decay rates. Interestingly, the onset of this effect is earlier in the full Lindblad master equation model by about five orders of magnitude in k_{pump} . This would imply a shortened steady-state timescale by around five magnitude orders once the full quantum master equations are considered. One possible explanation for this discrepancy is the assumption of a stationary RP state $|\overline{^3\text{RP}}\rangle$ being formed prior to its decay to the $|^1\text{GS}\rangle$ state [Eq. (D.79)], which occurs with a microsecond timescale. By contrast, in the full quantum simulation, the $|\overline{^3\text{RP}}\rangle$ state coherently evolves with the $|^1\text{RP}\rangle$ state (through the MFE) concurrently with their decay to the $|^1\text{GS}\rangle$ state. The latter decays faster at a sub-nanosecond timescale, thereby speeding up the approach towards steady state.

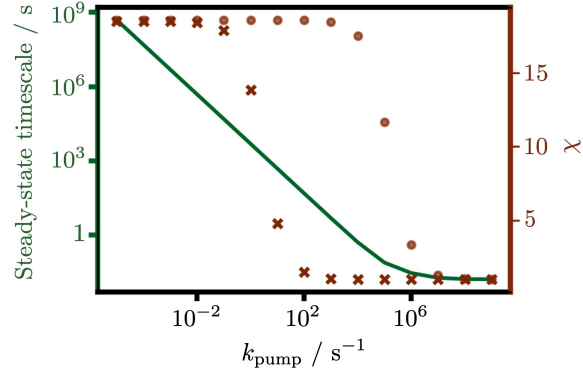


Figure D.2. Time to steady state (green) and chiral resolution χ (red) at different pump rates k_{pump} , computed using the simplified kinetic scheme (circles, where applicable). Also shown are the chiral resolution χ from the full Lindblad master equation model (red crosses), evaluated at $B_0 = 0.126$ T.

Next, we further extend the simplified kinetic model to account for additional hyperfine states. As mentioned in the discussion surrounding Eqs. (D.43)–(D.46), despite the potential for hyperfine couplings to mix the triplet RP state with its singlet counterpart, there will remain an electron-nuclear spin state of all up-spins that does not mix with the singlet RP state due to angular momentum conservation. As such, this state will continue to experience enantioselective decay of rates $w_+^{(R/S)}$, thereby contributing to chiral resolution, while all other states will decay at approximately the singlet’s decay rate w_S with little implication on the chiral resolution. For brevity, we shall label these states by $|\overline{3\text{RP}}\rangle_{(R/S)}$ and $|\overline{1\text{RP}}\rangle_{(R/S)}^{(j)}$ ($j = 1, 2, \dots, N$), respectively, to reflect their decay rates. Then, our kinetic scheme reads

$$\begin{aligned}
 & |\text{GS}\rangle_{(R)} \xrightleftharpoons[w_+^{(R)}]{k_{\text{pump}}/(N+1)} |\overline{3\text{RP}}\rangle_{(R)} \xrightleftharpoons[k_{\text{rac}}]{k_{\text{rac}}} |\overline{3\text{RP}}\rangle_{(S)} \xrightleftharpoons[k_{\text{pump}}/(N+1)]{w_+^{(S)}} |\text{GS}\rangle_{(S)}, \\
 & |\text{GS}\rangle_{(R)} \xrightleftharpoons[w_S]{k_{\text{pump}}/(N+1)} |\overline{1\text{RP}}\rangle_{(R)}^{(1)} \xrightleftharpoons[k_{\text{rac}}]{k_{\text{rac}}} |\overline{1\text{RP}}\rangle_{(S)}^{(1)} \xrightleftharpoons[k_{\text{pump}}/(N+1)]{w_S} |\text{GS}\rangle_{(S)}, \\
 & |\text{GS}\rangle_{(R)} \xrightleftharpoons[w_S]{k_{\text{pump}}/(N+1)} |\overline{1\text{RP}}\rangle_{(R)}^{(2)} \xrightleftharpoons[k_{\text{rac}}]{k_{\text{rac}}} |\overline{1\text{RP}}\rangle_{(S)}^{(2)} \xrightleftharpoons[k_{\text{pump}}/(N+1)]{w_S} |\text{GS}\rangle_{(S)}, \\
 & \vdots \\
 & |\text{GS}\rangle_{(R)} \xrightleftharpoons[w_S]{k_{\text{pump}}/(N+1)} |\overline{1\text{RP}}\rangle_{(R)}^{(N)} \xrightleftharpoons[k_{\text{rac}}]{k_{\text{rac}}} |\overline{1\text{RP}}\rangle_{(S)}^{(N)} \xrightleftharpoons[k_{\text{pump}}/(N+1)]{w_S} |\text{GS}\rangle_{(S)}, \tag{D.84}
 \end{aligned}$$

and the kinetics are solved in the same fashion as before.

The simulation results with a pump rate k_{pump} of 10^{-11} cm^{-1} (approximately 1 s^{-1}) are presented in Fig. D.3. Indeed, the chiral resolution χ remains relatively unchanged as the number of additional hyperfine states N increases. Interestingly, the steady-state timescale increases with N as more photoexcitation-decay cycles are needed for the differential decay rates to take effect. For our prototypical system, we expect the strongest hyperfine interactions to arise from the sixteen hydrogen atoms ($I = 1/2$), two nitrogen atoms ($I = 1$), and one boron atom ($I = 3/2$), contributing $N = 2^{16} \times 3^2 \times 4 - 1 \approx 10^6$ additional hyperfine states. Extrapolating from Fig. D.3, we would expect a 10^6 times increase in the steady-state timescale, which is easily countered by increasing the pump rate k_{pump} within the range accessible by our model teaching lab laser [Eq. (D.31)]. Importantly, the above timescale is likely to be overestimated because not all nuclear spins will have significant hyperfine interactions, which depend strongly on the electron spin density. Also, the increment in steady-state timescale might be smaller once the full quantum effects are considered, as discussed earlier in this section.

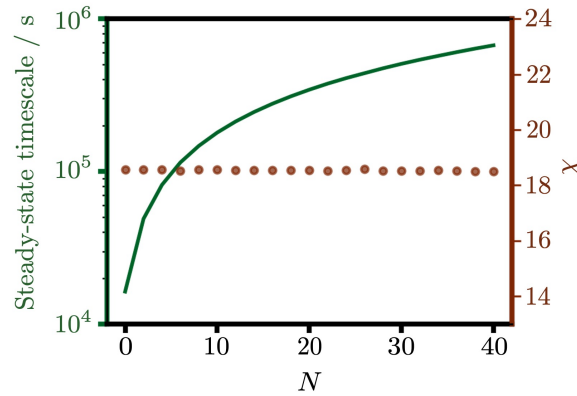


Figure D.3. Time to steady state (green) and chiral resolution χ (red) for different number of additional hyperfine states N , computed using the simplified kinetic scheme at a pump rate k_{pump} of 10^{-11} cm^{-1} (around 1 s^{-1}).

D.7 Ab initio calculations

D.7.1 Computational methods

The following DFT calculations were performed using the ORCA 5.0 code [166]. Unless otherwise indicated, we used the B3LYP functional, the D3BJ dispersion correction [86, 87], and the def2-SVPD basis set.

First, the molecular geometries of $\text{B}(\text{C}_2\text{F}_5)_3$ and (*R*)- NMI_2 were optimised as spin-restricted singlets. A local minimum was found for (*R*)- NMI_2 , confirmed by a harmonic frequency analysis. As for the $\text{B}(\text{C}_2\text{F}_5)_3$ geometry, three unstable modes of (imaginary) frequencies 31, 31, and 46 cm^{-1} were present. These unstable modes were tolerated because we envision the photosensitiser fragment to be embedded in a photocatalytic surface, which would anyway induce further distortions. The two geometries were then placed close to each other and the overall $\text{B}(\text{C}_2\text{F}_5)_3$ -(*R*)- NMI_2 geometry was relaxed as a spin-restricted singlet while locking the $\text{B}(\text{C}_2\text{F}_5)_3$ fragment in its in vacuo form. From here, the excited-state electronic structure, including the associated SOC matrix elements, was estimated using spin-restricted TDDFT within the Tamm–Dancoff approximation (TDA). Here, the electron spin states are reported in the high-symmetry coordinate frame of the C_{3h} -symmetric $\text{B}(\text{C}_2\text{F}_5)_3$ subunit.

Next, to estimate the activation barriers associated with the racemisation of (*R*)- NMI_2 , the ground-state geometry was also optimised for the cationic and anionic species, following which transition states corresponding to an approximately planar conformation were found for the neutral, cationic, and anionic electronic configurations. Again, these calculations were followed by the relevant frequency analyses. Calculations for the ionic configurations were conducted as spin-unrestricted doublets.

Finally, the ZFS parameters of the lowest triplet state of $\text{B}(\text{C}_2\text{F}_5)_3$ -(*R*)- NMI_2 were computed as a spin-unrestricted triplet. For that, we only included the spin-spin contributions because the spin-orbit contributions are expected to be small for organic systems. The RP *g*-tensors were also computed for the $\text{B}(\text{C}_2\text{F}_5)_3$ radical anion and (*R*)-

NMI₂ radical cation as spin-unrestricted doublets using the geometries relaxed for the B(C₂F₅)₃-(*R*)-NMI₂ system. These calculations were done using the EPR-II basis set.

D.7.2 B(C₂F₅)₃

The spin-restricted singlet SCF calculation converged to an energy of −1749.24093278 Hartree. The level of theory was B3LYP-D3BJ/def2-SVPD.

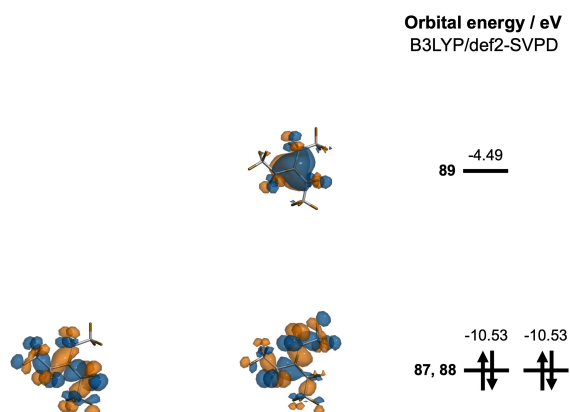


Figure D.4. Frontier MOs (isovalue = 0.020) of B(C₂F₅)₃ in the singlet ground state, calculated at the B3LYP/def2-SVPD level of theory.

Optimised geometry

```

B -0.00064927466988 -0.00132257980777 0.00000226473328
C 0.45080524747392 1.55970773405676 0.00000396655066
C 1.12685851345958 -1.17070953531015 0.00000179797415
C -1.57804826416141 -0.39118639714501 0.00000052689324
C -2.75035200679498 0.63612380622507 -0.00000400900729
C 1.92723511063647 2.06158535921500 -0.00000242016322
C 0.82546631857011 -2.69969653122337 0.00000073353322
F -0.12092330507419 2.11580622269249 1.11011424964128
F -0.12093489078894 2.11581224694588 -1.11009730867225
F 1.89156773954784 -0.95150432586674 1.11215218509977
F 1.89156790221405 -0.95150317686641 -1.11214818121968
F -1.77389107179005 -1.16207926809836 1.11218861196241

```

F -1.77388727065955 -1.16208472135383 -1.11218451717472
 F -2.71100852353276 1.40642073700720 1.08804210045225
 F -3.90494911911751 -0.03571165520100 -0.00000516842494
 F -2.71100398542072 1.40641619886495 -1.08805315092893
 F 2.57456909857138 1.64317546768234 1.08852965396854
 F 1.92221763487050 3.39710461127507 0.00000364611426
 F 2.57455638704562 1.64318549407629 -1.08854592096896
 F 0.13813928162385 -3.04967796021263 1.08834835460820
 F 1.98506518769880 -3.36233692337290 -0.00000165180259
 F 0.13813634048000 -3.04967561058146 -1.08834576316868

D.7.3 (R)-NMI₂

Ground state: The spin-restricted neutral singlet SCF calculation converged to an energy of -1559.58369063 Hartree. The spin-unrestricted cationic doublet SCF calculation converged to an energy of -1559.30071306 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 0.758568. Finally, the spin-unrestricted anionic doublet SCF calculation converged to an energy of -1559.65768285 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 0.757087. In all three cases, the level of theory was (U)B3LYP-D3BJ/def2-SVPD.

Transition state: The spin-restricted neutral singlet SCF calculation converged to an energy of -1559.54332933 Hartree. The spin-unrestricted cationic doublet SCF calculation converged to an energy of -1559.27440879 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 0.764633. Finally, the spin-unrestricted anionic doublet SCF calculation converged to an energy of -1559.63411284 Hartree and an $\langle \mathbf{S}^2 \rangle$ value of 0.760929. In all three cases, the level of theory was (U)B3LYP-D3BJ/def2-SVPD.

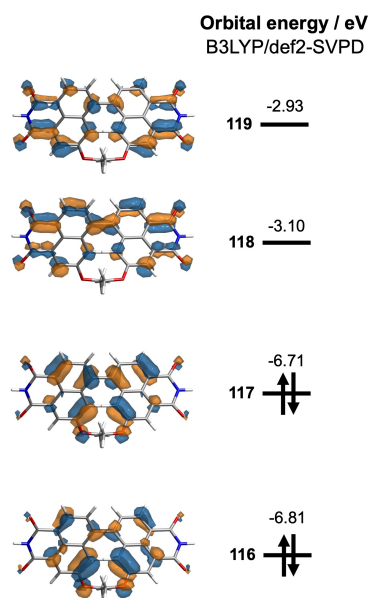


Figure D.5. Frontier MOs (isovalue = 0.040) of (*R*)-NMI₂ in the neutral singlet ground state, calculated at the B3LYP/def2-SVPD level of theory.

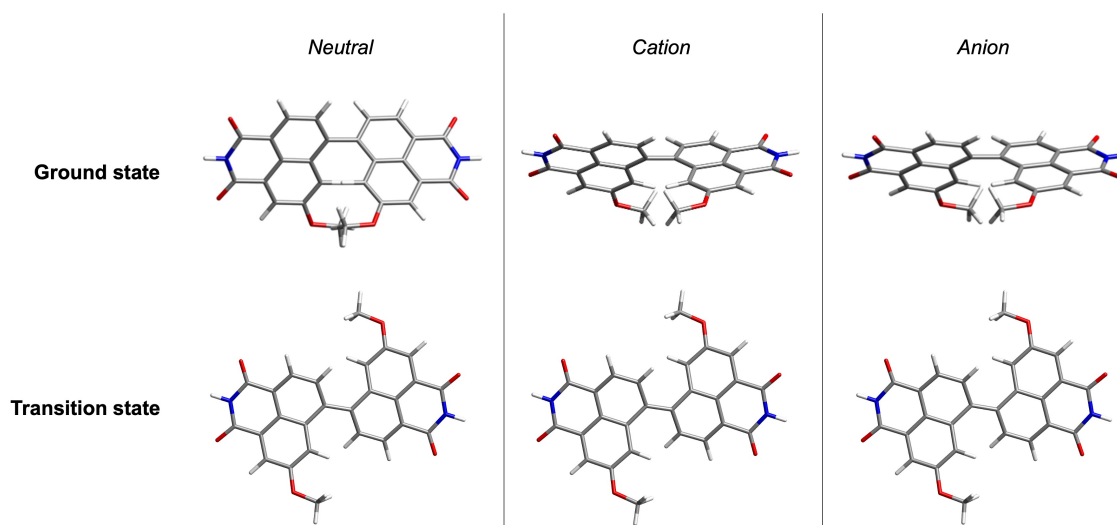


Figure D.6. Molecular geometries of (*R*)-NMI₂ in the ground and transition states, calculated at the (U)B3LYP/def2-SVPD level for the neutral singlet, cationic doublet, and anionic doublet electronic configurations.

Optimised neutral singlet geometry (ground state)

```

C 0.12887013453957 0.73240849095516 -1.45664428992883
C -0.39472173662508 1.57602596333556 -0.42263671762305
C -1.20087489987321 1.07047386947771 0.63371231700801

```

C -0.10091975418281 2.97325856734387 -0.46457525020664
C -0.60106380095647 3.81342848989342 0.57338634637037
C 0.66742509339870 3.50643503918075 -1.53230208222274
C 0.96303818435002 4.95964376931946 -1.58302748754577
C 1.14108331649188 2.67396129777790 -2.53223999181228
H 1.72722899322289 3.10737776900512 -3.34161909140361
C 0.87289345027033 1.29396682004136 -2.48693787505920
C -1.36101509967577 3.29515769507146 1.59891686275625
C -1.66830360777167 1.91097825224157 1.63071498697813
C -0.30891347734678 5.27181706197730 0.55139595852969
N 0.44956135068550 5.70957309118590 -0.52851722434023
O 1.60614588948519 5.49614185142517 -2.46707412929234
O -0.69029254194234 6.05679731425668 1.40000641486010
H -1.44004983914008 0.01292800478926 0.64395987576284
H -1.73556992166545 3.95162468783214 2.38312698038364
O -2.42804515844216 1.50855852459843 2.67416228576365
H 0.64837789002887 6.70529524832096 -0.55497262847816
C -0.12869633013706 -0.73241399868966 -1.45665354657206
C -0.87274121547786 -1.29394234640384 -2.48694781907809
C -1.14097639523051 -2.67392927978357 -2.53225559911957
H -1.72713446822572 -3.10732686043162 -3.34163655490668
C -0.66737993784461 -3.50641441633064 -1.53229661362172
C -0.96308126522913 -4.95960574007350 -1.58299948846790
C 0.10099066674029 -2.97326930825698 -0.46457248485597
C 0.60105160405479 -3.81344649745332 0.57342043391533
C 0.39484806931827 -1.57604834565105 -0.42264071521706
C 1.20100982960269 -1.07052257827985 0.63371631840921
C 1.36098878911983 -3.29519618756051 1.59897071997963

C 1.66836207799674 -1.91103532505711 1.63074843791637
 C 0.30883425629944 -5.27182197577885 0.55143982589310
 N -0.44966950461740 -5.70954585365178 -0.52846531306020
 O -1.60621066863107 -5.49608062638111 -2.46704406472028
 O 0.69017068959982 -6.05681301362561 1.40005942245607
 H 1.44026395210115 -0.01299484623115 0.64393012749259
 H 1.73547426669503 -3.95166759760762 2.38320959177399
 O 2.42809465911074 -1.50863712571404 2.67421010960850
 H -0.64854040721254 -6.70525694424139 -0.55490947506262
 H 1.26868230292847 0.64353761706401 -3.26672152203653
 H -1.26852801927293 -0.64349395820094 -3.26671613147392
 C -2.76527761610311 0.13540886712178 2.78388440361590
 H -3.35964598816880 0.03936523800778 3.69664264342762
 H -3.36194611571670 -0.19480819986447 1.91876971024148
 H -1.86066067848654 -0.48863722401337 2.86306329234703
 C 2.76538362521990 -0.13550050028904 2.78391850150171
 H 3.36210815435001 0.19467139671519 1.91882473699129
 H 1.86078916366666 0.48858607599177 2.86303853582563
 H 3.35971355364726 -0.03945951040571 3.69670199495587

Optimised neutral singlet geometry (transition state)

C 0.11763461132278 0.71458262824702 0.32914871336354
 C -0.90225735002293 1.75859651753928 0.25553548809977
 C -2.30692181608370 1.53560501063106 0.33593032765958
 C -0.47449924172384 3.12942477812723 0.19982213643570
 C -1.43819380477244 4.16252119996925 -0.00778598314804
 C 0.88286559996700 3.47323279916344 0.42904081805049
 C 1.34155353301120 4.87928873268254 0.34398248403917

C 1.76548880202530 2.48443786544518 0.82200360717800
 H 2.77546115730722 2.76201413682607 1.12108140017172
 C 1.37579847786450 1.14158732613238 0.77903721075229
 C -2.78644248525655 3.88700450134588 -0.04313092742270
 C -3.22593372103693 2.56533511360894 0.19035358735397
 C -1.00195387792033 5.57905132437472 -0.14712797823813
 N 0.35614923170218 5.80843439148880 0.03242164899964
 O 2.49476651266103 5.23159357311151 0.52219271189713
 O -1.75811866627091 6.49931760590653 -0.39934342413106
 H -2.67272401652463 0.55518315600059 0.60313206896196
 H -3.50674517971495 4.69164796134584 -0.18217034769782
 O -4.56597377822250 2.40310510230887 0.27995441824357
 H 0.65993736348189 6.77426342781460 -0.04776131784940
 C -0.11802191961850 -0.71470024235630 -0.02182310701040
 C -1.37631033886960 -1.14137202022634 -0.47170951729444
 C -1.76572820739357 -2.48418239510728 -0.51699891804750
 H -2.77572525775816 -2.76156886798913 -0.81616278884791
 C -0.88263348570178 -3.47340997372878 -0.12621766920136
 C -1.34121307602693 -4.87967624150270 -0.04353975006091
 C 0.47458567848057 -3.12964440307095 0.10376063864962
 C 1.43835265674298 -4.16304500405319 0.30939592813634
 C 0.90208529936429 -1.75853727981611 0.05084140869145
 C 2.30671032313310 -1.53516902897139 -0.02784012804025
 C 2.78656431898656 -3.88739804327880 0.34586033124628
 C 3.22586600397647 -2.56507147470515 0.11591325816911
 C 1.00251949705748 -5.58012399471658 0.44488657759105
 N -0.35569906359132 -5.80931306652640 0.26604327871963
 O -2.49437971597113 -5.23170653414146 -0.22258819370700

O 1.75910470371892 -6.50103309465134 0.69347210637554
 H 2.67308869078445 -0.55417548302859 -0.29190228116491
 H 3.50690678844982 -4.69231119984607 0.48311675020349
 O 4.56594397312589 -2.40223175038324 0.02807025729040
 H -0.65920066882318 -6.77543177205818 0.34377954548683
 H 2.10329280712050 0.40843125667962 1.09697094344365
 H -2.10442644768724 -0.40772122716869 -0.78687645323022
 C -5.09413720349379 1.10514145618631 0.48999366502529
 H -6.18202583464508 1.21612151315235 0.50097950302371
 H -4.80188307700915 0.42342389522920 -0.32500083296450
 H -4.75922399365243 0.68891602401528 1.45365785645817
 C 5.09388590264185 -1.10435318448909 -0.18308971869681
 H 4.75693621332950 -0.68814919319191 -1.14604619494148
 H 4.80354950002528 -0.42253202652602 0.63251965658530
 H 6.18172282549719 -1.21556386192118 -0.19630674778026

Optimised cationic doublet geometry (ground state)

C 0.17411280842572 0.71002529635804 -0.51782006457664
 C -0.74497962229455 1.71392035178121 -0.04298112789106
 C -1.91674883620880 1.39121752924281 0.67351124923146
 C -0.42082493314937 3.09240530775207 -0.25411128263163
 C -1.32791172720825 4.09949491569316 0.19685037052600
 C 0.79242579156658 3.44661196723204 -0.87311913459873
 C 1.14026569068473 4.88380672947777 -1.09355427492950
 C 1.69635094155261 2.46057547054791 -1.28467280753336
 H 2.61765461807292 2.77194890312495 -1.77550804084002
 C 1.39266381230001 1.11557779239408 -1.09875160719986
 C -2.48796750313132 3.76581769792439 0.85501415706877

C -2.78783801609951 2.40236606059060 1.11240724957897
C -1.01538846000722 5.54523858461622 -0.02996634009711
N 0.19668199776445 5.80290979534899 -0.66053135623853
O 2.17976449350900 5.23055609778832 -1.61407721505925
O -1.75613132861600 6.44102026208236 0.30969028656193
H -2.12752930611236 0.35432023627487 0.91502008861695
H -3.16803439263847 4.54514070161803 1.19709940230566
O -3.91203490169756 2.17522751761697 1.78403579791449
H 0.42118982190641 6.78333611102418 -0.81460270567963
C -0.17411247477281 -0.71002592237676 -0.51781937812800
C -1.39266629537090 -1.11557900149838 -1.09874424131970
C -1.69635276063127 -2.46057666601124 -1.28466632047375
H -2.61765915447152 -2.77195053787890 -1.77549588000305
C -0.79242440387596 -3.44661267720721 -0.87311920954523
C -1.14026504775577 -4.88380742457766 -1.09355237952956
C 0.42082819311495 -3.09240555149845 -0.25411540579625
C 1.32791696171449 -4.09949477030530 0.19684336451475
C 0.74498297965015 -1.71392059082484 -0.04298617290968
C 1.91675378214034 -1.39121714471611 0.67350308328531
C 2.48797346313661 -3.76581689696263 0.85500565049872
C 2.78784246103469 -2.40236527025296 1.11240020077822
C 1.01539203687112 -5.54523862241067 -0.02996987847007
N -0.19668051554420 -5.80291021197809 -0.66053081321313
O -2.17976618125954 -5.23055712217533 -1.61407046784018
O 1.75613416035748 -6.44102021944932 0.30968861543239
H 2.12753441751130 -0.35431995968571 0.91501166573776
H 3.16804058967991 -4.54513942790940 1.19709169345970
O 3.91203550943201 -2.17522624184708 1.78403485197178

H -0.42118975089806 -6.78333664477488 -0.81459915206057
 H 2.07072824127186 0.35484080092810 -1.48196274495383
 H -2.07073417365675 -0.35484214811441 -1.48194863481394
 C -4.32199306425096 0.84371344711057 2.09743996698083
 H -5.26889898564110 0.94195274906172 2.63287357268731
 H -4.47171689230816 0.26069976934630 1.17696470571124
 H -3.57817810869628 0.35412802981089 2.74300088283878
 C 4.32198634510748 -0.84371222517140 2.09744866724041
 H 4.47171346970520 -0.26069288850024 1.17697756453913
 H 3.57816514549770 -0.35413342807709 2.74300739754482
 H 5.26888910428899 -0.94195053054249 2.63288791182455

Optimised cationic doublet geometry (transition state)

C 0.10114216042032 0.68556114021256 0.48022171710160
 C -0.92671607938940 1.72817516059392 0.38553205412281
 C -2.31499032054604 1.50636902469140 0.46375226053208
 C -0.48338407297410 3.09336322359169 0.28799333631377
 C -1.43480891846079 4.13356129503588 0.04939826047330
 C 0.86142171605103 3.42573535299598 0.53089946096235
 C 1.34307399346072 4.83430671829236 0.40616506861074
 C 1.74889880011397 2.44207861279597 0.98660553406770
 H 2.74237899417423 2.74319128129836 1.31632034485979
 C 1.36164525232159 1.11432958809157 0.98280764277337
 C -2.78246685837219 3.87051118377387 0.01793557551261
 C -3.23545423438573 2.55418920865369 0.28167419418172
 C -0.97775301892110 5.54778298573937 -0.13011719627441
 N 0.38207314514815 5.76799033046149 0.05807428562715
 O 2.50391577480429 5.13990231152824 0.58637748203718

O -1.73027547089121 6.45057837299191 -0.42094459699995
 H -2.69117851007900 0.53432429273183 0.75545023546035
 H -3.49904103239828 4.67456700187123 -0.14504001560506
 O -4.55366717062102 2.40293528694907 0.36164668697694
 H 0.70097357947637 6.72801274915742 -0.05106314081199
 C -0.10254891118937 -0.68959691870909 0.06546028039665
 C -1.36322832570286 -1.12362075961706 -0.43164524997431
 C -1.74268844854096 -2.45369450629690 -0.43950607460619
 H -2.73578340861213 -2.75926512006350 -0.76627416357259
 C -0.84740753257004 -3.43429379448818 0.00770936308164
 C -1.31920854897325 -4.84701270565836 0.12416437377103
 C 0.49595984381066 -3.09482013346034 0.24793720208147
 C 1.45395539042311 -4.12988687018879 0.48189278833933
 C 0.93106997974481 -1.72697958707027 0.15291367657678
 C 2.31739871732673 -1.49711731932784 0.06806553209144
 C 2.80036169489467 -3.85959157957749 0.50700905583936
 C 3.24469623680231 -2.54053498517732 0.24190874587136
 C 1.00466234689561 -5.54587678421988 0.66641970826298
 N -0.35304506818616 -5.77498228276702 0.47338481559678
 O -2.47811338534092 -5.15940873362425 -0.05679959746393
 O 1.76207964285939 -6.44337192991539 0.96087799201119
 H 2.68713395123376 -0.52161667817208 -0.22057180248301
 H 3.52202589288413 -4.65977011073027 0.66661079138311
 O 4.56155850084440 -2.38190668138843 0.15489876538911
 H -0.66630198213103 -6.73684005721936 0.58270191289259
 H 2.05980851968947 0.37538497018287 1.35828228290016
 H -2.06861152999460 -0.38726741605206 -0.79787438105880
 C -5.13394945657134 1.12338473473218 0.61672246044126

H -6.21494371685339 1.27970462891986 0.60619970577908
H -4.85339171281927 0.40963917478596 -0.17183261539510
H -4.82328673639385 0.74692531612428 1.60240525670927
C 5.13313925064211 -1.10189290467932 -0.11697782441961
H 4.79597378033457 -0.72665748687148 -1.09434352491650
H 4.87272206796247 -0.38766518242250 0.67805787501463
H 6.21422732510803 -1.25686601208857 -0.13491859916270

Optimised anionic doublet geometry (ground state)

C 0.17787468747193 0.71056751675543 -0.57610978168537
C -0.73109420778284 1.72415332106045 -0.09271618540035
C -1.93363355105405 1.39803870211701 0.58452513037298
C -0.38771748892495 3.10957618544304 -0.24785585646069
C -1.30373838441798 4.09898564346398 0.21660483771120
C 0.85529531603721 3.47640323495466 -0.84019312670540
C 1.20311095234113 4.88122991066122 -1.00432508266670
C 1.74272217784982 2.47162965095354 -1.25751978575672
H 2.68277904887816 2.77216269907091 -1.71885341059630
C 1.40997008109023 1.13024652351752 -1.12138876801009
C -2.49523915871146 3.74305617401356 0.84100959888303
C -2.79970520201408 2.38762364389670 1.03946502979078
C -0.98234842433913 5.52827513406355 0.04957575027454
N 0.23938104095046 5.78908274609810 -0.54986798314089
O 2.24774064916313 5.31102380241501 -1.49809280665447
O -1.71067007774371 6.45398314901084 0.40398542524635
H -2.15751554382473 0.35125236227247 0.75725180506433
H -3.17299713263466 4.51957705868596 1.19116410736648
O -3.96997451267582 2.12396928801765 1.69640166910775

H 0.47379212523789 6.76880582262708 -0.66659031647613
C -0.17787519044297 -0.71057066222836 -0.57610307412711
C -1.40998067551957 -1.13025086814229 -1.12135597200583
C -1.74273838449487 -2.47163402215439 -1.25747172390735
H -2.68280742534903 -2.77216804769997 -1.71878024727347
C -0.85530022479905 -3.47640645409487 -0.84016645722150
C -1.20311393080763 -4.88123295874582 -1.00429947096503
C 0.38772545299868 -3.10957768214589 -0.24785671742808
C 1.30375764710197 -4.09898560289787 0.21658591888961
C 0.73110038653831 -1.72415463591794 -0.09271886733375
C 1.93363945050728 -1.39803748752850 0.58452148965206
C 2.49525953569800 -3.74305402334807 0.84098752891225
C 2.79971566993383 -2.38762097226379 1.03945651674845
C 0.98237511124232 -5.52827579611190 0.04954185158396
N -0.23936659610897 -5.78908424722859 -0.54987635704984
O -2.24775326712681 -5.31102893826963 -1.49804513074066
O 1.71070962582706 -6.45398418758825 0.40392383890611
H 2.15751319982704 -0.35125084890982 0.75725725228256
H 3.17302125444799 -4.51957329647889 1.19113742072640
O 3.96997513141843 -2.12396414861179 1.69641026388555
H -0.47377378046275 -6.76880756249238 -0.66660482132399
H 2.09206101584677 0.37125456470027 -1.50347114014660
H -2.09207762732343 -0.37125951832192 -1.50342696405130
C -4.33182066520848 0.77644634513359 1.90912740578868
H -5.29545086363320 0.79399283032950 2.42896811754072
H -4.43800218844709 0.23177657939558 0.95607292519534
H -3.58883544780890 0.25335384030430 2.53406664886390
C 4.33180009926714 -0.77644031754751 1.90916823360787

H 4.43798476813916 -0.23174850223858 0.95612686337792
H 3.58880074066531 -0.25337153391658 2.53411055576601
H 5.29542478317687 -0.79398441407834 2.42901947013708

Optimised anionic doublet geometry (transition state)

C 0.12198891878138 0.68937576068956 0.43828457301781
C -0.89280089451796 1.75232513706967 0.35765374919819
C -2.28837311521282 1.52355879431229 0.43243968834746
C -0.46232237331143 3.12301307852435 0.28329570811590
C -1.43237074759125 4.14404583586104 0.05752223777094
C 0.90374415927309 3.46480686218987 0.50748582654185
C 1.35279168776816 4.84152326413487 0.40576067565262
C 1.77233050610483 2.45548703161646 0.95380735665036
H 2.76686194489439 2.73988505490356 1.29770324406568
C 1.38427586700851 1.12934767133358 0.94154000682023
C -2.79185109374856 3.85784613716239 0.02232715664103
C -3.21955122620434 2.54797254488730 0.26571463962402
C -0.99932772440641 5.54791622660033 -0.09903672585251
N 0.35593732323189 5.76797308175972 0.06964413256967
O 2.50526023147060 5.24173894263641 0.58467678500111
O -1.75406436721372 6.48340498512907 -0.35669913651770
H -2.63805612467139 0.53102154255086 0.68023936358892
H -3.51034504583174 4.66023108097378 -0.13603626321976
O -4.57312384769120 2.35430823069480 0.33616809622098
H 0.66419540563506 6.72994131519832 -0.01916455116007
C -0.11130237845109 -0.68671139301083 0.05414683348532
C -1.37334500577230 -1.12696433937575 -0.44955320438919
C -1.76130900905214 -2.45311345535623 -0.46153667565091

H -2.75546321491848 -2.73796561653983 -0.80614300783104
C -0.89276551971464 -3.46214791192729 -0.01434084524473
C -1.34162411641128 -4.83891022598800 0.08762337374630
C 0.47317894869140 -3.12011536218701 0.21018478126506
C 1.44324811401023 -4.14098502302562 0.43650447731948
C 0.90367234281593 -1.74946967847821 0.13494962763728
C 2.29914065470094 -1.52083984245780 0.05922775810883
C 2.80277434198384 -3.85483906416959 0.47087037288525
C 3.23037537076872 -2.54520345272471 0.22608865507353
C 1.01008993216068 -5.54457814601686 0.59518298648018
N -0.34502061465630 -5.76494378957631 0.42567004144990
O -2.49395359750604 -5.23936127622353 -0.09170620341533
O 1.76468631613159 -6.47956392092071 0.85506881848341
H 2.64903773836223 -0.52851977021867 -0.18912848756309
H 3.52123681598629 -4.65711361803297 0.62991391887648
O 4.58388308324040 -2.35171548015722 0.15401184840979
H -0.65335397360886 -6.72678295558892 0.51559926391060
H 2.08353643672554 0.39401764255460 1.32141653599817
H -2.07207221912025 -0.39157840789818 -0.83033808984134
C -5.05821778387222 1.04593766041852 0.54744243321923
H -6.15094999351551 1.11800295408310 0.54696919192012
H -4.73638002578986 0.36121739740218 -0.25501945848409
H -4.72184833005730 0.63953106413960 1.51608562362538
C 5.06911658135093 -1.04266770609706 -0.05261113106121
H 4.73483516758931 -0.63373167137547 -1.02091816811067
H 4.74527172401951 -0.36018497058929 0.75094586694199
H 6.16186728089939 -1.11443475616929 -0.04979415355006

D.7.4 B(C₂F₅)₃-(*R*)-NMI₂

The spin-restricted singlet SCF calculation converged to an energy of -3308.84710132 Hartree. The level of theory was B3LYP-D3BJ/def2-SVPD.

The g -tensor of the B(C₂F₅)₃ anion was calculated on UB3LYP/EPR-II to be

$$\mathbf{g}_A = \begin{pmatrix} 2.0016519 & -0.0003434 & -0.0000000 \\ 0.0003430 & 2.0016494 & 0.0000000 \\ -0.0000000 & 0.0000000 & 2.0009638 \end{pmatrix}, \quad (\text{D.85})$$

while the g -tensor of the (*R*)-NMI₂ cation was calculated on UB3LYP/EPR-II to be

$$\mathbf{g}_B = \begin{pmatrix} 2.0041110 & 0.0000260 & 0.0004843 \\ -0.0000847 & 2.0040897 & 0.0000431 \\ 0.0004896 & 0.0001446 & 2.0035308 \end{pmatrix}. \quad (\text{D.86})$$

Finally, the ZFS tensor of the lowest triplet state of B(C₂F₅)₃-(*R*)-NMI₂ was computed on UB3LYP/EPR-II to be

$$\mathbf{D} = \begin{pmatrix} -0.000153 & -0.003166 & 0.000105 \\ -0.003166 & -0.007051 & 0.001746 \\ 0.000105 & 0.001746 & 0.007203 \end{pmatrix} \text{cm}^{-1}. \quad (\text{D.87})$$

In these three EPR parameters, the coordinate frame is aligned with the high-symmetry axes of the C_{3h} -symmetric B(C₂F₅)₃ subunit.

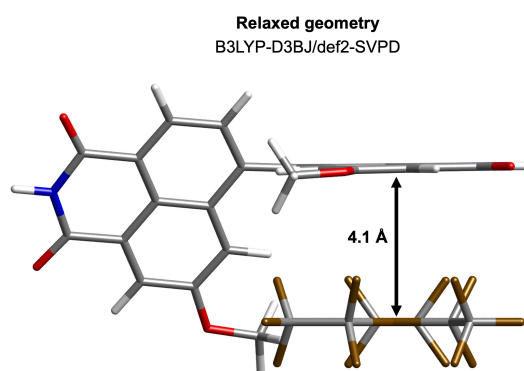


Figure D.7. Relaxed geometry of the $\text{B}(\text{C}_2\text{F}_5)_3$ -(*R*)- NMI_2 system in the singlet ground state, calculated at the B3LYP/def2-SVPD level of theory.

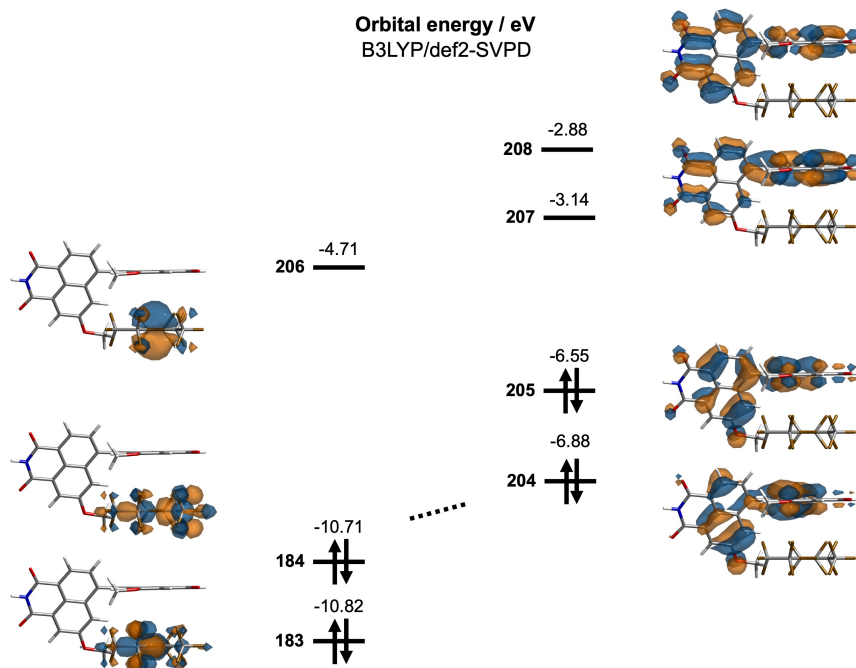


Figure D.8. Frontier MOs (isovalue = 0.030) of the $\text{B}(\text{C}_2\text{F}_5)_3$ -(*R*)- NMI_2 system in the singlet ground state, calculated at the B3LYP/def2-SVPD level of theory.

Relaxed geometry

```

H -4.09512232496611 -2.80019009897977 4.06722632171224
H -0.69506329719630 -3.82470761822676 6.00128128387042
C -4.25199732026423 -3.53002874496669 -0.37577100913286
C 3.19175407058096 -2.61704815506349 3.87774092636373
H -4.84077569180278 -3.48393167554465 -1.29598170676599
  
```

H -3.33803829463607 -2.93321504541360 -0.49421978624605
H -4.84526715184878 -3.12937104261707 0.46123492462720
H 4.28442356202002 -2.60481247606696 3.84261275133546
H 2.79860446008501 -3.08419188740942 2.96146991522813
H 2.85718634348976 -3.19190790362019 4.75543829381147
C -1.97472709994482 -2.50997448479853 4.06962645594560
C -0.90790622347134 -1.55271903728003 4.07373301939562
C 0.46053815424560 -1.93502143695054 4.03295403472888
C -1.23685499335768 -0.16160774026952 4.09087357818930
C -0.18114327933110 0.79614821094723 4.08610209997607
C -2.59470937394105 0.24923427734789 4.09289795696919
C -2.93632287123723 1.69209545683832 4.10800050800319
C -3.60669965415696 -0.69550733675596 4.07403045990617
H -4.64134270128822 -0.35539295604721 4.07880047613539
C -3.29145729321668 -2.06471872594903 4.06142151565627
C 1.13771906817456 0.39777978661004 4.05898421023919
C 1.46432229323301 -0.98060475440492 4.02659058537181
C -0.49666542664816 2.24927136004841 4.10951506331885
N -1.85039182565856 2.56274021729754 4.11830449801812
O -4.07446756120717 2.12469048062905 4.10842978271971
O 0.34567209692474 3.12737411234259 4.11879703125626
H 0.70476222024008 -2.98989404821378 3.98755202593504
H 1.93003372565309 1.14432265545331 4.05152209176801
O 2.78454844296097 -1.26198100297534 3.97147735314071
H -2.07625137314111 3.55285956291829 4.12917412865446
C -1.69163926724726 -3.96875404708882 4.11147651845442
C -1.01622187489033 -4.49762154490555 5.20675105231311
C -0.76590118961155 -5.87446179416847 5.32354798018293

H -0.24684117711199 -6.28215985755982 6.18998625950586
 C -1.19528425402952 -6.74294987928723 4.33374675297555
 C -0.93372434897414 -8.19705860488607 4.47030742705957
 C -1.88380301088094 -6.24508600830531 3.19741265446081
 C -2.33767865642718 -7.12638759189835 2.17272273242190
 C -2.13739502330948 -4.84324881297997 3.06665821661910
 C -2.81832164846183 -4.37135500343281 1.90936970433311
 C -3.01508365618862 -6.64560275683913 1.07446527899495
 C -3.26070835110601 -5.25632697990559 0.93876239837849
 C -2.09397091143989 -8.58870912802211 2.28792846073070
 N -1.41019694951920 -8.98914264154821 3.43050112174402
 O -0.34601128379744 -8.70009744089278 5.41133568347859
 O -2.45327534187966 -9.40736804500070 1.46177865041838
 H -2.98086333277649 -3.30562720194749 1.79935361417482
 H -3.36242442690954 -7.33466780132313 0.30600800684454
 O -3.94139444567446 -4.89868322920498 -0.17296131355564
 H -1.23925934777407 -9.98648483521521 3.51815810604220
 B -0.00064933831200 -0.00132264084859 0.00000257051728
 C 0.45080520251479 1.55970772701949 0.00000389724816
 C 1.12685853024172 -1.17070948480308 0.00000168623018
 C -1.57804820987825 -0.39118631056804 0.00000029887696
 C -2.75035202905363 0.63612378160728 -0.00000396897178
 C 1.92723509880288 2.06158539365097 -0.00000239556365
 C 0.82546625204777 -2.69969649998725 0.00000072515105
 F -0.12092329665662 2.11580619146232 1.11011420957161
 F -0.12093489895040 2.11581219841469 -1.11009729417333
 F 1.89156769655296 -0.95150429854413 1.11215220664083
 F 1.89156789286454 -0.95150320324846 -1.11214819709929

F -1.77389111806482 -1.16207932359343 1.11218861779922
 F -1.77388732788948 -1.16208472954223 -1.11218447109770
 F -2.71100849432646 1.40642070533385 1.08804209813757
 F -3.90494910231440 -0.03571169566587 -0.00000519685709
 F -2.71100399649463 1.40641619641059 -1.08805319816159
 F 2.57456910092988 1.64317549598589 1.08852969965658
 F 1.92221759725857 3.39710459943277 0.00000360396368
 F 2.57455639620072 1.64318550313986 -1.08854590261287
 F 0.13813931097010 -3.04967800116102 1.08834839448160
 F 1.98506521203961 -3.36233690369115 -0.00000169632651
 F 0.13813632416900 -3.04967559977709 -1.08834580382991

Singlet excited states from B3LYP/TDDFT/TDA/def2-SVPD

STATE 1: E= 0.048413 au 1.317 eV 10625.5 cm⁻¹ <S²> = 0.000000
 203a -> 205a : 0.052969 (c= 0.23015056)
 204a -> 205a : 0.944424 (c= -0.97181501)
 STATE 2: E= 0.060265 au 1.640 eV 13226.5 cm⁻¹ <S²> = 0.000000
 203a -> 205a : 0.938678 (c= -0.96885388)
 204a -> 205a : 0.053614 (c= -0.23154728)
 STATE 3: E= 0.076177 au 2.073 eV 16718.8 cm⁻¹ <S²> = 0.000000
 201a -> 205a : 0.214921 (c= 0.46359595)
 202a -> 205a : 0.776648 (c= 0.88127629)
 STATE 4: E= 0.084420 au 2.297 eV 18528.0 cm⁻¹ <S²> = 0.000000
 201a -> 205a : 0.780124 (c= -0.88324614)
 202a -> 205a : 0.215593 (c= 0.46432006)
 STATE 5: E= 0.092015 au 2.504 eV 20194.9 cm⁻¹ <S²> = 0.000000
 199a -> 205a : 0.990655 (c= -0.99531629)
 STATE 6: E= 0.098851 au 2.690 eV 21695.3 cm⁻¹ <S²> = 0.000000

200a -> 205a : 0.995450 (c= -0.99772222)
 STATE 7: E= 0.111178 au 3.025 eV 24400.8 cm⁻¹ <S²> = 0.000000
 203a -> 206a : 0.017605 (c= 0.13268550)
 203a -> 207a : 0.021189 (c= 0.14556406)
 204a -> 206a : 0.917661 (c= 0.95794615)
 204a -> 207a : 0.013828 (c= 0.11759229)
 STATE 8: E= 0.112049 au 3.049 eV 24591.9 cm⁻¹ <S²> = 0.000000
 196a -> 205a : 0.882543 (c= 0.93943779)
 198a -> 205a : 0.098248 (c= -0.31344554)
 STATE 9: E= 0.112461 au 3.060 eV 24682.4 cm⁻¹ <S²> = 0.000000
 195a -> 205a : 0.975882 (c= -0.98786738)
 198a -> 205a : 0.019714 (c= -0.14040652)
 STATE 10: E= 0.117808 au 3.206 eV 25855.9 cm⁻¹ <S²> = 0.000000
 203a -> 206a : 0.435768 (c= -0.66012750)
 203a -> 207a : 0.012917 (c= 0.11365430)
 204a -> 206a : 0.023318 (c= 0.15270243)
 204a -> 207a : 0.504480 (c= -0.71026729)
 STATE 11: E= 0.118695 au 3.230 eV 26050.5 cm⁻¹ <S²> = 0.000000
 193a -> 205a : 0.018278 (c= -0.13519548)
 194a -> 205a : 0.225693 (c= -0.47507122)
 195a -> 205a : 0.011854 (c= -0.10887445)
 196a -> 205a : 0.069405 (c= 0.26344804)
 197a -> 205a : 0.027978 (c= 0.16726632)
 198a -> 205a : 0.641345 (c= 0.80083991)
 STATE 12: E= 0.119340 au 3.247 eV 26192.2 cm⁻¹ <S²> = 0.000000
 194a -> 205a : 0.083726 (c= 0.28935516)
 196a -> 205a : 0.028863 (c= 0.16989250)
 197a -> 205a : 0.784843 (c= -0.88591356)

198a -> 205a : 0.093135 (c= 0.30517981)
 STATE 13: E= 0.119961 au 3.264 eV 26328.5 cm⁻¹ <S²> = 0.000000
 193a -> 205a : 0.049734 (c= 0.22301023)
 194a -> 205a : 0.609595 (c= 0.78076565)
 197a -> 205a : 0.180728 (c= 0.42512163)
 198a -> 205a : 0.145673 (c= 0.38167097)
 STATE 14: E= 0.127484 au 3.469 eV 27979.4 cm⁻¹ <S²> = 0.000000
 201a -> 206a : 0.057862 (c= 0.24054623)
 201a -> 209a : 0.020085 (c= 0.14172048)
 202a -> 210a : 0.013099 (c= -0.11445212)
 203a -> 206a : 0.460952 (c= -0.67893472)
 204a -> 207a : 0.367692 (c= 0.60637621)
 204a -> 210a : 0.018944 (c= 0.13763681)
 STATE 15: E= 0.131215 au 3.571 eV 28798.4 cm⁻¹ <S²> = 0.000000
 193a -> 205a : 0.060327 (c= 0.24561595)
 202a -> 206a : 0.056118 (c= 0.23689291)
 203a -> 207a : 0.785314 (c= -0.88617952)
 204a -> 206a : 0.012003 (c= 0.10955723)
 204a -> 209a : 0.022972 (c= -0.15156470)
 STATE 16: E= 0.131651 au 3.582 eV 28894.1 cm⁻¹ <S²> = 0.000000
 193a -> 205a : 0.862228 (c= 0.92856252)
 194a -> 205a : 0.063456 (c= -0.25190434)
 203a -> 207a : 0.056916 (c= 0.23857143)
 STATE 17: E= 0.134984 au 3.673 eV 29625.5 cm⁻¹ <S²> = 0.000000
 199a -> 206a : 0.730718 (c= -0.85482020)
 199a -> 207a : 0.218454 (c= -0.46739104)
 199a -> 212a : 0.010230 (c= -0.10114370)
 STATE 18: E= 0.135330 au 3.683 eV 29701.4 cm⁻¹ <S²> = 0.000000

200a -> 206a : 0.551511 (c= 0.74263755)
 200a -> 207a : 0.399501 (c= -0.63206078)
 STATE 19: E= 0.137391 au 3.739 eV 30153.9 cm⁻¹ <S²> = 0.000000
 201a -> 207a : 0.011918 (c= 0.10916861)
 202a -> 206a : 0.806061 (c= -0.89780927)
 202a -> 207a : 0.012326 (c= -0.11102040)
 203a -> 207a : 0.069649 (c= -0.26391174)
 204a -> 209a : 0.043727 (c= 0.20910968)
 STATE 20: E= 0.140398 au 3.820 eV 30813.7 cm⁻¹ <S²> = 0.000000
 191a -> 205a : 0.131163 (c= -0.36216425)
 192a -> 205a : 0.860773 (c= 0.92777828)
 STATE 21: E= 0.144675 au 3.937 eV 31752.6 cm⁻¹ <S²> = 0.000000
 201a -> 206a : 0.183468 (c= -0.42833116)
 202a -> 207a : 0.743149 (c= 0.86206082)
 204a -> 210a : 0.011912 (c= 0.10914231)
 STATE 22: E= 0.147132 au 4.004 eV 32291.7 cm⁻¹ <S²> = 0.000000
 201a -> 206a : 0.635556 (c= 0.79721787)
 202a -> 207a : 0.134286 (c= 0.36645007)
 203a -> 206a : 0.022315 (c= 0.14938092)
 203a -> 209a : 0.047152 (c= 0.21714599)
 204a -> 207a : 0.043134 (c= -0.20768742)
 204a -> 210a : 0.026666 (c= 0.16329744)
 204a -> 211a : 0.026117 (c= 0.16160878)
 STATE 23: E= 0.148590 au 4.043 eV 32611.7 cm⁻¹ <S²> = 0.000000
 191a -> 205a : 0.863382 (c= 0.92918331)
 192a -> 205a : 0.131822 (c= 0.36307267)
 STATE 24: E= 0.152993 au 4.163 eV 33578.0 cm⁻¹ <S²> = 0.000000
 196a -> 206a : 0.027929 (c= 0.16711862)

198a -> 206a : 0.026701 (c= 0.16340561)
 198a -> 207a : 0.037548 (c= -0.19377323)
 201a -> 207a : 0.731904 (c= -0.85551405)
 204a -> 209a : 0.094439 (c= 0.30730898)
 STATE 25: E= 0.153887 au 4.187 eV 33774.3 cm⁻¹ <S²> = 0.000000
 195a -> 206a : 0.075560 (c= 0.27488265)
 195a -> 207a : 0.034068 (c= 0.18457430)
 196a -> 206a : 0.373260 (c= -0.61095047)
 196a -> 207a : 0.181451 (c= -0.42597075)
 198a -> 206a : 0.216219 (c= 0.46499322)
 199a -> 207a : 0.016980 (c= 0.13030687)
 199a -> 208a : 0.028867 (c= 0.16990312)
 199a -> 211a : 0.010215 (c= -0.10107140)
 STATE 26: E= 0.154386 au 4.201 eV 33883.8 cm⁻¹ <S²> = 0.000000
 195a -> 206a : 0.024313 (c= 0.15592478)
 196a -> 206a : 0.146827 (c= -0.38318028)
 198a -> 206a : 0.262750 (c= -0.51259137)
 198a -> 207a : 0.304671 (c= 0.55196992)
 200a -> 206a : 0.017657 (c= 0.13287860)
 200a -> 207a : 0.039395 (c= 0.19848128)
 200a -> 208a : 0.020290 (c= -0.14244359)
 200a -> 211a : 0.011443 (c= -0.10697150)
 201a -> 207a : 0.089546 (c= -0.29924212)
 204a -> 209a : 0.013736 (c= 0.11720227)
 STATE 27: E= 0.160089 au 4.356 eV 35135.4 cm⁻¹ <S²> = 0.000000
 198a -> 206a : 0.031128 (c= -0.17643254)
 198a -> 207a : 0.027580 (c= 0.16607225)
 200a -> 206a : 0.398542 (c= -0.63130220)

200a -> 207a : 0.518415 (c= -0.72001062)
 STATE 28: E= 0.161330 au 4.390 eV 35407.8 cm⁻¹ <S²> = 0.000000
 194a -> 206a : 0.052206 (c= -0.22848629)
 195a -> 206a : 0.015087 (c= -0.12282756)
 197a -> 206a : 0.014254 (c= 0.11938934)
 204a -> 208a : 0.855279 (c= -0.92481275)
 STATE 29: E= 0.163694 au 4.454 eV 35926.6 cm⁻¹ <S²> = 0.000000
 196a -> 206a : 0.019390 (c= -0.13924823)
 199a -> 206a : 0.228469 (c= 0.47798391)
 199a -> 207a : 0.727010 (c= -0.85264859)
 STATE 30: E= 0.166939 au 4.543 eV 36638.9 cm⁻¹ <S²> = 0.000000
 189a -> 205a : 0.341394 (c= 0.58428903)
 190a -> 205a : 0.654350 (c= 0.80891932)
 STATE 31: E= 0.168990 au 4.598 eV 37089.0 cm⁻¹ <S²> = 0.000000
 193a -> 206a : 0.011927 (c= 0.10921194)
 193a -> 207a : 0.018893 (c= 0.13745032)
 194a -> 206a : 0.180815 (c= 0.42522366)
 195a -> 206a : 0.100700 (c= -0.31733201)
 195a -> 207a : 0.018763 (c= -0.13697750)
 196a -> 206a : 0.027819 (c= -0.16678973)
 197a -> 206a : 0.098972 (c= 0.31459783)
 197a -> 207a : 0.032041 (c= -0.17899959)
 201a -> 207a : 0.038980 (c= -0.19743340)
 202a -> 206a : 0.016310 (c= -0.12771210)
 203a -> 210a : 0.010569 (c= 0.10280420)
 204a -> 209a : 0.382976 (c= -0.61885058)
 204a -> 210a : 0.010581 (c= 0.10286192)
 STATE 32: E= 0.169883 au 4.623 eV 37285.0 cm⁻¹ <S²> = 0.000000

182a -> 205a : 0.010172 (c= 0.10085601)
 189a -> 205a : 0.646548 (c= -0.80408238)
 190a -> 205a : 0.331169 (c= 0.57547291)
 STATE 33: E= 0.170830 au 4.649 eV 37492.8 cm⁻¹ <S²> = 0.000000
 195a -> 206a : 0.192429 (c= -0.43866712)
 195a -> 207a : 0.021561 (c= -0.14683789)
 196a -> 206a : 0.034091 (c= -0.18463697)
 197a -> 206a : 0.202357 (c= -0.44984118)
 197a -> 207a : 0.041647 (c= 0.20407538)
 203a -> 208a : 0.246039 (c= 0.49602293)
 203a -> 209a : 0.020855 (c= 0.14441360)
 204a -> 210a : 0.024028 (c= -0.15501073)
 204a -> 211a : 0.167979 (c= 0.40985191)
 STATE 34: E= 0.171656 au 4.671 eV 37674.2 cm⁻¹ <S²> = 0.000000
 193a -> 206a : 0.097110 (c= -0.31162482)
 194a -> 206a : 0.033867 (c= 0.18403017)
 194a -> 207a : 0.112046 (c= -0.33473344)
 197a -> 206a : 0.104676 (c= 0.32353600)
 197a -> 207a : 0.015954 (c= -0.12630749)
 201a -> 206a : 0.011152 (c= 0.10560304)
 203a -> 208a : 0.010913 (c= 0.10446769)
 204a -> 209a : 0.016340 (c= 0.12782614)
 204a -> 210a : 0.545340 (c= -0.73847116)
 STATE 35: E= 0.173771 au 4.729 eV 38138.4 cm⁻¹ <S²> = 0.000000
 183a -> 205a : 0.905635 (c= -0.95164881)
 185a -> 205a : 0.016468 (c= -0.12832735)
 186a -> 205a : 0.029416 (c= 0.17151047)
 STATE 36: E= 0.174867 au 4.758 eV 38378.9 cm⁻¹ <S²> = 0.000000

183a -> 205a : 0.015258 (c= -0.12352378)
 193a -> 206a : 0.022358 (c= 0.14952524)
 194a -> 206a : 0.077257 (c= 0.27795109)
 194a -> 207a : 0.023976 (c= 0.15484076)
 195a -> 206a : 0.077597 (c= -0.27856176)
 196a -> 206a : 0.018451 (c= -0.13583612)
 197a -> 206a : 0.040352 (c= -0.20087802)
 201a -> 209a : 0.013632 (c= 0.11675638)
 203a -> 208a : 0.485383 (c= -0.69669448)
 203a -> 209a : 0.075841 (c= 0.27539315)
 203a -> 210a : 0.010452 (c= -0.10223408)
 204a -> 208a : 0.011609 (c= -0.10774730)
 204a -> 209a : 0.037805 (c= 0.19443454)
 204a -> 210a : 0.047267 (c= -0.21740948)
 STATE 37: E= 0.176855 au 4.812 eV 38815.1 cm⁻¹ <S²> = 0.000000
 195a -> 206a : 0.107040 (c= 0.32716996)
 196a -> 206a : 0.020597 (c= 0.14351761)
 197a -> 206a : 0.210974 (c= -0.45931908)
 201a -> 207a : 0.013619 (c= -0.11670071)
 203a -> 208a : 0.074513 (c= -0.27297073)
 203a -> 209a : 0.054281 (c= -0.23298337)
 203a -> 210a : 0.117737 (c= 0.34312892)
 203a -> 211a : 0.024303 (c= 0.15589325)
 204a -> 209a : 0.177751 (c= -0.42160561)
 204a -> 210a : 0.057792 (c= -0.24040024)
 204a -> 211a : 0.043147 (c= 0.20771854)
 STATE 38: E= 0.177734 au 4.836 eV 39008.0 cm⁻¹ <S²> = 0.000000
 182a -> 205a : 0.905271 (c= 0.95145705)

184a -> 205a : 0.012531 (c= 0.11193980)
 186a -> 205a : 0.020529 (c= 0.14327902)
 187a -> 205a : 0.016775 (c= -0.12951763)
 STATE 39: E= 0.178898 au 4.868 eV 39263.5 cm⁻¹ <S²> = 0.000000
 194a -> 206a : 0.398603 (c= -0.63135051)
 195a -> 206a : 0.109164 (c= -0.33039944)
 197a -> 206a : 0.079640 (c= 0.28220632)
 197a -> 207a : 0.032688 (c= 0.18079747)
 198a -> 206a : 0.043925 (c= 0.20958197)
 198a -> 207a : 0.034284 (c= 0.18515917)
 203a -> 208a : 0.059043 (c= -0.24298784)
 203a -> 210a : 0.074628 (c= 0.27318090)
 203a -> 211a : 0.014757 (c= -0.12147705)
 204a -> 208a : 0.058350 (c= 0.24155794)
 204a -> 209a : 0.011683 (c= -0.10808951)
 204a -> 210a : 0.022798 (c= -0.15099142)
 STATE 40: E= 0.179443 au 4.883 eV 39383.1 cm⁻¹ <S²> = 0.000000
 194a -> 206a : 0.044446 (c= -0.21082138)
 196a -> 206a : 0.037653 (c= -0.19404360)
 196a -> 207a : 0.026378 (c= -0.16241332)
 197a -> 206a : 0.011082 (c= 0.10526923)
 197a -> 207a : 0.012426 (c= 0.11147264)
 198a -> 206a : 0.340240 (c= -0.58330113)
 198a -> 207a : 0.413634 (c= -0.64314358)
 203a -> 209a : 0.018558 (c= 0.13622625)
 203a -> 210a : 0.019540 (c= 0.13978516)
 204a -> 211a : 0.027942 (c= -0.16715805)
 STATE 41: E= 0.179868 au 4.894 eV 39476.6 cm⁻¹ <S²> = 0.000000

194a -> 207a : 0.013182 (c= 0.11481303)
 197a -> 206a : 0.089956 (c= -0.29992742)
 197a -> 207a : 0.068813 (c= -0.26232201)
 198a -> 206a : 0.015360 (c= 0.12393635)
 198a -> 207a : 0.025009 (c= 0.15814133)
 203a -> 208a : 0.034402 (c= 0.18547680)
 203a -> 209a : 0.202231 (c= 0.44970072)
 203a -> 210a : 0.070368 (c= 0.26527040)
 204a -> 210a : 0.014190 (c= -0.11912165)
 204a -> 211a : 0.405252 (c= -0.63659411)
 STATE 42: E= 0.182420 au 4.964 eV 40036.5 cm⁻¹ <S²> = 0.000000
 193a -> 206a : 0.015120 (c= 0.12296333)
 194a -> 206a : 0.028278 (c= 0.16815987)
 194a -> 207a : 0.037695 (c= 0.19415122)
 195a -> 206a : 0.076486 (c= 0.27656123)
 195a -> 207a : 0.019679 (c= -0.14028216)
 196a -> 206a : 0.036447 (c= 0.19091164)
 196a -> 207a : 0.039910 (c= -0.19977548)
 197a -> 206a : 0.072953 (c= 0.27009776)
 197a -> 207a : 0.392817 (c= 0.62675143)
 198a -> 207a : 0.025676 (c= 0.16023692)
 202a -> 208a : 0.018788 (c= -0.13706787)
 203a -> 209a : 0.108913 (c= 0.33001998)
 203a -> 210a : 0.031402 (c= 0.17720613)
 203a -> 211a : 0.026764 (c= 0.16359766)
 STATE 43: E= 0.183110 au 4.983 eV 40188.1 cm⁻¹ <S²> = 0.000000
 195a -> 206a : 0.049688 (c= -0.22290700)
 195a -> 207a : 0.101782 (c= 0.31903299)

196a -> 206a : 0.184886 (c= 0.42998363)
 196a -> 207a : 0.541599 (c= -0.73593431)
 197a -> 207a : 0.022188 (c= -0.14895764)
 198a -> 206a : 0.021542 (c= -0.14677175)
 198a -> 207a : 0.032904 (c= 0.18139534)
 199a -> 208a : 0.012306 (c= 0.11093078)
 STATE 44: E= 0.185372 au 5.044 eV 40684.4 cm⁻¹ <S²> = 0.000000
 188a -> 205a : 0.055362 (c= 0.23529165)
 193a -> 206a : 0.022019 (c= 0.14838789)
 194a -> 206a : 0.043091 (c= -0.20758420)
 195a -> 206a : 0.062836 (c= 0.25067056)
 195a -> 207a : 0.506394 (c= -0.71161363)
 196a -> 206a : 0.010428 (c= 0.10211633)
 196a -> 207a : 0.076235 (c= -0.27610676)
 197a -> 207a : 0.068587 (c= -0.26189199)
 202a -> 208a : 0.025858 (c= 0.16080342)
 203a -> 209a : 0.011902 (c= 0.10909727)
 203a -> 210a : 0.015109 (c= -0.12291852)
 203a -> 211a : 0.032850 (c= -0.18124464)
 204a -> 211a : 0.015472 (c= 0.12438562)
 STATE 45: E= 0.185410 au 5.045 eV 40692.9 cm⁻¹ <S²> = 0.000000
 187a -> 205a : 0.017691 (c= -0.13300686)
 188a -> 205a : 0.906413 (c= -0.95205730)
 195a -> 207a : 0.032119 (c= -0.17921898)
 STATE 46: E= 0.187203 au 5.094 eV 41086.2 cm⁻¹ <S²> = 0.000000
 193a -> 206a : 0.200971 (c= 0.44829778)
 193a -> 207a : 0.020373 (c= 0.14273309)
 194a -> 206a : 0.011384 (c= -0.10669450)

194a -> 207a : 0.475607 (c= -0.68964281)
 197a -> 207a : 0.033209 (c= 0.18223382)
 201a -> 208a : 0.017447 (c= 0.13208762)
 202a -> 208a : 0.054773 (c= -0.23403573)
 203a -> 210a : 0.069893 (c= -0.26437322)
 203a -> 211a : 0.019628 (c= 0.14010147)
 204a -> 211a : 0.035581 (c= -0.18862936)
 STATE 47: E= 0.188436 au 5.128 eV 41357.0 cm⁻¹ <S²> = 0.000000
 185a -> 205a : 0.036401 (c= 0.19078978)
 186a -> 205a : 0.130395 (c= -0.36110198)
 187a -> 205a : 0.780455 (c= -0.88343360)
 188a -> 205a : 0.021878 (c= 0.14791090)
 STATE 48: E= 0.188980 au 5.142 eV 41476.3 cm⁻¹ <S²> = 0.000000
 192a -> 206a : 0.038651 (c= -0.19659818)
 193a -> 207a : 0.101381 (c= 0.31840428)
 194a -> 206a : 0.038794 (c= -0.19696249)
 194a -> 207a : 0.039731 (c= 0.19932620)
 195a -> 207a : 0.068313 (c= 0.26136723)
 201a -> 207a : 0.011189 (c= -0.10577793)
 201a -> 208a : 0.030474 (c= -0.17456788)
 202a -> 208a : 0.101352 (c= 0.31835780)
 202a -> 210a : 0.018049 (c= -0.13434607)
 203a -> 209a : 0.035169 (c= 0.18753348)
 203a -> 210a : 0.216621 (c= -0.46542585)
 203a -> 211a : 0.117018 (c= 0.34207876)
 204a -> 209a : 0.030074 (c= -0.17341761)
 204a -> 210a : 0.021851 (c= -0.14781941)
 204a -> 211a : 0.023207 (c= 0.15233921)

STATE 49: E= 0.189677 au 5.161 eV 41629.3 cm⁻¹ <S²> = 0.000000

187a -> 205a : 0.012644 (c= 0.11244477)

193a -> 207a : 0.060247 (c= -0.24545354)

194a -> 206a : 0.018778 (c= 0.13703422)

194a -> 207a : 0.024655 (c= -0.15701984)

194a -> 209a : 0.010013 (c= 0.10006735)

197a -> 207a : 0.048844 (c= 0.22100662)

201a -> 208a : 0.028017 (c= 0.16738290)

202a -> 208a : 0.583670 (c= 0.76398316)

203a -> 209a : 0.025725 (c= -0.16038923)

203a -> 210a : 0.010047 (c= 0.10023676)

203a -> 211a : 0.035242 (c= 0.18772741)

204a -> 211a : 0.035683 (c= -0.18890055)

STATE 50: E= 0.191363 au 5.207 eV 41999.4 cm⁻¹ <S²> = 0.000000

186a -> 205a : 0.042055 (c= -0.20507356)

192a -> 206a : 0.014426 (c= -0.12010878)

193a -> 206a : 0.304481 (c= -0.55179829)

193a -> 207a : 0.060264 (c= 0.24548737)

194a -> 207a : 0.024420 (c= 0.15627031)

195a -> 207a : 0.043758 (c= -0.20918347)

197a -> 207a : 0.049579 (c= 0.22266288)

201a -> 208a : 0.056255 (c= 0.23718172)

202a -> 208a : 0.024077 (c= -0.15516908)

202a -> 210a : 0.054524 (c= 0.23350457)

203a -> 210a : 0.091935 (c= -0.30320750)

204a -> 211a : 0.077627 (c= -0.27861671)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MO- MENTS

	State	Energy	Wavelength	fosc	T2	TX	TY	TZ
	(cm-1)	(nm)	(au**2)	(au)	(au)	(au)	(au)	(au)
1	10625.5	941.1	0.000653105	0.02024	0.04613	0.07286	-0.11313	
2	13226.5	756.1	0.000055355	0.00138	-0.00884	0.02664	0.02429	
3	16718.8	598.1	0.001365651	0.02689	0.02591	0.05005	-0.15400	
4	18528.0	539.7	0.000272712	0.00485	0.00262	0.04879	0.04958	
5	20194.9	495.2	0.000001921	0.00003	0.00225	-0.00248	0.00448	
6	21695.3	460.9	0.000008824	0.00013	0.00072	0.00657	-0.00950	
7	24400.8	409.8	0.265852978	3.58685	0.17014	1.86871	0.25660	
8	24591.9	406.6	0.000959674	0.01285	-0.00174	0.10612	0.03979	
9	24682.4	405.1	0.000069146	0.00092	0.01367	-0.02210	-0.01572	
10	25855.9	386.8	0.044216152	0.56298	0.15992	0.73177	-0.04383	
11	26050.5	383.9	0.000418203	0.00529	0.00457	0.07010	0.01869	
12	26192.2	381.8	0.000009045	0.00011	0.00600	-0.00052	-0.00880	
13	26328.5	379.8	0.000189190	0.00237	0.01081	0.00183	-0.04739	
14	27979.4	357.4	0.008060953	0.09485	0.11810	0.03408	-0.28238	
15	28798.4	347.2	0.122965697	1.40570	0.41520	1.05959	0.33252	
16	28894.1	346.1	0.009642353	0.10986	-0.12181	-0.30096	-0.06670	
17	29625.5	337.5	0.000548960	0.00610	0.02719	-0.06008	-0.04185	
18	29701.4	336.7	0.000321349	0.00356	-0.02954	-0.05150	0.00607	
19	30153.9	331.6	0.124253999	1.35657	-0.39635	1.08976	-0.10905	
20	30813.7	324.5	0.001642782	0.01755	-0.00219	0.03417	-0.12798	
21	31752.6	314.9	0.023452055	0.24315	-0.06483	0.44772	-0.19621	
22	32291.7	309.7	0.018814931	0.19182	0.24066	-0.04096	-0.36362	

23 32611.7 306.6 0.000778255 0.00786 0.01693 0.06010 0.06291
 24 33578.0 297.8 0.064802485 0.63535 -0.25852 0.74641 -0.10667
 25 33774.3 296.1 0.000300609 0.00293 -0.01412 0.05198 0.00535
 26 33883.8 295.1 0.009804668 0.09526 -0.07455 0.29733 -0.03602
 27 35135.4 284.6 0.000082278 0.00077 -0.00709 0.02459 -0.01076
 28 35407.8 282.4 0.000798732 0.00743 0.07621 -0.00948 0.03910
 29 35926.6 278.3 0.000115047 0.00105 -0.00515 0.03200 0.00186
 30 36638.9 272.9 0.000108321 0.00097 0.01313 -0.02827 0.00133
 31 37089.0 269.6 0.025129776 0.22306 -0.32760 0.32788 -0.09073
 32 37285.0 268.2 0.000562619 0.00497 -0.02546 -0.04619 0.04676
 33 37492.8 266.7 0.005066476 0.04449 0.08192 0.05697 -0.18582
 34 37674.2 265.4 0.010568444 0.09235 0.16298 0.23378 -0.10552
 35 38138.4 262.2 0.000667190 0.00576 -0.05995 -0.04262 0.01869
 36 38378.9 260.6 0.016939057 0.14530 0.26768 0.27044 0.02267
 37 38815.1 257.6 0.099314545 0.84234 -0.75169 -0.09906 -0.51720
 38 39008.0 256.4 0.000543607 0.00459 -0.04801 -0.03114 0.03623
 39 39263.5 254.7 0.064193345 0.53824 -0.02872 -0.72372 -0.11683
 40 39383.1 253.9 0.004697789 0.03927 -0.07304 -0.14678 -0.11131
 41 39476.6 253.3 0.018531598 0.15454 -0.21833 -0.16196 -0.28397
 42 40036.5 249.8 0.018977885 0.15605 -0.38871 0.06510 -0.02679
 43 40188.1 248.8 0.000938198 0.00769 0.06397 -0.05992 -0.00179
 44 40684.4 245.8 0.004167630 0.03372 -0.05946 -0.08020 0.15413
 45 40692.9 245.7 0.000057549 0.00047 0.00920 0.00700 0.01822
 46 41086.2 243.4 0.014749625 0.11818 -0.19030 0.14573 -0.24644
 47 41357.0 241.8 0.001033814 0.00823 0.08987 -0.00744 -0.00983
 48 41476.3 241.1 0.094460830 0.74977 -0.80867 0.20062 -0.23574
 49 41629.3 240.2 0.033599781 0.26571 0.19094 0.38743 -0.28134
 50 41999.4 238.1 0.045075086 0.35332 -0.12343 0.05713 -0.57864

Triplet excited states from B3LYP/TDDFT/TDA/def2-SVPD

STATE 1: E= 0.048255 au 1.313 eV 10590.6 cm⁻¹ <S²> = 2.000000

203a -> 205a : 0.055024 (c= -0.23457179)

204a -> 205a : 0.942323 (c= 0.97073324)

STATE 2: E= 0.060197 au 1.638 eV 13211.8 cm⁻¹ <S²> = 2.000000

203a -> 205a : 0.936594 (c= -0.96777768)

204a -> 205a : 0.055517 (c= -0.23562120)

STATE 3: E= 0.075917 au 2.066 eV 16661.9 cm⁻¹ <S²> = 2.000000

201a -> 205a : 0.226169 (c= -0.47557274)

202a -> 205a : 0.765317 (c= -0.87482372)

STATE 4: E= 0.083620 au 2.275 eV 18352.5 cm⁻¹ <S²> = 2.000000

201a -> 205a : 0.020267 (c= -0.14236087)

201a -> 207a : 0.023414 (c= -0.15301578)

203a -> 206a : 0.013042 (c= -0.11420043)

203a -> 207a : 0.121105 (c= -0.34800186)

204a -> 206a : 0.751967 (c= 0.86716010)

204a -> 207a : 0.014635 (c= -0.12097444)

STATE 5: E= 0.084351 au 2.295 eV 18513.0 cm⁻¹ <S²> = 2.000000

201a -> 205a : 0.748106 (c= -0.86493146)

202a -> 205a : 0.220286 (c= 0.46934684)

204a -> 206a : 0.021086 (c= -0.14521056)

STATE 6: E= 0.088528 au 2.409 eV 19429.7 cm⁻¹ <S²> = 2.000000

201a -> 206a : 0.037742 (c= -0.19427412)

203a -> 206a : 0.356891 (c= -0.59740354)

204a -> 207a : 0.555902 (c= 0.74558804)

STATE 7: E= 0.091998 au 2.503 eV 20191.3 cm⁻¹ <S²> = 2.000000

199a -> 205a : 0.990411 (c= 0.99519392)

STATE 8: E= 0.098845 au 2.690 eV 21694.1 cm⁻¹ <S²> = 2.000000

200a -> 205a : 0.995258 (c= -0.99762596)
 STATE 9: E= 0.110026 au 2.994 eV 24147.8 cm⁻¹ <S²> = 2.000000
 201a -> 206a : 0.250209 (c= 0.50020879)
 202a -> 206a : 0.015928 (c= 0.12620762)
 202a -> 207a : 0.215656 (c= 0.46438800)
 203a -> 206a : 0.356016 (c= -0.59667087)
 204a -> 206a : 0.017695 (c= -0.13302129)
 204a -> 207a : 0.096476 (c= -0.31060603)
 STATE 10: E= 0.110149 au 2.997 eV 24175.0 cm⁻¹ <S²> = 2.000000
 201a -> 207a : 0.129437 (c= -0.35977322)
 202a -> 206a : 0.504778 (c= -0.71047716)
 202a -> 207a : 0.078159 (c= 0.27956863)
 203a -> 207a : 0.241075 (c= 0.49099354)
 STATE 11: E= 0.112025 au 3.048 eV 24586.7 cm⁻¹ <S²> = 2.000000
 196a -> 205a : 0.884688 (c= 0.94057843)
 198a -> 205a : 0.097301 (c= -0.31193096)
 STATE 12: E= 0.112433 au 3.059 eV 24676.2 cm⁻¹ <S²> = 2.000000
 195a -> 205a : 0.972638 (c= -0.98622414)
 198a -> 205a : 0.020515 (c= -0.14322948)
 STATE 13: E= 0.117926 au 3.209 eV 25881.9 cm⁻¹ <S²> = 2.000000
 201a -> 206a : 0.243882 (c= 0.49384420)
 201a -> 207a : 0.047223 (c= 0.21730785)
 202a -> 206a : 0.032907 (c= 0.18140184)
 202a -> 207a : 0.083949 (c= 0.28973973)
 203a -> 206a : 0.148308 (c= 0.38510727)
 203a -> 207a : 0.096409 (c= 0.31049865)
 204a -> 206a : 0.092413 (c= 0.30399434)
 204a -> 207a : 0.197528 (c= 0.44444157)

STATE 14: E= 0.118661 au 3.229 eV 26043.0 cm⁻¹ <S²> = 2.000000

193a -> 205a : 0.020634 (c= 0.14364396)

194a -> 205a : 0.252852 (c= 0.50284423)

195a -> 205a : 0.011395 (c= 0.10674822)

196a -> 205a : 0.065646 (c= -0.25621521)

197a -> 205a : 0.031683 (c= -0.17799725)

198a -> 205a : 0.613830 (c= -0.78347273)

STATE 15: E= 0.119321 au 3.247 eV 26188.0 cm⁻¹ <S²> = 2.000000

194a -> 205a : 0.090786 (c= -0.30130743)

196a -> 205a : 0.032278 (c= -0.17966017)

197a -> 205a : 0.752341 (c= 0.86737619)

198a -> 205a : 0.113715 (c= -0.33721613)

STATE 16: E= 0.119908 au 3.263 eV 26316.9 cm⁻¹ <S²> = 2.000000

193a -> 205a : 0.047833 (c= 0.21870804)

194a -> 205a : 0.576722 (c= 0.75942198)

196a -> 205a : 0.010000 (c= 0.10000240)

197a -> 205a : 0.209045 (c= 0.45721489)

198a -> 205a : 0.153197 (c= 0.39140329)

STATE 17: E= 0.121043 au 3.294 eV 26565.9 cm⁻¹ <S²> = 2.000000

194a -> 206a : 0.014895 (c= 0.12204591)

201a -> 206a : 0.029088 (c= -0.17055261)

201a -> 207a : 0.065224 (c= 0.25538901)

202a -> 206a : 0.072431 (c= 0.26913062)

202a -> 207a : 0.071450 (c= -0.26730074)

203a -> 206a : 0.071998 (c= -0.26832515)

203a -> 207a : 0.416776 (c= 0.64558163)

204a -> 206a : 0.065314 (c= 0.25556529)

204a -> 207a : 0.105788 (c= -0.32525023)

204a -> 208a : 0.037333 (c= -0.19321814)
 STATE 18: E= 0.125614 au 3.418 eV 27569.2 cm⁻¹ <S²> = 2.000000
 196a -> 208a : 0.013855 (c= -0.11770736)
 199a -> 206a : 0.673982 (c= 0.82096406)
 199a -> 207a : 0.239273 (c= 0.48915549)
 199a -> 212a : 0.022163 (c= 0.14887224)
 STATE 19: E= 0.125988 au 3.428 eV 27651.2 cm⁻¹ <S²> = 2.000000
 198a -> 208a : 0.011294 (c= 0.10627179)
 198a -> 211a : 0.010013 (c= 0.10006602)
 200a -> 206a : 0.481631 (c= 0.69399657)
 200a -> 207a : 0.427657 (c= -0.65395502)
 200a -> 214a : 0.014173 (c= 0.11904898)
 200a -> 215a : 0.012720 (c= -0.11278208)
 STATE 20: E= 0.131579 au 3.580 eV 28878.3 cm⁻¹ <S²> = 2.000000
 193a -> 205a : 0.921618 (c= 0.96000924)
 194a -> 205a : 0.073062 (c= -0.27030075)
 STATE 21: E= 0.136263 au 3.708 eV 29906.4 cm⁻¹ <S²> = 2.000000
 191a -> 207a : 0.010070 (c= 0.10034856)
 193a -> 207a : 0.039147 (c= -0.19785497)
 194a -> 206a : 0.108029 (c= -0.32867810)
 195a -> 206a : 0.022272 (c= -0.14923790)
 197a -> 206a : 0.031869 (c= 0.17851969)
 197a -> 207a : 0.027484 (c= -0.16578383)
 201a -> 206a : 0.010558 (c= -0.10275274)
 201a -> 207a : 0.073518 (c= -0.27114181)
 201a -> 211a : 0.010405 (c= 0.10200460)
 202a -> 206a : 0.110911 (c= 0.33303348)
 202a -> 207a : 0.016111 (c= 0.12692931)

202a -> 208a : 0.023074 (c= -0.15190244)
 203a -> 207a : 0.079621 (c= 0.28217156)
 203a -> 210a : 0.019443 (c= -0.13943949)
 203a -> 211a : 0.026738 (c= 0.16351706)
 204a -> 206a : 0.016987 (c= 0.13033490)
 204a -> 208a : 0.277833 (c= 0.52709880)
 STATE 22: E= 0.138279 au 3.763 eV 30348.8 cm⁻¹ <S²> = 2.000000
 191a -> 206a : 0.013267 (c= -0.11518167)
 193a -> 206a : 0.113193 (c= 0.33644124)
 194a -> 207a : 0.112989 (c= 0.33613775)
 195a -> 206a : 0.075102 (c= 0.27404657)
 195a -> 207a : 0.034514 (c= 0.18578027)
 196a -> 206a : 0.019336 (c= 0.13905296)
 197a -> 206a : 0.032830 (c= 0.18119037)
 197a -> 207a : 0.033274 (c= -0.18241164)
 201a -> 208a : 0.045246 (c= 0.21271162)
 202a -> 207a : 0.012805 (c= 0.11315803)
 203a -> 208a : 0.168632 (c= 0.41064834)
 204a -> 208a : 0.011797 (c= -0.10861613)
 204a -> 210a : 0.130840 (c= -0.36171860)
 204a -> 211a : 0.087886 (c= 0.29645549)
 STATE 23: E= 0.140008 au 3.810 eV 30728.2 cm⁻¹ <S²> = 2.000000
 191a -> 205a : 0.040376 (c= 0.20093803)
 192a -> 205a : 0.255833 (c= -0.50579982)
 194a -> 206a : 0.011293 (c= -0.10627021)
 197a -> 206a : 0.012435 (c= 0.11151273)
 197a -> 207a : 0.016613 (c= -0.12889189)
 201a -> 206a : 0.095559 (c= 0.30912591)

201a -> 207a : 0.085483 (c= 0.29237394)
 202a -> 206a : 0.122713 (c= -0.35030454)
 202a -> 207a : 0.148494 (c= -0.38534972)
 203a -> 210a : 0.030233 (c= -0.17387584)
 204a -> 208a : 0.054414 (c= 0.23326856)
 204a -> 209a : 0.012867 (c= -0.11343400)
 204a -> 210a : 0.023833 (c= -0.15438028)
 STATE 24: E= 0.140147 au 3.814 eV 30758.6 cm⁻¹ <S²> = 2.000000
 191a -> 205a : 0.096331 (c= 0.31037179)
 192a -> 205a : 0.592495 (c= -0.76973679)
 201a -> 206a : 0.053229 (c= -0.23071318)
 201a -> 207a : 0.028463 (c= -0.16871068)
 202a -> 206a : 0.049479 (c= 0.22243952)
 202a -> 207a : 0.078945 (c= 0.28097226)
 203a -> 210a : 0.011898 (c= 0.10907572)
 204a -> 208a : 0.027454 (c= -0.16569190)
 STATE 25: E= 0.143112 au 3.894 eV 31409.5 cm⁻¹ <S²> = 2.000000
 195a -> 206a : 0.028704 (c= -0.16942378)
 195a -> 207a : 0.026415 (c= -0.16252699)
 196a -> 206a : 0.086751 (c= 0.29453495)
 196a -> 207a : 0.102334 (c= 0.31989694)
 197a -> 206a : 0.016795 (c= 0.12959615)
 198a -> 206a : 0.218334 (c= -0.46726235)
 198a -> 207a : 0.062411 (c= 0.24982205)
 199a -> 208a : 0.019651 (c= -0.14018271)
 200a -> 208a : 0.016937 (c= -0.13014039)
 201a -> 206a : 0.060649 (c= -0.24627112)
 201a -> 207a : 0.102973 (c= 0.32089451)

202a -> 206a : 0.011522 (c= -0.10733883)
 202a -> 207a : 0.057408 (c= 0.23960065)
 203a -> 210a : 0.016954 (c= -0.13020722)
 204a -> 209a : 0.041521 (c= -0.20376734)
 STATE 26: E= 0.143291 au 3.899 eV 31448.8 cm⁻¹ <S²> = 2.000000
 195a -> 206a : 0.067639 (c= 0.26007584)
 195a -> 207a : 0.014075 (c= 0.11863947)
 196a -> 206a : 0.366928 (c= -0.60574607)
 196a -> 207a : 0.078768 (c= -0.28065669)
 198a -> 207a : 0.104923 (c= 0.32391884)
 199a -> 208a : 0.041522 (c= 0.20376903)
 199a -> 211a : 0.015659 (c= -0.12513645)
 201a -> 206a : 0.069534 (c= -0.26369328)
 201a -> 207a : 0.049439 (c= 0.22234863)
 202a -> 207a : 0.071303 (c= 0.26702625)
 204a -> 209a : 0.012701 (c= -0.11269767)
 STATE 27: E= 0.143846 au 3.914 eV 31570.5 cm⁻¹ <S²> = 2.000000
 195a -> 206a : 0.010668 (c= -0.10328643)
 196a -> 206a : 0.015483 (c= 0.12443177)
 196a -> 207a : 0.012515 (c= -0.11187173)
 198a -> 206a : 0.212367 (c= 0.46083299)
 198a -> 207a : 0.208847 (c= -0.45699825)
 200a -> 207a : 0.011284 (c= -0.10622585)
 200a -> 208a : 0.025138 (c= 0.15854871)
 200a -> 210a : 0.010328 (c= -0.10162611)
 200a -> 211a : 0.017961 (c= 0.13401743)
 201a -> 206a : 0.091903 (c= -0.30315439)
 201a -> 207a : 0.094600 (c= 0.30757157)

202a -> 207a : 0.086600 (c= 0.29427804)
 203a -> 210a : 0.024523 (c= -0.15659901)
 204a -> 209a : 0.072259 (c= -0.26881086)
 STATE 28: E= 0.146511 au 3.987 eV 32155.6 cm⁻¹ <S²> = 2.000000
 194a -> 206a : 0.019882 (c= -0.14100404)
 195a -> 206a : 0.145407 (c= 0.38132317)
 195a -> 207a : 0.057461 (c= 0.23971117)
 196a -> 206a : 0.026142 (c= 0.16168413)
 197a -> 206a : 0.089419 (c= -0.29903035)
 197a -> 207a : 0.080447 (c= 0.28363254)
 201a -> 207a : 0.065169 (c= -0.25528191)
 202a -> 206a : 0.016676 (c= 0.12913744)
 203a -> 209a : 0.013770 (c= 0.11734664)
 203a -> 210a : 0.050503 (c= -0.22472951)
 203a -> 211a : 0.025805 (c= -0.16063848)
 204a -> 209a : 0.288958 (c= -0.53754787)
 204a -> 210a : 0.013081 (c= -0.11437142)
 STATE 29: E= 0.147293 au 4.008 eV 32327.0 cm⁻¹ <S²> = 2.000000
 193a -> 206a : 0.031295 (c= 0.17690278)
 194a -> 207a : 0.033642 (c= 0.18341784)
 195a -> 206a : 0.174284 (c= -0.41747352)
 195a -> 207a : 0.056318 (c= -0.23731427)
 196a -> 206a : 0.028661 (c= -0.16929513)
 196a -> 207a : 0.012512 (c= -0.11185510)
 197a -> 206a : 0.131232 (c= -0.36226018)
 197a -> 207a : 0.114549 (c= 0.33845083)
 203a -> 208a : 0.023782 (c= 0.15421345)
 203a -> 209a : 0.104151 (c= -0.32272484)

204a -> 210a : 0.181822 (c= -0.42640606)
 204a -> 211a : 0.016523 (c= -0.12854181)
 STATE 30: E= 0.147943 au 4.026 eV 32469.7 cm⁻¹ <S²> = 2.000000
 194a -> 206a : 0.032523 (c= -0.18034235)
 195a -> 206a : 0.075723 (c= 0.27517751)
 195a -> 207a : 0.031453 (c= 0.17734929)
 196a -> 206a : 0.029884 (c= 0.17286994)
 197a -> 206a : 0.112629 (c= -0.33560284)
 197a -> 207a : 0.101843 (c= 0.31912846)
 201a -> 207a : 0.100023 (c= 0.31626413)
 202a -> 206a : 0.021548 (c= -0.14679157)
 203a -> 209a : 0.010968 (c= -0.10472775)
 203a -> 211a : 0.053184 (c= 0.23061680)
 204a -> 208a : 0.092168 (c= 0.30359147)
 204a -> 209a : 0.238744 (c= 0.48861416)
 STATE 31: E= 0.148426 au 4.039 eV 32575.7 cm⁻¹ <S²> = 2.000000
 191a -> 205a : 0.827402 (c= 0.90961647)
 192a -> 205a : 0.131498 (c= 0.36262717)
 STATE 32: E= 0.148927 au 4.052 eV 32685.6 cm⁻¹ <S²> = 2.000000
 191a -> 205a : 0.026134 (c= 0.16165901)
 193a -> 206a : 0.016385 (c= -0.12800439)
 194a -> 207a : 0.036504 (c= -0.19106060)
 195a -> 206a : 0.051292 (c= 0.22647735)
 195a -> 207a : 0.014441 (c= 0.12017119)
 197a -> 206a : 0.045943 (c= 0.21434238)
 197a -> 207a : 0.038548 (c= -0.19633681)
 202a -> 210a : 0.028412 (c= -0.16855838)
 202a -> 211a : 0.013437 (c= -0.11591744)

203a -> 208a : 0.036102 (c= -0.19000542)
 203a -> 209a : 0.290784 (c= -0.53924423)
 204a -> 210a : 0.096446 (c= -0.31055680)
 204a -> 211a : 0.180328 (c= -0.42465026)
 STATE 33: E= 0.157123 au 4.276 eV 34484.6 cm⁻¹ <S²> = 2.000000
 165a -> 205a : 0.028970 (c= -0.17020710)
 183a -> 205a : 0.896449 (c= -0.94681002)
 185a -> 205a : 0.012907 (c= -0.11360684)
 186a -> 205a : 0.019156 (c= 0.13840465)
 STATE 34: E= 0.159602 au 4.343 eV 35028.6 cm⁻¹ <S²> = 2.000000
 198a -> 206a : 0.011728 (c= -0.10829545)
 200a -> 206a : 0.470328 (c= -0.68580460)
 200a -> 207a : 0.476816 (c= -0.69051833)
 STATE 35: E= 0.160731 au 4.374 eV 35276.3 cm⁻¹ <S²> = 2.000000
 164a -> 205a : 0.029810 (c= 0.17265616)
 182a -> 205a : 0.871021 (c= 0.93328497)
 184a -> 205a : 0.012521 (c= 0.11189535)
 186a -> 205a : 0.014682 (c= 0.12116768)
 187a -> 205a : 0.010465 (c= -0.10229829)
 189a -> 205a : 0.013849 (c= -0.11768376)
 190a -> 205a : 0.010030 (c= 0.10014957)
 STATE 36: E= 0.161207 au 4.387 eV 35380.9 cm⁻¹ <S²> = 2.000000
 192a -> 206a : 0.033054 (c= 0.18180760)
 193a -> 207a : 0.014102 (c= -0.11874979)
 201a -> 209a : 0.049472 (c= 0.22242225)
 201a -> 210a : 0.052785 (c= -0.22975071)
 201a -> 211a : 0.077326 (c= -0.27807527)
 202a -> 208a : 0.048538 (c= 0.22031260)

202a -> 209a : 0.356839 (c= 0.59736008)
 202a -> 210a : 0.012900 (c= 0.11357727)
 203a -> 210a : 0.015873 (c= 0.12598673)
 203a -> 211a : 0.087863 (c= 0.29641688)
 204a -> 209a : 0.092971 (c= -0.30491189)
 204a -> 212a : 0.011933 (c= -0.10924050)
 204a -> 213a : 0.011940 (c= 0.10927230)
 STATE 37: E= 0.162324 au 4.417 eV 35626.0 cm⁻¹ <S²> = 2.000000
 191a -> 206a : 0.044885 (c= -0.21186169)
 192a -> 207a : 0.053567 (c= 0.23144606)
 193a -> 207a : 0.010007 (c= -0.10003335)
 194a -> 206a : 0.102841 (c= -0.32068852)
 194a -> 207a : 0.038825 (c= 0.19704118)
 199a -> 206a : 0.035182 (c= -0.18756886)
 199a -> 207a : 0.088391 (c= 0.29730611)
 201a -> 208a : 0.071380 (c= 0.26716965)
 201a -> 209a : 0.041238 (c= 0.20307019)
 202a -> 208a : 0.038244 (c= -0.19555960)
 202a -> 211a : 0.113340 (c= -0.33666042)
 203a -> 208a : 0.071750 (c= -0.26786243)
 203a -> 209a : 0.026979 (c= -0.16425318)
 204a -> 208a : 0.084377 (c= -0.29047771)
 204a -> 210a : 0.059842 (c= 0.24462674)
 STATE 38: E= 0.162795 au 4.430 eV 35729.4 cm⁻¹ <S²> = 2.000000
 191a -> 206a : 0.018309 (c= 0.13531124)
 193a -> 206a : 0.011175 (c= -0.10571391)
 193a -> 207a : 0.045901 (c= -0.21424528)
 194a -> 206a : 0.272642 (c= -0.52215095)

199a -> 207a : 0.025753 (c= 0.16047800)
 201a -> 208a : 0.027848 (c= -0.16687841)
 201a -> 209a : 0.071008 (c= -0.26647282)
 202a -> 210a : 0.028443 (c= 0.16865020)
 202a -> 211a : 0.059290 (c= 0.24349523)
 203a -> 209a : 0.036789 (c= 0.19180543)
 204a -> 208a : 0.210175 (c= -0.45844800)
 204a -> 209a : 0.016594 (c= 0.12881844)
 204a -> 210a : 0.057999 (c= -0.24082977)
 204a -> 211a : 0.014559 (c= -0.12065965)
 STATE 39: E= 0.163570 au 4.451 eV 35899.4 cm⁻¹ <S²> = 2.000000
 193a -> 207a : 0.010214 (c= 0.10106599)
 194a -> 206a : 0.072023 (c= 0.26837126)
 196a -> 206a : 0.010471 (c= 0.10232606)
 199a -> 206a : 0.225375 (c= -0.47473675)
 199a -> 207a : 0.571649 (c= 0.75607458)
 204a -> 208a : 0.044089 (c= 0.20997458)
 STATE 40: E= 0.164441 au 4.475 eV 36090.6 cm⁻¹ <S²> = 2.000000
 191a -> 206a : 0.046760 (c= -0.21624159)
 192a -> 207a : 0.042912 (c= 0.20715264)
 194a -> 206a : 0.032078 (c= 0.17910232)
 194a -> 207a : 0.012987 (c= 0.11396068)
 201a -> 208a : 0.092433 (c= 0.30402868)
 201a -> 209a : 0.101325 (c= -0.31831522)
 202a -> 207a : 0.024187 (c= -0.15552304)
 202a -> 210a : 0.224583 (c= 0.47390193)
 203a -> 208a : 0.190118 (c= -0.43602559)
 203a -> 209a : 0.011130 (c= 0.10549868)

204a -> 210a : 0.092260 (c= -0.30374282)
 204a -> 211a : 0.049639 (c= -0.22279744)
 STATE 41: E= 0.165360 au 4.500 eV 36292.4 cm⁻¹ <S²> = 2.000000
 191a -> 206a : 0.014029 (c= -0.11844268)
 191a -> 207a : 0.058194 (c= -0.24123379)
 192a -> 206a : 0.145509 (c= 0.38145665)
 193a -> 207a : 0.010412 (c= -0.10203707)
 201a -> 207a : 0.076785 (c= -0.27710167)
 201a -> 208a : 0.018113 (c= 0.13458583)
 201a -> 210a : 0.063133 (c= 0.25126232)
 202a -> 208a : 0.238532 (c= 0.48839784)
 202a -> 209a : 0.046276 (c= -0.21511867)
 202a -> 210a : 0.032982 (c= -0.18160850)
 203a -> 210a : 0.106348 (c= -0.32610978)
 203a -> 211a : 0.012667 (c= 0.11254902)
 204a -> 208a : 0.010631 (c= -0.10310850)
 204a -> 209a : 0.050473 (c= 0.22466164)
 STATE 42: E= 0.166936 au 4.543 eV 36638.2 cm⁻¹ <S²> = 2.000000
 189a -> 205a : 0.354547 (c= 0.59543869)
 190a -> 205a : 0.641849 (c= 0.80115510)
 STATE 43: E= 0.170195 au 4.631 eV 37353.4 cm⁻¹ <S²> = 2.000000
 182a -> 205a : 0.021817 (c= -0.14770454)
 189a -> 205a : 0.629916 (c= -0.79367238)
 190a -> 205a : 0.343078 (c= 0.58572833)
 STATE 44: E= 0.171141 au 4.657 eV 37561.1 cm⁻¹ <S²> = 2.000000
 191a -> 206a : 0.030641 (c= 0.17504679)
 192a -> 207a : 0.063175 (c= -0.25134578)
 193a -> 206a : 0.327243 (c= 0.57205188)

194a -> 207a : 0.180395 (c= 0.42472888)
 201a -> 208a : 0.034859 (c= -0.18670459)
 202a -> 211a : 0.010513 (c= 0.10253504)
 203a -> 208a : 0.142829 (c= -0.37792784)
 204a -> 210a : 0.063722 (c= 0.25243191)
 204a -> 211a : 0.034236 (c= -0.18503051)
 204a -> 215a : 0.010149 (c= 0.10074047)
 STATE 45: E= 0.174894 au 4.759 eV 38384.9 cm⁻¹ <S²> = 2.000000
 191a -> 206a : 0.020926 (c= 0.14465883)
 192a -> 207a : 0.014781 (c= -0.12157671)
 194a -> 207a : 0.033348 (c= -0.18261337)
 201a -> 209a : 0.079626 (c= 0.28218113)
 202a -> 210a : 0.017619 (c= -0.13273650)
 202a -> 211a : 0.017012 (c= -0.13043002)
 203a -> 208a : 0.241335 (c= -0.49125832)
 203a -> 209a : 0.079796 (c= 0.28248168)
 204a -> 208a : 0.010104 (c= -0.10052061)
 204a -> 209a : 0.016195 (c= 0.12725793)
 204a -> 210a : 0.184344 (c= -0.42935281)
 204a -> 211a : 0.201968 (c= 0.44940876)
 STATE 46: E= 0.178672 au 4.862 eV 39214.1 cm⁻¹ <S²> = 2.000000
 196a -> 206a : 0.022031 (c= -0.14842992)
 196a -> 207a : 0.022467 (c= -0.14989116)
 198a -> 206a : 0.374364 (c= -0.61185303)
 198a -> 207a : 0.292843 (c= -0.54114949)
 200a -> 208a : 0.011691 (c= 0.10812528)
 201a -> 209a : 0.020248 (c= 0.14229699)
 201a -> 210a : 0.012109 (c= -0.11004061)

202a -> 208a : 0.015160 (c= -0.12312604)
 203a -> 209a : 0.046276 (c= 0.21511791)
 203a -> 210a : 0.049793 (c= -0.22314322)
 204a -> 209a : 0.016987 (c= 0.13033327)
 204a -> 211a : 0.037327 (c= -0.19320265)
 STATE 47: E= 0.179033 au 4.872 eV 39293.1 cm⁻¹ <S²> = 2.000000
 194a -> 206a : 0.025073 (c= 0.15834396)
 194a -> 207a : 0.010629 (c= 0.10309575)
 196a -> 207a : 0.010753 (c= 0.10369698)
 198a -> 206a : 0.105488 (c= 0.32478985)
 198a -> 207a : 0.090231 (c= 0.30038464)
 201a -> 209a : 0.051204 (c= 0.22628307)
 201a -> 210a : 0.024469 (c= -0.15642457)
 202a -> 208a : 0.023192 (c= -0.15229029)
 202a -> 209a : 0.022750 (c= 0.15083121)
 203a -> 208a : 0.018851 (c= 0.13729895)
 203a -> 209a : 0.146331 (c= 0.38253243)
 203a -> 210a : 0.134337 (c= -0.36652054)
 204a -> 209a : 0.050225 (c= 0.22410882)
 204a -> 211a : 0.166700 (c= -0.40828931)
 STATE 48: E= 0.179372 au 4.881 eV 39367.5 cm⁻¹ <S²> = 2.000000
 197a -> 206a : 0.417861 (c= 0.64642159)
 197a -> 207a : 0.456131 (c= 0.67537484)
 197a -> 208a : 0.025591 (c= -0.15997194)
 197a -> 211a : 0.010034 (c= -0.10016992)
 202a -> 208a : 0.014626 (c= -0.12093761)
 STATE 49: E= 0.180441 au 4.910 eV 39602.3 cm⁻¹ <S²> = 2.000000
 193a -> 206a : 0.040555 (c= -0.20138345)

193a -> 207a : 0.017354 (c= -0.13173484)
 194a -> 206a : 0.084788 (c= 0.29118423)
 197a -> 206a : 0.022615 (c= -0.15038207)
 197a -> 207a : 0.010807 (c= -0.10395572)
 201a -> 209a : 0.044689 (c= -0.21139682)
 201a -> 210a : 0.029989 (c= -0.17317331)
 202a -> 208a : 0.063805 (c= -0.25259578)
 202a -> 210a : 0.035918 (c= 0.18952127)
 202a -> 211a : 0.012752 (c= 0.11292695)
 203a -> 209a : 0.124945 (c= -0.35347574)
 203a -> 210a : 0.243953 (c= -0.49391573)
 204a -> 208a : 0.021038 (c= -0.14504449)
 204a -> 210a : 0.024009 (c= 0.15494714)
 204a -> 211a : 0.103391 (c= 0.32154477)
 STATE 50: E= 0.182279 au 4.960 eV 40005.6 cm**⁻¹ <S**2> = 2.000000
 191a -> 207a : 0.010547 (c= -0.10269879)
 192a -> 206a : 0.056406 (c= 0.23749909)
 196a -> 206a : 0.230746 (c= -0.48036015)
 196a -> 207a : 0.449149 (c= 0.67018546)
 196a -> 208a : 0.014088 (c= 0.11869254)
 198a -> 206a : 0.011249 (c= 0.10606233)
 198a -> 207a : 0.040656 (c= -0.20163407)
 199a -> 208a : 0.014651 (c= -0.12104124)
 202a -> 208a : 0.042988 (c= -0.20733554)
 203a -> 210a : 0.038834 (c= 0.19706296)

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