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Access to Corrole-Appended Persubstituted Benzofurans by a Multicomponent Reaction: The Dual Role of *p*-Chloranil

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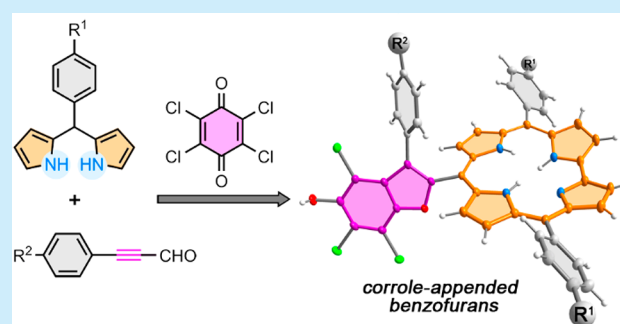


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Supporting Information

ABSTRACT: A multicomponent reaction among dipyrroles, aryl-propargyl aldehydes, and *p*-chloranil leading to 10-(benzofuran-2-yl)corroles is described. *p*-Chloranil was identified as a crucial reagent playing a twofold role: an oxidant taking part in the formation of the corrole macrocycle and a component undergoing heteroannulation to the incipient 10-arylethynylcorrole. A series of corroles bearing persubstituted benzofuran-2-yl moieties have been synthesized, and their fundamental electronic properties have been studied via UV–vis absorption and fluorescence spectroscopies.



Corroles are ring-contracted porphyrinoids lacking one *meso* bridge in comparison to the closely related porphyrins.^{1,2} Considerable synthetic advances in the past decade have inspired great progress in the chemistry of these aromatic macrocycles, fueled by considerable synthetic advances.^{3–5} For example, recent reports have demonstrated that essentially any metal center may be introduced into the cavity of these macrocycles^{6,7} and that a corrole macrocycle may be equipped with a variety of aryl substituents.² The coordination chemistry of corroles has been expanded,⁶ and these macrocycles have also been applied as a pivotal material in research related to cancer-targeting imaging and treatment⁸ and supramolecular chemistry⁹ and as catalysts for carbon dioxide reduction, water oxidation,^{10,11} and decomposition of reactive nitrogen species.¹²

In stark contrast to porphyrins, the π -expansion of corrole chromophores has been achieved only a few times.^{13–17} In particular, this striking difference exists as far as *meso*-arylethynyl derivatives are concerned. Indeed, arylethynyl substituents attached to the porphyrin core have become important structural motifs for tuning the photophysical properties of the parent chromophore;^{18–25} several strategies for the synthesis of arylethynyl porphyrins are well-established.²⁶ On the contrary, only a few reports have presented arylethynylcorroles.^{27–30}

Retrosynthetic analysis of a corrole bearing one arylethynyl unit at a *meso*-10 position indicates two possible strategies. The first approach includes the synthesis of silyl-protected ethynylcorrole, cleavage of a silyl group, followed by the coupling reaction between ethynylcorrole and an aryl coupling partner. The second strategy is based on a condensation between aryl-propargyl aldehyde and dipyrrole. It is worth

noting that the most routine synthesis of arylethynyl-porphyrins, i.e., from 5,10-dibromoporphyrins via Sonogashira reaction,³¹ could not be directly applied due to the lack of access to analogous 10-bromocorroles. Our positive experience with the preparation of 5,15-bis(phenylethynyl)-10,20-diphenyl-porphyrins from aryl-propargyl aldehydes³² inspired us to attempt an analogous approach toward corroles.

We selected electron-rich 5-(4-methoxyphenyl)dipyrrole and electron-poor 5-nitrophenylethynyl aldehyde for an initial test reaction (Table 1). The corrole synthesis was performed in a water/MeOH system using hydrochloric acid as a catalyst.⁵ Purification by column chromatography and size-exclusion chromatography, followed by crystallization, afforded a green solid of analytical purity in low yield, which we expected to be *trans*-A₂B-corrole possessing a 4-methoxyphenylethynyl substituent at position 10. Surprisingly, the ¹H NMR spectra of this dye possessed a pronounced fine structure (rarely observed for corrole spectra measured at room temperature). The signals in ¹H NMR spectra of A₃-corroles are typically broad due to various processes involving cavity NHs.³³ In the ¹H NMR spectrum of this new corrole, there were four doublets in the 8.80–8.35 ppm region of the spectrum with coupling constants *J* of 3.3–4.6 Hz, which were assigned to β protons, a doublet corresponding to the AA'BB' system of

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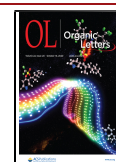
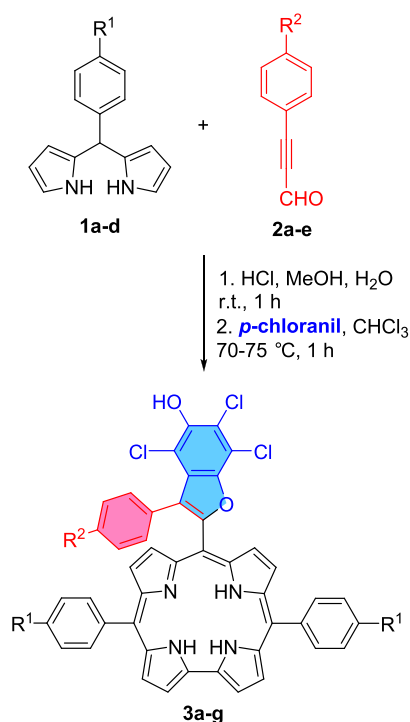


Table 1. Synthesis of Corrole-Appended Benzofurans from Dipyrroles, Aryl-propargyl Aldehydes, and *p*-Chloranil

dipyrrene	R ¹	aldehyde	R ²	corrole	yield (%)
1a	OMe	2a	NO ₂	3a	6.0
1a	OMe	2b	CN	3b	4.5
1a	OMe	2c	OMe	3c	3.1
1a	OMe	2d	H	3d	11.4
1b	Me	2b	CN	3e	11.0
1c	CO ₂ Me	2a	NO ₂	3f	2.7
1d	SMe	2a	NO ₂	3g	5.1

methoxyphenyl substituents with a *J* of 8.5 Hz, and an unusually broad singlet; these were ascribed to aromatic protons of (4-nitrophenyl)ethynyl (see the [Supporting Information](#)). The formation of a corrole core was supported by total integration of the proton NMR signals and their presence in a diagnostic region of the spectrum characteristic of corroles. Interestingly, however, the anticipated signal at *m/z* 655.2 was not found in mass spectra measured for 3a. Peaks located at *m/z* 865.1 in both MALDI and FD mass spectra were instead observed, indicating a different course of the reaction, in which a fragment derived from *p*-chloranil had to be incorporated into the corrole structure.

Intrigued by this finding, we resolved to investigate the scope of the reaction by carrying out analogous condensation with other combinations of aryl-dipyrroles **1a–d** bearing neutral or electron-donating substituents and phenylpropargylaldehydes **2a–d** (Table 1). Analogous nonpolar products **3a–g** were obtained in each case, although the yields vary significantly (2.7–11.4%). In contrast, electron-poor dipyrroles, such as 5-(pentafluorophenyl)dipyrromethene, did not afford the corresponding product.

We found that the presence of *p*-chloranil was crucial for this condensation. Analogous reactions between dipyrrene **1a** and aldehyde **2a** were performed using various oxidants in the second step, such as DDQ, *p*-benzoquinone, and BAIB. Formation of analogous products was not observed for the

last two oxidants, while the reaction with the structurally closest DDQ afforded a complex mixture. In this latter case, several green products were produced, albeit in only trace amounts. The results of these experiments led to the conclusion that *p*-chloranil plays a key role in stabilizing the structure of the resulting product. We note that the expected 10-(4-nitrophenylethynyl)corrole was not formed under any of these conditions.

Ultimately, we pursued X-ray crystallographic analysis of one of our corrole products to unambiguously assign its structure. We obtained X-ray quality crystals of product **3e** from a mixture of THF and hexanes and found that the product is an adduct of the desired 10-(arylethynyl)corrole with *p*-chloranil, in which the corrole is substituted with a highly functionalized benzofuran rather than the intended alkyne group. In the solid state, the benzofuran ring is oriented far out of the plane of the two closest pyrrole rings, with torsion angles of ~63°. The corrole ring itself is very contorted, with torsion angles between the pyrrole rings of ~4°, ~8°, ~10°, and nearly ~21°. The steric influence of the benzofuran ring and its specific rotational angle likely plays a role in how strain is distributed throughout the corrole ring. The corrole molecules assemble into hydrogen-bonded dimers in the solid state: these interactions involve two symmetry-related hydrogen bonds between the most out-of-plane pyrrole hydrogen of one molecule of **3e** and the basic pyrrole nitrogen of a second molecule of **3e** (Figure 1b). The molecules within the dimer are oriented in an antiparallel manner with an interplanar distance of ~3.57 Å. The dimer interacts with other dimers in a stack via C–H... π interactions between the 4-methylphenyl substituent and the corrole cores, and with neighboring stacks through chalcogen–chalcogen interactions (Figure S2). Importantly, determining the crystal structure of **3e** allowed

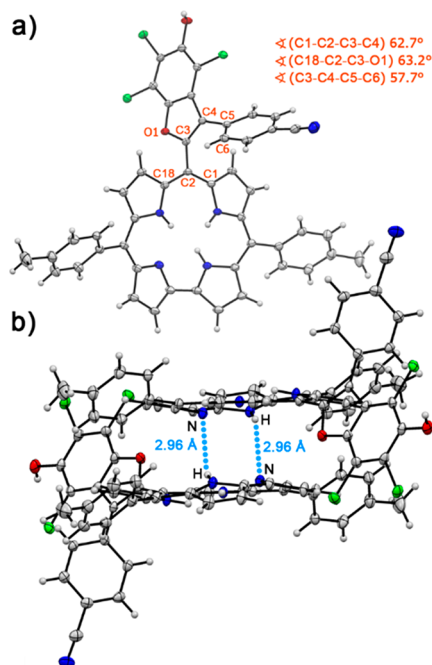


Figure 1. (a) Solid-state structure of **3e** determined by X-ray analysis at 100 K. The ORTEP drawing is shown with 50% probability. (b) Hydrogen-bonded dimer of **3e** as found in the solid state. Solvent molecules have been omitted for the sake of clarity. Legend: C, gray; N, blue; O, red; Cl, green; H, white.

us to also assign the structures of the other members of this unusual new class of corrole macrocycles. The optimized structure of **3e** at the B3LYP^{34–36}/def2-SVP³⁷ (CH₂Cl₂, PCM model) level of theory corresponds well to the geometry observed in the single crystal. All molecules show similar torsion angles between benzofuran and the corrole core (57–60°).

It is well-known that, due to its high electron affinity (first reduction potential of –0.42 V), *p*-chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) is a standard reagent, widely used as a stoichiometric oxidant.^{38,39} Although ubiquitous in organic chemistry, examples of *p*-chloranil acting as a coupling reagent whose core is embedded in the final product are rather limited, encompassing photochemical transformations,^{40–43} hydroquinone-bridged tripyrrins,⁴⁴ and bis-porphyrins,⁴⁵ as well as push–pull systems based on benzoquinones.⁴⁶

Benzofurans, as a class of compounds, are widespread in nature and have been found to display a wide spectrum of biological activities.^{47,48} Because of these features, benzofurans have attracted the particularly close attention of the pharmaceutical researchers as well as organic chemists.^{49–53} Notably, the metal-free, spontaneous formation of benzofurans has been seldom reported.

We investigated fundamental spectroscopic properties of all final corrole-appended persubstituted benzofurans, which are summarized in Table S1. They do not differ markedly from the spectral properties of other *trans*-A₂B-corroles bearing sterically hindered substituents. The Soret bands of this series of compounds are located at ~420 nm with the molar absorption coefficient (ϵ) reaching 110000–140000 M⁻¹ cm⁻¹, and Q bands are located in the spectral range of 580–640 nm. The emission maxima for all dyes are located at ~675 nm. The fluorescence quantum yields (Φ_f) are significantly lower than those of other *trans*-A₂B-corroles^{54,55} (0.3–3% vs 15–20%). Replacing toluene with DCM or 2-methyltetrahydrofuran had a negligible effect on the photophysical properties of these corroles (Supporting Information).

According to the time-dependent density functional theory calculations (CAM-B3LYP⁵⁶/def2-SVP, solvent CH₂Cl₂, PCM model), the lowest-energy electronic transition in these compounds involves mainly a transition from the HOMO to the LUMO. The main transitions are of charge transfer (CT) character for corroles **3a**, **3g**, and **3f** or arise from π – π^* transitions (see, e.g., Figure 2), with some contribution of CT for some corroles, which may contribute to quenching of fluorescence (for the detailed discussion, see the Supporting Information).

In conclusion, we have developed an atom-economic, multicomponent reaction leading to *trans*-A₂B-corroles possessing a sterically hindered, persubstituted benzofuran-2-yl substituents at position *meso*-10. *p*-Chloranil both oxidizes tetrapyrane to corrole and undergoes addition to the C≡C bond, which ultimately leads to formation of the benzofuran scaffold. The electron richness of the corrole appears to be essential in activating the C≡C bond toward this addition. The driving forces underlying addition of the triple bond to *p*-chloranil highlight its novel reactivity. Our findings enlarge the spectrum of possibilities within the synthetic chemistry of corroles and highlight uncommon coupling as well as opening the way to understanding the reactivity of tetrachloro-*p*-benzoquinone.

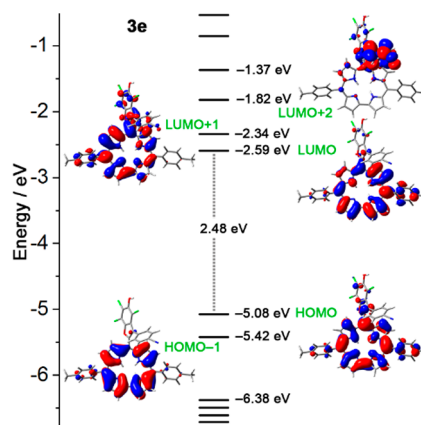


Figure 2. Kohn–Sham orbital energy level diagram of **3e** calculated at the B3LYP/def2-SVP (solvent CH₂Cl₂, PCM model) level of theory and contour plots of selected orbitals (isovalue of 0.02 au).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c03133>.

Experimental details and spectral data for all products as well as mechanistic considerations and photophysical data (PDF)

Accession Codes

CCDC 2012994 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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DEDICATION

In memory of Prof. François Diederich.

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