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Charged- and Multi-Exciton Dynamics in Colloidal Quantum Dot Molecules

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Abstract: Multicarrier states in quantum dots are confined to small volumes, resulting in increased nonradiative Auger recombination rates with implications for different optoelectronic applications. Recently, the synthesis of coupled colloidal quantum dot molecules obtained by the fusion of two core-shell quantum dots has been demonstrated, providing a new physical landscape for multiexciton states. In these nanostructures the excitons may now share a core (intra-dot, localized) or occupy different cores (inter-dot, segregated). Here we employ femtosecond transient absorption spectroscopy to investigate the multiexciton dynamics in coupled quantum dot dimers. We observe that multi-exciton populations in the dimers live significantly longer in comparison to the parent monomers, in contrast to the single exciton regime, where dimers show a faster excited state decay due to charging effects. We globally fit the transient absorption data at different excitation densities using a nonlinear kinetic model that accounts for both intra-dot and inter-dot recombination processes. We find that, while intra-dot multiexcitons show Auger rates similar to the monomers, inter-dot states have reduced Auger rates. These results pave the way for the rational design of new quantum dot molecules with tailored multiexciton properties.

Main Text

Semiconductor quantum dots (QDs) have attracted significant attention due to their unique optical and electronic properties arising from quantum confinement effects.¹ In well-passivated QDs the recombination dynamics of single excitons are predominantly governed by intrinsic radiative mechanisms, on a few to tens of nanoseconds timescale.^{2,3} However, these dynamics are significantly altered when multiple excitons are introduced into the QD, activating a non-radiative recombination pathway known as Auger recombination.^{4,5} In this process, many-body interactions between several carriers leads to an electron-hole recombination event releasing energy which promotes other carriers to higher energy levels, thus decreasing the overall excited carrier population. The timescales of multi-exciton (MX) Auger recombination, which depend on the QD size, composition and exciton multiplicity, range from a few to several hundred picoseconds.^{4,5} These timescales are typically significantly shorter than radiative lifetimes, resulting in low photoluminescence efficiencies of multicarrier states.^{5,6}

The short lifetime of MX states imposes challenges for the use of QDs in several applications, such as lasers⁷⁻⁹, displays¹⁰, light-emitting diodes^{8,11}, and quantum light sources¹². Early strategies to increase multicarrier lifetimes in QDs include the development of larger volume nanostructures, such as nanorods,¹³⁻¹⁵ dot-in-rod particles,¹⁶⁻¹⁸ and giant QDs with thick shells.¹⁹ Another approach has been the controlled alloying of the core-shell interface to smoothen the interface potentials,^{8,10,18,19} which also impact carrier localization.²² However, none of these approaches promoted the breakthrough required for QD applications where MX states are key.

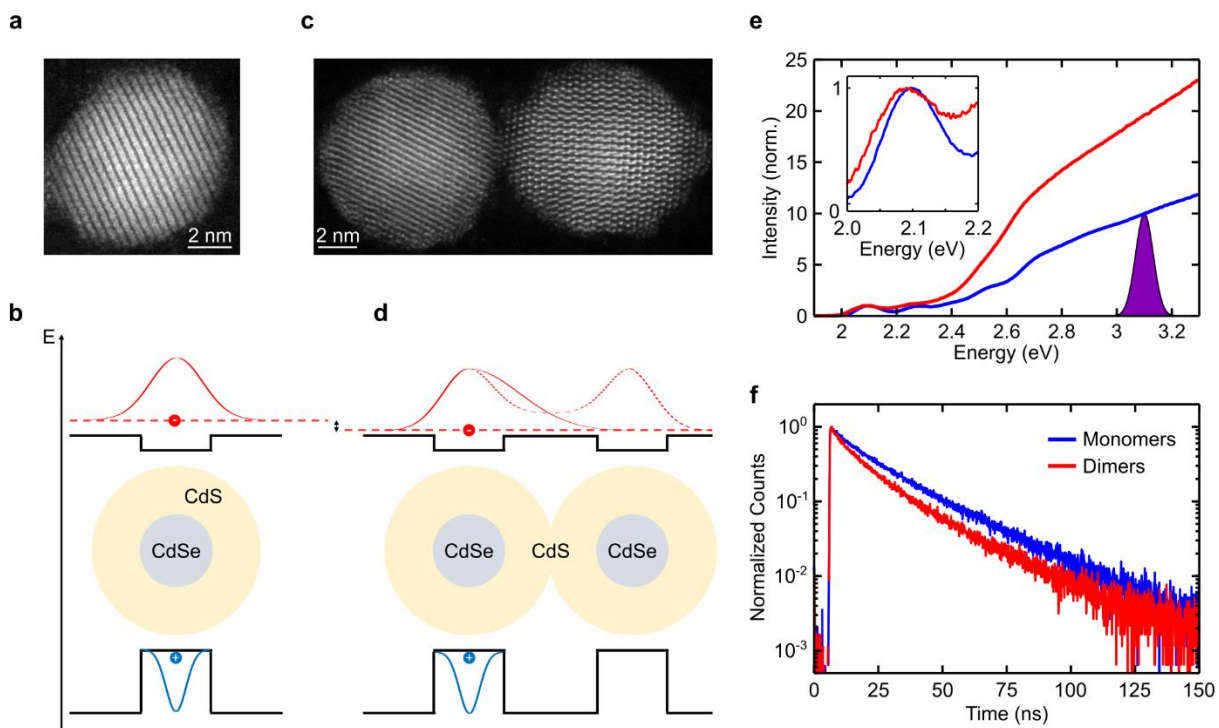


Figure 1. (a) STEM image of the monomer. (b) Scheme for the potential energy landscape of the monomer along with a cross section of the lowest state hole wave-function (blue), and the lowest state electron wavefunction (red). (c) STEM image of the dimer. (d) Scheme for the potential energy landscape of the dimer along with a cross section of the lowest state hole wavefunction (blue), and the lowest state electron wavefunction without (dashed red) and with Coulombic interaction (red). (e) Ensemble absorption spectra normalized to the bandgap absorption for the monomer (blue) and dimer (red) together with the spectrum of the 3.10 eV excitation pulses used in the ultrafast experiments (purple, normalized to 10). Inset: zoom in on the 1S exciton absorption peak of both monomer (blue) and dimer (red) to highlight the redshift upon fusion. (f) Normalized ensemble time-resolved photoluminescence measurements for monomers (blue) and dimers (red).

Recently, it was demonstrated that two QDs can be fused through a process known as constrained oriented attachment, resulting in the formation of a coupled QD molecule, hereafter

referred to as a dimer, while a single QD will be referred to as a monomer.^{23–29} As nanostructures formed by the fusion of two monomers — each independently exhibiting atom-like properties — dimers inherently possess the defining characteristics of artificial molecules. In dimers, the wavefunctions of charge carriers can hybridize as a result of the electronic coupling, which can be tuned via geometrical and compositional parameters.^{23,30} Consequently, dimers exhibit distinct optical properties compared to monomers, including a redshift and broadening of both absorption and emission spectra, as well as an absorption cross-section twice as intense at higher photon energies.^{23,24,28} Moreover, recent single-particle spectroscopy studies have shown that dimers display stronger and more diverse emission properties, attributed to the dominance of photon emission from MX states, in contrast to the well-characterized single-exciton emission of monomers.^{26,29} This observation brings to light a crucial difference between monomers and dimers: in the latter, MX states are not constrained to share the same core, and segregated MXs including carriers in both cores may benefit from the physical separation to possess much reduced Auger rates, potentially explaining the distinct emissive behavior of dimers compared to monomers.

Here we use femtosecond transient absorption (TA) spectroscopy to directly track the population dynamics of MXs and single excitons in QD monomers and dimers. By systematically increasing the excitation fluence, we explore both the single- and multi-exciton excitation regimes. We find that, although dimers present faster decay dynamics in the single-exciton regime, they show much slower population depletion in the multi-exciton regime in comparison to monomers. To rationalize this behavior, we develop a kinetic model that accounts for the presence of both localized and segregated MX species in dimers. We find that localized MXs exhibit an Auger recombination rate of approximately $(410 \text{ ps})^{-1}$, only moderately lower than that in monomers, attributable to the increased QD volume. However, segregated MX configurations, characterized

by a significantly lower Auger recombination rate of $(1.94 \text{ ns})^{-1}$, become statistically dominant at higher fluences, accounting for the prolonged lifetime of the MX population within the dimers.

The monomer studied is a CdSe/CdS core-shell QD, consisting of a core of CdSe (smaller bandgap material) embedded within a shell of CdS (larger bandgap material). A scanning transmission electron microscopy (STEM) image of the monomer is shown in Figure 1a. The core has a diameter of 2.7 nm, while the shell thickness is 2.1 nm. The conduction band offset between the core and the shell is relatively small, $\approx 0.1 \text{ eV}$.³¹ During the formation of the core-shell, the confinement energy surpasses the conduction band offset, resulting in a quasi-type II band alignment. In this configuration, the electron wavefunction, shown as red curve in Figure 1b, is partially delocalized into the shell region. Conversely, the valence band offset is significantly larger, about 0.64 eV. As a result, and due to its greater effective mass compared to the electron, the hole, represented by the blue wavefunction in Figure 1b, remains predominantly localized within the core.^{24,28}

Upon fusion of two monomers, we obtained a CdSe/CdS core-shell homodimer (Figure 1c), hereafter simply referred to as dimer, where the two cores are closely spaced, with a CdS region termed the "neck" separating them. The potential energy barrier of this neck region is determined by the band offsets between CdSe and CdS, as illustrated in Figure 1d. The delocalization of the electron wavefunction extending beyond each core into the neck region results in the emergence of electron states within the dimer formed by hybridization of the monomer electron states²⁴. Analogously to a diatomic molecule, the hybridized wavefunctions would ideally result in an anti-symmetric anti-bonding state and a symmetric bonding state, illustrated by the dashed red line in Figure 1d, with the latter exhibiting a redshift by the hopping energy compared to the monomer electron state (as indicated by the double-headed arrow in Figure

1b,d). In practice, the Coulomb interaction between the electron and the localized hole leads to a significant deviation from the ideal bonding and anti-bonding electron states, which ultimately results in the electron wavefunction represented as solid red line in Figure 1d. Nevertheless, significant tunneling coupling persists in the electron wavefunction, leading to a redshift of the lowest excitonic transition of the dimer compared with the monomer, shown in Figure 1e.

The monomer absorption spectrum, represented as a blue solid line in Figure 1e, includes several distinct bands in the visible. The lowest energy transition centered at 2.10 eV is associated with the CdSe core band-edge exciton, which will be hereafter referred to as the 1S exciton, using the conventional notation for QD states.³² The absorption spectrum of the dimers, represented as a red solid line in Figure 1e, shows the effects of electronic coupling. First, the dimer 1S exciton experiences a redshift by approximately 15 meV, emphasized in the inset in Figure 1e. Moreover, the dimer absorption spectrum appears broadened, lacking the distinctive features observed in the monomers. The normalized ensemble time-resolved photoluminescence dynamics of both the monomers (blue) and the dimers (red) are shown in Figure 1f. Both display a triexponential decay (see Figure S1), with the longest time constant (29.6 ns) representing the single-exciton radiative lifetime.

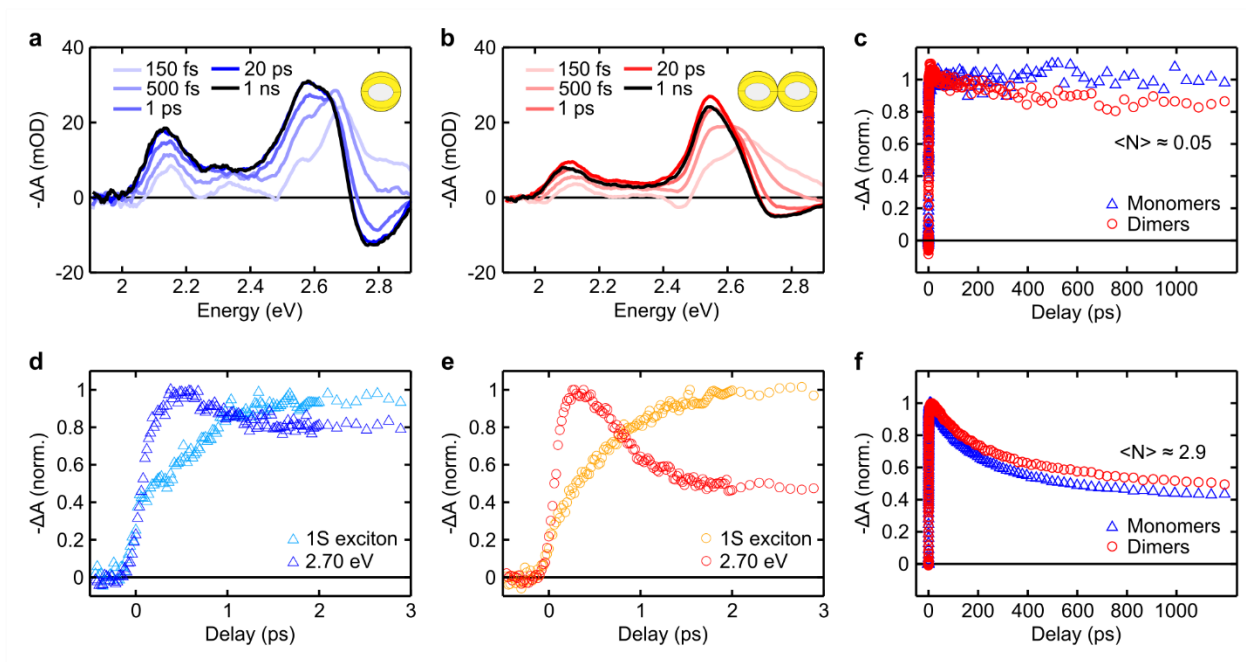


Figure 2. (a,b) Temporal evolution of the TA spectra of monomers (a) and dimers (b) for 3.10 eV photoexcitation in the single-exciton regime ($\langle N \rangle \approx 0.05$). (c) Normalized TA dynamics of the 1S exciton of the monomers (blue) and of the dimers (red) for 3.10 eV photoexcitation for $\langle N \rangle \approx 0.05$. (d,e) Normalized TA dynamics of the 1S exciton of the core (light color) and that corresponding to the onset of the shell absorption around 2.70 eV (dark color) of the monomers (d) and the dimers (e). (f) Normalized TA dynamics of the 1S exciton of the monomers (blue) and of the dimers (red) for 3.10 eV photoexcitation in the multi-exciton regime ($\langle N \rangle \approx 2.9$).

To study the sub-nanosecond dynamics of multi-carrier states in these systems we used femtosecond TA spectroscopy. We first examine the single-exciton regime, achieved by excitation with a pulse at 3.10 eV (whose spectrum is represented as a purple area in Figure 1e) and fluence that corresponds to an average number of excitons per QD $\langle N \rangle \approx 0.05$ (see SI for the calculation of $\langle N \rangle$). Figure 2a illustrates the temporal evolution of the TA spectra of the monomers in the single-exciton regime. Upon excitation at photon energies well above the 2.10 eV bandgap, high-energy electron-hole pairs are generated. These hot carriers undergo cooling towards lower energy

states on the few hundred femtosecond timescale (see Figure 2d).³³ This results in an instantaneous rise of the PB signal around 2.70 eV (already involving also CdS shell states), followed by the delayed rise of the PB of lower energy transitions. Following the relaxation to the 1S exciton, the TA dynamics of the monomers is flat in our 1.2 ns observation window, governed by the much slower radiative recombination (see Figure 1f).

When exciting the dimers under the same conditions (3.1 eV, $\langle N \rangle \approx 0.05$) the temporal evolution of the TA spectra (Figure 2b) shows similar features to that of the monomers, including the relaxation of hot carriers at early times, shown in Figure 2e. However, unlike the monomers, the dimers show a signal decay of approximately 20%, which can be observed both in the TA spectrum at 1 ns (black line in Figure 2b) and in the normalized relaxation dynamics of the 1S exciton (red circles in Figure 2c). This faster decay reveals an additional recombination mechanism in the dimers.

To reach the MX regime, we gradually increased the excitation fluence and the average number of excitons per QD. We are limited to $\langle N \rangle \leq 3$, as state filling effects compete with Auger processes above this threshold (see Figure S3). Figure 2f compares the 1S exciton relaxation dynamics in monomers and dimers for $\langle N \rangle = 2.9$. Interestingly, in the high fluence regime the dimer 1S exciton PB decays more slowly than in the monomers, reversing the trend observed in Figure 2c for the single-exciton regime.

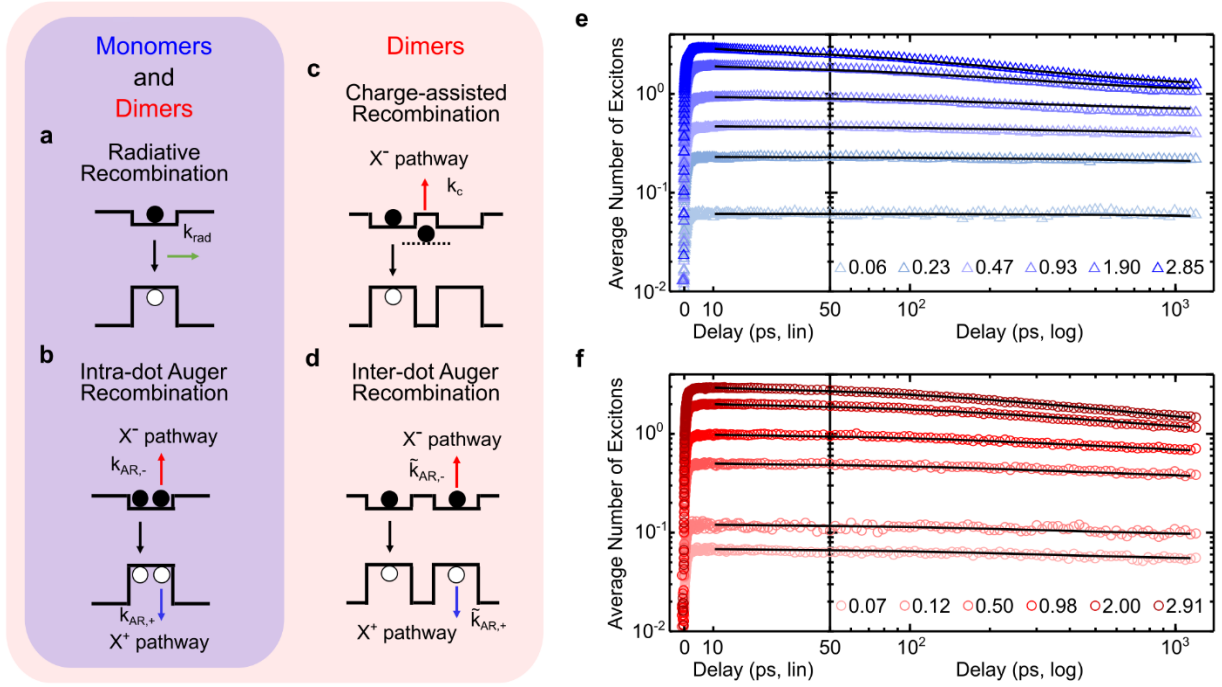


Figure 3. (a,b) Sketch of the one- and two-exciton annihilation mechanisms present in both the monomers and the dimers, namely (a) radiative recombination, and (b) intra-dot Auger recombination. (c,d) Sketch of the two extra exciton annihilation mechanisms present only in the dimers, namely (c) charge-assisted recombination, and (d) inter-dot Auger recombination. (e,f) Fluence-dependent TA dynamics of the 1S exciton of the monomer (e) and of the dimer (f) for 3.10 eV photoexcitation normalized to the average number of excitons photogenerated per nanocrystal, representing the dynamics of the average number of excitons per QD. The fits considering the exciton annihilation mechanisms presented in (a-d) are shown as black solid lines.

To investigate the mechanisms governing the MX decay dynamics, we developed a nonlinear kinetic model that accounts for exciton and biexciton recombination mechanisms in both monomers and dimers. The rate equation for exciton population n in the monomers reads

$$\frac{dn}{dt} = -k_{rad}n - k_{AR}\frac{n(n-1)}{2} \quad (1)$$

where the first term on the right-hand side represents linear exciton radiative decay with rate k_{rad} (Figure 3a), whereas the second term describes nonlinear Auger recombination.³⁴ In modeling biexciton Auger recombination, we adopted the electron-hole picture in the weak confinement regime, which allows us to treat it as a bimolecular annihilation process between two excitons, as opposed to the conventional interpretation of a three-particle collision involving separate electrons and holes.³⁵ Within this picture, Auger decay of a biexciton occurs with the rate k_{AR} that is the sum of the rates of the two independent pathways wherein either an electron (X^- pathway, $k_{\text{AR},-}$) or a hole (X^+ pathway, $k_{\text{AR},+}$) is excited within the same band during exciton recombination (Figure 3b). This process scales with the number of possible biexciton combinations that n excitons can form.

The value of $\langle N \rangle$ at each excitation fluence can be computed from experimental parameters (see SI). Knowing $\langle N \rangle$, we calculate the probability that a monomer contains $n_0 = 1, 2, \dots$, excitons, with the assumption that photon absorption transitions are independent events following a Poisson distribution:

$$P_{\text{Poisson}}(n_0) = \frac{\langle N \rangle^{n_0} e^{-\langle N \rangle}}{n_0!} \quad (2)$$

Finally, the monomer dynamics are simulated by the Poisson-weighted average of the different solutions of Equation 1 obtained starting from the initial conditions $n_0 = 1, 2, \dots, 10$, which suffices to contain 99.97% of the distribution for $\langle N \rangle = 3$.

In the dimer case, two fundamental differences arise in both the multi- and single-exciton regimes. First, absorption can occur in either core, enabling the formation of both MX configurations where all excitons are accommodated within a single core (localized MX), as in

monomers, and those where excitons form in both cores (segregated MX). To independently account for the occupancy of the two cores, we separately consider the exciton population in the right and left cores, denoted as n_R and n_L , respectively. Initially, $n_{0,R}$ and $n_{0,L}$ such that $n_0 = n_{0,R} + n_{0,L}$ are photogenerated. In our model, photon absorption is treated symmetrically between the two cores, even when they contain different numbers of excitons. Consequently, we determine the probability that the left (right) core contains $n_{0,L}$ ($n_{0,R}$) excitons using a symmetric binomial distribution:

$$P_{Binomial}(n_{0,L,R}) = \binom{n_0}{n_{0,L,R}} \left(\frac{1}{2}\right)^{n_0} \quad (3)$$

In the segregated MX configuration, excitons located in the two distinct cores, despite being physically separated by the dimer's neck, can still undergo Auger recombination because of the aforementioned partial delocalization onto the other core (Figure 1d). Therefore, there is sufficient wavefunction overlap to enable interaction between excitons in different cores. To address this, we introduce the Auger recombination mechanism between segregated biexcitons, depicted in Figure 3d and associated with the inter-dot Auger rate $\tilde{k}_{AR}$ in addition to the Auger recombination mechanism between biexcitons localized within the same core, represented in Figure 3b and characterized by the intra-dot Auger rate k_{AR} .

The second difference between dimers and monomers is suggested by the faster decay component observed in the dimers TA in the single-exciton regime (see Figure 2c). This reveals the presence of a distinct recombination mechanism that occurs exclusively in dimers and is already active for $n_0 = 1$ exciton. It is reasonable to assume that, during fusion of two QDs, defects may form in the neck region where the shells merge. These defects can trap charges, which we represent in our model with a population n_c . Given that excitons in the dimers are delocalized onto

the neck, they can interact with those charges and be annihilated via a charge-assisted Auger recombination mechanism, depicted in Figure 3c, with a rate k_c .

Considering all the relevant processes, the rates of change of the excitons populations n_R and n_L in the two cores and of the charges n_c in the dimers are described by the following coupled equations

$$\begin{aligned}\frac{dn_R}{dt} &= -k_{rad}n_R - k_{AR}\frac{n_R(n_R-1)}{2} - k_cn_cn_R - \tilde{k}_{AR}n_Rn_L \\ \frac{dn_L}{dt} &= -k_{rad}n_L - k_{AR}\frac{n_L(n_L-1)}{2} - k_cn_cn_L - \tilde{k}_{AR}n_Rn_L \\ \frac{dn_c}{dt} &= -k_cn_c(n_R + n_L) \quad (4)\end{aligned}$$

As for the monomers, to simulate the decay dynamics of the dimers with $\langle N \rangle$ average photogenerated excitons per QD, we compute the Poisson-weighted average (Equation 2) of the decay dynamics obtained for different initial exciton numbers $n_0=1, 2, \dots, 10$. To determine the average decay dynamics of a dimer initially containing n_0 excitons, we first solve Equation 4 for all possible distributions of excitons between the right ($n_{0,R}$) and left ($n_{0,L}$) cores. The solutions are then summed, weighted by the corresponding binomial coefficients obtained from Equation 3.

We fit the simulated decay dynamics to experimental exciton density-dependent dynamics of the 1S exciton in monomers and dimers, respectively, for six excitation fluences corresponding to $\langle N \rangle$ ranging from ≈ 0.05 (Figure 2c) to ≈ 2.9 (Figure 2f). The radiative recombination rate k_{rad} has been kept fixed for both samples, since it can be directly extracted from the time-resolved emission kinetics in Figure 1f (See SI). The complete datasets for monomers and dimers are shown

in Figure 3e (blue triangles) and Figure 3f (red circles), respectively. The fit results are overlaid with the data in Figure 3e,f as black solid lines and the rate constants are listed in Table 1.

Rate	Monomers	Dimers
k_{rad}	$1/29.6 \text{ ns}^{-1}$	$1/29.6 \text{ ns}^{-1}$
k_{AR}	$1/240 \text{ ps}^{-1}$	$1/410 \text{ ps}^{-1}$
$\tilde{k}_{\text{AR}}$	/	$1/1.94 \text{ ns}^{-1}$
k_{c}	/	$1/240 \text{ ps}^{-1}$

Table 1. Summary of the results of the fits of the dynamics of the 1S exciton of both monomers and dimers.

The Auger recombination rate in monomers is $(240 \text{ ps})^{-1}$, in agreement with both experimentally and theoretically determined biexciton Auger rates previously reported for monomers.^{4,5,35,36} The intra-dot Auger recombination rate in dimers, instead, is reduced to $(410 \text{ ps})^{-1}$, which can be attributed to two factors. First, in dimers, excitons can occupy a larger volume, as they are partially delocalized across the two cores, decreasing the wavefunction overlap and the likelihood of interaction between excitons in the same core. Second, on a sub-nanosecond timescale, charge-assisted Auger recombination also takes place with rate $k_{\text{c}} = (240 \text{ ps})^{-1}$. This value was obtained from fitting the low-fluence dynamics, corresponding to $\langle N \rangle \approx 0.05$ (see Figure 2c) and kept fixed for all other excitation densities, effectively accounting for the extra decay observed in dimers at low fluences (see Figure 3f). We note that despite k_{c} being fixed, this term is still dependent on the exciton populations in the two cores and can influence the extracted intra-dot Auger recombination rate of $(410 \text{ ps})^{-1}$, possibly causing an underestimation.

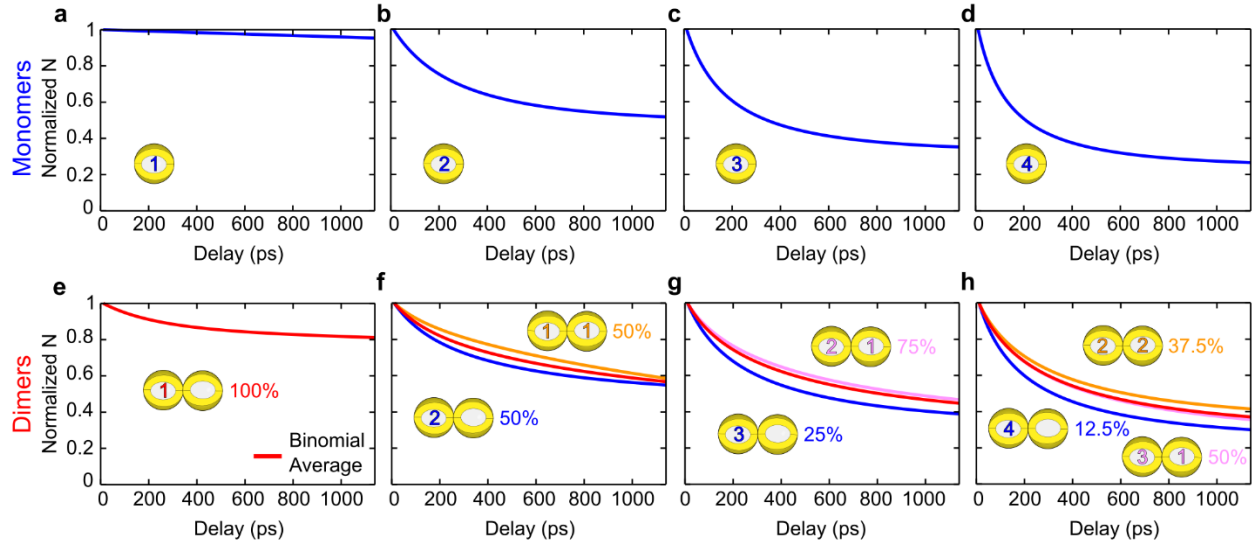


Figure 4. Simulated normalized decay dynamics of the 1S exciton of the monomers (a-d) and the dimers (e-h) calculated solving Equation 1 and Equation 4 starting from an initial number of photogenerated excitons n_0 from 1 (a,e) to 4 (d,h). For the dimers, for each value of n_0 , the panels show the dynamics obtained for all possible MX configurations, represented as colored solid lines. In each panel, monomers and dimers sketches represent schematically the cores occupation with numbers colored like the solid lines representing the dynamics to which they are related. Beside the sketches of the dimers, symmetric binomial probabilities calculated using Equation 3 are shown. The average dimer dynamics are represented as red solid lines.

The modest increase of the intra-dot Auger recombination time alone is insufficient to explain the reversal in the decay trend between monomers and dimers in the multi-exciton regime observed in Figure 2f. Instead, we find that the most significant effect is the formation of segregated MX configurations, in which biexcitons recombine via an inter-dot Auger process with a characteristic rate approximately five times smaller than that of intra-dot recombination: $(1.94 \text{ ns})^{-1}$ vs $(410 \text{ ps})^{-1}$.

Figure 4 presents the simulated exciton population dynamics obtained using Equation 1 and Equation 4 for n_0 ranging from 1 to 4. In monomers, when $n_0 = 1$ (Figure 4a), excitons decay solely via radiative recombination on a timescale of 29.6 ns. From $n_0 = 2$, instead, Auger recombination processes become increasingly dominant (Figure 4b–d). In dimers, Figure 4e shows the dynamics for $n_0 = 1$, which is governed by radiative recombination and by charge-assisted Auger recombination. For $n_0 = 2$, the second exciton has a 50% probability of being photogenerated in the previously excited core, forming a localized biexciton (blue line in Figure 2f), or in the other core, forming a segregated biexciton state (orange line in Figure 2f) with much lower Auger rate. Moreover, the probability of MXs to be localized within one core, under the assumption of perfect homodimer, scales with the total number of excitons n_0 as $\left(\frac{1}{2}\right)^{n_0-1}$. Therefore, as n_0 increases, the average MX configuration in the dimers becomes increasingly dominated by a segregated character (Figure 4g,h), ultimately leading to a significant reduction in depopulation rate compared to monomers, reversing the trend observed for $n_0 = 1$.

We note that our observation of a long-lived MX population in dimers is consistent with previously reported emission studies.²⁶ Specifically, fluorescence-lifetime-intensity distribution experiments have revealed a continuous intensity distribution of emission in dimers, manifested as an intensity flickering. This behavior stands in stark contrast to the blinking effect observed in monomers, where the intensity distribution is characterized by well-defined ON and OFF states. This phenomenon has been attributed to the coexistence of multiple multi-carrier configurations in dimers, exhibiting similar lifetimes.²⁶ Furthermore, Hanbury-Brown–Twiss experiments have shown a bunching behavior in dimers, in contrast to the strong antibunching observed in monomers. In other words, while in monomers the dominant recombination process is non-

radiative Auger recombination, in dimers photon-pair emission events arising from radiative biexciton recombination are predominant.²⁶

To summarize, we studied ultrafast exciton dynamics in QD dimers exploring both the single and the multi-exciton regimes and found that, in both cases, dimers show distinct ultrafast dynamics compared to monomers. We find that under low excitation densities exciton recombination in dimers is accelerated due to a nonradiative mechanism, that we attribute to charge-assisted Auger recombination. On the other hand, at increased exciton densities corresponding to $\langle N \rangle = 2.9$, this trend is reversed and dimers show significantly more population after several hundreds of picoseconds, despite the extra decay mechanism present in the single exciton regime. We rationalize these findings by globally fitting the data with a nonlinear kinetic model that accounts for exciton-density dependent recombination mechanisms which describe the different ways to generate MX states in the dimers, and considers the lower recombination rates of segregated biexcitons.

Our findings help understand the interplay between radiative and nonradiative processes in dimers. In these systems the limitations imposed by Auger recombination in traditional QDs can potentially be mitigated by the reduced Auger rates of the segregated MX states, thus promoting the potential application of coupled QD molecules across various emerging fields. These include display technologies, where dual-color emission can be achieved by varying core sizes;²⁷ quantum information processing, where dimers can function as qubits;³⁷ light harvesting, enabled by the spatial separation of electron and hole wave functions between the two cores; and electric field sensing, which takes advantage of their sensitivity to external perturbations.

ASSOCIATED CONTENT

Supporting Information. Details on the sample preparation, ultrafast spectroscopy experiments, calculation of the average number of excitons per quantum dot, supporting figures and tables.

The following files are available free of charge.

Supporting Information (PDF)

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Notes

The authors declare no competing financial interest.

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