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Optical Control of Exciton and Trap-State Recombination in Quantum Dots Pairs Through Förster Resonance Energy Transfer

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ABSTRACT

The electron-hole recombination dynamics of colloidal quantum dots (QDs) is critically driven by charge carrier trapping. Surface traps lead to long-lived electron-hole pairs and play a pivotal role in the photochemical reactivity and the charge transfer at the interface between QDs and their medium. Here, we demonstrate that both band-edge exciton and surface trap electron-hole recombination kinetics can be optically manipulated thanks to Förster Resonance Energy Transfer (FRET) within suspensions of donor/acceptor QD pairs. To identify the specific roles of the different radiative states at play, we monitor the time evolution of their photoluminescence decays as QDs assemble, observing in real time the arising of FRET and its effects on carrier dynamics. We deduce that the time decoupling between the cooling process of photoexcited electron-hole pairs (~ 1 ps) and the FRET excitation of band-edge excitons (~ 1 ns) enables the surface trap states (of acceptor QDs) to slow down the relaxation of the FRET-excited states (induced by donor QDs): We typically observe a 400% increase in the exciton lifetime of acceptor QDs. As the rate-determining step of carrier dynamics within QD-QD pairs, FRET emerges as a regulating mechanism that can be used to optimise electron-hole recombination for targeted application.

1 | Introduction

Nanophysics covers both fundamental and applied sciences, producing various nanoscale objects with multifunctional and highly tuneable optoelectronic properties. As artificial atoms, semiconductor quantum dots (QDs) are as well able to host qubits for quantum information processing at the scale of single nanocrystals [1–3] and to generate finely controlled transient photocurrents when assembled in solid films [4]. As quantum emitters, QDs are also used to design coherent single-photon sources [5, 6], with radiative lifetimes ranging from tens of picoseconds to hundreds of nanoseconds [6, 7]. These fundamental features arise from the size-tuneable quantum confinement of electron-hole pairs [8]. In applied physics and chemistry, QDs

are then used for the design of light sources [9, 10], photodetectors [11, 12], photovoltaic cells [13, 14], field-effect transistors [15] and biosensors [16–18]. For all those functionalities, the understanding of recombination dynamics and charge transport is necessary to optimise: first, the QD properties at the single-particle and collective levels and, second, the QD coupling with its material and electromagnetic environment. According to the desired application, we may as well need to employ isolated QDs embed in nanocavities or assemble them in arrays and clusters of coupled dots (through tunnel coupling [4, 19], charge transfer [20–22], or resonant energy transfer [23–26]). Given the mesoscopic complexity of such QD-based architectures and of the interdot couplings, we still need fundamental investigations to reach the finest control possible.

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In addition to quantum confinement, the surface trapping of charge carriers also play a crucial role in the specific case of colloidal quantum dots [27–34]. These additional states, classified into shallow and deep traps according to their energy location within the QD interband gap, are conditioned by coordination chemistry at the QD surface [35]. They may come from dangling bonds [36], chalcogene vacancies [37], oxidation [38], hydroxylation [39], and adsorption of molecular ligands [40–42]. Due to the electron (or hole) localisation and the resulting partial charge separation, such trap states are often characterised by long lifetimes (between 10 and 100 ns). Long viewed as hindrances and drawbacks for photonic applications and charge transport, surface states are more and more considered beneficial for photocatalysis [43], charge transfer [44], redox sensing [45] and photovoltaics [46]. Compared with fast decaying band-edge excitons delocalised over the QD core, the trapped electron-hole pairs are, first, long-lived enough to allow (photo)chemical processes to occur and, second, localised at the QD surface, providing a high reactivity at the interface with the medium and facilitating charge carrier extraction.

In this context, we aimed at examining the recombination dynamics within binary QD-QD systems thanks to 2D time-resolved photoluminescence (PL) spectroscopy. Achieving the pairing of colloidal CdTe QDs by wet chemistry to reach the regime of Förster electromagnetic coupling [47], we show here that small QDs (playing as energy donors) are able to enhance the lifetime of their bigger partners (as acceptors) thanks to resonance energy transfer (FRET). This phenomenon has already been observed by some research teams [26, 48, 49] but has essentially been considered so far as a trivial property of acceptor QDs. The few observations of such lifetime enhancements are indeed reported at the margin [26, 48] and briefly described as a ‘logical’ consequence of FRET. However, Förster’s theory does not predict such a slowdown in the acceptor decay: It only accounts for the enhancement of the acceptor PL intensity. Actually, a resonance energy transfer from a donor to an acceptor fosters the excitation of the latter (increasing the number of photons subsequently emitted) but is not supposed to change its probability of spontaneous emission. The decay rate of any radiative state, characterised by memorylessness, is in principle related to the structural properties of the system. Hence, from Förster’s theory, the FRET-induced increasing in acceptor QDs’ lifetimes is rather unexpected. In this study, we take full measure of this intriguing QD-specific phenomenon and propose a deep study of it. While QD-QD FRET has been previously studied in QD solid films and multilayers without focusing on its special effect on acceptor QD’s lifetime [25, 26, 50, 51], here we scrutinise the FRET-induced recombination dynamics within colloidal QD nanoclusters. Given the slowness of the clusterisation driven by the addition of organosilane molecules, we monitor in real time the arising of FRET throughout the assembly of QD-QD pairs. Theoretical considerations and mathematical modelling of the fluorescence decays (obtained by Time-Correlated Single Photon Counting [TCSPC] at different excitation and detection wavelengths) strongly suggest that the time decoupling between the cooling process of the photoexcited electron-hole pairs (on a picosecond timescale) and the FRET-excitation of band-edge excitons (on a nanosecond timescale) enables the surface trap states (of acceptor QDs) to slow down the recombination of the FRET-excited states (induced by donor QDs). This mechanism is

here explained in the light of the localised carrier-induced Stark effect [52].

2 | Results and Discussion

2.1 | Band-Edge Excitons and Surface Trap States

Before examining interdot coupling processes within bipartite QD-QD systems, the size-dependence of the QD lifetime enables us to appreciate how determining carrier trapping is for the intrinsic emission properties of QDs. Here, we study three samples of COOH-capped CdTe QDs, named QD1, QD2, and QD3, with mean radii of 1.98 nm ($\pm 6.3\%$), 2.26 nm ($\pm 7.6\%$), and 2.49 nm ($\pm 9.4\%$), respectively. Their structural and chemical properties have been previously characterised using HR-TEM, EDX, XPS, UV-visible and photoluminescence (PL) spectroscopies, PL imaging, and pH measurements [47, 53–55]. According to XPS studies, the ligands increase the average radii of the QDs to 2.49, 2.77, and 3.12 nm for QD1, QD2, and QD3, respectively [47]. The PL spectra are displayed in Figure 1a. The bandwidths are due to the heterogeneous broadening of the colloidal suspensions, so the spectra are the images of the Gaussian distribution of the QD sizes. We take advantage of this size dispersion in order to measure the QD fluorescence lifetime as a function of the emission wavelength, which is in bijection with the QD size (i.e. each value of the emission wavelength corresponds, in a univocal manner, to a precise value of the QD diameter): in virtue of quantum confinement [8, 56], the larger the QD, the smaller its optical bandgap, the higher its emission wavelength. With our homemade TCSPC setup dedicated to 2D time-resolved fluorescence spectroscopy (see Methods), the detection wavelength is scanned with a monochromator whose window is set for a spectral width of 6 nm. The decays of the fluorescence intensity I are then well fitted by biexponential functions:

$$I(t) = I_0 + I_X \exp(-t/\tau_X) + I_S \exp(-t/\tau_S) \quad (1)$$

leading us to identify a short and a long lifetimes, depicted by τ_X and τ_S , respectively. The literature indeed reports such biexponential decays for CdTe [38, 41], CdSe [29] and CdS [31, 37] colloidal quantum dots. Interestingly, only the long lifetime is size-dependent: considering the three overlapping QD populations as a continuous statistical distribution of CdTe QDs’ emission wavelengths λ , Figure 1b shows that τ_S increases roughly linearly with respect to λ (from 30 to 50 ns), whereas τ_X is pretty much constant (around 13 ns). It suggests a surface-related process for the slow decay, while the fast one may be linked to the core properties of the nanocrystals. Moreover, the statistical weights of these two exponential decays (Figure 1c), defined as $a_S = I_S/(I_S + I_X)$ and $a_X = I_X/(I_S + I_X)$, clearly show that the slow component becomes more and more predominant as the QD size increases. This undoubtedly indicates the existence of two emissive states of different natures driven by two distinct physical mechanisms.

To identify them, we construct the two decay-associated spectra (DAS) of each sample. The procedure is detailed in Supporting Information (Section S1). It consists in the extraction of the spectral components associated with the two lifetimes τ_X and τ_S , hence deduced from the steady-state PL spectrum weighted by the λ -dependent number of photons collected from each decay

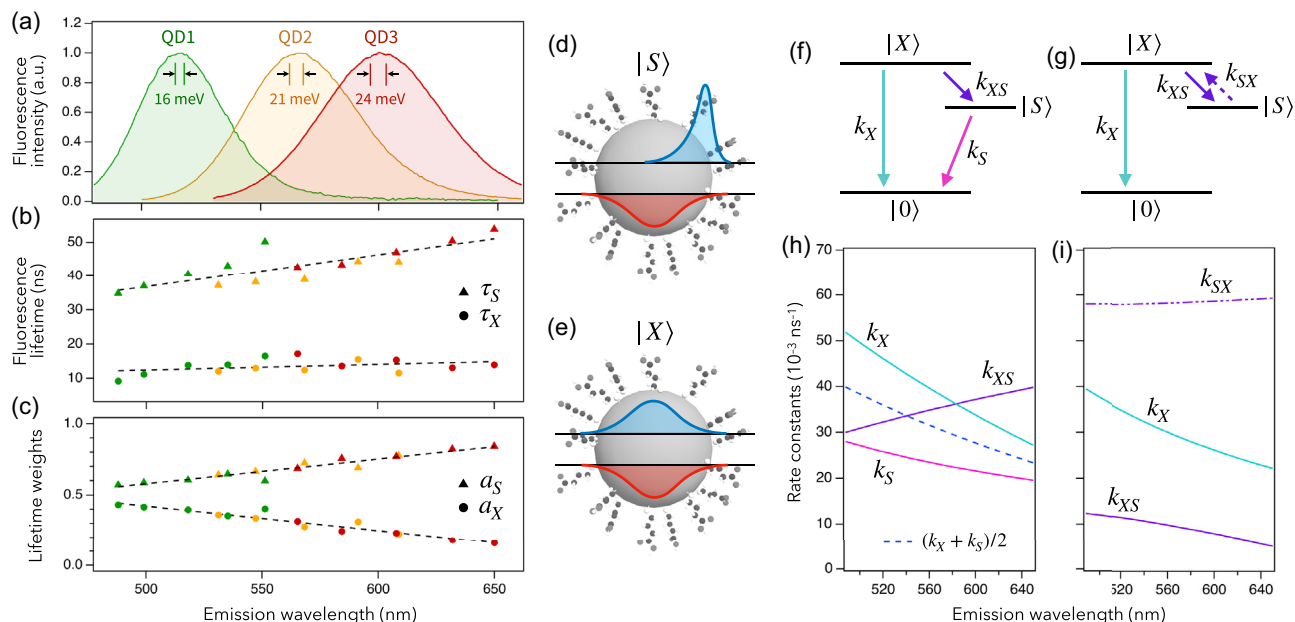


FIGURE 1 | Intrinsic emission properties of CdTe QDs. (a) Emission spectra of the three CdTe QD colloidal suspensions. For each sample, the vertical lines locate the maxima of the two decay-associated spectra (DAS, see Section S1). (b) Short and long fluorescence lifetimes τ_X and τ_S as functions of the emission wavelength [see Equation (1) 1] acquired for an excitation wavelength $\lambda_{\text{ex}} = 470$ nm. (c) Statistical weights a_X and a_S of the slow and fast components of the biexponential QD fluorescence decay [see Equation (1)]. Schematic representation of the electron (blue) and the hole (red) envelope wave functions in the cases of (d) a shallow surface trap state and (e) a band-edge exciton state. Three-level model of electron-hole recombination under the assumption of (f) the existence of a radiative decay or (g) the absence of decay from state $|S\rangle$. Rate constants associated to (h) the three-level model (f) and (i) the three-level model (g), as deduced from our experimental data, Equation (2) and the treatment detailed in Section S2.

[31, 57, 58]. The DAS are drawn in Figure S1 for QD1, QD2, and QD3, and the spectral positions of their maxima are displayed in Figure 1a. For each sample, the fast DAS is blue-shifted from the steady-state PL spectrum, while the slow DAS is slightly red-shifted. We can then ascribe the fast decay to the relaxation of band-edge excitons, whose eigenstate is named $|X\rangle$, and the slow decay to a trap-mediated electron-hole recombination [29, 31, 38, 41], associated with a surface state named $|S\rangle$. Given the weak energy gap between $|X\rangle$ and $|S\rangle$, ranging from 16 to 24 meV (Figure 1a), and the high values of $\tau_S \geq 30$ ns, we are here dealing with a shallow electron trap state rather than a deep trap state [59, 60]. It is further known that CdTe QDs capped with mercaptocarboxylic acids do not experience hole trapping, unlike CdSe QDs [42]. Figure 1d,e gives a schematic representation of the electron and hole envelope wave functions for both $|S\rangle$ and $|X\rangle$ states. Although these ones depend on the QD nature and capping, we represented them by gaussians in the figures. Indeed, as we will explain later in the manuscript, what is important here is that the presence of an internal electric field will lead to an increasing of the asymmetry of the function, whatever its nature (whether it is symmetric or not, initially).

Despite the extensive literature on surface trap states, their radiative nature remains controversial. Even though nonradiative shallow trap states are often invoked to explain the mechanisms of blinking and delayed emission in core-shell QDs (within which the charge carrier separation is strong) [28, 61], shallow traps are sometimes considered radiative in core-type QDs (which are not specifically designed for electron-hole separation) [29, 31, 38]. We can notice that the question does not arise for deep traps, which are characterised by a wide and Stokes-shifted

emission band in core-type QDs [37, 40]. In all these cases, the trap-mediated kinetics are accounted for by a three-state model, involving the band-edge exciton state $|X\rangle$, a surface trapped-electron state $|S\rangle$ and the ground state $|0\rangle$. The difference lies in the considered connections between the three states through hypothetical relaxation paths. We count three main configurations: (i) Both $|X\rangle$ and $|S\rangle$ are assumed radiative, and the band-edge exciton can irreversibly relax to the surface trap state [31, 38] (Figure 1f); (ii) the band-edge exciton is the only radiative state, the surface trap state cannot relax to the ground state, and there is a dynamic equilibrium between $|X\rangle$ and $|S\rangle$ [27, 61] (Figure 1g); and (iii) the band-edge exciton is the only radiative state, $|S\rangle$ can relax nonradiatively to the ground state, and there is a dynamic equilibrium between $|X\rangle$ and $|S\rangle$ [28]. In Figure 1h,i, we compare the results we obtained for the first two configurations, translating in biexponential laws whose derivations are given in Section S2. The third configuration is here discarded as it leads to a monoexponential decay [28]. It is worth noting that the rate constant k_X associated to the band-edge exciton relaxation in the second configuration (Figure 1i) coincides with the arithmetic average of the two rate constants k_X and k_S computed in the frame of the first configuration (see the dashed line in Figure 1h). It means that both configurations lead to the same phenomenological description. However, they are distinguished by the size dependence of k_{XS} , that is the probability (per unit time) for an electron initially bound to its hole partner to be trapped at the QD surface. This probability is expected to be roughly proportional to the number of surface traps, increasing itself with the QD surface and the QD size. Therefore, the first configuration of the three-state model appears to be the most relevant. In this framework, we understand that (i) k_X is indeed

greater than k_S due to the higher overlap between the electron and hole envelope wave functions in state $|X\rangle$ than in state $|S\rangle$ (Figure 1d,e), (ii) k_S decreases when the QD size increases because the envelope overlap between the delocalised hole and the localised trapped electron shrinks, and (iii) k_X decreases when the QD size increases because of the energy densification of the band-edge exciton fine structure and the thermal activation of dark states [62]. From the kinetic picture of Figure 1f, the biexponential decay then reads:

$$I(t) = \left(1 - \frac{k_{XS}}{k_X + k_{XS} - k_S}\right) e^{-(k_X + k_{XS})t} + \frac{k_{XS}}{k_X + k_{XS} - k_S} e^{-k_S t} \quad (2)$$

wherein we identify $\tau_X = 1/(k_X + k_{XS})$ and $k_S = 1/\tau_S$ (see Section S2, for the detailed derivation). In the following, the effective decay rate of $|X\rangle$ is depicted by $\bar{k}_X = k_X + k_{XS}$.

2.2 | FRET-Induced Enhancement of Acceptors' Lifetimes

Resonance energy transfer can happen between colloidal QDs of different sizes when they are close enough to each other. This condition is obviously satisfied within solid films and bilayers [25, 26, 50, 51, 63, 64], but, in such cases, QDs are closely packed so that each nanocrystal may couple and exchange energy with several partners. The analysis of the results is then complicated, and it is hard to extract the photophysical parameters which characterise the properties of individual QDs. In addition to the unavoidable heterogeneous distribution of the single QD emission properties (due to size dispersion), one faces a high heterogeneity in the QD-QD interactions. The measured FRET efficiency hence consists in a rough average over the densely packed QD sample (as for aggregated molecular assemblies [65]) and can hardly be decoupled from possible other quenching mechanisms, since it is computed from the quenching factor of donors'

fluorescence intensity. Actually, assuming that donors' emission light is only quenched by FRET in close-packed samples is highly questionable. In order to overcome those difficulties, here we propose a chemical approach to get closer to the ideal configuration of a binary QD-QD system wherein the donor and the acceptor are distinguishable, separate by a definite interdistance. As described previously [47, 55], this consists in adding an amino-organosilane, namely (3-aminopropyl)triethoxysilane (APTES, see Methods), to the QD suspensions. In aqueous solution, APTES polymerises and captures protons, thus acquiring positively charged NH_3^+ groups and stabilising the carboxylate form COO^- of the QD ligands. QDs thus keep their repulsive colloidal interactions preventing their aggregation into close-packed aggregates. With this protocol, our previous work shew that each QD has 0.9 neighbours in average (cf. parameter S in Reference [47]), which confirms that we are close to the ideal bipartite QD-QD system.

Defining the quenching factor $Q = 1 - \tau^{(\text{APTES})}/\tau$ as the relative decrease in the QD fluorescence lifetime $\tau = a_X \tau_X + a_S \tau_S$ through addition of APTES, we observe in Figure 2a that the electron-hole recombination is not affected by APTES in the same manner according to the emission wavelength (i.e. the QD size): For each sample, the smallest QDs (points D) are almost totally quenched ($\sim 100\%$) while the largest (points A) are weakly quenched (from 50%, for QD1, to $\sim 0\%$, for QD3). This behaviour is noticeable in the fluorescence decays associated to these two extreme regimes (Figure 2b). While small QDs are fast quenched with a sharp initial decrease of their intensity (curves D1 and D3), the decays of the large ones are preceded by a first rising (curves A1 and A3). This is the signature of an energy transfer: The excitation of the large QDs is mediated by the transient intermediate photoexcitation of the small QDs. Henceforth, the former play as acceptors and the latter as donors. These observations are in accordance with our spectral characterisations of the so-called Homogeneous FRET process (Homo-FRET) occurring within quasi-monodisperse QD suspensions [55].

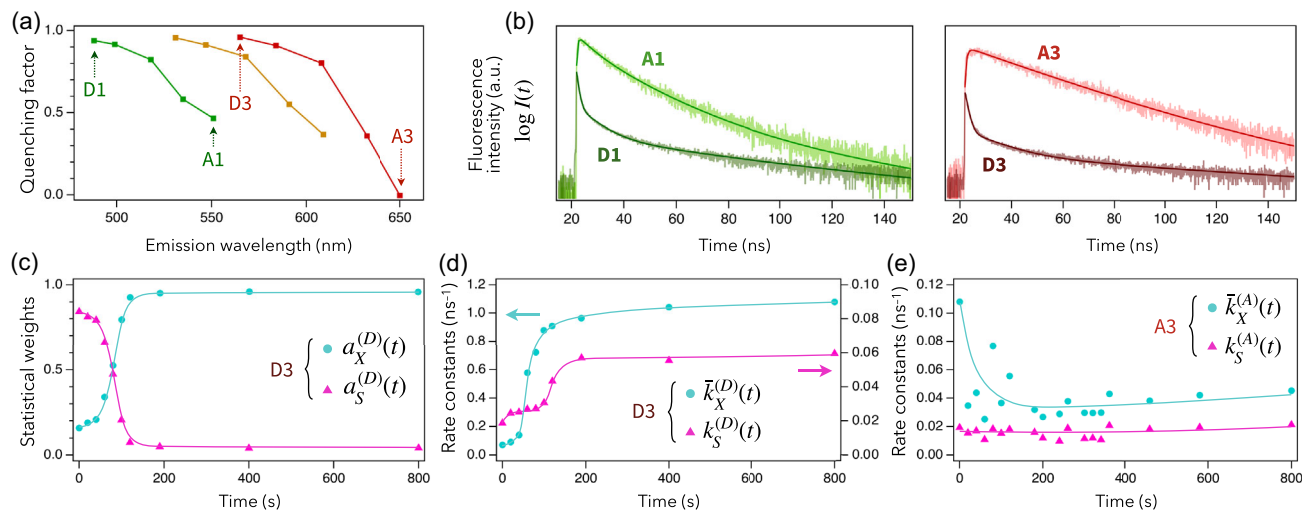


FIGURE 2 | Homogeneous resonant energy transfer. (a) Quenching factor (i.e. relative decrease) of the fluorescence lifetime $\tau = a_X \tau_X + a_S \tau_S$ according to the emission wavelength, 20 min after addition of APTES (QD1 in green, QD2 in yellow, QD3 in red). (b) Fluorescence decays $\log I(t)$ of QD1 (left) and QD3 (right) corresponding to the points D1, A1, D3 and A3 indicated in (a). Time evolution of (c) the statistical weights $a_X(t)$ and $a_S(t)$ associated to decay D3, (d) the rate constants $\bar{k}_X(t)$ and $k_S(t)$ associated to decay D3 and (e) the rate constants $\bar{k}_X(t)$ and $k_S(t)$ associated to decay A3. The chemical QD-QD pairing starts with the addition of APTES at $t = 0$. Trend curves are drawn to guide the eye. See Section S3 for details about data treatment. All the measurements are here acquired with an excitation wavelength $\lambda_{\text{ex}} = 470$ nm.

The donor-associated decays D1 and D3 are fitted by biexponential functions similar to the previous ones, with the difference that an additional non-radiative decay related to FRET must be included, characterised by its own rate constant k_{ET} . For each population QDn , $n \in \{1, 2, 3\}$, the global rate constant $k_n^{(D)}$ of the donor-associated biexponential decay reads:

$$k_n^{(D)} = a_X^{(D)} \bar{k}_X^{(D)} + a_S^{(D)} k_S^{(D)} + k_{ET}^{[nn]} \quad (3)$$

The superscript $[nn]$ means that it accounts for a Homo-FRET process between two QDs coming from the same population QDn . As for the acceptor-associated kinetics A1 and A3, we model them by a combination of a biexponential decay with an exponential rise. Theory teaches us that the intensity $I_A(t)$ of the FRET-excited QDs follows [66, 67]:

$$I_A(t) = I_X^{(A)} e^{-\bar{k}_X^{(A)} t} + I_S^{(A)} e^{-k_S^{(A)} t} - I_{\uparrow} e^{-k^{(D)} t} \quad (4)$$

where $I_{\uparrow}$ is the amplitude of the rise component, driven by the global rate constant $k^{(D)}$ of the donor. Henceforth, the Homo-FRET rate constant can be independently extracted from both the donor-associated decay and the rise component of the acceptor transient emission. As reported in Table 1, we get 1.35 and 1.98 ns⁻¹ for $k_{ET}^{[11]}$ and 1.05 and 1.24 ns⁻¹ for $k_{ET}^{[33]}$. The details of the data treatment are provided in Section S3.

Table 2 gathers the lifetimes and decay rates describing the recombination dynamics of the largest QD3 (point A3, Figure 2a,b). The statistical distribution of the fast and slow decay components and the values of the associated lifetimes change upon addition of APTES. Especially, both short and long lifetimes increase (from 13 to 51 ns, and 35 to 100 ns, respectively) when QDs benefit from Homo-FRET (as acceptors). Despite what is sometimes claimed, this effect is surprising: whether donors' lifetime is supposed to decrease because of the addition of FRET as a nonradiative relaxation path, acceptors' lifetime is not supposed

TABLE 1 | Rate constants of Homo- and Hetero-FRET as extracted from both the donor and the acceptor time-resolved PL signals (cf. Sections S3 and S4).

Method	$k_{ET}^{[11]}$	$k_{ET}^{[33]}$	$k_{ET}^{[13]}$
Donor quenching	1.35 ns ⁻¹	1.05 ns ⁻¹	1.6 ns ⁻¹
Acceptor rising	1.98 ns ⁻¹	1.24 ns ⁻¹	1.0 ns ⁻¹

TABLE 2 | Lifetimes, rate constants and statistical weights of the fast and slow decay components of the largest QD3 (spectral position A3, Figure 2) before and after (30 min) addition of APTES, in the case of Homo-FRET.

Parameter	Before addition of APTES	After addition of APTES
$\tau_X(a_X)$	13 ns (17%)	35 ns (88%)
$\bar{k}_X$	77·10 ⁻³ ns ⁻¹	29·10 ⁻³ ns ⁻¹
$\tau_S(a_S)$	51 ns (83%)	100 ns (12%)
k_S	20·10 ⁻³ ns ⁻¹	1.0·10 ⁻³ ns ⁻¹

to change, and even less expected to increase. At least, such an increasing is not predicted by Förster's theory: the fluorescence decay time of an acceptor is only driven by its own relaxation processes, independently from the way it is excited (whether by direct light excitation or through FRET). At this stage, this apparent FRET-induced enhancement of acceptor QD3 lifetime suggests an intrinsic modification of acceptors' relaxation dynamics by Homo-FRET.

2.3 | Dynamic Correlation Between Chemical Pairing and Energy Transfer

The kinetics of QD-QD chemical pairing induced by APTES is actually slow. The process has been imaged in real time (such as in Reference [55]). A modification of the solution colour from orange to red clearly supports a FRET mechanism between QDs (see Section S5). Acquiring the emitted photons by TCSPC over 30 min from the addition of APTES enables us to track the two exponential components of the decay throughout the APTES-induced QD-QD pairing. Each parameter $\bar{k}_X = 1/\tau_X$, $k_S = 1/\tau_S$, a_X , and a_S is now measured as a function of the 'pairing time' t . For the donor-associated decay D3, the experimental values of these parameters are given in Figure 2c,d. The band-edge exciton is significantly quenched: Its effective decay rate $\bar{k}_X^{(D)}(t)$ is multiplied by a factor 13 over 800 s, reaching a limit value of 1.08 ns⁻¹. In comparison, that of the surface trap state, $k_S^{(D)}(t)$, increases by a factor of 2, with a maximum value of 59 · 10⁻³ ns⁻¹. These trends confirm the arising of an energy transfer characterised by $k_{ET}^{[33]} = a_X(\infty) k_{ET}^{(X)} + a_S(\infty) k_{ET}^{(S)}$ with:

$$k_{ET}^{(X)} = \bar{k}_X^{(D)}(\infty) - \bar{k}_X^{(D)}(0) \sim 1 \text{ ns}^{-1} \quad (5)$$

and:

$$k_{ET}^{(S)} = k_S^{(D)}(\infty) - k_S^{(D)}(0) \sim 5 \cdot 10^{-3} \text{ ns}^{-1} \quad (6)$$

As shown in Figure 2c, the statistical weight $a_X^{(D)}(t)$ of the band-edge exciton paths tends toward 1 while $a_S^{(D)}(t)$ vanishes. According to Equation (2), it means that $k_X^{(D)} + k_{XS}^{(D)} - k_S^{(D)} \gg k_{XS}^{(D)}$ after QD pairing, i.e. $\bar{k}_X^{(D)}(\infty) \gg k_{XS}^{(D)}(\infty)$ [given that $\bar{k}_X^{(D)}(\infty) \gg k_S^{(D)}(\infty)$, experimentally]. In other words, the increasing of $\bar{k}_X^{(D)} = k_X^{(D)} + k_{XS}^{(D)}$ is only related to an increase in $k_X^{(D)}$. We deduce that FRET is mainly driven by state $|X\rangle$ (as $k_{ET}^{(X)} \gg k_{ET}^{(S)}$ and $a_X^{(D)} \rightarrow 1$), which is coherent with its stronger oscillator strength (arising from the electron-hole envelope wave function overlap, cf. Figure 1e). Interestingly, the rise of $k_S^{(D)}(t)$ starts at $t = 100$ s, whereas that of $\bar{k}_X^{(D)}(t)$ begins a bit earlier at $t = 40$ s. Since the QD-QD distance decreases with respect to the pairing time t , it seems that state $|S\rangle$ requires a shorter QD-QD distance to transfer its energy with an acceptor partner, compared with state $|X\rangle$. This observation suggests that the shallow surface trap state exchanges energy through charge transfer, whose spatial range behaves as $e^{-d/\delta}$ (with d the edge-to-edge distance and δ the span length), whereas FRET is characterised by a longer range behaving as r^{-6} (with r the centre-to-centre distance) [68, 69]. Henceforth, the global rate constant $k_{ET}^{[33]}$ is mainly ascribed to a FRET process from the band-edge exciton, with

a small contribution of charge transfer from the surface trap state. Eventually, the time-dependence of the acceptor-associated rate constants $\bar{k}_X^{(A)}(t)$ and $k_S^{(A)}(t)$ presented in Figure 2e evidences an interesting feature. While $k_S^{(A)}(t)$ is pretty much constant over time, the band-edge exciton recombination proves to significantly change due to FRET: $\bar{k}_X^{(A)}(t)$ loses 60% of its initial value, well accounting for a slowdown in the electron-hole recombination dynamics. We can conclude that the aforementioned FRET-related enhancement of acceptors' lifetime mainly involves the band-edge excitons. To scrutinise more precisely this new phenomenon, it is necessary to spectrally separate donors from acceptors. This is actually impossible within a quasi-monodisperse sample, for which all the QDs are simultaneously excited. This is why we study now the case of Heterogeneous Resonance Energy Transfer (Hetero-FRET) [47].

2.4 | Statistical Decoupling of Homo- and Hetero-FRET

Now as we have characterised the statistics and the emission properties of samples QD1 and QD3, independently, we can examine the Hetero-FRET process occurring as soon as we mix them in the same APTES-polymerised solution. Here, sample QD2 is discarded because its emission band exhibits a significant overlap with those of QD1 and QD3 (Figure 1a): It would be difficult to discriminate Homo- and Hetero-FRET within QD1-QD2 and QD2-QD3 mixed populations. In contrast, QD1 and QD3 can be considered distinct quasi-monodisperse populations experiencing Hetero-FRET when mixed, leading to the formation of heterodimers [47]. Their respective PL intensities are then acquired at their wavelengths of maximum emission (i.e. 518 and 608 nm, respectively) with a spectral window of 6 nm. In this configuration, Homo- and Hetero-FRET can be decoupled by varying the donor/acceptor ratio $x = \text{QD1/QD3}$. We can easily identify two extreme regimes, for which QD1 or QD3 constitutes the predominant QD population. At low QD1/QD3 ratio

(i.e. $x \ll 1$), the QD3 predominate and each QD1 involved in a QD-QD pair is coupled with a QD3 (Figure 3a). In this case, the QD1 only behave like hetero-donors, and their decay rate is:

$$k_1 = k_1^o + k_{ET}^{[13]} \quad (7)$$

where $k_{ET}^{[13]}$ is the Hetero-FRET rate from QD1 to QD3, and $k_1^o = 43.3 \cdot 10^{-3} \text{ ns}^{-1}$ is the "native" rate constant of QD1 (measured as $k = a_X k_X + a_S k_S$ before addition APTES). Assuming that this statistical regime is achieved for $x = 0.1$ (Figure 3c), the fitting of the QD1-associated decays leads to $k_{ET}^{[13]} = 1.6 \text{ ns}^{-1}$ (see Section S4). Conversely, at high QD1/QD3 ratio (i.e. $x \gg 1$), the QD1 predominate and mainly experience Homo-FRET (Figure 3b). But more importantly, the probability for a QD3 to spatially couple with another QD3 is near zero so that we can consider each paired QD3 as engaged in a heterodimer. Assuming this condition is satisfied for $x = 10$ (Figure 3e, bottom), the fitting of the QD3-associated kinetics with Equation (4) leads to $k_{ET}^{[13]} = 1.0 \text{ ns}^{-1}$ (see Section S4). The two values are slightly different due to the limit approximations we made about the ratio x but are both compatible with the values we obtained for Homo-FRET rates $k_{ET}^{[11]} = 1.6 \text{ ns}^{-1}$ and $k_{ET}^{[33]} = 1.1 \text{ ns}^{-1}$. They are also consistent with the order of magnitude given by the theoretical expression:

$$k_{ET}^{\text{th}} = k_1^o \left(\frac{R_0}{r} \right)^6 = 0.82 \text{ ns}^{-1} \quad (8)$$

obtained from the QD1-QD3 Förster radius $R_0 = 9.28 \text{ nm}$ [47] and the centre-to-centre QD1-QD3 distance $r = 5.68 \text{ nm}$ (taking the mercaptocarboxylic ligand lengths into account) [47]. It may be worth remembering that Förster's theory of resonant energy transfer is more a model than a theory. It is based on the dipolar approximation of electromagnetic interactions and likens the interacting fluorescent species to point-like electric dipoles. If it seems to well account for FRET between molecular fluorophores, it becomes questionable when the definition of the donor-acceptor

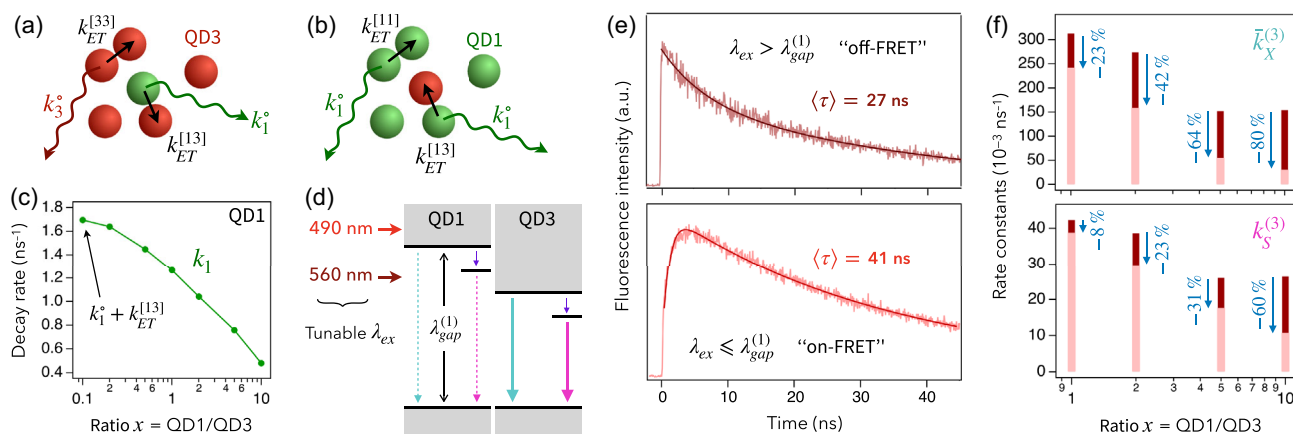


FIGURE 3 | Heterogeneous resonant energy transfer. Illustration of radiative and non-radiative relaxation processes occurring within QDs when (a) QD3 (red) are predominant and (b) QD1 (green) are predominant. (c) Fluorescence decay rate of QD1 with respect to the ratio x . (d) Scheme of the energy diagram of a QD1-QD3 heterodimer. According to the excitation wavelength, the photon energy hc/λ_{ex} is below ($hc/560 \text{ nm}$) or above ($hc/490 \text{ nm}$) the donor bandgap ($hc/\lambda_{\text{gap}}^{(1)}$). (e) Fluorescence decays acquired at a detection wavelength of 608 nm (i.e. QD3 maximum emission) for a QD1-QD3 mix at $x = 10$ with $\lambda_{\text{ex}} = 560 \text{ nm} > \lambda_{\text{gap}}^{(1)}$ (top) and $\lambda_{\text{ex}} = 490 \text{ nm} \leq \lambda_{\text{gap}}^{(1)}$ (bottom). The curves are fitting to the data (see Section S4). (f) Values of the QD3 rate constants $\bar{k}_X^{(3)}$ (top) and $k_S^{(3)}$ (bottom) acquired with $\lambda_{\text{ex}} = 490 \text{ nm}$ (light red) and 560 nm (dark red) according to the ratio x .

interdistance is ambiguous, especially when there is a significant difference between the centre-to-centre and edge-to-edge distances [65, 70]. The value of 0.82 ns^{-1} is here indicative.

2.5 | Spectral Selection of ‘off-FRET’ and ‘on-FRET’ Regimes

As the bandgaps of QD1 and QD3 are 80 nm apart in wavelength, it is possible to activate FRET or not by tuning the excitation wavelength λ_{ex} (Figure 3d). In order to analyse how Hetero-FRET acts on the electron-hole recombination within QD3, we set the detection wavelength at 608 nm and vary λ_{ex} between 550 and 450 nm. We notice two different behaviours. First, when λ_{ex} is greater than the wavelength $\lambda_{\text{gap}}^{(1)}$ of the QD1 optical bandgap, located between 490 and 500 nm [47], we observe a common decay driven by Equation (2): Indeed, the QD1 are not photoexcited and do not contribute to the relaxation dynamics of the QD3. Second, when $\lambda_{\text{ex}} \leq \lambda_{\text{gap}}^{(1)}$, the QD3 intensity exhibits a first rise, characteristic of a FRET process, followed by a slower decay [Equation (4)]. Figure 3e illustrates these two behaviours for the QD1/QD3 ratio $x = 10$. The corresponding mean decay times are 27 ns when $\lambda_{\text{ex}} > \lambda_{\text{gap}}^{(1)}$ and 41 ns when $\lambda_{\text{ex}} \leq \lambda_{\text{gap}}^{(1)}$. Here again, we evidence that FRET leads to the enhancement of acceptor QDs’ lifetimes.

The relative spectral positions of λ_{ex} and $\lambda_{\text{gap}}^{(1)}$ hence define an ‘on-FRET’ ($\lambda_{\text{ex}} \leq \lambda_{\text{gap}}^{(1)}$) and an ‘off-FRET’ ($\lambda_{\text{ex}} > \lambda_{\text{gap}}^{(1)}$) regimes. A specific analysis of the band-edge exciton and surface trap states dynamics is performed in Figure 3f, based on the measurement of the QD3-associated rate constants $k_X^{(3)}$ and $k_S^{(3)}$ in both regimes. The two relaxation paths of QD3 are all the more affected by FRET that the number x of QD1 per QD3 is high. It evidences a direct correlation between the proportion of QD3 which are involved in a QD1-QD3 heterodimer and the relative decrease of the QD3 recombination rates. It is worth noting that the chemistry of the system is exactly the same in both on- and off-FRET regimes. We can thus be sure that the observed slowdown of the carrier recombination is truly due to FRET and not to the chemical mechanism of QD-QD pairing.

2.6 | Slowdown Mechanism by Localised Carrier-Induced Stark Effect

The description of resonant energy transfer by Förster’s theory cannot account for such a slowdown. To our knowledge, the literature does not provide any direct explanation of it. It is true that the apparent lifetime of an acceptor A can increase when coupled with a long-lived donor D (i.e. $k_D \ll k_A$) provided that the donor decay time remains higher than that of the acceptor even after their FRET coupling (i.e. $k_D + k_{\text{ET}} \ll k_A$). In this case, well described by Kang and Lakowicz et al. [71], the acceptor dynamics is then dictated by that of the donor, whose decay is the rate-determining step. In contrast, here we have $k_1 = 0.5\text{--}2 \text{ ns}^{-1}$ (Figure 3c), $k_{\text{ET}}^{[13]} = 1\text{--}2 \text{ ns}^{-1}$ and $k_3 = 0.03\text{--}0.1 \text{ ns}^{-1}$ (Figure 3f), so the condition $k_1 + k_{\text{ET}}^{[13]} \ll k_3$ is not satisfied.

The FRET-induced slowdown of acceptors’ dynamics must come from the very special properties of QDs. In our view, three interesting features have to be considered. First, the main difference between QDs and other common fluorophores (e.g. organic dyes and fluorescent proteins) lies in their broad and unbounded absorption spectra, with the result that we necessarily excite the acceptor QDs as soon as we excite their donor partners: Here, $\lambda_{\text{ex}} \leq \lambda_{\text{gap}}^{(1)} < \lambda_{\text{gap}}^{(3)}$ (Figure 3d), and both QD1 and QD3 are concomitantly photoexcited. Second, from the point of view of acceptor QDs, the direct light excitation (by absorption of a photon with energy hc/λ_{ex}) can be seen as playing the role of a ‘pump’ pulse, while the nanosecond-delayed FRET-mediated excitation can play the role of a ‘probe’ pulse: The interaction with the latter may depend on the former. Third, the electron-hole recombination within QDs involves localised carrier trap states which are sources of symmetry breaking. In the light of these considerations, we propose an interpretation based on localised carrier-induced Stark effect [52, 72] with the following scenario (Figure 4): (1) Within a QD heterodimer, the direct photoexcitation of the acceptor QD leads to a long-lived trapped-electron surface state $|S\rangle$ which generates a small intradot electric field and breaks the centrosymmetry of the nanocrystal; (2) within the lifetime of this trap state, a band-edge exciton $|X\rangle$ is generated by FRET from the donor QD and acquires a slight polarisation due to the intradot electric field; and (3) due to this localised carrier-induced charge separation, the lifetime of state $|X\rangle$ is enhanced (its electron-hole envelope wave function

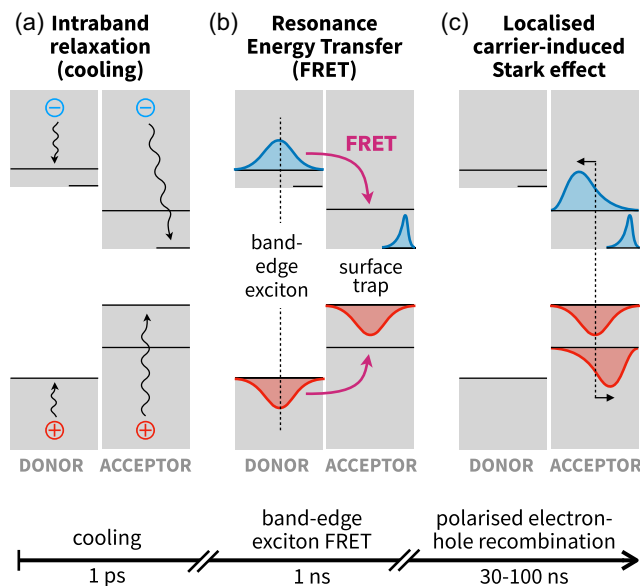


FIGURE 4 | Slowdown mechanism based on localised carrier-induced Stark effect. The conduction and valence bands of a donor/acceptor heterodimer are pictured in grey. (a) The photoexcited carriers (electrons in blue, holes in red) relax through intraband cooling. For the sake of clarity, we only represent a band-edge exciton for the donor QD and a surface trapped-electron state for the acceptor QD. (b) The band-edge exciton of the donor QD (whose envelope wave functions are symmetric) is transferred through FRET to the acceptor QD (hosting a trapped-electron/hole pair). (c) The resulting band-edge exciton within the acceptor QD is then polarised due to the intradot electric field induced by the surface state. The electron-hole envelope wave function overlap and the recombination probability are thus reduced.

overlap is reduced). In other words, the charge separation of the first electron-hole pair induces a Stark effect on the subsequent FRET-excitation of a band-edge exciton and slows down its recombination. In the frame of this mechanism, Figure 2e can be interpreted in a new light. Since state $|S\rangle$ is the cause of the Stark effect, its rate constant $k_S^{(3)}(t)$ does not vary significantly but, in contrast, state $|S\rangle$ polarises state $|X\rangle$, slows it down and makes the rate constant $\bar{k}_X^{(3)}(t)$ converge to an $|S\rangle$ -like value. Eventually, the FRET-excited band-edge exciton can be trapped into a more highly polarised surface state $|S'\rangle$ exhibiting an even longer lifetime.

Interestingly, using pump-probe absorption spectroscopy, Trinh et al. have shown that hot electron-hole pairs can also produce a transient Stark effect on optical transitions in PbSe QDs [73], which enables us to draw a parallel with our results. In their case, the bulk-like behaviour of the carriers translates into a transient and fluctuating dipole moment which breaks the QD symmetry and induces a redistribution of the optical transition strengths to dipole-forbidden states (often qualified as dark states due to their long radiative lifetimes). In the present situation of FRET, the surface trap states $|S\rangle$ play a role analogous to hot pairs: Both are sources of symmetry breaking. Moreover, the FRET process is a thousand times slower than the intraband cooling of hot carriers (occurring over 1 ps) [59, 73] and thus constitutes the rate-determining step of the mechanism. Within heterodimers, the population rate of band-edge excitons into acceptor QDs is then driven by FRET, implying a time decoupling between the photoexcited electron-hole pairs (sources of Stark effect) and the FRET-excited ones (influenced by Stark effect). In other words, the localisation of carriers at surface traps must precede the excitation of another state to affect it. This explains why FRET is required to observe such a surface trap-induced slowdown of electron-hole recombination.

3 | Conclusion

Thanks to 2D time-resolved fluorescence spectroscopy and APTES-mediated chemical pairing of CdTe QDs, we have provided a complete study of the intrinsic and collective emission properties of colloidal QDs. Benefiting from the optical and chemical tunabilities of, first, the excitation and detection wavelengths and, second, the donor/acceptor ratio, we have precisely examined QDs' intrinsic lifetimes and their behaviours when coupled through resonance energy transfer (FRET). On the one hand, we identified two emissive states of different natures: a fast exponential decay ascribed to band-edge excitons and a slow decay driven by shallow surface trapped-electron states. On the other hand, thanks to a three-level model involving these band-edge and surface trap states, we succeeded in decoupling the different relaxation processes occurring within QDs, namely the radiative exciton recombination (k_X), the surface trapping (k_{XS}), the radiative surface trap relaxation (k_S), the homogeneous and heterogeneous resonance energy transfers (k_{ET}). Such a fundamental analysis was made possible thanks to the real-time tracking of all these rate constants throughout the APTES-induced QD-QD pairing, unveiling the interplay between band-edge excitons and surface traps. Drawing on our understanding of the intrinsic and statistical behaviours of QDs, we

have indeed evidenced a FRET-dependent enhancement of acceptor QDs' lifetimes within QD heterodimers. When the donors are photoexcited, we observed that the electron-hole recombination rates decrease by 80% and 60% for the band-edge exciton and the surface trap states, respectively, translating into increases of +400% and +150% in the corresponding lifetimes. According to the light excitation wavelength λ_{ex} and the donor optical bandgap λ_D , it is therefore possible to control acceptors' relaxation dynamics with light, switching between an 'off-FRET' ($\lambda_{ex} > \lambda_D$) and an 'on-FRET' ($\lambda_{ex} \leq \lambda_D$) regimes, characterised by their own kinetics. To explain this behaviour, we proposed a slowdown mechanism based on localised carrier-induced Stark effect according to which the photoexcited electron-hole pairs trapped into the surface states polarise the FRET-excited band-edge excitons, slowing down their recombination.

4 | Experimental Section

4.1 | QD Samples

The three types of COOH-capped CdTe QDs were purchased from Sigma-Aldrich (Reference 777935, 777943 and 777951 core-type CdTe), named QD1, QD2 and QD3, respectively. QDs are provided as water-soluble powders and we disperse them in milliQ water (18 M Ω -cm) to reach stock solutions of 16×10^{-6} , 33×10^{-6} , and 22×10^{-6} M for QD1, QD2 and QD3, respectively. Their structural, chemical and optical characteristics are given in previous works [47, 53–55]: HR-TEM and EDX analyses of QD cores, X-ray photoelectron spectroscopy of QD ligands, UV-visible and PL spectroscopies of QD colloids, UV-visible spectroscopy and PL imaging of APTES-induced QD clusterisation, and analyses of pH-dependence of the QD photophysical properties. To achieve FRET, we mixed QD1 and QD3 solutions, for a total QD concentration set at a maximum of 6 μ M (to avoid inner filter effects [53]) and a total volume of 1 mL, then aggregated them by adding 1 μ L of (3-aminopropyl) triethoxysilane (APTES, A3648-100ML, 98%, Sigma-Aldrich). Given the QD concentrations of our experiments, the pH value is 7.5 ± 0.3 . When APTES is added to QDs solution to favour aggregation, the pH remains stable. Let's point out that we have previously used these pH conditions and studied their influence on photoluminescence in the cases of monodisperse colloidal quantum dots as well as mixture of QDs [47, 54]. These previous works demonstrate, in particular, that a pH value greater than 7 is conducive to the aggregation of QDs and ensures the stability of the ligands. The details of the QD concentrations and their mixing are given in Section S6.

4.2 | 2D Time-Resolved Fluorescence Spectroscopy.2D

All measurements were performed using 10 mm path length PPMA disposable cuvettes. 1 mL of QD solutions were prepared directly in the cuvette by diluting QDs in milliQ water at a final concentration ranging from 1 to 5 μ M. 1 μ L of pure APTES was added to the solution directly in the cuvette 15 min before the measurement except for Figure 2c–e wherein the evolution of the fluorescence lifetime was directly monitored upon APTES

addition. The fluorescence decay curves were recorded using the time-correlated single photon counting technique (TCSPC) with, as an excitation source, either a 470 nm pulsed laser diode (PicoQuant) or a pulsed white laser (Fianium, NKTPhotonics) at repetition rates from 2 to 20 MHz. The repetition rate was reduced for the longer lifetimes in order to avoid any pile-up effect. To spectrally select the QD fluorescence, a monochromator was used before the detection by an MCP-PMT detector (Hamamatsu Photonics). The signals were amplified by a fast pulse preamplifier (Phillips Scientific) before reaching the PicoHarp300 TCSPC module (PicoQuant). The amount of fluorescence photons was about $1\text{--}10 \times 10^5$ total counts for each decay. All experiments were performed at controlled sample temperatures ($20 \pm 0.5^\circ\text{C}$). The instrumental response function (IRF), obtained by measuring the light scattered from a LUDOX solution (Dupont), was characterised by a typical full width at half maximum (FWHM) of 75–85 ps. All data were processed with SymPhoTime32 software (PicoQuant). Decays were fitted with multiexponential models and IRF deconvoluted for the shorter lifetimes below 1.2 ns.

Additional information concerning the methodology used for each experiment is set out in the Section S7 so as not to make the main document too lengthy.

Author Contributions

Thomas Noblet: conceptualisation (lead), formal analysis (lead), methodology (lead), writing – original draft (lead), writing – review and editing (equal). **Marie Erard:** investigation (equal), resources (equal), supervision (equal), writing – review and editing (equal). **Hippolyte Stassart:** writing – review and editing (supporting). **Laurent Dreesen:** funding acquisition (lead), supervision (lead), validation (lead).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data available on request from the authors.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.