

Supporting Information to:

Homogeneous Resonant Energy Transfer within Clusters of Monodisperse Colloidal Quantum Dots

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1 Modeling of UV-visible spectra

The absorbance $\mathcal{A}(\omega)$ at pulsation ω of any system can be derived from its linear susceptibility $\chi(\omega)$:

$$\mathcal{A}(\omega) = \frac{\omega \ell}{c\sqrt{\epsilon_r} \ln 10} \text{Im}\chi(\omega). \quad (\text{S1})$$

In the case of a colloidal suspension of QDs, $\epsilon_r = 78.5$ is the relative permittivity of the solvent (water) and $\ell = 1$ cm the optical path-length through the cuvette. As derived from quantum mechanics, the susceptibility of QDs reads:

$$\chi(\omega) = -\frac{N}{\hbar\epsilon_0} \sum_{\nu} p_{\nu}^2 \left(\frac{1}{\omega - \omega_{\nu} + i\gamma_{\nu}} - \frac{1}{\omega + \omega_{\nu} + i\gamma_{\nu}} \right), \quad (\text{S2})$$

where ν labels the individual eigenstates of QDs: p_{ν} are the transition dipole moments, ω_{ν} the eigenenergies and γ_{ν} the damping factors. The parameter N is the QD concentration (m^{-3}). The eigenenergies $\omega_{\nu} = \omega_{\nu}(R)$ depend on the QD radius R , which follows a Gaussian distribution. Hence:

$$\mathcal{A}(\omega) = \frac{\omega \ell}{c\sqrt{\epsilon_r} \ln 10} \frac{N}{\hbar\epsilon_0} \sum_{\nu} p_{\nu}^2 \int_0^{+\infty} dR \frac{\gamma_{\nu}}{(\omega - \omega_{\nu}(R))^2 + \gamma_{\nu}^2} \frac{\exp\left[-\frac{1}{2} \left(\frac{R - \langle R \rangle}{\delta R}\right)^2\right]}{\delta R \sqrt{2\pi}}, \quad (\text{S3})$$

where $\langle R \rangle$ is the mean radius and δR the standard deviation. As shown in section 3, the lifetimes of the QD eigenstates range from 20 to 50 ns. This corresponds to an homogeneous spectral width of 10^{-5} nm, quite smaller than the spectral bandwidth of the whole QD population. We can thus consider that $\gamma_{\nu} \rightarrow 0$ (the damping constant is the inverse of the lifetime). At the scale of absorption and emission spectra, each QD of radius R contributes as a Dirac delta function:

$$\lim_{\gamma_{\nu} \rightarrow 0^+} \frac{1}{\pi} \frac{\gamma_{\nu}}{(\omega - \omega_{\nu}(R))^2 + \gamma_{\nu}^2} = \delta(\omega - \omega_{\nu}(R)). \quad (\text{S4})$$

As a result, the absorbance can be written:

$$\mathcal{A}(\omega) = \frac{\omega \ell}{c \ln 10} \frac{N}{\hbar\epsilon_0} \frac{1}{\delta R} \sqrt{\frac{\pi}{2\epsilon_r}} \sum_{\nu} \frac{p_{\nu}^2}{G_{\nu}(\omega)} \exp\left[-\frac{1}{2} \left(\frac{R_{\nu}(\omega) - \langle R \rangle}{\delta R}\right)^2\right], \quad (\text{S5})$$

with:

$$R_{\nu}(\omega) = \frac{-\eta_{\nu} + \sqrt{\eta_{\nu}^2 + 4(\hbar\omega - E_g)\kappa_{\nu}}}{2(\hbar\omega_{\nu} - E_g)} \quad \text{and} \quad G_{\nu}(\omega) = \frac{2\kappa_{\nu}}{\hbar R_{\nu}^3(\omega)} - \frac{\eta_{\nu}}{\hbar R_{\nu}^2(\omega)}. \quad (\text{S6})$$

Here we used the dispersion relation:

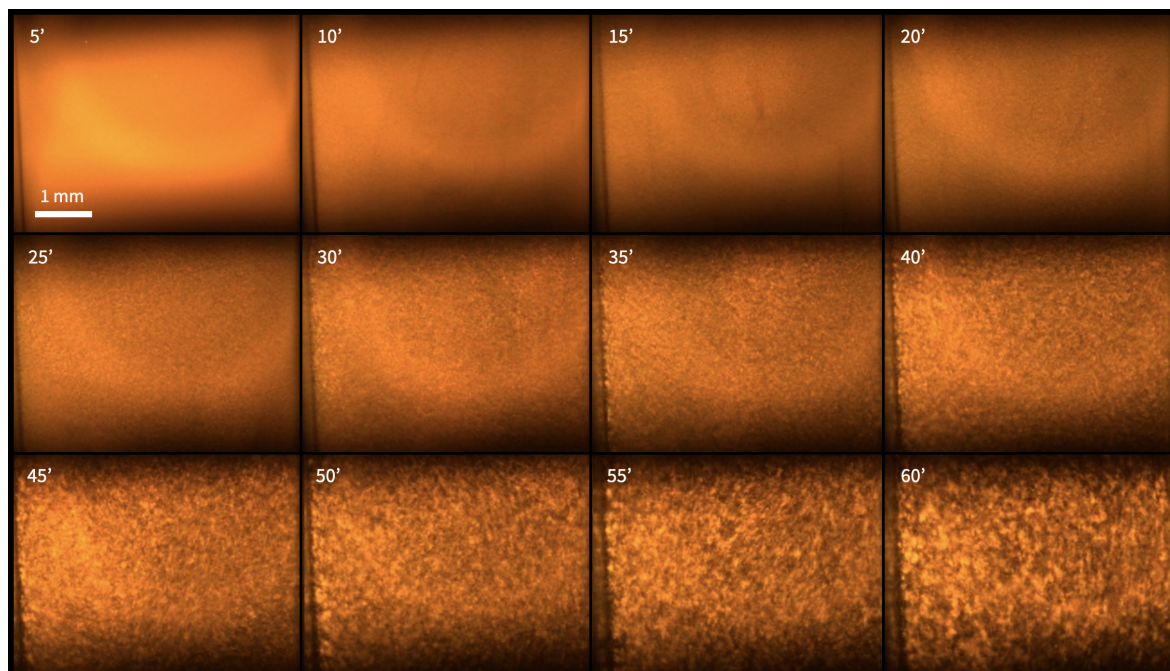
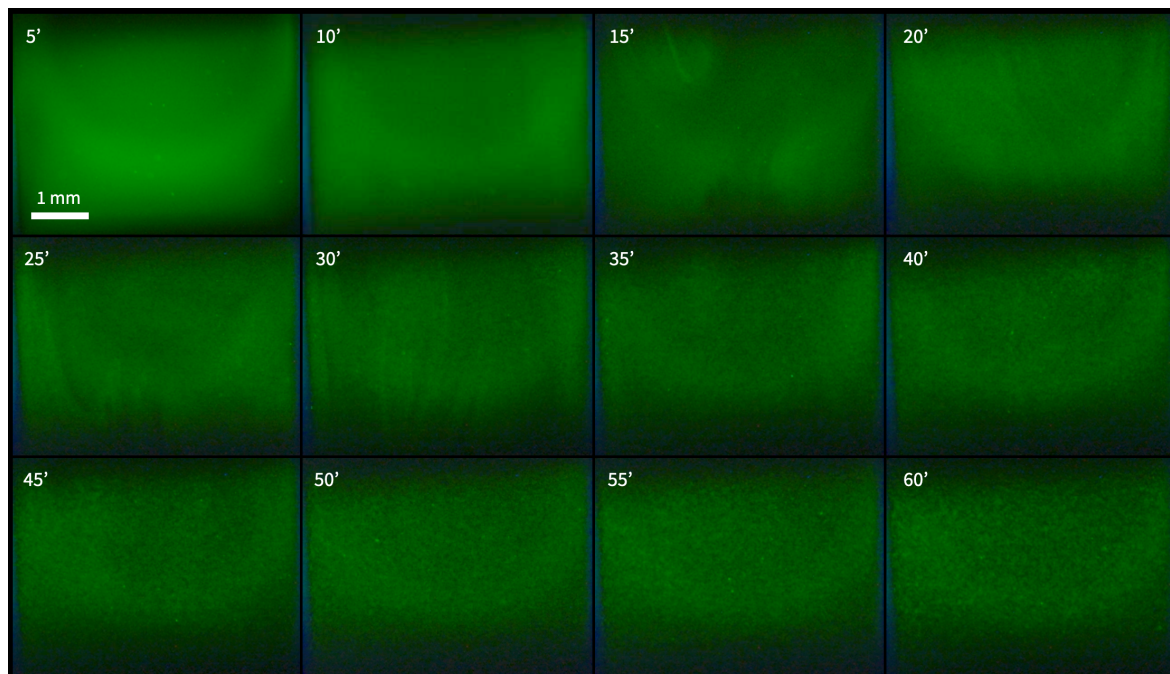
$$\hbar\omega_{\nu}(R) = E_g + \frac{\kappa_{\nu}}{R^2} - \frac{\eta_{\nu}}{R}, \quad (\text{S7})$$

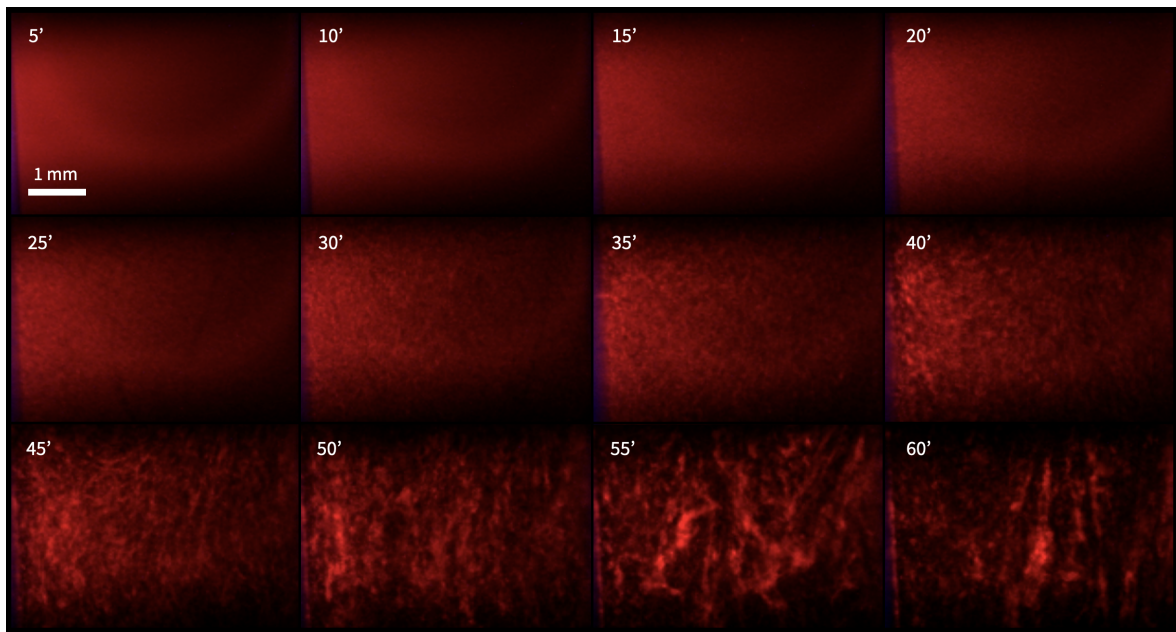
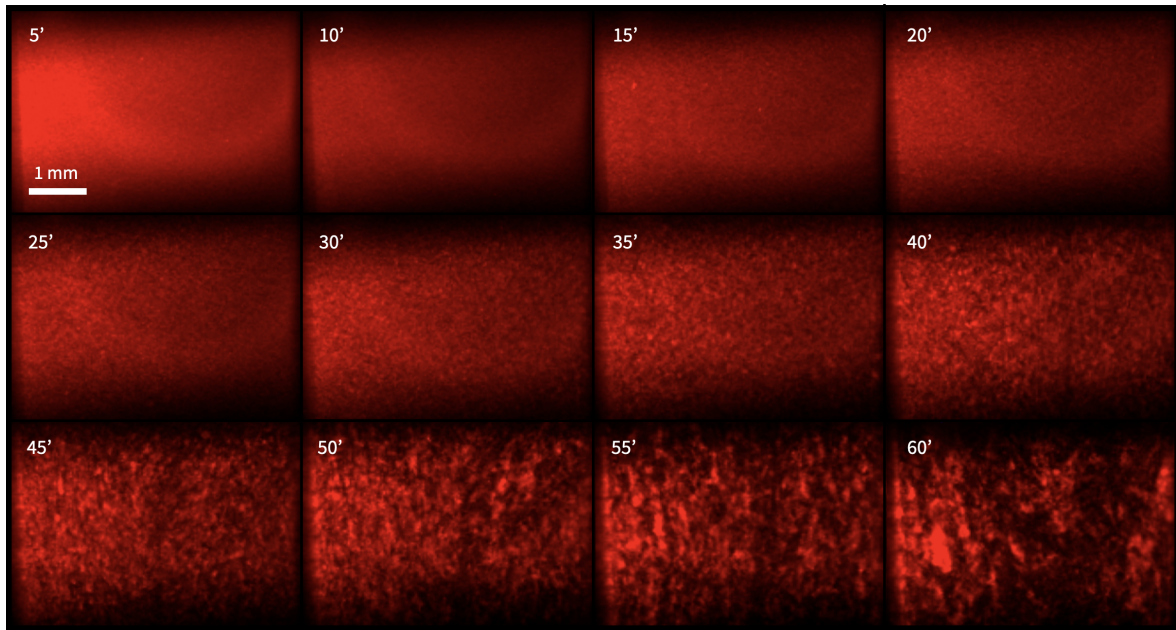
where $E_g = 1.61$ eV is the CdTe bandgap, κ_{ν}/R^2 the confinement energy in state ν , arising from the quantum confinement theory for electron/hole pairs, and η_{ν}/R the Coulomb energy between the electron and the hole of the pair in state ν . To fit the data, we considered the first six states from $\nu = 1$ to $\nu = 6$, for which κ_{ν} and η_{ν} are known [2, 1]. The resulting fitting parameters are given by the following table:

		QD1	QD2	QD3	QD4
$\langle R \rangle$	(nm)	1.98	2.26	2.49	3.24
$\delta R / \langle R \rangle$	(1)	0.0627	0.0756	0.0935	0.245
p_1	(D)	5.42	5.87	7.74	7.19
p_2	(D)	2.56	2.19	0.0732	0.0723
p_3	(D)	3.29	3.62	3.90	1.40
p_4	(D)	5.25	5.05	6.77	0.104
p_5	(D)	5.68	0.890	0.0256	4.39
p_6	(D)	5.96	9.66	9.55	8.17

2 Dynamics of aggregation

Hereafter we present the photographs of the four QD samples acquired every 5 minutes over one hour, as from the addition of APTES into the QD solutions (1 cm × 5 mm cuvettes). The colors are not artificial, but recorded thanks to a Color Sensor provided by ThorLabs (see ‘Methods’). The four sets of photographs correspond to the four samples QD1, QD2, QD3 and QD4, respectively.





3 Fluorescence lifetimes

Figure S1 gives the fluorescence decays of the four QD samples (without addition of APTES). Their fitting with a double exponential function:

$$I_f(t) = \text{bkgnd} + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \quad (\text{S8})$$

enables us to compute the mean lifetimes τ_f :

$$\tau_f = \frac{\tau_1 A_1 + \tau_2 A_2}{A_1 + A_2}. \quad (\text{S9})$$

The results range from 23 to 47 ns, i.e. $\tau_f \sim 30$ ns. This time can be seen as the coherence time of the QD emission light, thus related to the homogeneous bandwidth $d\lambda$ of individual QDs (independent from the size dispersion):

$$d\lambda = \frac{\lambda_f^2}{c\tau_f} \sim \frac{(600 \text{ nm})^2}{3 \cdot 10^8 \text{ m/s} \times 30 \text{ ns}} \sim 10^{-5} \text{ nm}. \quad (\text{S10})$$

The heterogeneous bandwidth due to size dispersion is $\delta\lambda \sim 30$ nm. Hence:

$$d\lambda \ll \delta\lambda, \quad (\text{S11})$$

so we can consider that QDs individually contribute to the absorption and emission spectra as Dirac delta functions, infinitely narrow.

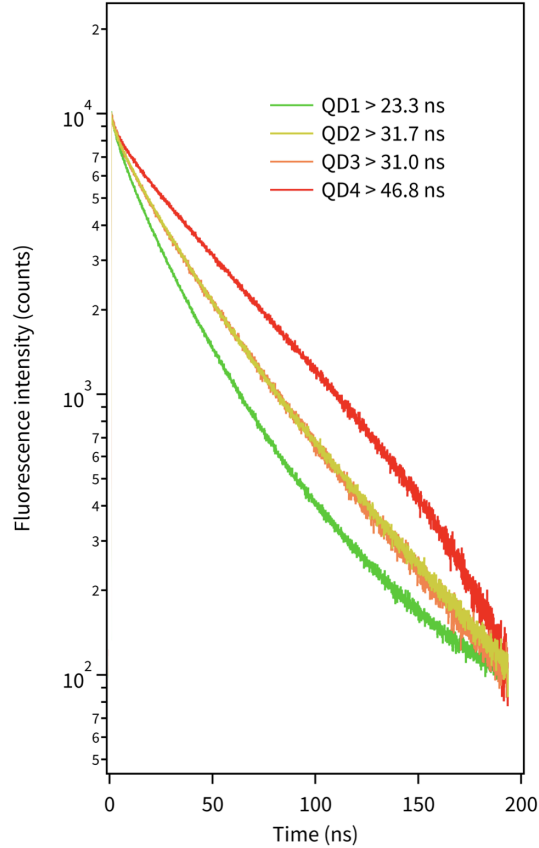


Figure S1: Fluorescence decays of colloidal QD samples QD1, QD2, QD3 and QD4.

4 Derivations of homo-FRET efficiency and redshift amplitude

4.1 Homo-FRET efficiency F_T

The normalized emission spectrum of a given monodisperse QD population follows a Gaussian distribution centered at the mean emission wavelength λ_f :

$$\hat{I}_0(\lambda) = A e^{-\left(\frac{\lambda-\lambda_f}{\delta\lambda}\right)^2}, \quad A = \frac{1}{\delta\lambda\sqrt{\pi}}. \quad (\text{S12})$$

The probability density $P(\lambda)$ for a donor QD emitting at λ to transfer its energy to another QD reads:

$$P(\lambda) = \frac{1}{\alpha} \hat{I}_0(\lambda) \hat{I}_0(\lambda + \Delta_S). \quad (\text{S13})$$

where α (nm^{-1}) is a normalization factor defined as:

$$\int_{-\infty}^{+\infty} d\lambda P(\lambda) \Big|_{\Delta_S=0} = 1. \quad (\text{S14})$$

Indeed, $P(\lambda)$ must be theoretically maximum when the Stokes shift is zero (the matching condition between donors and acceptors is instantaneously fulfilled as QDs emit at the same wavelength they absorb). Hence:

$$\alpha = \int_{-\infty}^{+\infty} d\lambda \hat{I}_0^2(\lambda) = \frac{1}{\pi \delta\lambda} \int_{-\infty}^{+\infty} d\xi e^{-2\xi^2}. \quad (\text{S15})$$

From Eq. (S12):

$$P(\lambda) = \frac{A^2}{\alpha} e^{-2\left(\frac{\lambda-\lambda_f}{\delta\lambda}\right)^2} e^{-2\frac{(\lambda-\lambda_f)\Delta_S}{\delta\lambda^2}} e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2}. \quad (\text{S16})$$

Summing over the whole QD population, the homo-FRET efficiency is defined by:

$$F_T = \int_{-\infty}^{+\infty} d\lambda P(\lambda). \quad (\text{S17})$$

Given Eq. (S16), we split the integral on both sides of the centroid λ_f :

$$F_T = \int_{-\infty}^{\lambda_f} d\lambda P(\lambda) + \int_{\lambda_f}^{+\infty} d\lambda P(\lambda), \quad (\text{S18})$$

and perform the changes of variable $x = \lambda_f - \lambda$ and $y = \lambda - \lambda_f$, respectively:

$$F_T = \frac{A^2}{\alpha} e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2} \left(\int_{+\infty}^0 (-dx) e^{-2\left(\frac{x}{\delta\lambda}\right)^2} e^{2\frac{x\Delta_S}{\delta\lambda^2}} + \int_0^{+\infty} dy e^{-2\left(\frac{y}{\delta\lambda}\right)^2} e^{-2\frac{y\Delta_S}{\delta\lambda^2}} \right) \quad (\text{S19})$$

$$= \frac{A^2}{\alpha} e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2} \int_0^{+\infty} dy e^{-2\left(\frac{y}{\delta\lambda}\right)^2} \left(e^{2\frac{y\Delta_S}{\delta\lambda^2}} + e^{-2\frac{y\Delta_S}{\delta\lambda^2}} \right) \quad (\text{S20})$$

$$= 2\frac{A^2}{\alpha} e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2} \int_0^{+\infty} dy e^{-2\left(\frac{y}{\delta\lambda}\right)^2} \cosh\left(2\frac{y\Delta_S}{\delta\lambda^2}\right) \quad (\text{S21})$$

$$= J(\Delta_S, \delta\lambda) e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2}, \quad (\text{S22})$$

with:

$$J(\Delta_S, \delta\lambda) = 2\frac{A^2}{\alpha} \int_0^{+\infty} dy e^{-2\left(\frac{y}{\delta\lambda}\right)^2} \cosh\left(2\frac{y\Delta_S}{\delta\lambda^2}\right). \quad (\text{S23})$$

We now perform the change of variable $\xi = y/\delta\lambda$:

$$J(\Delta_S, \delta\lambda) = 2\frac{A^2}{\alpha} \int_0^{+\infty} \delta\lambda d\xi e^{-2\xi^2} \cosh\left(2\frac{\Delta_S}{\delta\lambda}\xi\right). \quad (\text{S24})$$

As the hyperbolic cosine is an even function, we eventually get:

$$J(\Delta_S, \delta\lambda) = \frac{A^2 \delta\lambda}{\alpha} \int_{-\infty}^{+\infty} d\xi e^{-2\xi^2} \cosh\left(2\frac{\Delta_S}{\delta\lambda}\xi\right). \quad (\text{S25})$$

From Eqs. (S12) and (S15):

$$\frac{A^2 \delta \lambda}{\alpha} = \left(\int_{-\infty}^{+\infty} d\xi e^{-2\xi^2} \right)^{-1}, \quad (\text{S26})$$

and then $J(\Delta_S, \delta\lambda) = J(\frac{\Delta_S}{\delta\lambda})$ only depends on the ratio between the Stokes shift and the emission bandwidth. Eventually, we obtain:

$$F_T = J\left(\frac{\Delta_S}{\delta\lambda}\right) e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2}, \quad (\text{S27})$$

with:

$$J(x) = \frac{\int_{-\infty}^{+\infty} d\xi e^{-2\xi^2} \cosh(2\xi x)}{\int_{-\infty}^{+\infty} d\xi e^{-2\xi^2}}. \quad (\text{S28})$$

As a probability, F_T admits 1 as its upper value. The function $x \mapsto J(x) e^{-2x^2}$ is maximum at $x = 0$, and this is logical: on a physical point of view, the homo-FRET efficiency is expected to be maximum and equal to 1 when $\Delta_S = 0$ or $\delta\lambda = +\infty$. Besides, $J(\frac{\Delta_S}{\delta\lambda})$ is the mean value of $\cosh(2\frac{\Delta_S}{\delta\lambda}\xi)$ with respect to the statistical weight of the squared Gaussian function $\xi \mapsto (e^{-\xi^2})^2$. Such a distribution is consistent with a statistics of paired objects: here, donor/acceptor QD-QD couples. Defining the pair correlation average operator:

$$\langle f(\xi) \rangle_\xi = \frac{\int_{-\infty}^{+\infty} d\xi e^{-2\xi^2} f(\xi)}{\int_{-\infty}^{+\infty} d\xi e^{-2\xi^2}}, \quad (\text{S29})$$

we can simply write:

$$F_T = \langle \cosh\left(2\frac{\Delta_S}{\delta\lambda}\xi\right) \rangle_\xi e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2}. \quad (\text{S30})$$

As discussed in the main text of the article, $J(x) = \langle \cosh(2x\xi) \rangle_\xi$ quantifies the differentiation between donor and acceptor QDs.

4.2 Asymptotic behavior of F_T

When $x \rightarrow +\infty$, the hyperbolic cosine behaves like an exponential:

$$\cosh(2\xi x) = \frac{e^{2\xi x} + e^{-2\xi x}}{2} \sim \frac{e^{2|\xi|x}}{2}. \quad (\text{S31})$$

From Eq. (S30):

$$F_T = \frac{1}{2} \langle e^{2|\xi|x} \rangle_\xi e^{-x^2}. \quad (\text{S32})$$

Given the square of its argument, the factor e^{-x^2} tends to zero faster than $\langle e^{2|\xi|x} \rangle_\xi$ tends to the infinity. As a result, $F_T \rightarrow 0$ when $x \rightarrow +\infty$.

4.3 Redshift amplitude $\Delta\lambda$

The process of homo-FRET lies on the spectral overlap between donor emission and acceptor absorption. It occurs only if the QDs are close enough to each other. This is why we add APTES to aggregate them into clusters. The associated transfer of energy, from small to large wavelengths, thus leads to a redshift of the emission band of the QD population.

Phenomenologically, this redshift is similar to that observed when we increase the QD concentration within a colloidal suspension. In this case, QDs are not aggregated and not coupled to each other, so they cannot achieve homo-FRET. However, given their high concentration, inner filter effects (IFEs) come into play. Each QD still emits light but significantly absorbs the light of the others. It is a purely collective phenomenon of self-absorption, at the scale of the whole QD population, relying on the spectral overlap between absorption and emission [3].

Given Eq. (S13), homo-FRET can be formally described as a statistical phenomenon involving the effective overlap between absorption $\mathcal{A}(\lambda)$ and emission spectra $I_0(\lambda)$ of the whole QD population in an analogous way than IFEs, as far as $\Delta_S \gtrsim \delta\lambda$, i.e. $\mathcal{A}(\lambda) \approx I_0(\lambda + \Delta_S)$ over the spectral range of the overlap (see Figure S2). For these reasons, here we propose to, first, calculate the redshift due to inner filter effects (IFEs) and, second, extrapolate the result to the formally similar case of homo-FRET.

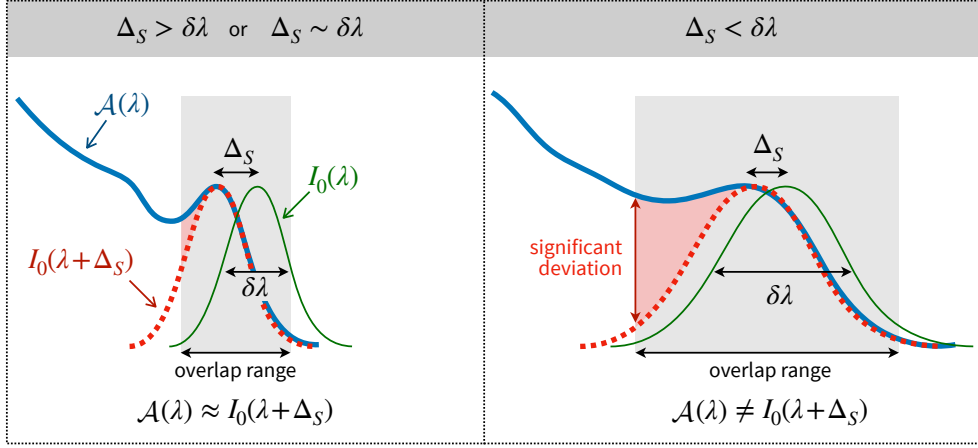


Figure S2: Principle of the approximation $\mathcal{A}(\lambda) \approx I_0(\lambda + \Delta_S)$ when $\Delta_S \gtrsim \delta\lambda$ over the spectral range of the overlap. When $\Delta_S < \delta\lambda$, the deviation between $\mathcal{A}(\lambda)$ and $I_0(\lambda + \Delta_S)$ is too important.

From our previous study about IFEs [3], the fluorescence intensity $F(\lambda)$ of a QD population at concentration N is related to the fluorescence intensity $F_0(\lambda)$ at concentration $N_0 < N$ through:

$$F(\lambda) = F_0(\lambda) \frac{N}{N_0} e^{-(N-N_0)(\sigma(\lambda_{\text{ex}}) + \sigma(\lambda))\ell}, \quad (\text{S33})$$

where σ is the absorption cross-section, λ_{ex} the excitation wavelength, and ℓ the optical path-length (i.e. the size of the cuvette). The redshift between the two spectra $F(\lambda)$ and $F_0(\lambda)$ can be deduced from the position λ_f of the maximum of emission, defined as:

$$\frac{\partial F}{\partial \lambda}(\lambda_f) = 0, \quad (\text{S34})$$

that is, from Eq. (S33):

$$\frac{\partial F_0}{\partial \lambda}(\lambda_f) = (N - N_0)\ell F_0(\lambda_f) \frac{\partial \sigma}{\partial \lambda}(\lambda_f). \quad (\text{S35})$$

Given the Gaussian distribution of the fluorescence intensity:

$$F_0(\lambda) = f_0 e^{-\left(\frac{\lambda - \lambda_f^{(0)}}{\delta\lambda}\right)^2}, \quad (\text{S36})$$

and that $\frac{\partial \sigma}{\partial \lambda}$ is approximately constant over the spectral range $[\lambda_f^{(0)}, \lambda_f]$, we get from Eqs. (S35-S36):

$$\Delta\lambda = \lambda_f - \lambda_f^{(0)} = -\frac{\delta\lambda^2}{2}(N - N_0)\ell \frac{\partial \sigma}{\partial \lambda}(\lambda_f^{(0)}). \quad (\text{S37})$$

In the case of IFEs, we find that a decreasing $\sigma(\lambda)$ leads to a redshift, while an increasing $\sigma(\lambda)$ leads to a blueshift, as expected. The amplitude of the redshift $\Delta\lambda$ is also driven by the increasing of the concentration, encoded by $N - N_0$. In other words, the data of $(N - N_0)$ and $\sigma(\lambda)$ determine the strength of the IFEs-related redshift. To observe such a redshift, two conditions must be fulfilled:

$$(\text{C1}) : \frac{\partial \sigma}{\partial \lambda}(\lambda_f^{(0)}) < 0 \quad \text{and} \quad (\text{C2}) : N > N_0.$$

In the case of homo-FRET, the total concentration of the QDs does not change ($N = N_0$), so we must find a substitute for condition (C2). As discussed in the main text of the article, the homo-FRET is efficient if the QD population is polarized in terms of donors and acceptors. We easily understand that the homo-FRET-related redshift is all the more important that small QDs are only donors and do not emit light anymore (at small wavelengths), while large QDs are only acceptors and emit more light (at large wavelengths). Such a donor/acceptor polarization of the QD population is quantized by function $J(x)$, Eq. (S28). Under these considerations, condition (C2) may be substituted by a condition over $J(x)$ (with $x = \frac{\Delta_S}{\delta\lambda}$), in such a manner that the contribution of $(N - N_0)\ell\sigma(\lambda)$ to the IFEs-related redshift is

replaced by an effective dimensionless cross-section $\hat{\sigma}$ proportional to the absorption cross-section $\sigma(\lambda)$ and function $J(x)$. Henceforth, the new condition reads:

$$(C2') : \hat{\sigma}(\lambda) \propto J(x) \sigma(\lambda).$$

so that Eq. (S37) is formally written:

$$\Delta\lambda = -\frac{\delta\lambda^2}{2} \frac{\partial\hat{\sigma}}{\partial\lambda}(\lambda_f^{(0)}), \quad (S38)$$

quantifying the strength of the IFEs-like redshift observed through homo-FRET.

The contribution of the absorption spectrum to its spectral overlap with the emission band can be reduced to the first absorption band corresponding to the first local maximum of absorption centered at λ_a (as far as $\Delta_S \gtrsim \delta\lambda$, Figure S2). It is then possible to consider $\hat{\sigma}(\lambda)$ as a Gaussian distribution of the absorption wavelengths, whose amplitude satisfies condition (C2'):

$$\hat{\sigma}(\lambda) = J(x) e^{-\left(\frac{\lambda-\lambda_a}{\delta\lambda}\right)^2} \implies \frac{\partial\hat{\sigma}}{\partial\lambda} = -2\frac{\lambda-\lambda_a}{\delta\lambda^2} J(x) e^{-\left(\frac{\lambda-\lambda_a}{\delta\lambda}\right)^2}. \quad (S39)$$

It is worth noting that, given the factor $-2(\lambda-\lambda_a)$ in Eq. (S39), condition (C1) directly flows from the hypothesis of a Gaussian cross-section. At this stage, all is thus consistent.

As a consequence, Eq. (S38) translates into:

$$\Delta\lambda = (\lambda_f^{(0)} - \lambda_a) J(x) e^{-\left(\frac{\lambda_f^{(0)} - \lambda_a}{\delta\lambda}\right)^2}. \quad (S40)$$

The difference between $\lambda_f^{(0)}$ and λ_a is nothing but the Stokes shift $\Delta_S = \lambda_f^{(0)} - \lambda_a$, so we eventually get:

$$\Delta\lambda = \Delta_S J\left(\frac{\Delta_S}{\delta\lambda}\right) e^{-\left(\frac{\Delta_S}{\delta\lambda}\right)^2} = \Delta_S \times F_T, \quad (S41)$$

which corresponds to Eq. (9) in the main text.

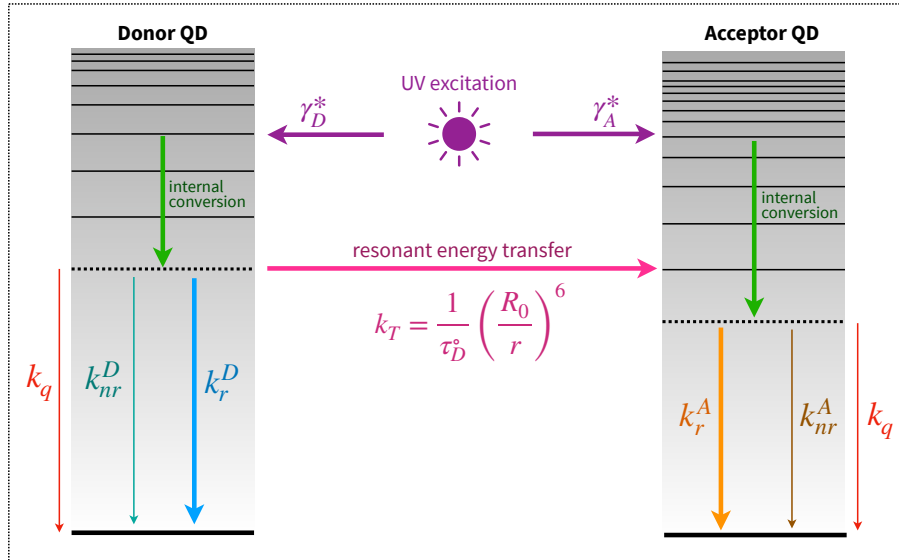


Figure S3: Model of the relaxation pathways considered to account for the processes of homo-FRET and molecular quenching. γ^* depicts the stocking rates of the donor/acceptor QDs (number of photons absorbed by unit time). k_r and k_{nr} are the radiative and non-radiative decay rates (before aggregation), and k_q encodes the existence of an additional dissipative coupling between QDs and APTES (after aggregation).

5 Rate equations of QD-QD FRET

5.1 Hypothesis of a FRET-related quenching

We consider a couple of QDs able to perform FRET as depicted in Figure S3, without additional source of quenching nor dissipative coupling (i.e. $k_q = 0$). Before addition of APTES (i.e. $k_T = 0$), the rate equations driving the fluorescence intensities $I_{D/A}^\circ$ of the two QDs read:

$$\frac{dI_D^\circ}{dt} = \gamma_D^* - (k_r^D + k_{nr}^D)I_D^\circ \quad \text{and} \quad \frac{dI_A^\circ}{dt} = \gamma_A^* - (k_r^A + k_{nr}^A)I_A^\circ. \quad (\text{S42})$$

After aggregation, the addition of the FRET process gives:

$$\frac{dI_D}{dt} = \gamma_D^* - (k_r^D + k_{nr}^D + k_T)I_D \quad \text{and} \quad \frac{dI_A}{dt} = \gamma_A^* + k_T I_D - (k_r^A + k_{nr}^A)I_A. \quad (\text{S43})$$

In steady-state regime, all the derivatives vanish and we obtain:

$$I_D = \frac{I_D^\circ}{1 + k_T \tau_D^\circ} \quad \text{and} \quad I_A = I_A^\circ + \frac{k_T \tau_A^\circ}{1 + k_T \tau_D^\circ} I_D^\circ, \quad (\text{S44})$$

with:

$$\tau_{D/A}^\circ = \frac{1}{k_r^{D/A} + k_{nr}^{D/A}} \quad \text{and} \quad k_T = \frac{1}{\tau_D^\circ} \left(\frac{R_0}{r} \right)^6, \quad (\text{S45})$$

and:

$$I_D^\circ = \gamma_D^* \tau_D^\circ \quad \text{and} \quad I_A^\circ = \gamma_A^* \tau_A^\circ. \quad (\text{S46})$$

Hence, the total fluorescence intensity after addition of APTES is given by:

$$F = I_D + I_A = \frac{1 + k_T \tau_A^\circ}{1 + k_T \tau_D^\circ} I_D^\circ + I_A^\circ. \quad (\text{S47})$$

We notice that F is poorly sensitive to the ratio between the quantum yields of the partners, i.e. the ratio between τ_D° and τ_A° . In the ideal case of a QD-QD distance $r = R_0$:

$$F = \frac{1}{2} \left(1 + \frac{\tau_A^\circ}{\tau_D^\circ} \right) I_D^\circ + I_A^\circ, \quad (\text{S48})$$

and we see that a quenching of $Q \sim 50\%$ is strictly impossible (we should have $\frac{\tau_A^\circ}{\tau_D^\circ} < 0$).

More importantly, Eq. (S44) shows that the intensity of the acceptor is necessarily enhanced. At the macroscopic scale of a whole QD population, this would translate into a systematic enhancement of the ‘red side’ of the global emission band (associated to predominantly acceptor QDs), which is not the case for samples QD1 and QD2. Even if we assume cascade energy transfers (when $\Delta_S \ll \delta\lambda$), it is not possible to explain quenching factors $Q \sim 50\%$. For interested readers, this point is discussed in details in section 5.4.

5.2 Necessity of an external source of quenching

We now assume that the aggregation induced by APTES gives rise to a new non-radiative relaxation path for both the donor and the acceptor, encoded by the rate constant k_q (Figure S3). The rate equations read:

$$\frac{dI_D}{dt} = \gamma_D^* - (k_r^D + k_{nr}^D + k_T + k_q)I_D \quad \text{and} \quad \frac{dI_A}{dt} = \gamma_A^* + k_T I_D - (k_r^A + k_{nr}^A + k_q)I_A. \quad (\text{S49})$$

In steady-state regime, we get:

$$I_D = \frac{I_D^\circ}{1 + (k_T + k_q)\tau_D^\circ} \quad \text{and} \quad I_A = \frac{I_A^\circ}{1 + k_q \tau_A^\circ} + \frac{k_T I_D^\circ}{(k_q + 1/\tau_A^\circ)[1 + (k_T + k_q)\tau_D^\circ]}. \quad (\text{S50})$$

In other words:

$$\frac{I_A}{I_A^\circ} = \frac{1}{1 + k_q \tau_A^\circ} \left(1 + \frac{\gamma_D^*}{\gamma_A^*} \cdot \frac{k_T \tau_D^\circ}{1 + (k_q + k_T)\tau_D^\circ} \right). \quad (\text{S51})$$

This corresponds to Eq. (11) in the manuscript, with the approximation $\gamma_D^* = \gamma_A^*$. Of course, we retrieve the fact that I_A is necessarily enhanced when $k_q = 0$. Interestingly, the ratio I_A/I_A° does not depend on τ_A° when $k_q = 0$. It means that any discrepancy between the QYs of the donor and the acceptor does not affect the enhancement factor of the acceptor QD, unless we do consider an additional dissipative coupling with the medium or a non-FRET mechanism (i.e. $k_q \neq 0$).

5.3 Condition over k_q

In order to account for the possibility of a quenching affecting acceptor QDs, we must determine the values of k_q satisfying:

$$\frac{I_A}{I_A^\circ} < 1. \quad (\text{S52})$$

From Eq. (S51), this is equivalent to the inequation:

$$\tau_D^\circ k_q^2 + (1 + k_T \tau_D^\circ) k_q - \frac{\gamma_D^* \tau_D^\circ}{\gamma_A^* \tau_A^\circ} k_T > 0. \quad (\text{S53})$$

The corresponding positive root is given by:

$$k_q^{\min} = \frac{-(1 + k_T \tau_D^\circ) + \sqrt{(1 + k_T \tau_D^\circ)^2 + 4 \frac{\gamma_D^* (\tau_D^\circ)^2}{\gamma_A^* \tau_A^\circ} k_T}}{2 \tau_D^\circ}. \quad (\text{S54})$$

Assuming a QD-QD distance r close to the theoretical Förster radius R_0 (since FRET occurs):

$$r = R_0 + \epsilon R_0, \quad \text{with} \quad \epsilon \ll 1. \quad (\text{S55})$$

Hence:

$$k_T \tau_D^\circ = \left(\frac{R_0}{r} \right)^6 = \left(\frac{1}{1 + \epsilon} \right)^6 \approx (1 - 6\epsilon) \quad (\text{S56})$$

By performing the Taylor expansion of Eq. (S54) with respect to ϵ , we find:

$$\frac{k_q^{\min}}{k_T} \approx \left(\sqrt{1 + \frac{\gamma_D^* \tau_D^\circ}{\gamma_A^* \tau_A^\circ}} - 1 \right) (1 + 3\epsilon). \quad (\text{S57})$$

As a first approximation, all the QDs individually get the same propensity to absorb the UV excitation light (i.e. $\gamma_D^* \sim \gamma_A^*$) and exhibit fluorescence lifetimes of the same order of magnitude (i.e. $\tau_D^\circ \sim \tau_A^\circ$), so that:

$$k_q^{\min} \sim 0.4 k_T. \quad (\text{S58})$$

Henceforth, it is possible to account for a quenching of the acceptor QDs if $k_q > k_q^{\min} \sim 0.4 k_T$. The fact that the condition over the quenching rate constant reduces to $k_q \gtrsim k_T$ clearly means that the quenching mechanism must be uncorrelated to a FRET-related process.

5.4 Discussion about cascade energy transfers

To further examine the hypothesis of a FRET-related quenching mechanism, we discuss here the assumption of a decreasing of the effective QD population quantum yield from cascade energy transfers. Without considering a new source of non-radiative decay, this hypothesis leads to the increasing of the emission intensity of the QDs involved in the end of the cascade, despite their intrinsic quantum yield. Indeed, if any QD transfers its energy to a partner by FRET, the energy remains within the system (i.e. the QD population) until, first, it is emitted by another partner or, second, it is dissipated into the medium with the same probability than if the energy had been absorbed from a direct light excitation. As a result, there would still be a region of the emission spectra satisfying $I(\lambda) > I_0(\lambda)$. Moreover, to strengthen our position, let us notice that, from QD1 to QD4:

$$x = \frac{\Delta_S}{\delta\lambda} \text{ decreases}$$

↓

$$J(x) \text{ decreases}$$

↓

The QD population is less and less statistically polarized in terms of donor and acceptor behaviors

↓

They are more and more QDs playing both the roles of donor and acceptor

↓

The cascade energy transfer is longer and longer

Henceforth, under the hypothesis of a quenching due to the length of the FRET cascade, sample QD4 should be more quenched than QD1, which is not experimentally the case.

As a result, the quenching observed for the samples QD1 to QD4 cannot be ascribed to the non-unity (i.e. the unknown statistical distribution) of the intrinsic quantum yield of QDs, nor to a would-be decreasing effective quantum yield driven by the length of the cascade energy transfer from the smallest to the biggest QDs.

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