Supplementary Information

Statistical Analysis of Photoluminescence Decay Kinetics in Quantum Dot Ensembles:
Effects of Inorganic Shell Composition and Environment

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S1. Derivation of the stretched exponential decay function

Under the assumption that the resonant electromagnetic energy transfer (FRET) from an excited donor to an unexcited acceptor is irreversible, the donor survival probability, i.e., the probability of the energy donor being in its excited state at a time $t$, is given by:

$$\phi(t, R_A) = \exp \left[ -\gamma(R_A) t \right],$$

(S1)

where $R_A$ is the donor-acceptor distance and $\gamma$, in the case of dipole-dipole interaction, is given by Eq. (10) of the main text.

With $N$ independent acceptors as possible transfer channels for one excited donor (located at positions $\{R_i\}$ relative to the donor), the survival probability is given by:

$$\phi(t, \{R_i\}) = \prod_i^{N} \exp \left[ -\gamma(R_i) t \right].$$

(S2)

Assuming that the number of acceptors is not too small, one can define a distribution function $g(R_i, j)$, which defines the probability of having $j$ acceptors in the vicinity of a point $R_i$. It can be taken as a Poisson distribution with a mean equal to the average number of acceptors in a physically infinitesimal volume element near a point $R$, $\Delta R$ (defined as $\Delta n_A = \Delta R C_A(R)$, where $C_A(R)$ is the volume concentration of acceptors),

$$g(R, j) = \exp \left[ -\Delta n_A(R) \right] \frac{[\Delta n_A(R)]^j}{j!}.$$  

(S3)

With the help of this function, the excited donor survival probability can be written as follows:

$$\phi(t, \{R_i\}) = \prod_i^{\infty} \left\{ \sum_{j=0}^{N} g(R_i, j) \exp \left[ -\gamma(R_i) t \right] \right\}. $$

(S4)

The advantage of Eq. (S4) is that it can be applied to an inhomogeneous distribution of donors. It also takes into account local fluctuations of their concentration.
Substituting (S3) into (S4), we have:

\[
\phi(t, \{R_i\}) = \prod_i \exp \left[ -\Delta n_A(R_i) \right] \left\{ \sum_{j=0}^{N} \frac{\Delta n_A(R_i) \exp \left[ -\gamma(R_i) t \right]}{j!} \right\}
\]

\[
\approx \prod_i \exp \left[ -\Delta n_A(R_i) \right] \left\{ \exp \left[ \Delta n_A(R_i) e^{-\gamma(R_i) t} \right] \left[1 - e^{-\gamma(R_i) t} \right] \right\}
\]

where we took the limit \( N \to \infty \) in the second line. Taking the continuous limit (i.e. assuming that \( C_A(R) \) is a smooth function) and replacing \( \sum_i \) by an integral, we arrive at the expression for \( \phi(t) \) given in the main text, Eq. (10).

Similar arguments used for the "fixed-shell" model (Sec. 3.3.2) lead to Eq. (17) of the main text, valid for a finite number of acteptors in the shell.

S2. QD-in-PMMA films

We fabricated thin-film hybrid structures by spin-coating using a Model KW-4A Spin-Coater using a previously developed technique. Initially semiconductor QDs were deposited onto a glass surface from a hexane solution with a molar concentration of \( 3 \times 10^{-11} \) M at 1000 RPM during 60 s. Then a toluene solution of poly(methyl methacrylate) (PMMA) with an average molecular weight of 120,000 by GPC (Sigma Aldrich, 182230) was used to prepare a polymer spacer layer. Thin films were fabricated by spin-coating at 1000 RPM during 60 s. To change the thickness of the PMMA layer, we varied the concentration of the PMMA solution used for the spin-coating. The thicknesses of the PMMA layers were estimated using the AFM height profiling method after cutting off a part of the deposited film (see Figures 1-3 below).
Figure 1: AFM profiling of the cut “10 nm” PMMA layer.

Figure 2: AFM profiling of the cut “25 nm” PMMA layer.
S3. Single-particle measurements

In order to check that we collected signals only from a single QD in our measurements of the QD-in-PMMA films, we used the photon-correlation technique. In the Hanbury-Brown-Twiss geometry with a beam-splitter and two photodetectors, we measured the second-order cross-correlation function, $g^{(2)}$, from each QD:

$$g^{(2)}(\tau) = \frac{\langle I_1(t)I_2(t+\tau)\rangle}{\langle I_1(t) \rangle \langle I_2(t+\tau) \rangle},$$  

(1)

where $\langle \cdots \rangle$ means time-averaging, $I_1(t)$ and $I_2(t)$ are time-resolved signals from the first and second detectors, and $\tau$ is the time delay between two detectors. For PL decay measurements we used only those QDs that showed a near-zero central part of the $g^{(2)}$ function (a typical $g^{(2)}$ function is presented in Figure 4), which means the single-photon emission$^2$. For samples covered with silver nanospheres, we checked $g^{(2)}$ before the deposition of nanospheres following the procedure developed in our previous studies$^3,4$. We found single QDs by measuring the $g^{(2)}$ function, then we fixed the objective, carefully deposited silver nanoparticles by dropping the water solution on the surface of the QD-in-PMMA film, and measured found QDs again being sure that they are single.
Figure 4: A typical $g^{(2)}(\tau)$ function for QDs chosen for single-particle measurement before the deposition of silver nanoparticles.

S4. "Dark fraction" of QDs

The presence of a "dark fraction" in QD ensembles is a well-known phenomenon and here we present a brief note on (i) how it is related to the fluorescence intermittency (blinking) of QDs, (ii) how it affects the PL decay kinetics, and (iii) how one can use the statistical analysis to identify the formation of a "dark fraction" in a QD ensemble without measurement of QY and single-particle measurements. We also provide information about the average exciton occupancy during our measurements of less than 10%, which is far away from the saturation limit and possible nonlinear processes.

The presence of an extra charge in the core of QDs causes a decrease of their PL quantum yield (QY) and lifetime and leads to the formation of two fractions of QDs, one with a longer lifetime and a higher QY and the other ("dark fraction") with a much shorter lifetime and lower QY. For a single QD, one can observe this effect as the well-known blinking phenomenon, which is a temporary switching of a QD into a low-emitting state with a short lifetime. In most types of QDs this effect is observable even at low-intensity
excitations⁶. Thus, the measured time-averaged PL kinetics is non-monoexponential even for single QDs if the blinking is present. During a blinking event, the PL lifetime is much shorter and it contributes to the overall collected PL lifetime histogram (measured PL kinetics), so only a measurement of only “on” or “off” states can yield the monoexponential behavior. The explanation of the blinking phenomenon (A-type, with reduced lifetime) is a nonradiative Auger recombination due to the presence of the extra-charge inside the QD core. The origin of the extra-charge may be associated with either a high-intensity excitation and biexciton recombination, or with a (low-intensity) excitation of the exciton with a subsequent thermonduction of one of the charge carries to the trap state on the QD surface⁷. Moreover, the process of charging may be irreversible in the dissolved solutions where surface ligands can desorb and take this trapped charge with it, then during the chemical processes of purification and washing these extra-charges may leave solution forever. In QDs with a thick shell, the blinking is suppressed⁸, thus the formation of “dark fraction” in their solutions are suppressed too, giving a nearly-monoexponential PL decay in their ensembles. This type of kinetics is easily detectable via the $R_n$ distribution, as explained in the main text.

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