

Supporting information:

S1 Estimation of photoinduced electron transfer

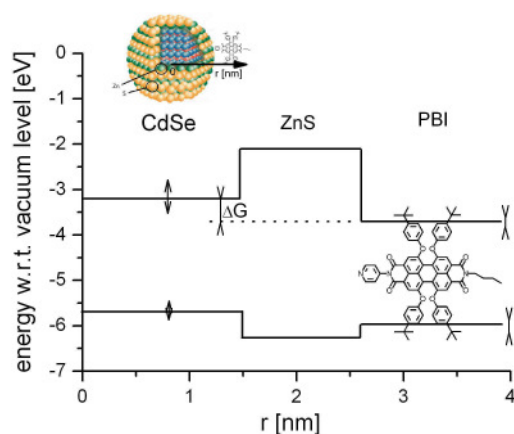


Fig. S1.1 Redox potentials of CdSe/ZnS QD and PBI dye molecules; the arrows indicate the range of variation know from literature data. In the case of PBI variations are caused by different conformations. Data taken from references¹⁻⁷.

Most reports on electron transfer refer to core-only system, so far there are only few reports on electron and/or hole transfer between core/shell nanocrystals and organic dye molecules^{8,9}. A quantitative analysis of such systems is missing.

A system with a similar redox potential situation to the one applied here, shown in Fig. S1.1, was presented by Bakkers et al.¹⁰ The electron transfer rate k_{ET} of their gold/spacer/QD system was determined experimentally via cyclic voltammetry varying the length of the spacer molecules. The obtained rates are in the range of 10^5 to 10^4 s⁻¹ at distances of 3 to 12 Å respectively. These values may be even lower in systems where the spacer is realised by higher band gap materials (like a ZnS shell). Hence, electron transfer should not be a competitive process to the QD decay rate $k_{rad} = 5 \cdot 10^7$ s⁻¹.

In the following, some further arguments against efficient electron transfer will be discussed. Huang et al.¹¹ suggest the description of electron transfer based on Marcus theory¹², whereat the non-adiabatic electron transfer rate can be calculated according to Equ. (S1.1)

$$k_{ET} \propto H_{DA}^2 F(\Delta G, \lambda) \quad (\text{S1.1})$$

with

$$H_{DA}^2 = H_{DA,\max}^2 e^{-\beta r}. \quad (\text{S1.2})$$

$F(\Delta G, \lambda)$ is the Franck-Condon-Factor and H_{DA} describes the electronic coupling between donor and acceptor. As described by Bakkers et al. the parameter β was found to be in the range of 0,1 to 1,5 Å for amorphous and crystalline solids and biological relevant systems¹⁰. According to Kuno and coworkers¹³, the “carrier attempt frequency” - which may be regarded as $k_{ET,\max}$ - is in the order of 10^{14} to 10^{15} s^{-1} . Estimating a distance of 1.5 nm between QD core surface and the chromophoric unit of the PBI, the electronic coupling constant H_{DA} is reduced and $k_{ET,\max}$ becomes smaller by a factor of 10^4 to 10^5 (for maximum β factors of 15 Å).

The reorganisation energy λ consists of solvational (λ_0) and vibrational (λ_i) term. The first term - calculated by assuming spheres for donor and acceptor - is 0.03eV in our system. Electron transfer is very efficient when ΔG is close to λ (see Fig. S1.2) and thus λ_i is the critical, but unknown parameter. The difference in Gibbs free energy for the system shown in Fig. S1.1 is between 0.5 and 1 eV, leading to by several orders of magnitude reduced electron transfer rates in the case of small λ_i values.

Finally rates determined from Equ. (S1.1) are still overestimated since so far the ZnS barrier shell is not taken into account.

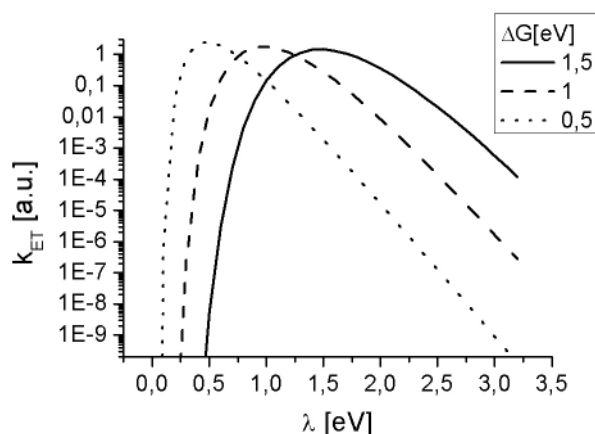


Fig. S1.2 Electron transfer according to (S1.1) for different ΔG .

Besides the mentioned lack of changes in the dye fluorescence quantum yield as described in the paper, the above mentioned considerations lead to the conclusion that charge transfer is not competitive with the PL decay or FRET rates in the investigated systems.

literature:

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S2 Calculation of the number of ligands

According to Nie et al.¹, the number n_{SA} of surface atoms and related Volume V_{SA} for QD can be estimated according to eq. (S2.1) and (S2.2)

$$n_{SA} = 2 \frac{V_{SA} \cdot D \cdot N_A}{MW}, \quad (S2.1)$$

and

$$V_{SA} = \frac{4}{3} \pi (r^3 - (r - d)^3), \quad (S2.2)$$

whereat V_{SA} is volume of the surface atoms, calculated from the total QD volume, approximated by a sphere with radius r and the thickness $d_{ZnS} = 0.35$ nm of the outer monolayer, determined from the lattice constant. We assume for each Cd (Zn) one dangling bond at the surface, which might be saturated by ligands or functionalised pbi: By calculating the total number of atoms in the QD from density $D_{ZnS} = 4.01$ g/cm³ and molar weight $MW_{ZnS} = 97$ g/mol; Avogadro's number N_A , the ratio of surface atoms (SA) to atoms in the complete volume can be used to get the number of surface atoms resulting in eq. (S2.1), where the factor 2 accounts for the number of atoms per ZnS molecule. Lattice constants d have been taken from² and ³, resulting in more than 400 (600) Cd (Zn) surface atoms for a CdSeZnS QD of 5.1nm diameter including 3 ZnS monolayers

Number of surface atoms blocked by one PP molecule

Maximum radius of PP: $r_{PP} = 1$ nm

Maximum ratio of surface area covered by 1 PP molecule to total QD surface: $\frac{\pi r_{PP}^2}{4\pi r_{QD}^2} = 3,7\%$.

This value commensurates with the creation of at most 22 free surface atoms, while occupying only one by the pyridyl group.

Assuming 30% surface coverage with ligands after the dilution of the stock solution, 1.1% (6-7 atoms) of the surface will be blocked for reattachment of surfactants by one PP molecule on average.

The ligand exchange related absolute loss of QY is thus **0.66%** on average (presuming the maximum surface coverage is realised at the maximal measured QY of the stock solution being 60%). From ensemble experiments we know that at $x = 1$, PP quenches the QY from 15% QY to 13.2%, correcting for the incomplete labelling of $f_{DA} = 0.24$ the absolute QY would be effectively quenched to **7.8%** (75 free surface atoms) in case of complete (1:1) labelling. To explain the experimentally observed quenching a ligand depletion of 75 ligands would be necessary which is a factor of 12 larger than expected value (*vide supra*).

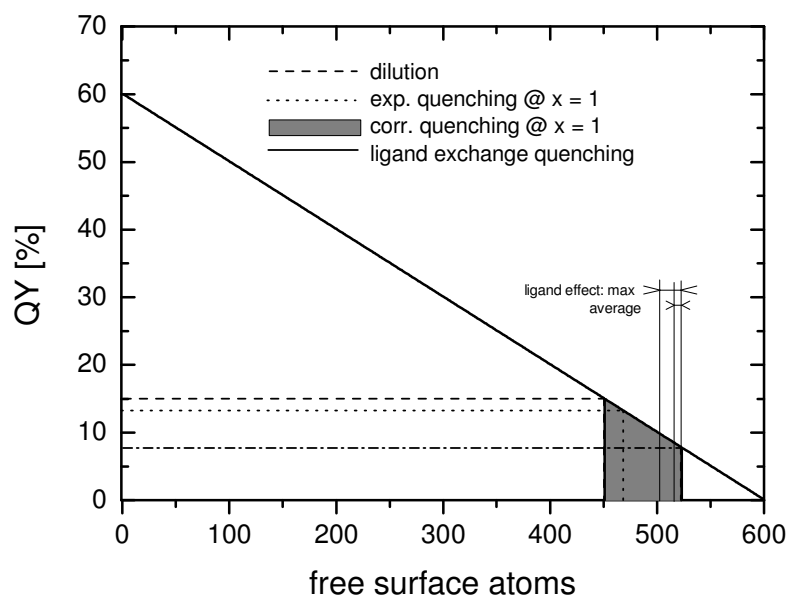


Fig. S2.1 Model according to⁴ describing QD quenching by linear function of ligand coverage (directly related to number of free surface atoms). Ligand loss upon dilution from stock (dashed line) or displacement/blockage of ligands by one PP dye molecule (vertical lines); Grey shaded area represents quantity of ligand removal necessary to explain quenching at $x = 1$ (corrected quenching for complete labelling).

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S3 Control experiments of PL quenching for CdSe/ZnS QD by pyridine

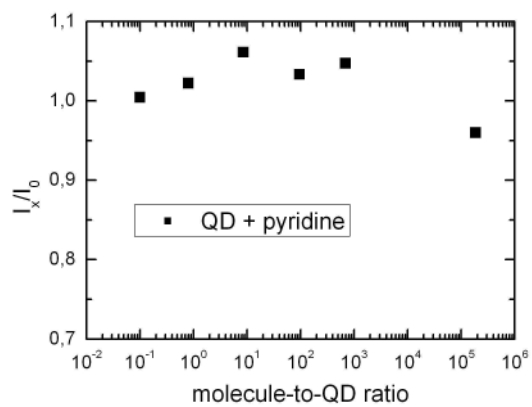


Fig. S3.1 PL quenching by titration of 10^{-7} molar CdSe/ZnS QD-AM nanocrystals with pyridine in toluene solution. Note the logarithmic x-axis.

S4 Estimation of FRET efficiency

It is somewhat surprising that the FRET efficiency estimated from the acceptor enhancement of our QD-PP assemblies is quite low since PBI molecules have large transition dipole moments¹. According to Förster theory FRET efficiency is²

$$E_{Förster} = \frac{R_0^6}{R_0^6 + r_{D-A}^6}, \text{ with } R_0 = 0.211 \cdot [\kappa^2 n^{-4} QY_D J(\lambda)]^{1/6}, \quad (\text{S4.1})$$

where $J(\lambda)$ is the spectral overlap between donor emission and acceptor absorption, κ^2 represents a coupling parameter due to the geometrical orientation of the corresponding dipoles and n , QY_D and r_{D-A} are the refractive index of the embedding medium, the donor quantum yield and the donor-acceptor distance, respectively.

Assuming tolerances of these parameters occurring in solution or single particle experiments, FRET efficiencies are calculated as the extreme (maximal or minimal) and “typical” efficiencies in case of QD-PP as shown in Fig. S4.1.

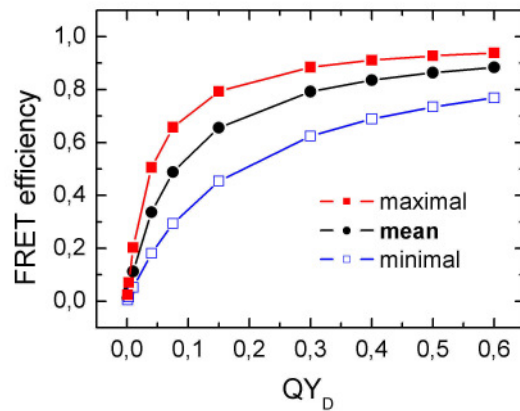


Fig. S4.1 FRET efficiency of QD-PP, depending on QD (PP) diameter d_{QD} (d_{PP}) and their respective emission and absorption wavelengths λ_{em-QD} , λ_{abs-PP} . Mean E_{FRET} (bold filled circles), minimum FRET (unfilled squares) and maximum FRET (filled squares). Values obtained for parameter according to table S4.1.

It is seen that the efficiency can be reduced below 0.18 upon reduction of the QY from values close to 0.15 to values close to 0.05 and lower. Such reductions in QY may result from extremely low concentrated QD samples accompanied by ligand shell depletion²² and intrinsic NON-FRET contributions due to assembly formation.

The following parameters have been used to calculate FRET:

- Diameter distribution of QD: $d_{\text{QD}} = (5.1 \pm 0.5) \text{ nm}$
- PP centre to QD surface distance variation due to functional group (alkyl/pyridyl): $d_{\text{PP}}/2 = (1.02 \pm 0.06) \text{ nm}$ (see Fig. S4.2)
- Range of spectral diffusion of QD: $\lambda_{\text{em-QD}} = (560 \pm 10) \text{ nm}$
- Spectral range related to changes in conformation of PP³: $\lambda_{\text{abs-PP}} = (576 \pm 10) \text{ nm}$

Table S4.1 shows the molecule/particle diameters, emission and absorption parameters used for calculation of the mean, minimal and maximal FRET efficiencies in the case of QD-PP assemblies.

E_{FRET}	Mean	Minimal	Maximal
d_{QD} [nm]	5.1	5.6	4.6
d_{PP} [nm]	2.04	2.16	1.92
$\lambda_{\text{em-QD}}$ [nm]	560	550	570
$\lambda_{\text{abs-PP}}$ [nm]	576	586	566

Table S4.1 Parameters for calculations of FRET efficiency.

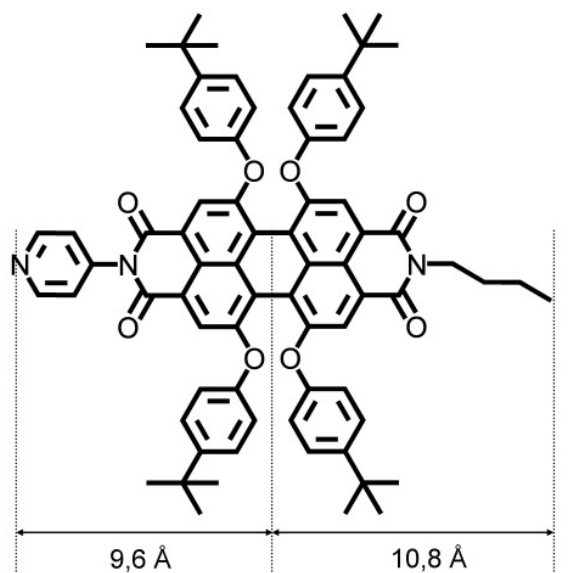


Fig. S4.2 Scheme of a PP molecule, values represent maximal and minimal PP radius

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