<u>Supplementary Information</u>

Luminescence Quenching in Supramolecular Assemblies of Quantum Dots and Bipyridinium Dications

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Calculation of the size of the inorganic nanocrystals

The uncoated CdSe core size was evaluated according to the onset of visible absorption (539 nm, see thick line in Fig. 4).[1] By this approach, a diameter of 2.8 nm was calculated. The CdSe core absorption coefficient was also evaluated by previously reported equations,[1] using the above reported size. The amount of zinc or sulfur required for each layer was determined by the number of the surface atoms for a given size of a core–shell nanocrystal, and the ratio between the core and shell volumes was considered on the basis of bulk lattice parameters for CdSe and ZnS. The calculations were based on the wurtzite structure for the CdSe nanocrystal and zinc blend for the ZnS shell. The average contribution of one hemi-layer of ZnS to the particle diameter was taken as 0.31 nm. Considering that 4 full monolayers of ZnS were grown on the 2.8 nm CdSe core, and assuming that the shell precursors reacted completely, a final size of 5.3 nm for the CdSe–ZnS core–shell QDs was estimated.

DLS experiments

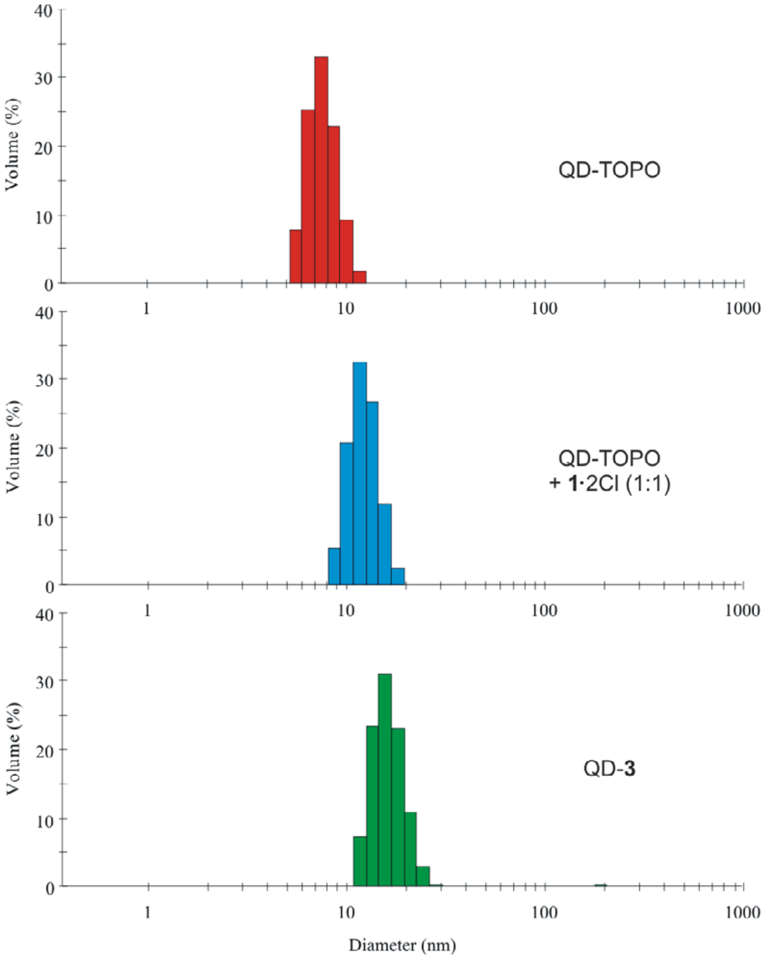

Fig. S1. Examples of size distribution analysis, extrapolated by DLS experiment, for QD–TOPO (top), QD–TOPO and **1**·2Cl (1:1) (center), and QD–**3** (bottom).

^{1}H NMR and ESIMS Spectra of 3

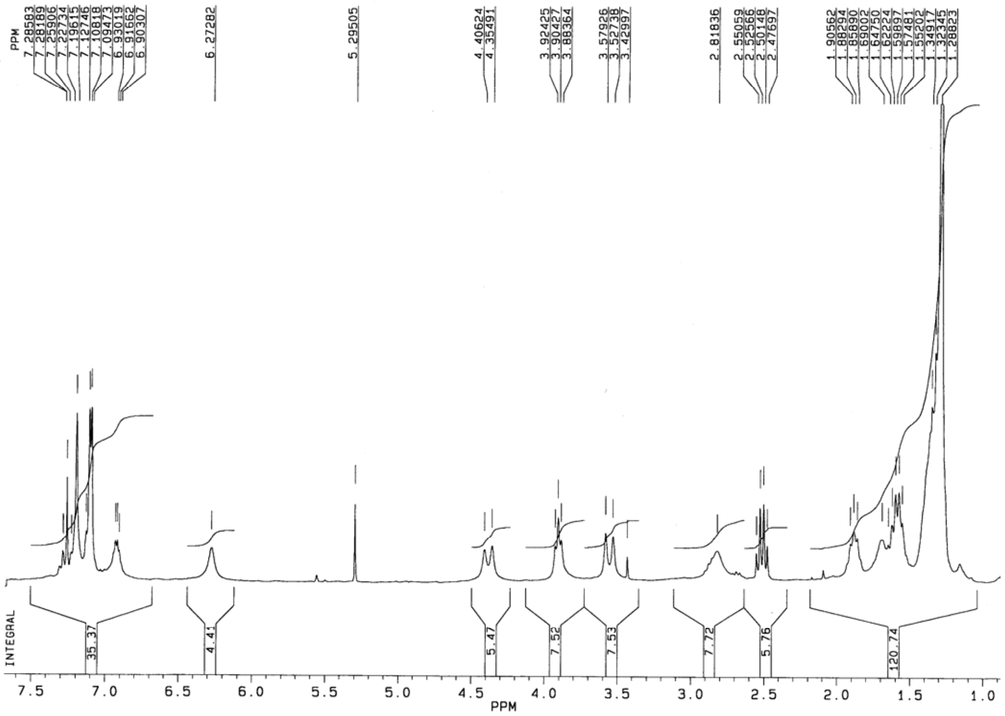

Fig. S2. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of **3**.

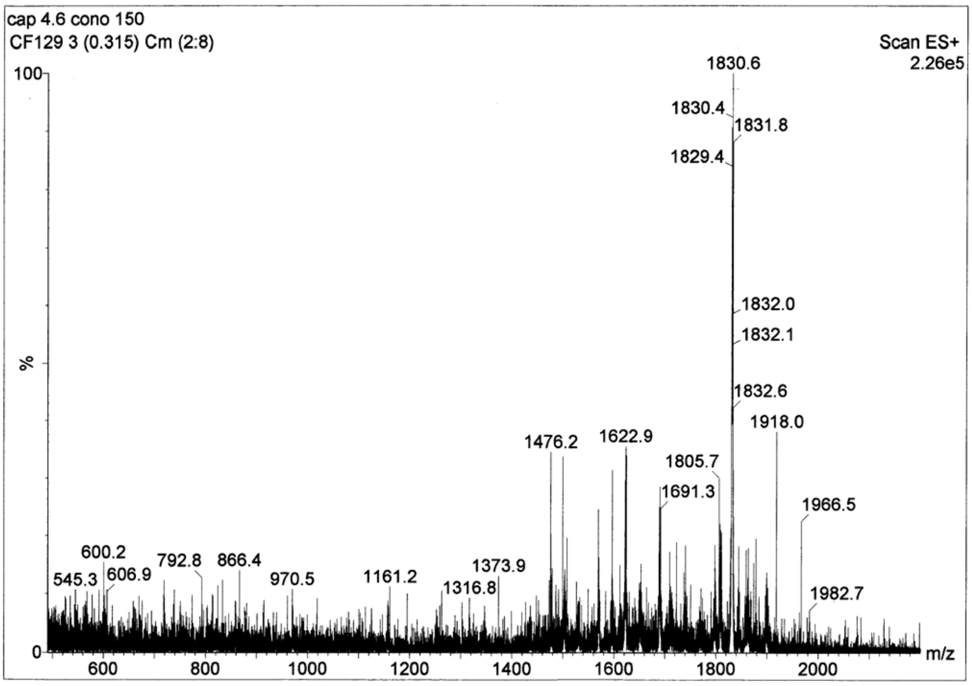

Fig. S3. ESIMS spectrum of **3**.

Analysis of the Stern–Volmer Plots

Fig. S4 shows the Stern–Volmer plots obtained from luminescence intensity and lifetime measurements upon addition of **1**·2Cl to QD–TOPO. Qualitatively similar results have been obtained with **1**·$2PF_6$ or **2**·$2PF_6$ as the quenchers or with QD–**3** as the luminophore. The non-linearity of the Stern–Volmer plot for luminescence intensity and the invariance of the luminescence lifetime on increasing the quencher concentration indicate that the quenching is static in nature, *i.e.*, the QD and bipyridinium dications are associated in their ground state.

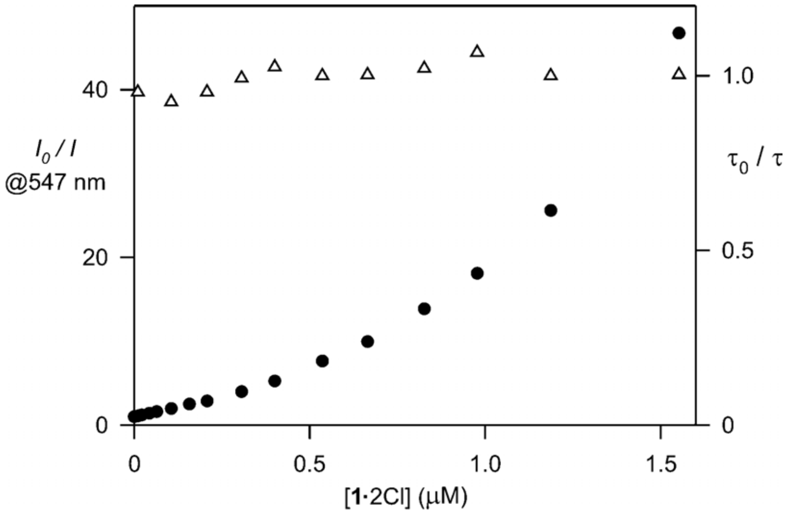

Fig. S4. Stern–Volmer plots obtained from luminescence intensity (circles; left scale, I_0/I) and lifetime (triangles; right scale, τ_0/τ) measurements upon addition of **1**·2Cl to QD–TOPO in $CHCl_3$.

In case of static quenching the luminescence behavior of the system can be described[2] by means of the following equation:

$$\frac{I_0}{I} = 1 + \left(k_q \tau_0 + K \frac{\varepsilon_{L.Q}}{\varepsilon_L} \right)[Q] + k_q \tau_0 K \frac{\varepsilon_{L.Q}}{\varepsilon_L}[Q]^2 \qquad (1)$$

wherein: I_0 and I are the luminescence intensity of the luminophore in the absence and in the presence of the quencher, respectively; τ_0 is the luminescence lifetime of the luminophore in the absence of quencher; k_q is the bimolecular (dynamic) quenching rate constant; K is the stability constant of the luminophore-quencher complex; [Q] is the molar concentration of the quencher; and ε_L and $\varepsilon_{L.Q}$ are the molar absorption coefficients of the luminophore and of the luminophore–quencher complex, respectively, at the excitation wavelength (in this case $\varepsilon_{L.Q}/\varepsilon_L \approx 0.8$ at 400 nm, see Fig. 4). Since in our case $K\varepsilon_{L.Q}/\varepsilon_L$ is certainly much larger than $k_q\tau_0$, at small quencher concentrations the third term of the equation can be neglected and a linear Stern–Volmer plot, whose slope is equal to $[k_q\tau_0 + K\varepsilon_{L.Q}/\varepsilon_L] \approx K\varepsilon_{L.Q}/\varepsilon_L$, is obtained.

As a matter of fact, the first part of the Stern–Volmer plot can be satisfactorily fitted by a linear regression (Fig. S5), yielding a slope of 9.1 μM^{-1} and an association constant of 11.4 μM^{-1}. The same value, within experimental error, is obtained by fitting the luminescence spectral changes with the Specfit software[3] by assuming a 1:1 binding model.

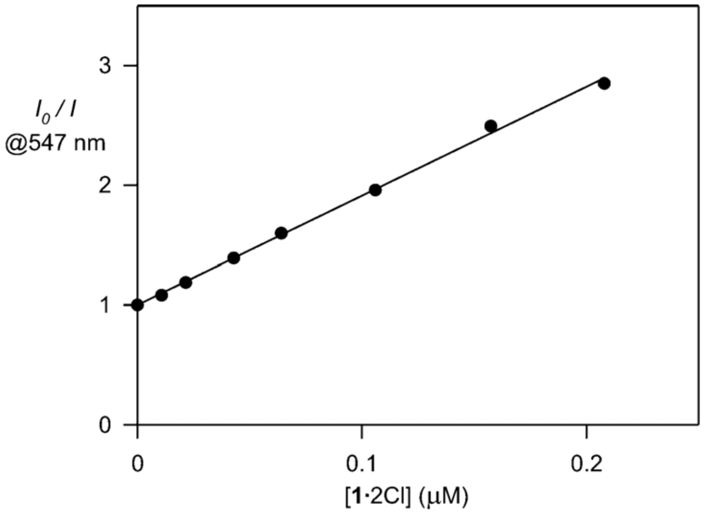

Fig. S5. Stern–Volmer plot obtained from luminescence intensity measurements (I_0/I) upon addition of up to 2.0 mM of **1**·2Cl to QD–TOPO in $CHCl_3$. The line represents the fitting to the data points according to eq. (1).

The quenching rate constant was estimated from equation (2),

$$k_q = 1/\tau_0\,(I_0/I - 1) \qquad (2)$$

where τ_0 and I_0 are the luminescence lifetime and intensity of the luminophore in the absence of the quencher, respectively, and I is the luminescence intensity observed for the luminophore-quencher complex (taken as that corresponding to the plateau at end of the titration). For example, in the case of the QD–TOPO/**1**·2Cl pair,

$$k_q = 1/(16\times10^{-9}) \times (180/5 - 1) = 2.2 \times 10^9\ s^{-1} \qquad (3)$$

The above described analysis of the Stern–Volmer plot was applied to all the examined luminophore–quencher pairs.

References

1. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.* 2003, **15**, 2854.
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3. R. A. Binstead, SPECFIT, Spectrum Software Associates, Chapel Hill, NC, 1996.