Observation of Non-Förster Type Energy Transfer Behavior in Quantum Dot-Phthalocyanine Conjugates

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Supporting Material

1. Synthesis of CdSe Quantum Dots (QDs) and their Conjugates with Phthalocyanines (Pcs):

CdSe QDs were synthesized by using cadmium oxide (STREM), selenium powder (STREM), trioctylphosphine (TOP, Fluka), trioctylphosphine oxide (TOPO, Aldrich) and hexadecylamine (HDA, Aldrich) with slight modification to a previously reported method[1]. In brief, 0.510 g CdO, 3.75 g TOPO and 2 g HDA were heated at 320 °C to get a colorless solution. The temperature was lowered to 270 °C. The selenium precursor (TOPSe) was obtained by dissolving 0.0410 g Se in 2 ml TOP and injected into CdO precursor at 270 °C. The QDs were allowed to grow at 250 °C. The reaction was quenched by adding anhydrous toluene at 60 °C. The synthesized QDs were washed twice by using methanol as precipitating solvent to get rid of excess TOPO. A final solution of QDs was made in anhydrous toluene and mixed with Pc solutions of different linker chain lengths in toluene. Each mixture was allowed 24 hrs for conjugation. All the solvents used were anhydrous and measurements were carried out at room temperature. Synthesized QDs were characterized by UV-VIS absorption (Varian Cary 50) and fluorescence spectroscopy (Varian Eclipse Fluorescence Spectrophotometer).

CdSe QDs capped with tributylphosphine oxide (TBPO) was synthesized in the same manner as discussed above but by replacing TOPO and TOP with TBPO and TBP, respectively. Both CdSe QDs sample capped with TOPO and TBPO, show an absorption maximum at 557 nm and emission maximum at 580 nm, respectively. Therefore, we were able to keep the spectral overlap integral constant and the only variable factor was the Pc linker chain length.

2. Adjustment of QD and Pc Concentration for Optimum Energy Transfer Efficiency:

The energy transfer efficiency was observed to increase with increasing Pc/QD concentration ratio. However, at the same time increasing the Pc concentrations led to self-quenching of Pc emission. Therefore, in our study we used a Pc/QD concentration ratio of 2:1 to observe the highest ET efficiency but still keeping the Pc self-quenching minimal. The Pc concentration was 8×10^{-6} M and the QD concentration as calculated based on Peng's method (Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G. *Chem. Mater.* **2003**, 15, 2854.) was 5×10^{-6} M in all the investigated solutions. The solutions were prepared by adjusting the optical density with the following molar extinction coefficients: $\varepsilon_{(QD,\ 557\ nm)} = 2.1\times10^5\ M^{-1}cm^{-1}$ and $\varepsilon_{(Pc,\ 673\ nm)} = 3\times10^5\ M^{-1}cm^{-1}$. While the emission quantum yield of the Pcs varies slightly with linker chain length, the absorption did not. Therefore, the extinction coefficient of all Pcs was a constant and so was the overlap integral between QD emission and Pc absorption.

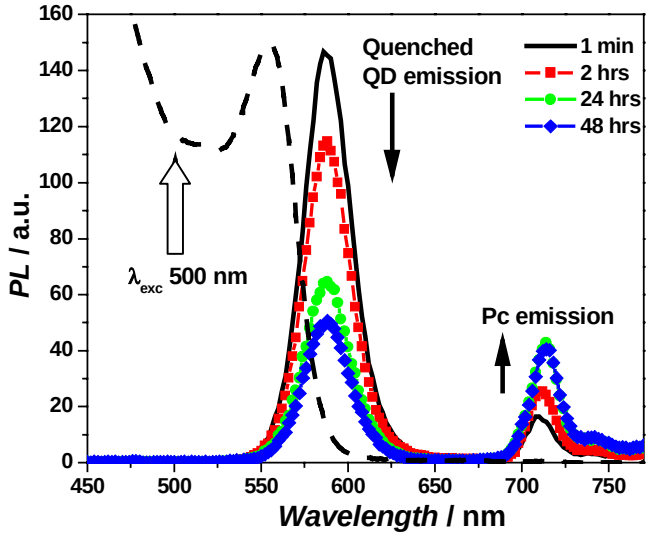

Figure S1. Monitoring of the energy transfer efficiency as a function of incubation time after mixing solutions of 5×10^{-6} M CdSe QDs and 8×10^{-6} M Pcs, both in toluene. Maximum efficiency was observed after 24 hrs. Longer times did not improve ET, while higher concentration of Pc led to self-quenching.

3. Femtosecond (fs) time-resolved measurements:

FS measurements were carried out after 24 hrs of conjugation time. 500 nm excitation wavelength was used for the excitation of both pure QDs and their conjugates with Pc. All measurements were performed at room temperature. The femtosecond laser pump–probe system consists of an amplified erbium-doped fiber laser, which is frequency doubled to 780 nm and amplified in a regenerative amplifier (Clark MXR CPA 2001). This femtosecond laser produces pulses with 120 fs FWHM duration and 800 mJ output energy per pulse at a repetition rate of 1 kHz. A small portion of the fundamental output pulse train is used to generate white light in a 2 mm sapphire crystal while the remaining laser light is used to frequency-double the 780 nm light in order to achieve 390 nm. To obtain 500 nm excitation wavelength, an optical parametric amplifier (OPA) is employed to facilitate the sum-frequency mixing and doubling of the signal or idler. For the femtosecond laser spectroscopy measurements, the excitation beam was modulated by a chopper with a 100 Hz frequency. The probe light was used with reflective optics in order to avoid white light dispersion. Measurements are conducted with the excitation beam focused to a spot diameter of about 500 mm and the probe beam to 100 mm. For measurements in this study, the QD solutions were placed in a 2mm path length quartz cuvette. Labview-assisted data acquisition resulted in 3-dimensional matrixes (ΔOD vs. wavelength vs. delay time). Experimentally obtained excitation lifetimes are summarized in table S1.

4. Energy transfer (ET) efficiency from steady state and lifetime measurements:

The steady state ET efficiency Φ_{ET} was calculated using the relative intensity of the integrated donor emission, in the absence (I_D) and presence (I_{DA}) of acceptor.

$$\phi_{ET} = 1 - \frac{I_{DA}}{I_D} \qquad (1)$$

The ET efficiency in these conjugates can also be calculated by measuring the excited-state lifetimes of the QDs in absence (τ_D) and presence of the energy acceptor (τ_{DA}).

$$\phi_{ET,kin} = 1 - \frac{\tau_{DA}}{\tau_D} \quad (2)$$

In order to obtain the lifetime of QDs the observed decay traces were fitted with mono-exponential functions.

	Lifetimes for TOPO capped QDs / ps	ET efficiency for TOPO capped QDs	Lifetimes for TBPO capped QDs / ps	ET efficiency for TBPO capped QDs
Pure QDs	55.1	-	58.09	-
Conj 1	42.4	0.23	48.38	0.17
Conj 2	40.8	0.26	37.73	0.35
Conj 3	38.1	0.31	32.26	0.45
Conj 4	34.1	0.38	29.05	0.5
Conj 5	30.4	0.45	42.93	0.26
Conj 6	27.3	0.50	48.54	0.16

5. Pc bond lengths and interdigitization scheme:

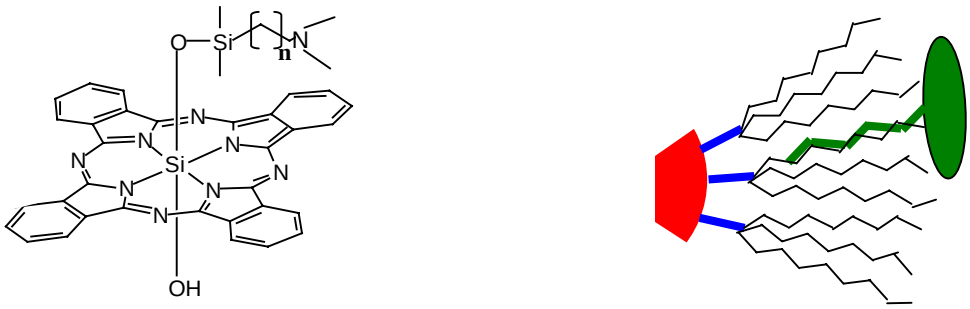

Figure S2. On the right is the backbone structure of the Silicon Pc used in this study, where the total linker chain length is described as the distance between the Pc ring and the amino group given as # bonds = n + 3 (i.e. n methylene groups together with an oxygen, a silicon and nitrogen atom) . On the right is the schematic diagram of the interdigitization process of the capping layer (e.g. TOPO) with the linker chain of the Pc.

The question still remains for some of the QD-based D-A systems, if FRET and this other process are operating at the same time and how much is one dominant? These questions are currently under investigation in our lab.

6. On the possibility of Charge Transfer vs. Energy Transfer:

In the case of charge transfer (CT) one would observe in the transient spectra the occurrence of radial cations of the electron donor and radical anions of the electron acceptor. This was however not observed. On the other hand, clearly the uncharged excited states for the QDs and subsequently of

the Pc were monitored. This allows safely the interpretation of the observed process as energy transfer. More electron-poor adsorbents can on the other hand lead to CT, as recently demonstrated by Klimov et al. (REF: Sykora, M.; Petruska, M. A.; Alstrum-Acevedo, J.; Bezel, I.; Meyer, T. J.; Klimov, V. I. **Photoinduced Charge Transfer between CdSe Nanocrystal Quantum Dots and Ru-Polypyridine Complexes.** J. Am. Chem. Soc. 2006, 128(31), 9984.). Note: in this study the D:A concentration ratio on the QDs was not directly controlled. Instead the A was added in an excess concentration and allowed to incubate until good measurement were possible. Here, defined concentration ratios of [Pc]:[QD] = 2:1 were used.

7. Additional References:

Due to limited space there are many interesting references on the topic of our studies that we were not able to include that we have added in this supporting information.

1. Stryer, L. *Annual Rev. Biochem.* **1978**, 47, 819.
2. (a) Anikeeva, P. O.; Madigan, C. F.; Coe-Sullivan, S. A.; Steckel, J. S.; Bawendi, M. G.; Bulovic, V. Chem. Phys. Lett. **2006**, 424, 120. (b) Clapp, A. R.; Medintz, I. L.; Mauro, J. M.; Fisher, B. R.; Bawendi, M. G.; Mattoussi, H. *J. Am. Chem. Soc*. **2004**, 126, 301. (d) Kagan, C. R.; Murray, C. B.; Bawendi, M. G. *Phys. Rev. B* **1996**, 54, 8633.
3. (a) Pons, T.; Medintz, I. L.; Sykora, M.; Mattoussi, H. *Phys. Rev. B* **2006**, 73, 245302/1. (b) (b) Clapp, A. R.; Medintz, I. L.; Mattoussi, H. *Chem. Phys. Chem*. **2006**, 7, 47. (c) Medintz, I. L.; Clapp, A. R.; Melinger, J. S.; Deschamps, J. R.; Mattoussi, H. *Adv. Mat*. **2005**, 17, 2450.
4. (a) Achermann, M.; Petruska, M. A.; Koleske, D. D.; Crawford, M. H.; Klimov, V. I. *Nano Lett.* **2006**, 6, 1396. (b) Kos, S.; Achermann, M.; Klimov, V. I.; Smith, D. L. *Phys. Rev. B* **2005**, 71, 205309/1. (c) Achermann, M.; Petruska, M. A.; Crooker, S. A.; Klimov, V. I. *J. Phys. Chem. B* **2003**, 107, 13782.
5. (a) Schoonover, J.R.; Dattelbaum, D. M.; Malko, A.; Klimov, V. I.; Meyer, T. J.; Styers-Barnett, D. J.; Gannon, E. Z.; Granger, J. C.; Aldridge, W. S., III; Papanikolas, J. M. *J. Phys. Chem. A* **2005**, 109, 2472. (b) Bandichhor, R.; Petrescu, A. D.; Vespa, A.; Kier, A. B.; Schroeder, F.; Burgess, K. *J. Am. Chem. Soc.* **2006**, 128, 10688. (c) Harriman, A.; Izzet, G.; Ziessel, R. *J. Am. Chem. Soc*. **2006**, 128, 10868.
6. Minkowski, C.; Calzaferri, G. *Angew. Chem. Int. Ed.* **2005**, 44, 5325.
7. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York and London, 1983.