

Electronic Supplementary Information for

## Core size Dependent Hole Transfer from a Photoexcited CdSe/ZnS

### Quantum Dot to a Conductive Polymer

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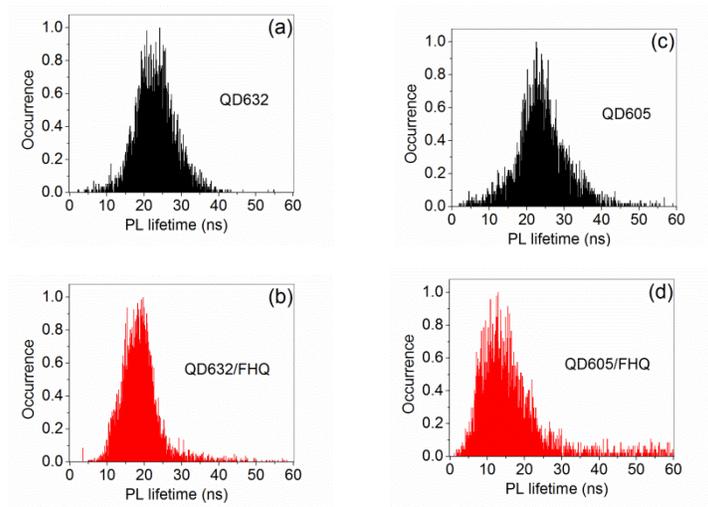
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#### 1. Single Particle Photoluminescence Microscopy.

Time-resolved single-particle photoluminescence microscopy measurements were performed on a home-built confocal scanning stage microscope based on an inverted microscope (Olympus IX81, 1.4 NA 100× oil objective) equipped with a piezo scanning stage (Physik Instruments, Germany) and coupled to a 532nm pulsed (10 MHz) diode-pumped solid-state laser system (LHD-532 Picoquant, Germany). The average power at the sample was kept at about 2 μW. Photoluminescence was collected in epi-illumination scheme, spectrally separated from the excitation laser light by a dichroic (Semrock, DiO-532) and by a band-pass filter (Semrock FF01-628/40 and FF01-605/50 for QD632 and QD605, respectively), spatially filtered by a 75 μm pinhole and finally imaged onto a single photon counting avalanche photodiode (MPD Picoquant) coupled to a time-analyzer (PicoHarp 300, PicoQuant). Data acquisition and data analysis were performed with the Symphotime analysis software (Picoquant).

#### 2. PL lifetime histograms of QDs and QDs/FHQ.

PL lifetime distributions from isolated QDs and QD/FHQ are shown in Figure S1. Each distribution includes data from 35 isolated QDs or QD/FHQ hybrids, each observed for 60 seconds, and with each point in the distribution obtained as a single exponent fit of a single particle PL decay of 1000 total photon counts binned in 128 channels by using a Maximum Likelihood Estimation minimization procedure<sup>1</sup>. Average PL lifetimes for QDs and QD/FHQ hybrids reported in the manuscript were the result of Gauss fits of the distributions from Fig.S1.



**Fig. S1.** Distributions of PL lifetimes for isolated QDs (upper panels, black colors) and QD/FHQ hybrids (lower panels, red colors).

### 3. $P_{on}(t)$ and $P_{off}(t)$ probabilities generation and analysis.

Probability densities  $P_{on}(t)$  and  $P_{off}(t)$  were calculated according to<sup>2-4</sup>

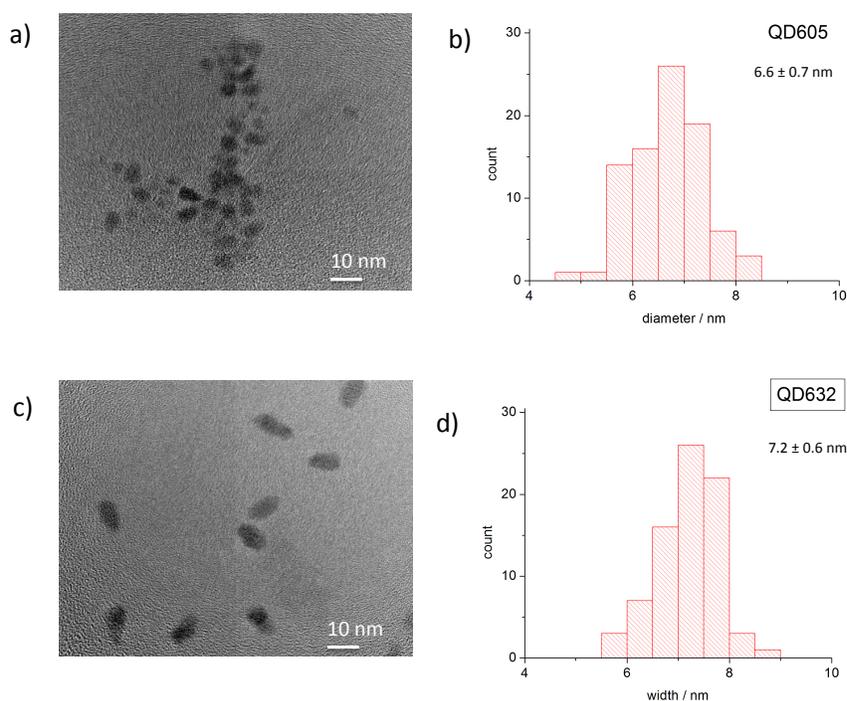
$$p_i(t) = \frac{N_i}{N_{i,total}} \times \frac{1}{\Delta t_{avg}} \quad (i = on \text{ or } off)$$

with  $N_i$  representing the number of *on* (*off*-) events with duration time  $t$ ,  $N_{i,total}$  the total number of *on* (*off*) events, and  $\Delta t_{avg}$  the average duration time between nearest neighbor event. Separation of *on* and *off* events was done using a threshold equal to the background signal in single particle PL intensity traces binned at 1 ms dwell time plus three times the standard deviation. Each of the probabilities shown in Fig.3 main text are normalized and sum up events from 35 molecules, each observed for 60 seconds.

### 4. QD synthesis and self assembly of QD/FHQ hybrids.

Poly(9,9'-bis(6-N,N,N-trimethylammoniumhexyl)fluorene-*alt*-1,4-(2,5-bis(6-N,N,N-trimethylammoniumhexyloxy))phenylene) containing bromide (FHQ, MW: 15 kDa) was received as a kind gift from Dr. H.L.Wang of Los Alamos National Laboratory, New Mexico and Dr. H.Y.Woo from Pusan National University in South Korea. Details on polymer synthesis can be found in reference.<sup>5</sup> Negatively charged 3-mercaptopropionic acid (MPA) core/shell CdSe/ZnS QD605

were synthesized following standard methods using trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) as the capping agents.<sup>6, 7</sup> Core diameters were estimated based on the first band edge absorption of the core only QDs (3.6nm according to reference<sup>6</sup>). ZnS shell was deposited using the SILAR approach<sup>7-9</sup> and successful ZnS deposition was observed by an increase in QDs photoluminescence quantum yield and a slight red-shift in absorption and emission peaks.<sup>8, 10</sup> CdSe/ZnS QD605 diameters were estimated from TEM images to be  $\approx 6.6 \pm 0.7$  nm for QD605 (Fig. S2a-b), indicating an average ZnS shell thickness of  $\sim 1.5$ . CdSe/ZnS QD632 were synthesized following Alivisatos's method using alkylphosphonic acids (PA) in addition to TOPO.<sup>11, 12</sup> This method prepares QDs with emission in the red, and due to the PA ligands directing growth, results in somewhat oblong CdSe QDs. In this system, a mixture of methylphosphonic acid (MPA) ligands and TOPO were used,<sup>13</sup> and annealing time after TOP=Se injection was monitored to prepare CdSe cores with a diameter (width) of  $\approx 4.6$  nm, and aspect ratio (length/width) of  $\sim 1.8$  (based on TEM micrographs). For such shape and slightly increased volume, the first band edge absorption and the PL emission



**Fig. S2.** TEM micrographs and corresponding particle size distributions for MPA-capped QD605 (a-b) and QD632 (c-d).

peaks are red-shifted by 5-10 nm compared to spherical CdSe QDs of similar diameter.<sup>11</sup> For low (<3) aspect ration, the photophysical properties of such oblongue CdSe/ZnS QDs, including the blinking, is similar to spherical CdSe/ZnS QDs of similar absorption and emission peaks.<sup>14, 15</sup> The ZnS shell was deposited following the SILAR approach, as described above for QD605 and successful ZnS deposition was observed by an increase in photoluminescence quantum yield, and by the red-shift in absorption and emission peaks(5-10 nm). The final QD632 morphology was determined by TEM, and the QDs possessed a width of  $\approx 7.2 \pm 0.6$  nm (Fig. S2d), indicating an average ZnS shell thickness of  $\sim 1.3$  nm. After purification, QDs were phase transferred to borate buffer and monolayer exchanged with MPA as described recently.<sup>16</sup> QD/FHQ hybrids were assembled by electrostatic interaction by blending QDs and FHQ at 1:20 molar ratio (100 nM, 2  $\mu$ M FHQ) and blended solutions were diluted 1000 times and spin coated on cover-glasses cleaned by piranha solution.

1. M. Maus, M. Cotlet, J. Hofkens, T. Gensch, F. C. De Schryver, J. Schaffer and C. A. M. Seidel, *Analytical Chemistry*, 2001, **73**, 2078-2086.
2. M. Kuno, D. P. Fromm, H. F. Hamann, A. Gallagher and D. J. Nesbitt, *The Journal of Chemical Physics*, 2001, **115**, 1028-1040.
3. S. Y. Jin, J. C. Hsiang, H. M. Zhu, N. H. Song, R. M. Dickson and T. Q. Lian, *Chemical Science*, 2010, **1**, 519-526.
4. N. H. Song, H. M. Zhu, S. Y. Jin, W. Zhan and T. Q. Lian, *Acs Nano*, 2011, **5**, 613-621.
5. M. Kang, O. K. Nag, R. R. Nayak, S. Hwang, H. Suh and H. Y. Woo, *Macromolecules*, 2009, **42**, 2708-2714.
6. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chemistry of Materials*, 2003, **15**, 2854-2860.
7. J. J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson and X. Peng, *Journal of the American Chemical Society*, 2003, **125**, 12567-12575.
8. D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase and H. Weller, *Nano Letters*, 2001, **1**, 207-211.
9. D. V. Talapin, I. Mekis, S. Götzinger, A. Kornowski, O. Benson and H. Weller, *The Journal of Physical Chemistry B*, 2004, **108**, 18826-18831.
10. B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen and M. G. Bawendi, *J. Phys. Chem. B*, 1997, **101**, 9463-9475.
11. L.-s. Li, J. Hu, W. Yang and A. P. Alivisatos, *Nano Letters*, 2001, **1**, 349-351.
12. D. V. Talapin, J. H. Nelson, E. V. Shevchenko, S. Aloni, B. Sadtler and A. P. Alivisatos, *Nano Letters*, 2007, **7**, 2951-2959.
13. R. Alam, D. M. Fontaine, B. R. Branchini and M. M. Maye, *Nano Letters*, 2012, **12**, 3251-3256.
14. S. Wang, C. Querner, T. Emmons, M. Drndic and C. H. Crouch, *J Phys Chem B*, 2006, **110**, 23221-23227.
15. Z. H. Xu, C. R. Hine, M. M. Maye, Q. P. Meng and M. Cotlet, *Acs Nano*, 2012, **6**, 4984-4992.
16. J. Zylstra, J. Amey, N. J. Miska, L. Pang, C. R. Hine, J. Langer, R. P. Doyle and M. M. Maye, *Langmuir*, 2011, **27**, 4371-4379.