Electronic Supplementary Information

Triplet energy migration pathways from PbS quantum dots to surface-anchored polyacenes controlled by charge transfer

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Experimental Methods

Chemicals. Lead chloride ($PbCl_2$, 99.9%) and oleylamine (OLA, Tech. grade, 70%) were purchased from Aladdin. Oleic acid (OA, Tech. grade, 90%), 1-octadecene (ODE, Tech. grade, 90%) and zinc stearate (ZnO 12.5-14%) were purchased from Alfa Aesar. Ethanol (≥ 99.7%), hexane (≥ 97%), octane (≥ 98.0%), acetonitrile (≥ 99.8%), acetone (≥ 99.5%), and thioacetamide (TAA, ≥ 99%) were purchased from Sinopharm Chemical Reagent. Tetrachloroethylene (TCE, ≥98.5%), hexane (≥97%), ethanol (≥99.7%) and acetone (≥99.5%) were purchased from Sinopharm Chemical Reagent. All the chemicals were used as received.

Synthesis of Cl-passivated PbS QDs. PbS QDs with their first excitonic absorption peak at ~800 nm were synthesized by a cation exchange synthesis using small ZnS QDs as the sacrificing materials.[1] *ZnS QDs:* Zinc stearate (4.41 g), 0.225 g (3 mmol) of TAA, 6 ml of OLA, and 50 ml of ODE were mixed in a three-neck round-bottom flask. After degassing, the mixture was heated to 140 ^{o}C and maintained for 50 minutes. Subsequently, the mixture was cooled to room temperature, and the ZnS QDs were precipitated by centrifuge using ethanol as the antisolvent. Lastly, the oily ZnS QDs were obtained, then hexane and anhydrous ethanol were added again for further purification, and this process was repeated for another 1 to 2 times. Finally, the ZnS QDs were dispersed in ODE for the synthesis of PbS QDs. *PbS QDs:* 2.919 g (10.5 mmol) of PbCl2 and 35 mL of OLA were loaded in a three-neck round-bottom flask, and the mixture was degassed at room temperature for 30 min. Then, the temperature of the mixture was raised to 140 °C under N_2 and maintained for 30 min to form the lead precursor (Pb-OLA). Subsequently, the lead precursor was set to 30 °C for the injection of the ZnS QDs (diluted in 5 mL ODE). Then the mixture was heat to 45 °C and the growth was maintained for 30 s, and then was quenched using a water bath. Hexane (20 mL) was injected into the reaction flask and 28 mL of OA was injected at 40 °C. At last, the reaction mixture was stirred for 10 min. The raw solution was centrifuged to remove the unreacted $PbCl_2$ and the supernatant was subjected to purification using acetone and ethanol as the antisolvent.

Preparation of PbS-Acenes complexes. The Cl-passivated PbS-Acenes complexes were prepared by adding acenes (Pc or Tc) powders into a QDs solution in hexane, followed by sonication for controlled time (~5 min). The mixture was filtered to obtain a clear solution containing PbS-Acenes complexes; because the solubility of carboxyl functionalized acenes in hexane is negligible, all the acenes were believed to be anchored to NC surfaces. For comparison, we also prepared PbS-Pc complexes using a long-time ligand exchange procedure reported in the literature.[22] This sample displayed considerable blue-shift of the QD absorption peak due to QD etching (Fig. S2).

Cyclic voltammetry. Cyclic voltammetry (CV) measurements were conducted on a Model CHI700e electrochemical analyser with a three-electrode system under inert gas atmosphere. For Tc and Pc, an anhydrous dichloromethane solution containing tetra-n-butylammonium hexafluorophosphate (0.1 M) was used as the electrolyte. For the PbS QDs, a mixture of solvents (acetonitrile and toluene (1:4 v/v)) containing tetra-butylammonium perchlorate (0.1 M) was used as the electrolyte. Glassy carbon, Pt-wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. Prior to use, the working electrode was polished over 0.5 μm alumina powder and rinsed with Milli-Q water. The CVs were performed at a scan speed of 100 mVs^{-1}. The CV curves were calibrated with the ferrocene/ferrocenium (Fc/Fc^+) redox couple as a standard measured under the same conditions. The energy level of Fc/Fc^+ was taken to be −4.8 eV with respect to vacuum.

According to the CV measurements, the lowest energy electron and hole levels in PbS QDs were -3.0 and -4.7 eV, respectively, vs. vacuum. The difference between them (1.7 eV) is higher than the optical gap of the sample (~1.55 eV) because of a sizable electron-hole binding energy in PbS QDs. The oxidation potential energy of Tc (E_{ox}) was measured by CV as -5.1 eV vs. vacuum, from which we further estimate the reduction potential energies for the Tc cations to form singlet and triplet excited states (E_{red} and $E_{\mathrm{red,T}}$, respectively) by adding the respective singlet and triplet transition energies (E_{S} and E_{T} are 2.4 and 1.3 eV, respectively, for Tc) . The oxidation potential energy of Pc (E_{ox}) was measured by CV as -4.6 eV vs. vacuum, from which we further estimate the reduction potential energies for the Pc cations to form singlet and triplet excited states (E_{red} and $E_{\mathrm{red,T}}$, respectively) by adding the respective singlet and triplet transition energies (E_{S} and E_{T} are 1.9 and 0.9 eV, respectively, for Pc).

Transient absorption. The femtosecond pump-probe TA measurements were performed using a regenerative amplified Ti:sapphire laser system (Coherent; 800 nm, 70 fs, 6 mJ/pulse and 1 kHz repetition rate) as the laser source and a Femto-100 spectrometer (Time-Tech LLC). Briefly, the 800 nm output pulse from the regenerative amplifier was split in two parts with a 50% beam splitter. The transmitted part was used to pump a TOPAS Optical Parametric Amplifier (OPA) which generated a wavelength-tunable laser pulse from 250 nm to 2.5 μm as pump beam. The reflected 800 nm beam was split again into two parts. One part with <10% was attenuated with a neutral-density filter and focused into a crystal to generate a white light continuum (WLC) used for probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. After the sample, the probe beam was collimated and then focused into a fibre-coupled spectrometer with CMOS sensors and detected at a frequency of 1 KHz. The intensity of the pump pulse used in the experiment was controlled by a variable neutral-density filter wheel. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 500 Hz and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked). The samples were placed in 1mm airtight cuvettes in a N_2-filled glove box and measured under ambient conditions. Nanosecond TA was performed with the EOS spectrometer (Ultrafast Systems LLC). The pump beam is generated in the same way as the femtosecond TA experiment described above. A different white light continuum (380–1700 nm, 0.5 ns pulse width, 20 kHz repetition rate) was used, which was generated by focusing a Nd:YAG laser into a photonic crystal fibre. The delay time between the pump and probe beam was controlled by a digital delay generator (CNT-90, Pendulum Instruments).

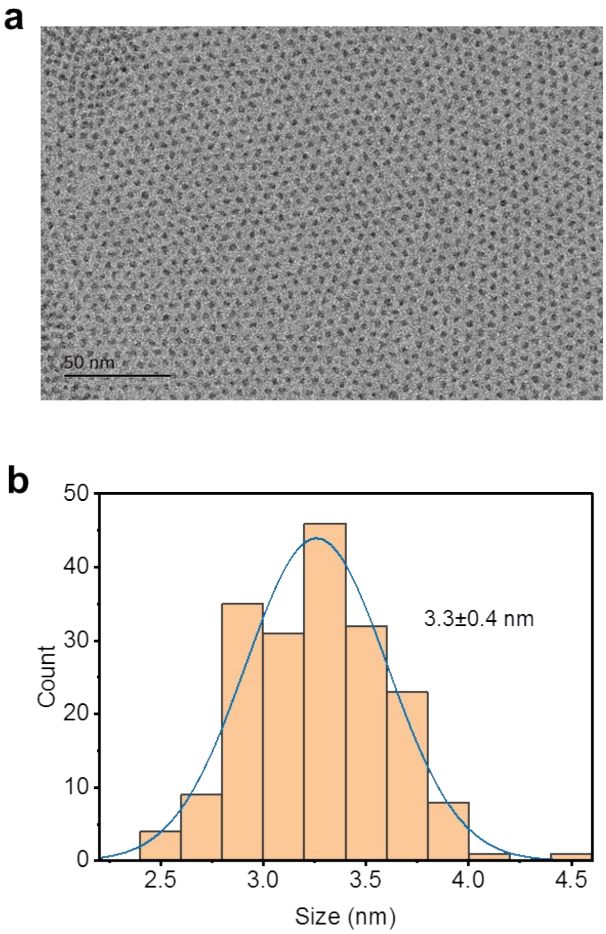

Figure S1. Large-scale TEM image (a) and diameter distribution (b) of the PbS QDs used in this study.

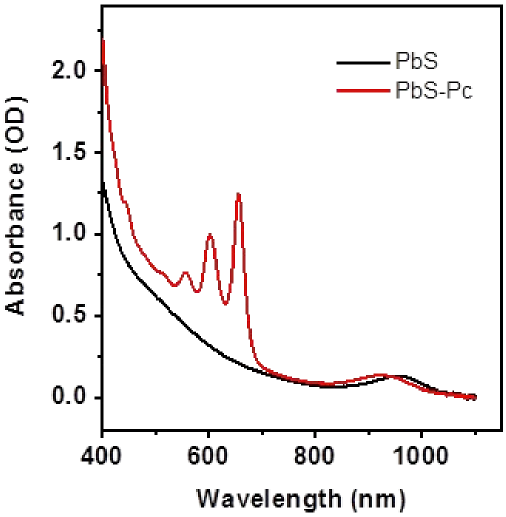

Figure S2. UV-vis absorption spectra of PbS QDs and QD-Pc complexes prepared using a long-time ligand-exchange procedure. The first excitonic absorption peak of QDs was considerably blue-shifted after ligand exchange.

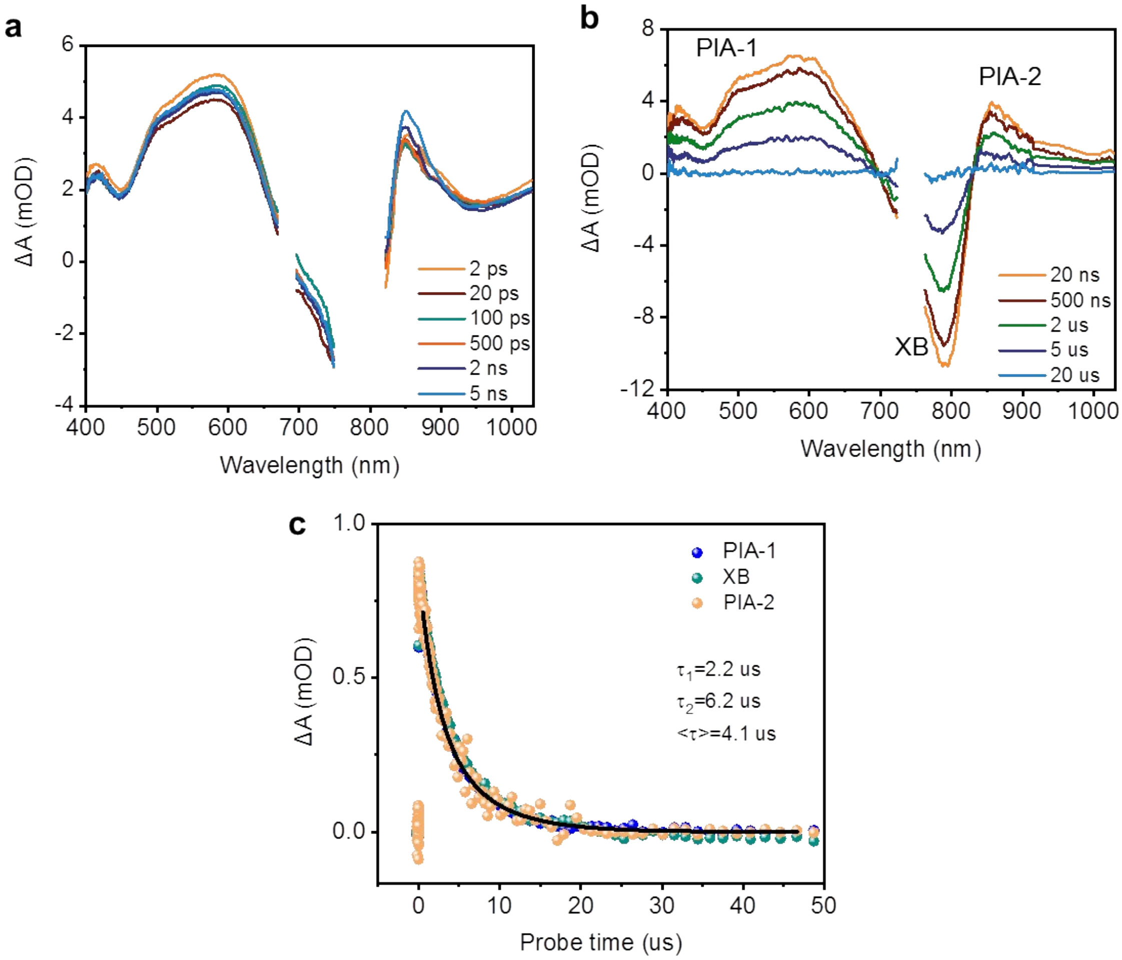

Figure S3. (a,b) TA spectra of free PbS QDs at indicated time delays following excitation at the QD band edge. The QD exciton bleach (XB) and two photoinduced absorption features (PIA-1 and PIA-2) are indicated. (c) TA kinetics of free QDs probed at the XB (green), PIA-1 (blue) and PIA-2 (yellow) features. The black solid line is a bi-exponential fit to the kinetics.

Supplementary references:

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2. S. Garakyaraghi, C. Mongin, D. B. Granger, J. E. Anthony and F. N. Castellano, *J. Phys. Chem. Lett.*, 2017, **8**, 1458-1463.