The Direct Observation of Charge Separated State in a CdSe Quantum Dot/Cobaloxime Hybrid

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1. General Method.

Starting materials and reagents were purchased from VWR. All chemicals were used as received without further purification.

2. Standard Characterization

UV-Visible absorption spectra were taken using an Agilent 8453 spectrometer. The sample cuvette path length was 2 mm. ^{1}H NMR experiments were carried out on a Bruker DMX 500 spectrometer. ESI-MS was conducted on a ThermoFisher LCQ Fleet from dilute methanol solutions.

3. The Synthesis of CdSe QDs.

CdSe QDs was synthesized by hot-injection method (*Chemistry of Materials* **2003**, *15*, 2854-2860.). In a typical synthesis, 7 ml octadecene (ODE) containing 0.62 mL oleic acid and 0.051 g CdO (0.4 mmol) was first heated to 180 °C to form a clear solution under N_2 atmosphere. The mixture solution was then heated up to 250 °C. 0.34 mL tributylphosphine (TBP, 1.35mmol) and 1.3 mmol Se (102 mg) was dissolved in 10 mL ODE under sonication to make a TBP-Se stock solution. 1 mL TBP-Se solution was quickly injected into the cadmium solution

to initiate the nucleation. The heater was removed until desired size of QDs was obtained. After cooling to room temperature, the QDs was precipitated by 20 mL acetone and separated by centrifugation. The product was dissolved in toluene for further experiment.

4. Femtosecond absorption spectroscopy

The femtosecond absorption spectrometer is based on a regenerative amplified Ti-Sapphire laser system (Solstice, 800nm, < 100 fs FWHM, 3.5 mJ/pulse, 1 KHz repetition rate). The tunable pump is generated in TOPAS which has output with tunable wavelength ranging from 254 nm to 1100 nm. The tunable UV-visible probe pulses are generated by while light generation in a Sapphire window (430-750 nm) on a translation stage. The femtosecond transient absorption is performed in Helios ultrafast spectrometer (Ultrafast Systems LLC). The sample cuvette path length was 2 mm.

5. Time resolved X-ray absorption spectroscopy was performed at beamline 11ID-D, Advanced Photon Source (APS) at Argonne National Laboratory. The laser pump was based on a Nd:YLF regenerative amplified laser (1054nm, 1.6 kHz repetition rate, 5 ps FWHM). The pump wavelength at 527 nm was obtained from the output of second harmonic generation. The X-ray pulse with 80 ps FWHM width at 6.5 MHz repetition rate was used as the probe. The laser pump and X-ray probe intersect at a flowing sample stream with 550 μm in diameter. The X-ray fluorescence signals were collected at 90˚ angle on both sides of the incident X-ray beam by two avalanche photodiodes (APDs).