

# Control of Electron Transfer from Lead-Salt Nanocrystals to $\text{TiO}_2$

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## **Absorption and Emission Spectrum Measurements:**

Absorption spectra were measured on a Shimadzu UV-3101PC spectrophotometer at room temperature. Emission spectra were recorded at room temperature with an infrared fluorometer equipped with a 200-mm focal length monochromator, a single mode fiber coupled laser source (S1FC635PM, 635 nm, Thorlabs, Inc) as the excitation source, and an Si photodiode (New Focus Femtowatt model 2151).

## **Fluorescence lifetime measurements:**

The samples were excited at a repetition rate of 1 kHz by femtosecond pulses of a Ti:sapphire laser system with an optical parametric amplifier (OPA) (at 680 nm) or regenerative amplifier (at 800 nm). The sample was exposed to intensity levels below  $10 \text{ mW/cm}^2$  so that the excitation level was always well below one electron-hole pair per dot. Fluorescence was monitored with a Si avalanche photodiode (APD) single photon counting module (PerkinElmer, SPCM-AQRH-44-FC). The output was fed into a multichannel scalar (Stanford Research Systems, SR430), which provides an instrument response of a 5 nanoseconds, and adequate dynamic range to monitor decay times in the microsecond range. In the sub-

microsecond range, time-resolved fluorescence measurements were performed in the time-correlated single photon counting (TCSPC) mode with a TCSPC board (PicoQuant, TimeHarp 200) and a digital delay generator (Stanford Research Systems, DG645) under right-angle sample geometry.

## **Synthesis.**

- 1) The colloidal  $\text{TiO}_2$  and  $\text{ZrO}_2$  suspension in ethanol was prepared by the hydrolysis of titanium isopropoxide and zirconium (IV) n-propoxide,<sup>1,2</sup> involving dropwise addition of 297/211  $\mu\text{L}$  of titanium isopropoxide/zirconium n-propoxide to an ethanol (10mL) kept under vigorous stirring. The diameter of the  $\text{TiO}_2$  nanoparticles is between 40 and 50 nm.<sup>1,2</sup> To functionalize the  $\text{TiO}_2$  and  $\text{ZrO}_2$  nanoparticles, 25 mM of linker molecules in ethanol or methanol were added into the nanoparticle suspension in ethanol. The anchoring group moiety of molecules strongly interacts with the positively charged surface of nanoparticles as the hydrolysis-condensation reaction takes place. This reaction leaves the thiol groups of the bridge molecule-capped nanoparticles facing outwards for coupling with the PbS nanocrystals (NCs). Following rotary evaporation at 45 °C, a film-like powder was obtained, which could be resuspended in organic solvents, such as tetrachloroethylene (TCE), chloroform, chlorobenzene, and dichloromethane. Functionalized  $\text{TiO}_2$  nanoparticles were mixed with PbS NCs in organic solvent, and the resulting solution was used for the spectroscopic measurements.
- 2)  $\text{TiO}_2$  mesoporous film was prepared with Degussa P25 titania powder. The porous film was formed by adding 6 wt% of titania into the tetraethyleneglycol dimethylether. This suspension is sonicated for 10 min. to aid in dispersion of the titania nanoparticles. Once the titania slurry is formed, it was deposited by “doctor blading” onto a glass substrate cleaned by oxygen plasma. The resulting paste was sintered at 450 °C for 1 hr. The temperature was then lowered to 120 °C for 10 min. The hot films were placed directly into a 0.1 M of linker solution (See Table 1) for 12 h to allow for attachment of linker molecules. The films were subsequently washed with acetonitrile/methanol and toluene and placed directly in PbS NCs solution.

Table 1. Linker molecules and their dispersing solvents

Linker molecule	Solvent
2-mercaptoacetic acid (MAA)	Acetonitrile
3-mercaptopropionic acid (MPA)	Acetonitrile
4-mercaptopbutyric acid (MBA)	Methanol
Sodium 3-mercaptopropane-1-sulfonate (S3MPS)	Methanol
4-mercaptobenzoic acid (MBZA)	Acetonitrile
6-mercaptopyridine-3-carboxylic acid (MPCA)	Tetrahydrofuran
4-mercaptobutylphosphonic acid (MBPA)	Methanol
3-(mercaptopropyl)-trimethoxysilane (MPTMS)	Toluene

### **PbS NC-linker-ZrO<sub>2</sub> composite system**

The lack of charge transfer from PbS NCs to all of these linker molecules was confirmed by a control experiment with ZrO<sub>2</sub> colloids. The electron affinity and ionization potential of ZrO<sub>2</sub> is 2.99<sup>3</sup> and 8.47<sup>4</sup>, respectively. Thus, no charge transfer from PbS NCs to ZrO<sub>2</sub> is expected. Figure S1 shows the typical fluorescence transients of PbS NC-linker-ZrO<sub>2</sub> composites in TCE. The fluorescence of the PbS QDs decays with a time constant of 1.7 μs. The decay time constants of PbS NC-linker-ZrO<sub>2</sub> are nearly identical. This leads us to conclude that there is no charge transfer between the PbS NCs and the linker molecules.

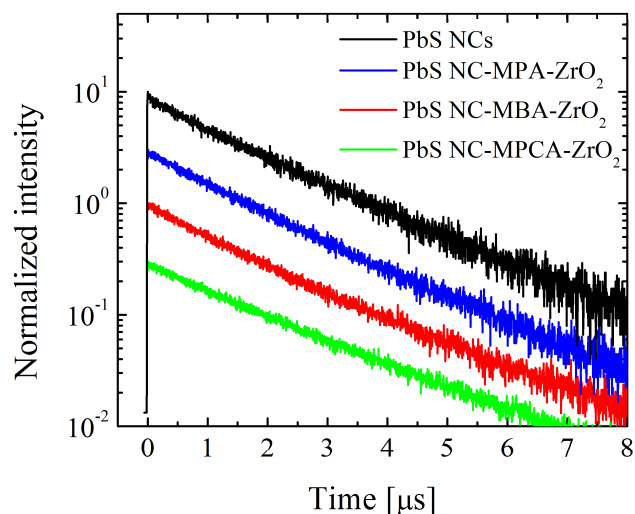


Figure S1. The transient fluorescence lifetime decay of PbS NCs (solid black line) and PbS NC-linker-ZrO<sub>2</sub> composites (solid blue line: MPA, solid red line: MBA, solid green line: MPCA).

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