# Gating of Hole Transfer from Photoexcited PbS Quantum Dots to Aminoferrocene by the Ligand Shell of the Dots

Michał Malicki, Kathryn E. Knowles and Emily A. Weiss\*

E-mail: e-weiss@northwestern.edu

Department of Chemistry, Northwestern University, 2145 Sheridan Rd Evanston, IL 60208-3113

# **Experimental Section**

# 1. Materials

Lead(II) oxide (99.999% trace metal basis), oleic acid, and 1-octadecene, were purchased from Sigma-Aldrich and were used as received. Hexamethyldisilathiane (synth. grade) was purchased from Sigma-Aldrich and was stored in a glove box. All solvents were purchased and used as received unless air-free atmosphere was required; air-free solvents were prepared by performing three freeze-pump-thaw cycles.

# 2. Synthesis of PbS Quantum Dots

# Oleate-coated PbS quantum dots (OL-PbS)

We deaerated a mixture comprising 18 mL of 1-octadecene and 2.0 mL (6.3 mmol) of oleic acid in a three-neck 50 mL round-bottomed flask equipped with a magnetic stirrer by bubbling nitrogen gas through the mixture for 30 minutes. Addition of lead(II) oxide (0.36 g; 1.6 mmol) followed by heating to 150 °C under nitrogen gas atmosphere for 45 minutes produced a clear, colorless solution. We allowed this solution to cool down to 110 °C before quickly injecting a solution of hexamethyldisilathiane (0.17 mL; 0.8 mmol) in 8 mL of air-free octadecene.. After stirring for 10 minutes at 110 °C, we cooled the resulting dark brown solution to room temperature in an ice bath and washed the reaction mixture with methanol ( $2 \times 50$  mL). Addition of acetone (50 mL) followed by centrifugation (20 min at 3500 rpm) produced a dark brown solid that was redissolved in hexanes (5 mL), precipitated again by addition of 5 mL of methanol, centrifuged (5 min at 3500 rpm), washed copiously with acetone and redissolved in 10 mL of hexanes. After 12 hours, the hexanes solution was centrifuged (5 min at 3500 rpm), and the supernatant was collected. Evaporation of the solvent under reduced pressure yielded 0.41 g of dark solid comprising OL-PbS. UV-Vis-NIR spectrum of a diluted hexanes solution of OL-PbS showed the band-edge absorption maximum at 979 nm, which, based on the calibration curve reported by Cademartiri *et al.*,<sup>1</sup> corresponds to the average particle diameter of 3.4 nm.

We prepared smaller OL-PbS by adjusting the ratio of oleic acid to PbO; we used 1.0 mL of oleic acid and 19 mL of 1-octadecene. This adjustment produced QDs with a band-edge absorption maximum at 920 nm in hexanes, which corresponds to an average particle diameter of 3.1 nm.<sup>1</sup>

## Decanethiolate-coated PbS quantum dots (DT-PbS)

We transferred 3.1-nm OL-PbS (0.38 g) into a glove box and dissolved it in 8 mL of air-free hexanes. We added decanethiol (0.5 mL, 2.4 mmol,  $820 \times$  excess with respect to OL-PbS) and transferred the mixture to a three-neck round-bottomed flask equipped with a magnetic stirrer. The flask was transferred outside of the glove box and the mixture was stirred for one hour under nitrogen gas atmosphere. Injection of 10 mL of air-free acetone followed by centrifugation (3 min at 3500 rpm) in air produced a dark brown solid (DT-PbS) that was then washed with air-free acetone (3  $\times$  10 mL), transferred to a glove box, and dissolved in 30 mL of air-free toluene.

## Calculation of the stoichiometry in the reaction of decanethiolate with OL-PbS

We experimentally established the molar weight of 3.1 nm OL-PbS using Vis-NIR spectroscopy. We prepared 2.0 g/L hexanes solution of 3.1 nm OL-PbS and measured a Vis-NIR spectrum of the solution in a 1.0 cm cuvette. Using the molar extinction coefficient of 3.1 nm OL-PbS,  $\varepsilon_{OL-PbS}$ , based on the calibration curve of Cademartiri *et al.*,<sup>1</sup> and the measured absorbance at the maximum of the band-edge absorption,  $A_{max}$ , we calculated the molar weight of the dots:

$$MW_{OL-PbS} = \frac{2\frac{g}{L} \times \varepsilon_{OL-PbS} \times 1cm}{A_{max}} = 1.3 \times 10^5 \frac{g}{mol}$$
(S1)

With the value of  $M_{OL-PbS}$  we calculated the molar ratio of decanethiol to OL-PbS QDs to be 820.

#### 3. Calculation of the length of decanethiolate and oleate ligands

We optimized geometries of oleic acid and decanethiol using an MM2 force field approach in ChemBio 3D software. We found the distance from the oxygen atom in the hydroxyl group to the carbon of the methyl group in oleic acid to be 2.05 nm while the distance from the sulfur atom to the carbon atom in the methyl group in fully extended decanethiol was measured to be 1.11 nm. Thus, we conclude that oleate is 0.9 nm longer than decanethiolate.

# 4. Calculation of the driving force of the hole transfer from PbS QD to amFc.

We calculated the free energy of the hole transfer from PbS QD to amFc,  $\Delta G_{PHT}$ , from:

$$\Delta G_{pHT} = IE_{amFc} - IE_{pbS} \tag{S2}$$

where  $IE_{PbS}$  is the ionization energy of PbS QDs and  $IE_{amFc}$  is the ionization energy of amFc. We used the value of 5.0 eV for  $IE_{PbS}$  according to photoelectron-spectroscopy measurements of films of PbS QDs reported by Jasieniak *et al.*<sup>2</sup> The ionization energy of amFc was calculated

from its electrochemical oxidation potential (-0.37 V vs  $\text{FeCp}_2^+/\text{FeCp}_2)^3$ , using the empirical dependence between the electrochemical potential of organic compounds and the ionization energies of the corresponding neat films;<sup>4</sup> we found  $IE_{amFc} = 4.1$  eV. According to equation S2:  $\Delta G_{PHT} = -0.9$  eV.

#### 4. Experimental details

#### Steady-State NIR spectroscopy

We took ground state absorption spectra of the PbS QDs in hexanes in 1-cm quartz cuvettes using a Varian Cary 5000 spectrophotometer. We baseline-corrected all spectra with neat solvent prior to measurement.

#### Transient-absorption measurements

We split the 2.5-mJ output of a commercial amplified Ti-sapphire laser (Solstice, 1 kHz, 100 fs, Spectra Physics), and guided 95% to an optical parametric amplifier (TOPAS-C, Light Conversion) used to produce the pump wavelength for sample excitation at 970 nm, and 5% to a commercial TA spectrometer (Helios, Ultrafast Systems) for use as the probe. Within the spectrometer, a broadband continuum of wavelengths from 800 nm to 1500 nm was generated in a 1.2-cm thick sapphire plate. We focused the pump beam to a gaussian-profile spot with FWHM of 500  $\mu$ m and overlapped it with the probe beam (FWHM = 300  $\mu$ m) at the sample in a 2-mm guartz cuvette. All samples were prepared with an absorbance of  $0.13 \pm 0.03$  OD at the maximum of the first absorption feature, which corresponds to the first excitonic state resonant with the pump light, to ensure low attenuation of the pump light within the sample. The polarization of the probe light was set to the magic angle (54.7°) with respect to the pump light. The transmitted probe signal was passed through an 850-nm long-wave pass filter (placed before the sample) and collected in optical fiber. The output of the fiber was dispersed onto an array detector. The output differential absorption spectrum ( $\Delta A$ ) was obtained through active background subtraction of the ground state spectrum by chopping the pump at 500 Hz. The pump-pulse energy was adjusted such that the expected excited-state population was lower than 0.6 to ensure that multi-photon absorption effects were small. The solution was stirred with a small magnetic stir bar assembly to minimize local heating. We collected two consecutive spectra for each sample in order to check for any changes in the spectrum due to sample instability. All of the studied samples were stable during the TA experiment.

## <sup>1</sup>H NMR measurements

<sup>1</sup>H NMR spectra were recorded using either a Bruker Avance-III 600 MHz or a Varian Inova 500 MHz spectrometers. Measurements of <sup>1</sup>H NMR T<sub>1</sub> relaxation times of toluene-d<sub>8</sub> solutions of Au NPs were performed using the conventional population-inversion recovery method. We acquired 1D-NOESY spectra of OL-PbS/amFc and DT-PbS/amFc in air-free toluene-d<sub>8</sub> with the use of Bruker's "selnog" program and by choosing the 180° selective excitation of Cp5 protons in amFc. We set the mixing time to 300 ms and the delay between pulses to 32 s. We acquired 2000

scans for each sample. We recorded DOSY spectra for a sample of OL-PbS/amFc (amFc:QD ratio of *ca*. 100) in air-saturated benzene- $d_6$  solution using Bruker's "dstebpgp3s" program. We ran two DOSY experiments for the same sample: one with a diffusion delay,  $\Delta$ , of 0.25 s and gradient length,  $\delta$ , of 1500 µs, and another with  $\Delta = 0.025$  s and  $\delta = 5000$  µs. We also ran the DOSY experiment on a benzene- $d_6$  solution of amFc (c = 1×10<sup>-2</sup> M) using  $\Delta = 0.1$  s and  $\delta = 1500$  µs. The gradient strength in DOSY experiments was varied from 5% to 95%.

#### 5. Transient-absorption data analysis

The kinetic traces at 961 nm were analyzed using a global fitting routine with a fitting function described by equation 1 (see the main text). The global fitting routine was implemented in the Origin 8.6 software. In order to avoid issues with instrument-response function convolution in the fitting procedure we only used a portion of the kinetic traces starting from *ca*. 300 fs after the initial pump/probe temporal overlap.

The rate of the decay component that we attribute to the phonon-induced decay,  $k_{ph}$  in equation 1 (see the main text), was determined from an independent fit of the dynamics measured for OL-PbS (no amFc) at 961 nm and 1060 nm (see figure S1). The two kinetic traces were globally fit using a monoexponential decay function with shared  $k_{ph}$ . The oscillations seen in figure S1b are due to acoustic phonon-induced modifications of the absorption spectrum of PbS QDs.<sup>5</sup> The fit yielded  $k_{ph} = 1.2 \times 10^{12} \text{ s}^{-1}$ .



**Figure S1.** Transient-absorption kinetic traces recorded at **a**) 961 nm and **b**) 1060 nm for  $8.6 \times 10^{-6}$  M OL-PbS QDs in air-free toluene excited at 970 nm. The best-fit monoexponential functions from the global fit of the two kinetic traces are shown with solid lines.



**Figure S2.** Transient-absorption spectra recorded for **a**)  $8.6 \times 10^{-6}$  M OL-PbS QDs in toluene solution and **b**)  $8.6 \times 10^{-6}$  M OL-PbS QDs with  $2.1 \times 10^{-3}$  M amFc in toluene solution excited at 970 nm.

# 6. <sup>1</sup>H NMR analysis

#### Surface coverage of PbS QDs before and after ligand exchange

We experimentally established the number of oleate ligands per each QD by employing an internal standard (FeCp<sub>2</sub>) in the <sup>1</sup>H NMR experiment (Figure S3a). We prepared  $3.9 \times 10^{-4}$  M solution of 3.1 nm OL-PbS in hexane- $d_{14}$  which contained 0.030 M FeCp<sub>2</sub> as internal standard. We collected 8 scans and set the relaxation time of 40 s between the scans in order to allow for complete sample relaxation. We used the integral of Cp5 protons in FcCp<sub>2</sub>,  $I_{Cp5}$  (4.61 ppm, 10 protons), and of the vinyl protons in oleate ligands,  $I_{vinyl}$  (5.92 ppm, 2 protons), in order to calculate the concentration of oleate ligands,  $c_{OL}$ , in the sample:

$$c_{OL} = \frac{5 \times I_{\text{vinyl}} \times \sigma_{FeCp_{2}}}{I_{Cps}} = 6.1 \times 10^{-2} \frac{mol}{L}$$
(S3)

We calculated the average number of oleate ligands per each QD from the ratio of  $c_{OL}$  to the concentration of OL-PbS; we found the number to be *ca*. 160.

We also established an average number of decanethiolate ligands per each DT-PbS QD following the same approach as described above. Figure S3b shows the 1H NMR spectrum of a mixture of  $3.9 \times 10^{-4}$  M OL-PbS (3.1 nm), 0.030 M FeCp<sub>2</sub>, and 0.30 M decanethiol in hexane- $d_{14}$ . We used the integral of the broad signal originating from the methylene group alpha to sulfur,  $I_{alpha}$  (4.02-5.42 ppm, 2 protons), and the integral of Cp5 protons from FeCp<sub>2</sub>,  $I_{Cp5}$  (4.61 ppm, 10 protons), in order to establish the concentration of decanethiolate ligands,  $c_{DT}$ , in the sample:

$$c_{DT} = \frac{5 \times I_{alpha} \times \sigma_{FeCp_2}}{I_{Cps}} = 4.9 \times 10^{-2} \frac{mol}{L}$$
(S4)

The average number of DT ligands per each QD is ca. 130.



**Figure S3.** <sup>1</sup>H NMR spectra of **a**)  $3.9 \times 10^{-4}$  M OL-PbS QDs (3.1 nm in diameter) and 0.030 M FcCp<sub>2</sub> in hexane- $d_{14}$  solution and **b**)  $3.9 \times 10^{-4}$  M OL-PbS QDs (3.1 nm in diameter), 0.030 M FcCp<sub>2</sub>  $8.6 \times 10^{-6}$  M, and 0.30 M decanethiol in hexane-d14.

We analyzed the <sup>1</sup>H NMR spectrum of DT-PbS (Figure 1b, red trace) in order to establish the amount of residual oleate ligands present on the surface of QDs after ligand exchange. We integrated the broad signal originating from the methylene group alpha to sulfur in DT (3.80-5.22 ppm, 2 protons, Integral = 1.0) and the signal originating from the vinyl group in OL (5.43-5.67

ppm, 2 protons, Integral = 0.15). Based on the obtained integral values we found that the residual OL ligands on the surface of DT-PbS constitute 13% of all the ligands stabilizing the QDs.

This information, together with the calculated average number of DT ligands per each QD (see above), allowed us to calculate the surface coverage of DT-PbS. We found that on average each DT-PbS QD is coated with *ca*. 130 DT and *ca*. 20 OL ligands; thus, the total number of ligands present on the surface of DT-PbS is *ca*. 150 – nearly the same as in the case of OL-PbS. We conclude that the coverage of DT is nearly the same as the coverage of OL ligands on the surface of 3.1 nm PbS QDs.

## OL-PbS and OL-PbS/amFc

Addition of  $100 \times$  excess of amFc to OL-PbS in toluene- $d_8$  does not result in detachment of OL ligands from QD surface. As can be seen in figure S4, there is almost no change in the shape of the signals originating from OL protons upon addition of amFc. Most importantly, the lack of development of sharp signals that could be assigned to OL protons upon addition of amFc supports the hypothesis that the vast majority of OL ligands stay adsorbed to the QD surface.



**Figure S4.** <sup>1</sup>H NMR spectra of toluene- $d_8$  solutions of  $1.0 \times 10^{-4}$  M OL-PbS (black) and  $1.0 \times 10^{-4}$  M OL-PbS with  $1.0 \times 10^{-2}$  amFc (red). The intensities of both spectra were normalized at the signal originating from vinyl group protons (ca. 5.6 ppm). The signals from residual solvent at 2.1 ppm have been removed from the spectra. The spectra were displaced vertically for clarity.

#### 7. DOSY of amFc and OL-PbS/amFc

Provided there is only one diffusional species present, the signal attenuation in a DOSY experiment can be described with:<sup>6</sup>

$$I(G^2) = I_0 e^{-D(\gamma g \delta)^2 (\Delta - \frac{2\delta}{s})} = I_0 e^{-DG^2}$$
(S5)

where D is a diffusion coefficient,  $\gamma$  is the gyromagnetic ratio of a proton (2.68×10<sup>4</sup> s<sup>-1</sup>G<sup>-1</sup>), g is the gradient strength (G/cm),  $\delta$  is the duration of the gradient pulse, and  $\Delta$  is the diffusion delay.

Figure S5 shows the dependence of the integrated signal of Cp5 protons in amFc on the gradient function  $G^2$  in DOSY experiments.



**Figure S5.** Dependence of Cp5 proton signal attenuation on the gradient strength function, G<sup>2</sup>, measured in a DOSY experiment for  $1 \times 10^{-2}$  M amFc in benzene- $d_6$  ( $\Delta_1 = 0.1$  s,  $\delta_1 = 1500$  µs; black squares) and for  $1 \times 10^{-4}$  M OL-PbS QDs with  $1 \times 10^{-2}$  M amFc in benzene- $d_6$  ( $\Delta_2 = 0.25$  s,  $\delta_2 = 1500$  µs, red circles;  $\Delta_3 = 0.025$  s,  $\delta_3 = 5000$  µs, blue triangles)

Clearly, Cp5 signal attenuation is nearly identical for amFc and for OL-PbS/amFc. We found diffusion coefficients for amFc from fitting the data in figure S5 to equation S5:  $D_1 = (1.56 \pm 0.01) \times 10^{-5} \text{ cm}^2/\text{s}$  - amFc only sample ( $\Delta_1 = 0.1 \text{ s}$  and  $\delta_1 = 1500 \text{ }\mu\text{s}$ )  $D_2 = (1.54 \pm 0.01) \times 10^{-5} \text{ cm}^2/\text{s}$  - OL-PbS/amFc sample ( $\Delta_2 = 0.25 \text{ s}$  and  $\delta_2 = 1500 \text{ }\mu\text{s}$ )  $D_3 = (1.56 \pm 0.01) \times 10^{-5} \text{ cm}^2/\text{s}$  - OL-PbS/amFc sample ( $\Delta_3 = 0.025 \text{ s}$  and  $\delta_3 = 5000 \text{ }\mu\text{s}$ )

We find that (i) no new amFc diffusional species appears in the sample after addition of OL-PbS and (ii) there is no change in the diffusion coefficient of amFc upon addition of OL-PbS to the amFc solution. Combining these findings with the 1D-NOESY spectrum for the OL-PbS/amFc system (Fig. 2e) suggests that amFc undergoes fast exchange on the surface of PbS QDs.<sup>7</sup> Following the same methodology as Fritzinger *et al.* we set the low limit of the exchange rate constant at  $1/\Delta_3 = 50 \text{ s}^{-1.7}$ 

#### 8. Langmuir Isotherm of OL-PbS/amFc

The average number of amFc molecules adsorbed to the surface of each QD,  $\lambda$ , was found from fitting TA dynamics (Fig. 2a in the main text) with a fitting function that includes  $\lambda$  as a fitting parameter (see equation 1 in the main text). The values of  $\lambda$  that best fit the experimental data are

shown as a function of total concentration of amFc in figure S5. These data were fit to the Langmuir adsorption equation:<sup>8</sup>

$$\lambda = \lambda_{max} \frac{K_a[aminoFc]}{1 + K_a[aminoFc]}$$
(S6)

where  $\lambda_{max}$  is the average number of empty adsorption sites per QD and  $K_a$  is the adsorption equilibrium constant. We find the best fit of the experimental data with  $K_a = 5 \times 10^2 \text{ M}^{-1}$  and  $\lambda_{max} = 5.1$ .



**Figure S6.** Langmuir isotherm plot of OL-PbS/amFc system;  $\lambda$  is the average number of amFc molecules adsorbed to each QD. The best fit of the experimental data using equation S6 is shown with the blue line.

#### 9. Binding constants of propanoic acid and 2-amino-ehtylthiol to Pb(2+)

The equilibrium constants of the reaction Pb(2+) with 2-aminoethanethiol in water and with propanoic acid in water were reported to be logK=11.1 and logK=2.64, respectively.<sup>9</sup>

# **10. References**

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