In-situ Spectroscopic Characterization of a Solution-Phase X-Type Ligand Exchange at Colloidal Lead Sulphide Quantum Dot Surfaces

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Supplementary Information

Materials and Methods

a) Materials

All chemicals were used as received without further purification unless noted. Anhydrous octane (≥99%), anhydrous diethylene glycol dimethyl ether (diglyme, 99.5%), N,N'-diphenylthiourea (98%), anhydrous toluene (99.5%), anhydrous tetrachloroethylene (TCE, ≥99.9%), anhydrous methyl acetate (MeOAc, 99%), anhydrous hexane (≥99%), trans-2,6-difluorocinnamic acid (2,6F-CAH, 99%), anhydrous chloroform ($CHCl_3$, ≥99%), anhydrous chloroform-d ($CDCl_3$, ≥99.8%), anhydrous α,α,α-trifluorotoluene (≥99%), and ferrocene (Cp_2Fe, 98%) were obtained from Sigma Aldrich.

b) Oleate Terminated PbS QD Synthesis

Oleate capped PbS QDs with a core diameter of 3.5 nm corresponding to a first exciton transition energy centered at 1.2 eV were synthesized following the substituted thiourea protocol developed by Owen and co-workers.[1] First, hydroxide-free $Pb(oleate)_2$ was prepared and purified. In a nitrogen glove box, 8.83 g $Pb(oleate)_2$ and 150 mL anhydrous octane were added to a 2-neck 250 mL Schlenk flask equipped with a magnetic stirbar and sealed using a glass stopcock and two rubber septa. Separately, 1.75 g of N,N'-diphenylthiourea and 5 mL of diglyme were mixed in a 20 mL scintillation vial and sealed with a rubber septa. After transferring to a Schlenk line, both vessels were brought to 95 °C in an oil bath under nitrogen and allowed to stir for approximately 30 minutes or until both solutions were clear. Subsequently, the N,N'-diphenylthiourea diglyme solution was quickly injected into the $Pb(oleate)_2$ octane solution under vigorous stirring. After a few minutes, the flask now containing a dark brown solution was removed from the oil bath and allowed to cool to room temperature, and the volatiles were removed from the flask under vacuum. The flask was transferred to a nitrogen filled glovebox and the sticky, brown reaction crude was dispersed in approximately 40 mL toluene and split between four 50 mL centrifuge tubes and centrifuged at 7000 RPM for 10 minutes. The brown nanocrystal solution was decanted into four new centrifuge tubes and the remaining dark pellets were discarded. To each centrifuge tube, approximately 30 mL of methyl acetate was added to precipitate the QDs and then centrifuged at 7000 RPM for 10 minutes. This cycle of precipitation, centrifugation, and redissolution using toluene and methyl acetate was repeated a total of three times. The QD product was dried under vacuum and finally suspended in hexane for storage in a nitrogen-filled glove box. Due to the large yield (multi-gram scale) of the QD synthesis, we performed all experiments on the same precursor QD sample, thereby eliminating the effects of sample-to-sample variations.

c) Quantitative ^1H and $^{19}F\{^1H\}$ NMR Spectroscopy

^1H and $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker Avance III 400 MHz instrument and acquired with sufficiently long delay to allow complete relaxation between pulses (30 seconds and 10 seconds, respectively). Surface bound OA^- ligand density was estimated using a combination of UV-Vis-NIR and ^1H NMR spectra. First, the concentration of a TCE solution of QDs was standardized using UV-Vis-NIR absorbance at 400 nm. The addition of a known amount of ferrocene (10 H's) as an internal standard to the QD ^1H NMR sample allowed us to estimate the total number of surface bound oleate ligands using the well-resolved vinyl proton peak. We find that there are approximately 120 ± 0.2 ligands per PbS QD, giving an estimated OA^- surface grafting density of 3.1 ligands / nm^2. We perform a similar procedure for ^1H NMR spectroscopic characterization of the *in-situ*

ligand exchange samples. Following ^{1}H NMR spectroscopy, we take the samples back into in a nitrogen-filled glovebox and add a known amount of α,α,α-trifluorotoluene (3 F's) as an internal standard for $^{19}F\{^{1}H\}$ NMR spectroscopy to quantify the number of surface bound 2,6-F-CA^{-} and free 2,6-F-CAH in solution.

d) Quantitative Spectrophotometric Absorbance Titration with 2,6-F-CAH

Optical absorbance spectra were collected using a Cary 6000i UV-Vis-NIR spectrometer. A stock solution of 10 μM PbS QDs in $CHCl_3$, standardized from absorbance measurements taken in TCE, was prepared under ambient conditions. Separately, a stock ligand solution was prepared by dissolving a known amount of the ligand in $CHCl_3$. The stock ligand solution was combined with neat ligand solvent in separate vials to make diluted ligand samples of varying ligand concentration. In a 2 mm path length cuvette, 0.1 mL of the diluted ligand solution was added to 0.6 mL of the stock QD solution to always maintain a constant sample volume of 0.7 mL. The sample was thoroughly mixed, and an absorbance spectrum was immediately taken. This protocol was followed for diluted ligand samples with ligand content ranging from 0 – 1500 ligands per QD per addition. Solution measurement and mixing was performed with calibrated micropipettes.

e) Large-Scale Solution-Phase Ligand Exchange

In a nitrogen-filled glovebox, a QD $CHCl_3$ solution was prepared and its concentration determined using absorbance spectroscopy.[2] A $CHCl_3$ solution containing approximately 450 equivalents of 2,6-F-CAH was added dropwise to the QD solution with vigorous stirring, and the exchange was allowed to proceed for approximately 10 minutes. The ligand exchanged QDs were purified *via* three precipitation, centrifugation, and redissolution cycles using $CHCl_3$ and hexane as a solvent and anti-solvent, respectively. The exchanged QD product was dried under vacuum and finally resuspended in $CDCl_3$ for NMR spectroscopic analysis.

Additional NMR Spectroscopy Data

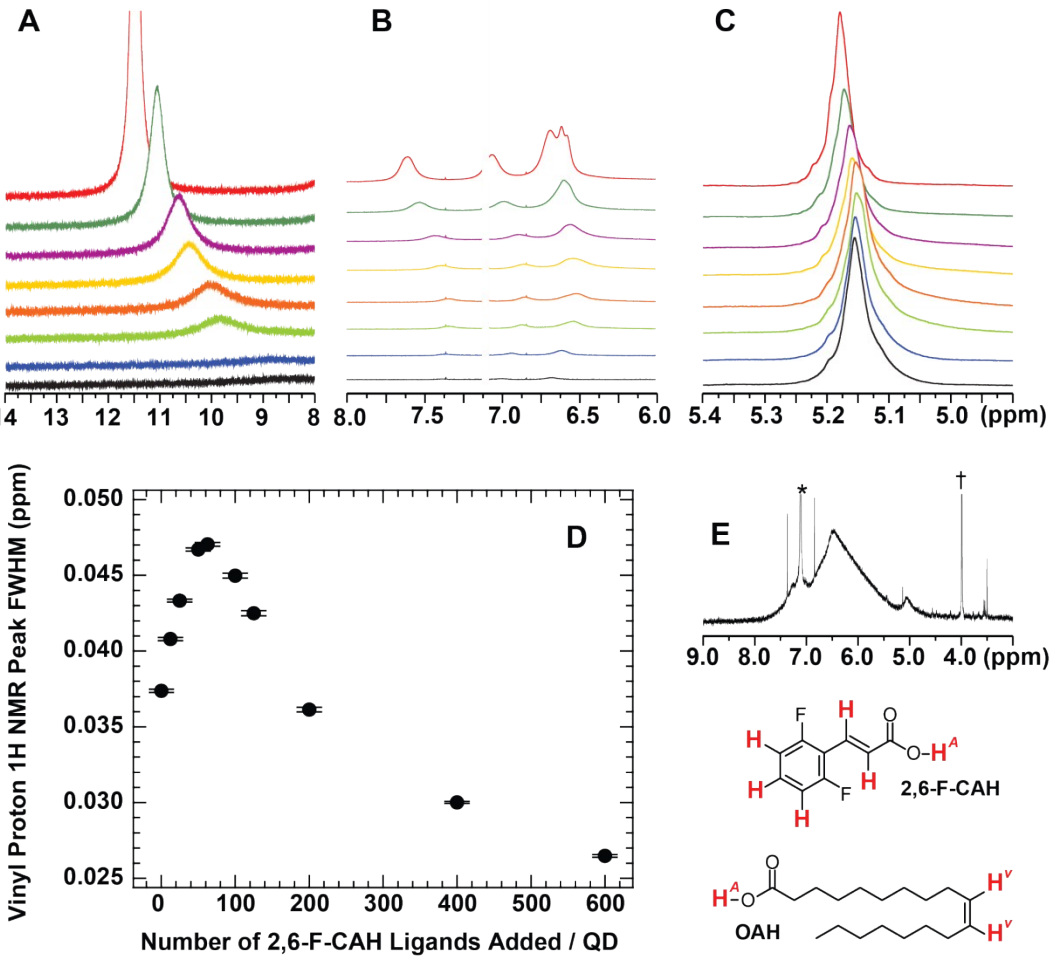

Fig. S1 ^{1}H NMR spectra of (A-C) *in-situ* ligand exchange QD solutions and (D) purified partially ligand exchanged QD solutions. (A) The acidic protons (δ = 8 - 13 ppm) of both OAH and 2,6-F-CAH, labelled ' H^A' in the above chemical structures, measured *via* ^{1}H NMR spectroscopy. The peaks sharpen and shift downfield with increased 2,6-F-CAH equivalent addition. (B) The aromatic protons of 2,6-F-CA^-/2,6-F-CAH are broad at low ligand equivalent addition, but sharpen at higher ligand equivalents. (C) The vinylic proton region of OAH and OA^- (δ = 5.0 - 5.3 ppm), labelled ' H^v' in the above chemical structure (right), measured *via* ^{1}H NMR spectroscopy. The peak is shifted upfield from the sharp vinylic multiplet of free OAH in solution. (D) Fitting the sharp, symmetrical portion of the vinylic peak of OAH and OA^- to a Lorentzian line shape, we find that the peak full-width half-maximum (FWHM) initially broadens, but then narrows with increasing 2,6-F-CAH ligand equivalent additions. The broadening of NMR linewidths is characteristic of slow rotational diffusion due to association with the QD or dynamic exchange on the NMR timescale. We suspect the initial broadening is due to relatively fast exchange of OA^- for 2,6-F-CA^- on the NMR time scale, but as more 2,6-F-CA^- coordinates the QD surface and more free OAH is generated in solution the vinylic peak then sharpens. (E) The ^{1}H NMR spectrum of an isolated, partially 2,6-F-CA^- exchanged QD solution. Using ^{1}H NMR spectroscopy, we can clearly distinguish the broad OA^- vinylic proton peak (δ = 5.2 ppm) and the aromatic 2,6-F-CA^- peaks (δ = 5.5-8 ppm) that are evidence for both ligand species coordinating the QD surface. The peaks labelled '*' and '†' indicate the protic solvent impurity, $CHCl_3$, and ^{1}H NMR internal standard, Cp_2Fe, respectively.

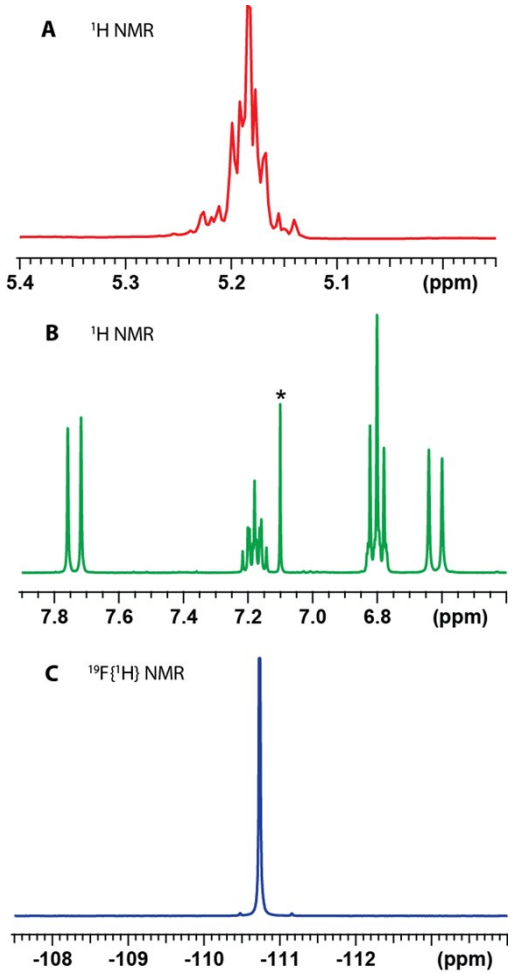

Fig. S2. NMR spectra of neat ligand molecules in $CDCl_3$. (A) The vinylic proton region of OAH. (B) The aromatic proton region of 2,6-F-CAH. The peak labelled '*' indicates the protic solvent impurity, $CHCl_3$. (C) The aryl fluorine atom region of 2,6-F-CAH.

References

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2 I. Moreels, K. Lambert, D. Smeets, D. De Muynck, T. Nollet, J. C. Martins, F. Vanhaecke, A. Vantomme, C. Delerue, G. Allan and Z. Hens, *ACS Nano*, 2009, **3**, 3023–3030.