

Supporting Information

Liquid contacting as a method to study photovoltaic properties of PbS quantum dot solids

Vitalii A. Dereviankin, Erik Johansson

Department of Chemistry, Portland State University

Address: 1719 SW 10th Avenue, Portland OR, 97201, USA

Phone number: 503-725-2566

E-mail: ejohansson@pdx.edu

Contents

1.1.1.	Chemicals and Materials	3
1.1.2.	Instruments	3
1.1.3.	PbS QDs synthesis	3
1.1.4.	Test-cell preparation/assembly	4
1.1.4.1.	<i>Working electrode preparation</i>	4
1.1.4.2.	<i>Counter electrode preparation</i>	4
1.1.4.3.	<i>Electrolyte preparation</i>	4
1.1.4.4.	<i>Determination of solution reduction potentials (E)</i>	5
1.1.4.5.	<i>Cell assembly</i>	5
	Figure S1. Exploded schematic of the test cell ("sandwich cell").	6
	Figure S2. Cross-sectional schematic of the test cell, band-edge energy diagram in the dark, and under illumination	6
	Figure S3 – S6. <i>J-V</i> characteristics in the dark and under illumination, open-circuit voltage (V_{oc}), and short-circuit current density (J_{sc}) data	7-8
	Figure S7. Photovoltage (V_{ph}) values of MPA-PbS QD solid in contact with electrolytes with different energetics	8
	Figure S8. Photo voltage response to light as a function of directionality of illumination	9
	Figure S9. Absorption spectra of the as-synthesized OA capped PbS QDs	9
	Figure S10. Absorption spectra of the 3-MPA exchanged PbS solid films prior and after soaking in the electrolytes.	10
	Figure S11. TEM of OA capped PbS quantum dots and the size distribution histogram.	11
	Figure S12. Thin film GIXRD of 3-MPA exchanged PbS QD solid deposited on FTO and wide angle XRD of as synthesized OA capped PbS QDs	12

1.1.1. Chemicals and Materials

All chemicals were used as received unless specified otherwise. Lead oxide (PbO, 99.999+ %, Strem Chemicals), oleic acid (OA, 90 %, Sigma-Aldrich), 1-octadecene (ODE) (90%, Sigma-Aldrich), bis(trimethylsilyl) sulfide (TMS, $(\text{CH}_3)_3\text{Si})_2\text{S}$, 96%, ACROS Organics), 3-mercaptopropionic acid (3-MPA, $\text{HSC}_2\text{H}_4\text{COOH}$, $\geq 99\%$, Sigma-Aldrich), ferrocene (Cp_2Fe , 98%, Sigma-Aldrich), ferrocenium tetrafluoroborate (Cp_2FeBF_4 , tech. grade, Sigma-Aldrich), decamethylferrocene ($\text{Me}_{10}\text{Cp}_2\text{Fe}$, 99%, Alfa Aesar), methyl viologen ($\text{MVCl}_2 \cdot x\text{H}_2\text{O}$, 1,1'-dimethyl-4,4'-bipyridinium dichloride hydrate, 98%, Sigma-Aldrich), ammonium hexafluorophosphate (NH_4PF_6 , 99%, ACROS Organics), bis(cyclopentadienyl)cobalt(II) (Cp_2Co , Sigma-Aldrich), bis(cyclopentadienyl)cobalt(III) hexafluorophosphate (Cp_2CoPF_6 , $>95.0\%$ (T), TCI America), nitrosonium tetrafluoroborate (NOBF_4 , 98%, Alfa Aesar). Acetone ($>99.5\%$, BAKER ANALYZED® A.C.S. Reagent), n-hexane (anhydrous, 99.99%, Alfa Aesar), acetonitrile (anhydrous, 99.8%, DriSOLV, EMD), methanol (anhydrous, 99.8%, DriSOLV, EMD Millipore), ethanol (absolute, $\geq 99.5\%$, Sigma-Aldrich) and Sparkleen laboratory detergent (Fisher Scientific) were used as received. Ferrocenium tetrafluoroborate (Cp_2FeBF_4 , tech. grade) was purchased from Sigma-Aldrich, and purified by sublimation. Methyl viologen dichloride hydrate (98%, Sigma-Aldrich) was purified by recrystallization from ethanol.

Fluorine doped tin oxide (FTO) (TEC 15, 13 $\Omega/\text{sq.}$, 2.3 mm, Sigma-Aldrich), aluminium foil tape (0.3 mil, All-Spec), thermoplastic sealant (Surlyn) (TPS 065096-30, Dyesol) and Vycor® Porous Glass Frits (Gamry instruments) were used as received unless additional cleaning steps and treatments are specified.

1.1.2. Instruments

Mbraun Labstar 1200 Glovebox (Mbraun), Gamry Reference 600 potentiostat/galvanostat/ZRA instrument (Gamry), UV005 photodiode (OSI Optoelectronics), ABET solar simulator Model 10500, FEI Tecnai F-20 TEM/STEM microscope, Rigaku Ultima IV X-Ray diffractometer, UV-3600 Shimadzu UV-VIS-NIR spectrophotometer

1.1.3. PbS QDs synthesis

Oleic acid capped quantum dots were synthesized using a previously reported method,¹ with small modifications. Briefly, 10 ml of ODE in a 3-neck round-bottom flask was degassed for 24 hours by heating to 80 °C under active vacuum. After that, while keeping the temperature at 80 °C, the flask was refilled and maintained under positive pressure with N_2 gas and 0.213 ml of TMS was added. The mixture's temperature was then increased to 100 °C. In a separate 3-neck round bottom flask 0.45 g PbO, 18 ml of ODE, and 1.51 ml OA were mixed, and similarly degassed under vacuum at 95 °C for 24 hours after which temperature was increased to 125 °C to achieve a clear solution. After this the TMS/ODE mixture was injected into the Pb-oleate/ODE solution using a syringe. The solution immediately turned black, and was kept at 125 °C for 1

minute, after which it was gradually cooled to 50 °C with tap water. The content was divided into two 50 ml centrifuge tubes, which were then filled with acetone, mixed, centrifuged, and decanted. Precipitated QDs in both centrifuge tubes were re-dispersed into 20 ml of toluene each, mixed, and 30 ml of acetone was again added to each tube to cause flocculation after which solutions were centrifuged and decanted again. The last step was repeated two more times. Finally, the solid QDs were dried under vacuum, and stored in the N₂ filled glovebox.

1.1.4. Test-cell preparation/assembly

1.1.4.1. Working electrode preparation

The working electrode (WE) consisted of 3-MPA linked PbS QDs on FTO. Working electrodes were prepared in accord with published procedures for preparing 3-MPA linked PbS QDs on metal-oxide substrates.² Briefly, a typical WE slide was prepared as follows. A 1.3 x 1.8 cm² FTO slide was cleaned by sonicating in 5% DI water/Sparkleen solution followed by rinses in isopropanol and DI water. The substrate was dried and partially masked using low adhesion paint tape to prevent QD deposition onto the contacting area. After QD deposition a 0.5 cm wide strip of aluminium tape was adhered to this area to serve as a contacting pad (see Figure S). The masked FTO substrate was placed on a spin coater. The spin coater speed was set to 2500 rpm and the substrate was spinning continuously during the QD film deposition. A cycle of QD deposition consisted of 50 µL of OA-capped PbS QDs in n-hexane (10 mg/ml) deposited onto the FTO substrate followed by 150 uL of 10% v/v mercaptopropionic acid (MPA) in methanol, and finally 300 uL of methanol. QD solids were made using 15 consecutive deposition cycles. For preparation of optically thick FTO/QD solid electrodes, used for studying illumination through the working or counter electrode, 50 deposition cycles were used instead.

1.1.4.2. Counter electrode preparation

The counter electrode (CE) was prepared by drilling a 1.5 mm diameter hole in a 1.3 x 1.8 cm² FTO substrate. Sonication in 5% Sparkleen soap solution and isopropanol rinsing and drying preceded Au sputtering to a thickness of 60 nm using a 108auto Cressington sputter coater. Similar to the WE, a contact pad was created using aluminium tape.

1.1.4.3. Electrolyte preparation

All electrolytes were prepared to contain the same ratio (1:1) and equal concentrations (1 mM) of reduced and oxidized species. This was done in a N₂(g) filled glovebox containing less than 0.5 ppm H₂O(g) and O₂(g). Maintaining equal concentrations and ratio of reduced and oxidized species across all redox couples is important. Varying the concentrations of reduced and oxidized species can change both solution potential and minority and majority charge-transfer rates, which can affect the open-circuit voltage under illumination of semiconductor/liquid junctions.³ Thus, to allow results to be compared more easily across a series of redox couples the concentrations of reduced and oxidized species were prepared to nominally 1 mM. 1 mM is

a low concentration compared to what is commonly used for photoelectrochemical experiments. The concentration was chosen due to solubility limitations of some of the redox species in acetonitrile. Ferrocenium tetrafluoroborate /ferrocene ($\text{Cp}_2\text{Fe}^{+/0}$) electrolyte was prepared by dissolving ferrocene and ferrocenium tetrafluoroborate in acetonitrile to 1 mM each. Decamethylferrocenium tetrafluoroborate / decamethylferrocene ($\text{Me}_{10}\text{Cp}_2\text{Fe}^{+/0}$) was prepared by dissolving decamethylferrocene in acetonitrile to 2 mM followed by addition of 1mM nitrosonium tetrafluoroborate to nominally oxidize half of the decamethylferrocene to decamethylferrocenium tetrafluoroborate. Methyl viologen bis(hexafluorophosphate)/methyl viologen radical hexafluorophosphate ($\text{MV}^{2+/+}$) electrolytes were prepared as follows. Methyl viologen bis(hexafluorophosphate) ($\text{MV}(\text{PF}_6)_2$) was synthesized according to a previously published method.⁴ Briefly, 55 mg (0.2 mmols) of methyl viologen dichloride hydrate and 65 mg (0.4 mmols) of ammonium hexafluorophosphate were dissolved in 9 ml of DI water by gentle heating to ~ 50 °C. When the solution was clear it was placed in an ice bath for 2 hours. Clear-white needle-like crystals of $\text{MV}(\text{PF}_6)_2$ were recovered by centrifugation and filtration. The crystals were dried under vacuum and kept in N_2 filled glovebox. A solution of 6.8 mM solution of $\text{MV}(\text{PF}_6)_2$ in dry acetonitrile was prepared in the glovebox and *in-situ* reduced via controlled potential electrolysis in order to form 1:1 ratio of oxidized (MV^{2+}) and reduced (MV^{+}) species which yielded an intense blue colouration of the solution. Prior to use this solution was diluted with anhydrous acetonitrile to 1mM $\text{MV}^{2+/+}$ electrolyte. Cobaltocenium hexafluorophosphate /cobaltocene ($\text{Cp}_2\text{Co}^{+/0}$) electrolyte was prepared by dissolving bis(cyclopentadienyl)cobalt(II) and bis(cyclopentadienyl)cobalt(III) hexafluorophosphate in acetonitrile to 1mM each.

1.1.4.4. Determination of solution reduction potentials (*E*)

Solution potentials were measured vs. ferrocene/ferrocenium tetrafluoroborate ($\text{Cp}_2\text{Fe}^{+/0}$) (1/1 mM in acetonitrile) using a two-electrode setup. A Pt button working-electrode (WE) was submerged in the electrolyte along with the $\text{Fc}^{+/0}$ reference electrode (RE). The solution was stirred and the open circuit potential between the two electrodes was recorded using the potentiostat. The $\text{Fc}^{+/0}$ reference electrode consisted of a Pt wire inserted in a 3 mm OD glass tube with attached Vycor® porous frit tip and filled with the $\text{Cp}_2\text{Fe}^{+/0}$ electrolyte. Solution potentials were in all cases close to calculated formal potentials, based on measured solution potentials and relative concentrations of redox species, estimated using experimentally observed limiting currents measured during separate three-electrode experiments. Differences between measured solution potentials and calculated formal potentials were in all cases small, being at most 20 mV

1.1.4.5. Cell assembly

A 1.4 x 1.4 cm^2 Surllyn spacer with a 0.50 cm^2 circular hole was made to provide an electrolyte chamber. The working electrode, Surllyn spacer, and the counter electrode were assembled at ambient conditions according to Figure S. The cell was placed on a hotplate (105 °C), counter electrode facing down, and moderate pressure was applied to ensure good adhesion of softened surllyn spacer to both electrodes. The cell was immediately taken into a N_2 filled glovebox,

where it was filled with electrolyte using a syringe with a soft tip. A slight vacuum was created inside the cell by retracting the syringe plunger, which, when released, injected the electrolyte into the cell. Finally, the predrilled hole was sealed using adhesive tape and the cell could be taken out from the glovebox to the test station.

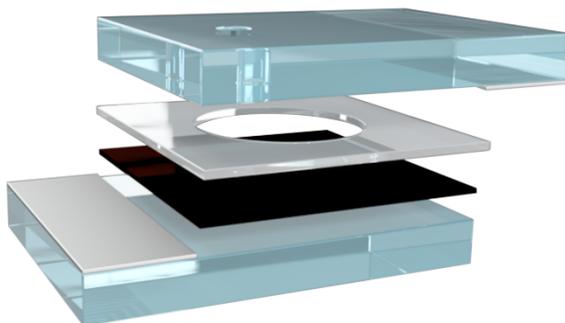


Figure S1. Exploded schematic of the test cell ("sandwich cell"). The components are, from top to bottom, Au coated FTO electrode (CE), surlyn spacer, PbS QD solid film, and FTO electrode (WE).

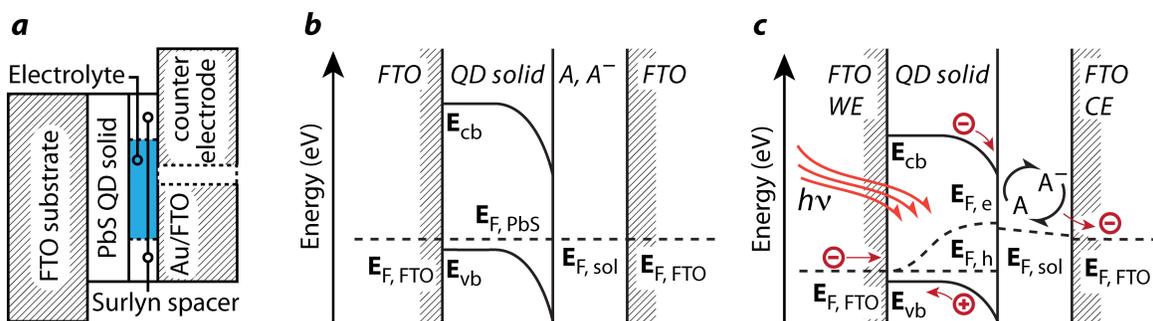


Figure S2. (a) Cross-sectional schematic of the test cell, (b) proposed band-edge energy diagram in the dark, and (c) under illumination showing the flow of electrons and holes at the PbS and FTO solid/liquid and solid/solid interfaces. E_{vb} and E_{cb} are the valence band and conduction band edge energies, respectively. $E_{F, FTO}$, and $E_{F, sol}$ are the Fermi levels in FTO and the electrolyte solution, respectively. $E_{F, e}$, and $E_{F, h}$, are the electron and hole quasi-Fermi levels, respectively.

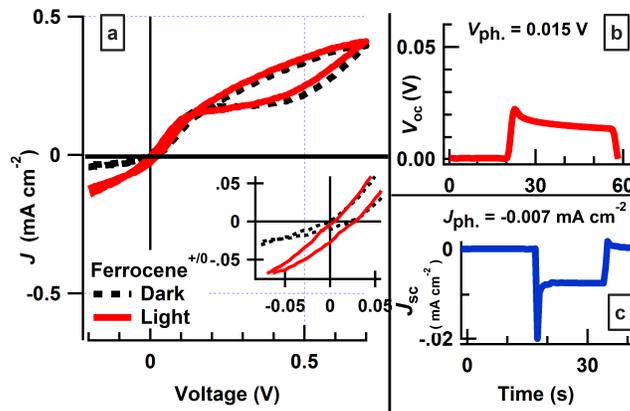


Figure S3. (a) J - V characteristics in the dark (dotted) and under illumination (solid), (b) open-circuit voltage (V_{oc}) change, and (c) short-circuit current density (J_{sc}) change with illumination of the 3-MPA-linked PbS QD solids contacted with a $\text{Cp}_2\text{Fe}^{+/0}$ electrolyte.

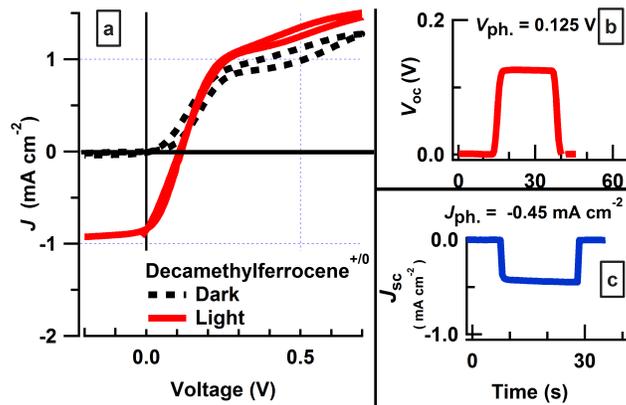


Figure S4. (a) J - V characteristics in the dark (dotted) and under illumination (solid), (b) open-circuit voltage (V_{oc}) change, and (c) short-circuit current density (J_{sc}) change with illumination of the 3-MPA-linked PbS QD solids contacted with a $\text{Me}_{10}\text{Cp}_2\text{Fe}^{+/0}$ electrolyte.

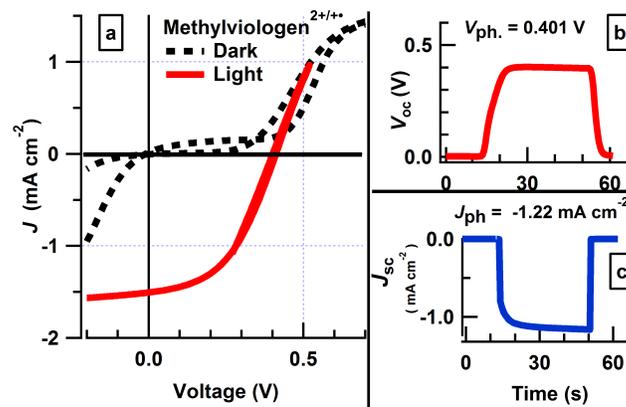


Figure S5. (a) J - V characteristics in the dark (dotted) and under illumination (solid), (b) open-circuit voltage (V_{oc}) change, and (c) short-circuit current density (J_{sc}) change with illumination of the 3-MPA-linked PbS QD solids contacted with a $\text{MV}^{2+/+}$ electrolyte.

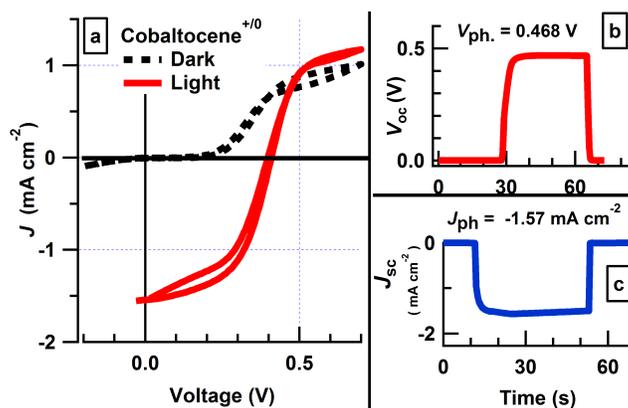


Figure S6 (a) J - V characteristics in the dark (dotted) and under illumination (solid), (b) open-circuit voltage (V_{oc}) change, and (c) short-circuit current density (J_{sc}) change with illumination of the 3-MPA-linked PbS QD solids contacted with a $\text{Cp}_2\text{Co}^{+/0}$ electrolyte.

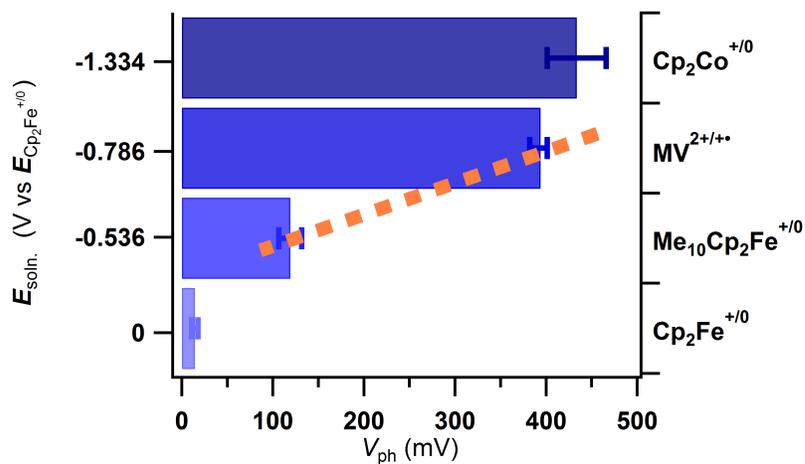


Figure S7. Photovoltages as a function of the solution potential for 3-MPA PbS QD solid contacted with different electrolytes.

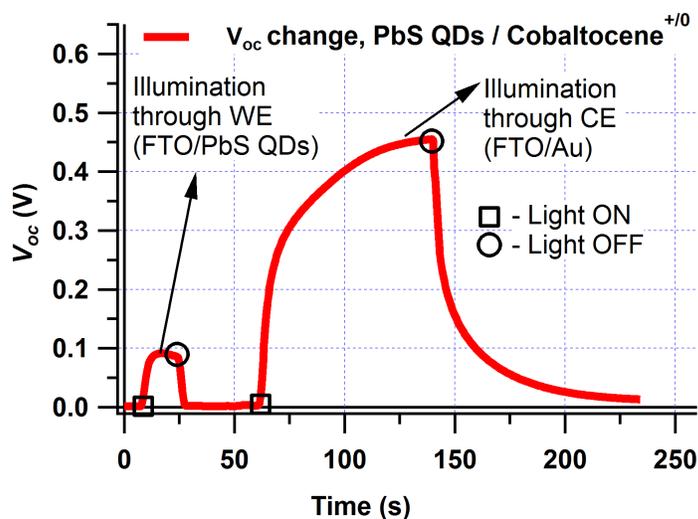


Figure S8. Photovoltage response as a function of illuminating a sandwich cell through the working electrode versus through the counter electrode. Thicker (50 cycles) PbS QD films were used for this study.

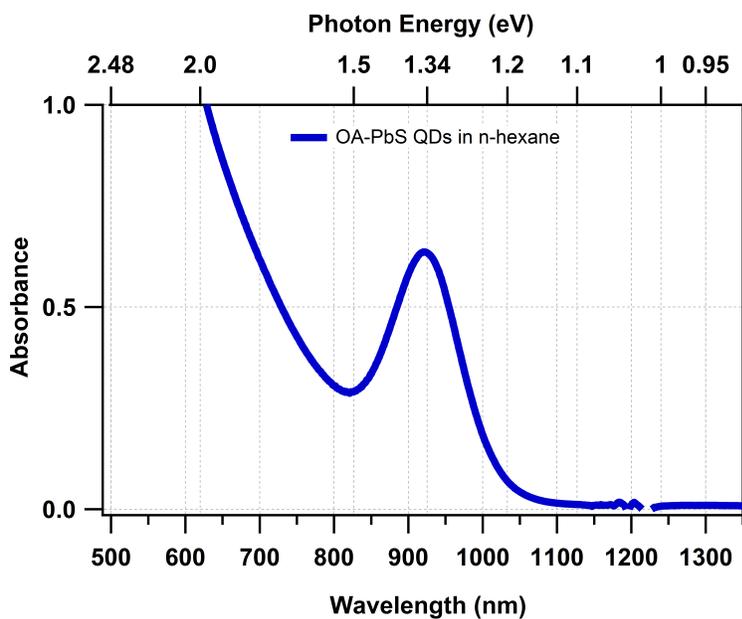


Figure S9. Absorption spectra of the as-synthesized OA capped PbS QDs, showing explicit excitonic absorption peak at 1.34 eV.

The lowest-energy excitonic peak red-shifted (~ 68 meV) upon ligand exchange (during deposition of films) from OA to 3-MPA (figures S9 and S10). This is consistent with previous reports for both solution and solid-state ligand exchange⁵⁻⁸

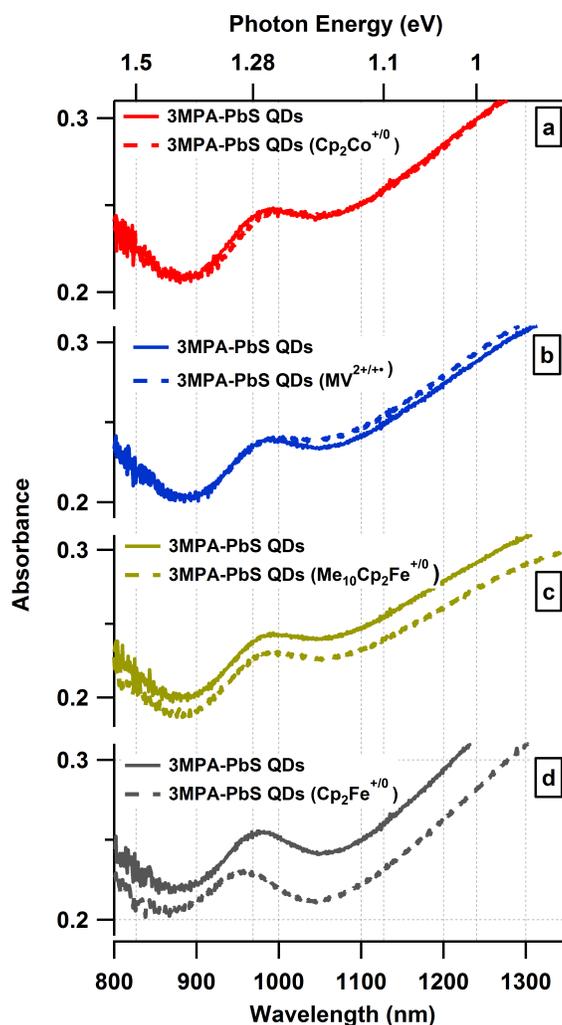


Figure S10. Absorption spectra of the 3-MPA exchanged PbS solid films deposited on 4 different FTO substrates used for study of the effects of (a) cobaltocenium hexafluorophosphate/cobaltocene, (b) methyl viologen bis(hexafluorophosphate) / methyl viologen radical hexafluorophosphate, (c) decamethylferrocenium tetrafluoroborate/decamethylferrocene and (d) ferrocenium tetrafluoroborate/ferrocene electrolytes on the QD solids. 3-MPA PbS solids were deposited according with the procedure described above in section 1.1.4.1. Each of the four substrates with the PbS solid were soaked in their respective electrolyte for 45 hours. Absorption spectra of the solids were acquired prior to (solid lines) and after the soaking (dashed lines).

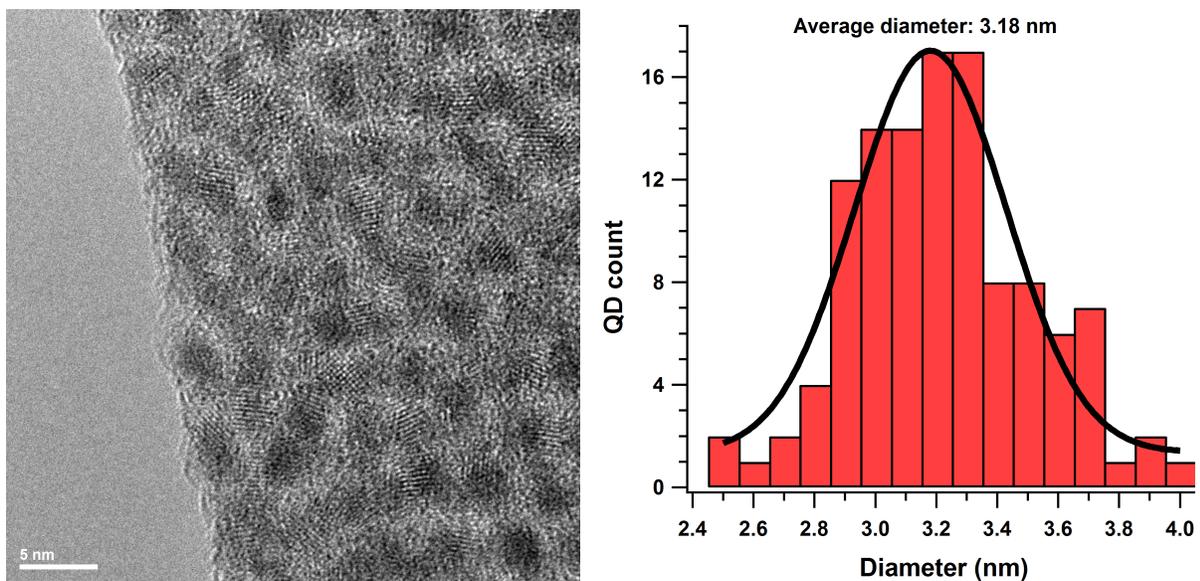


Figure S11. Transmission electron micrograph of OA capped PbS quantum dots and the size distribution histogram for QD particles.

To assess QDs size information, multiple TEM images of same batch QDs were manually analyzed using ImageJ software.

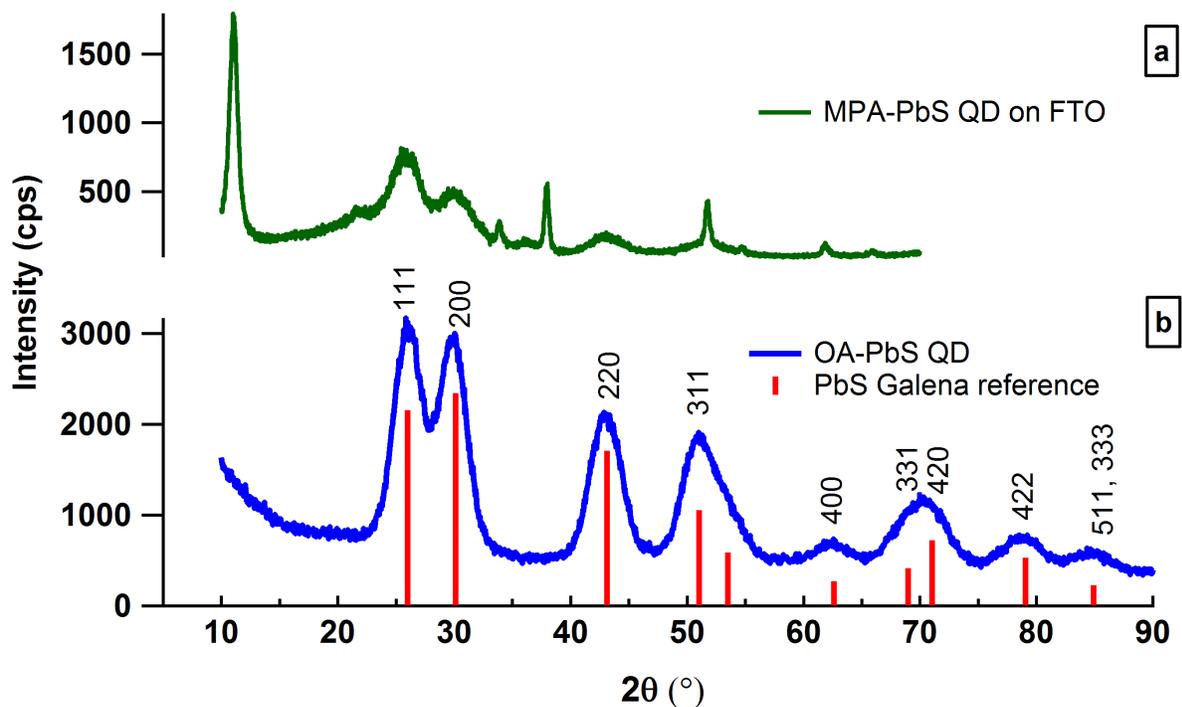


Figure S12. (a) X-ray diffraction patterns of 3-MPA exchanged PbS QD solid deposited on FTO (green line) and (b) as synthesized OA capped PbS QDs (blue line) along with PbS galena reference (red, vertical lines). Analysis of peak broadening using Scherrer equation yielded particle diameter of 3.04 ± 0.17 nm for OA capped QDs. The sharp peaks in the top spectrum (a) come from the substrate.

Bibliography

- 1 D. A. R. Barkhouse, R. Debnath, I. J. Kramer, D. Zhitomirsky, A. G. Pattantyus-Abraham, L. Levina, L. Etgar, M. Grätzel and E. H. Sargent, *Adv. Mater.*, 2011, **23**, 3134–8.
- 2 D. Zhitomirsky, O. Voznyy, L. Levina, S. Hoogland, K. W. Kemp, A. H. Ip, S. M. Thon and E. H. Sargent, *Nat. Commun.*, 2014, **5**, 1–7.
- 3 M. L. Rosenbluth and N. S. Lewis, *J. Phys. Chem.*, 1989, **93**, 3735–3740.
- 4 A. Manjula and M. Nagarajan, *Arkivoc*, 2001, **2001**, 165.
- 5 C. C. Reinhart and E. Johansson, *Chem. Mater.*, 2015, **27**, 7313–7320.
- 6 I. Mora-Sero, L. Bertoluzzi, V. Gonzalez-Pedro, S.-S. Gimenez, F. Fabregat-Santiago, K. W. Kemp, E. H. Sargent and J. Bisquert, *Nat. Commun.*, 2013, **4**, 2272.
- 7 K. J. Williams, W. A. Tisdale, K. S. Leschkies, G. Haugstad, D. J. Norris, E. S. Aydil and X.-Y. Zhu, *ACS Nano*, 2009, **3**, 1532–1538.
- 8 A. Wolcott, V. Doyeux, C. A. Nelson, R. Gearba, K. W. Lei, K. G. Yager, A. D. Dolocan, K. Williams, D. Nguyen and X.-Y. Zhu, *J. Phys. Chem. Lett.*, 2011, **2**, 795–800.