Supplementary Information

Optimizing Solid-State Ligand Exchange for Colloidal Quantum Dot Optoelectronics: How Much is Enough?

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Figure S1. Infra-red variable-angle spectroscopic ellipsometry (IR-VASE) measurements for tracking MPA ligand exchange on PbS CQD films. (a) 2852 cm⁻¹ and 2922 cm⁻¹ C-H stretching vibrations of OA are studied for various ligand exchange times. No C-H intensity is observed after \sim 3 seconds of MPA treatment, suggesting that the exchange is complete at this point. Any remaining OA after this stage is negligible and below the resolution limit of the technique. This data is plotted as a function of exchange time in (b). Y-axis is normalized to the initial intensity of the C-H stretch (2922 cm⁻¹ peak) for the pristine, OA-capped PbS CQD film. Reproduced with permission from Ref. [1]. Copyright 2014, Wiley.



Figure S2. QCM-D data showing frequency vs time trends for various [MPA] in ACN.

Frequency change (Δf (Hz)) was converted into mass change (Δm) using Sauerbrey equation:

 $\Delta m = -(C. \Delta f)/n$

where, Δm (ng.cm⁻²) is the areal mass change corresponding to the frequency change of the nth overtone. C (17.7 ng.cm⁻².Hz⁻¹) is the vibrational constant. This information allowed us to convert the net mass changes (Δm) into N, the total number of ligands exchanged per unit area, for each [MPA], using the following equation:

$$\Delta m = N.(M_{MPA} - M_{OA})$$

Here, Δm is the mass-change detected by QCM-D, M_{MPA} is the molecular weight of MPA, M_{OA} is the molecular weight of OA, and N is the total number of ligands exchanged per unit area. To convert this into number of ligands exchanged per CQD, we used the interdot spacing from Figure

1d, and assumed random packing of the CQDs (given the invasive and rough nature of solid-state exchange).²⁻³



Figure S3. Effect of [MPA] on refractive index (signifying film density) and absorption of OA-PbS CQD solids, as measured by VASE.



Figure S4. Effect of [MPA] on the various film properties when ACN is used as the carrier solvent.



Figure S5. FTIR spectra showing the impact of (a) MeOH and (b) ACN on OA-PbS CQDs. The films were soaked for 10 minutes in the solvents. C-H stretching vibration of OA was found to significantly decrease for MeOH, but remained unchanged for ACN. (c) IR-VASE data showing the reduction of OA content for MeOH exposure (solid line), (d) mass loss from the OA-PbS CQD film for MeOH (solid line) signifying loss of OA ligands. Reproduced with permission from Ref. [1]. Copyright 2014, Wiley.



Figure S6. Thickness of OA-PbS CQD films measured using spectroscopic ellipsometry (SE) for MeOH and ACN. MeOH leads to ~60 % reduction in film thickness due to loss of OA. (b) Excitonic peak undergoes a blue shift as OA is removed. No change is detected upon ACN interaction. (c) As OA is removed by MeOH, film densification is observed and the refractive index increases. (d) Inter-dot spacing is found to reduce upon extended exposure to MeOH due to loss of OA. No noticeable change is found for ACN. Reproduced with permission from Ref. [1]. Copyright 2014, Wiley.



Figure S7. No noticeable change in the overall shape of XPS core level peaks was observed upon interaction of the OA-PbS CQD films with neat MeOH. In particular, the intensity of the Pb_{OA} component (red) is found to reduce relative to the Pb_{QD} component (blue), as expected due a loss of OA. Reproduced with permission from Ref. [1]. Copyright 2014, Wiley.



Figure S8. *MPA-exchange:* High resolution S 2p core level peaks as found from XPS. The OA-PbS CQD film (a) shows a doublet as expected, arising from the S atoms in the CQD (S_{QD}). S 2p peaks for the MPA-exchanged films (b)-(d) show a new component arising from S atoms of MPA ligands bonded to Pb (red-shaded components, S_{MPA}). The S $2p_{1/2}$ peak shifts to a lower binding energy from 162.2 eV for the OA-capped CQDs to 161.6 eV for 10% [MPA] case. This is roughly similar to peak shifts observed for all the other core levels (Pb 4f, O 1s, C 1s) and is likely due to the corresponding Fermi level shift that occurs upon *p*-doping induced by the ligand exchange.



Figure S9. *MPA-exchange:* High resolution Pb 4f core level peaks as found from XPS. The OA-PbS CQD film (a) shows two components: arising from the Pb atoms in the CQD (Pb_{QD}), and the surface Pb atoms bonded to OA (Pb_{OA}). In the case of Pb 4f peaks for the MPA-exchanged films (b)-(d), the Pb_{OA} component is replaced by Pb_{MPA} , arising from surface Pb atoms bonded to MPA. As can be seen, no other peak components at any different binding energy position are observed in the exchanged films, indicating that either all of the OA has been exchanged, or Pb_{OA} and Pb_{MPA} components overlap. It is also likely that some Pb-O exists in minimal amounts (around 139 eV and 144 eV), as is evident from the O 1s peaks (Figure S6). Due to the short lengths of the MPA ligands compared to OA, the exchanged CQDs are more likely to get oxidized due to more bare sites available for atmospheric oxygen to attach once the bulky OA ligands have been removed.



Figure S10. *MPA-exchange:* High resolution O 1s core level peaks as found from XPS. OA-PbS CQDs, (a), exhibit a single component likely originating from the oxygen in OA and hydroxides on CQD surfaces. For the MPA-exchanged films (b)-(d), a lower binding energy component centered at 530 eV (green), likely corresponding to Pb-O is also found.



Figure S11. *MPA-exchange:* High resolution C 1s core level peaks as found from XPS. Red peaks correspond to amorphous carbon, likely originating from the alkyl chains of OA and MPA. The higher binding energy component (black) is due to the C=O group. A relative increase in this black component is found compared to the red component after MPA-exchange, since there is lesser alkyl content in MPA compared to OA.

Table S1. Summary of XPS on OA-PbS CQD solids exchanged with various [MPA]

	Relative atomic concentration, %						
[MPA]	Pb	S	С	Cd	Cl	0	(Pb+Cd)/(S+Cl)
0	11.2	6.1	74.6	0.4	2.0	5.7	1.43
1	21.2	18.6	42.5	1.2	4.1	12.0	0.99
5	20.2	17.9	46.0	1.0	4.7	10.2	0.94
10	23.6	19.8	35.5	1.3	4.7	12.7	1.02



Figure S12. (a) QD absorber layer made out using a 9 LbL deposition with [MPA] >1%. The top few layers start showing roughness, cracks and delamination resulting in shorted and malfunctioning cells. (b) Thin films/single layers of QDs made using [MPA] >1% for spectroscopic characterization were smooth and uniform.



Figure S13. *EDT-exchange:* High resolution Pb 4f and S 2p core level peaks as found from XPS. In accordance with our recent finding of oxygen doping,⁴ these films were stored in an oxygenrich environment upon ligand exchange. Consequently, a higher binding energy component (grey) is observed in Pb 4f, (b), and corresponds to oxidized species. Evolution of S 2p upon EDT exchange and oxygen storage is more drastic and results in a complex peak which is fit using multiple components, as shown in (d).⁴ Besides appearance of S_{EDT}, unbound ligands are also found (green), besides the oxidation species, PbSO₃ and PbSO₄, at higher binding energies. We have discussed about in detail elsewhere.⁴



Figure S14. *EDT-exchange:* High resolution O 1s and C 1s core level peaks as found from XPS. Upon ligand exchange, O 1s shows a low binding energy feature centered at 529 eV corresponding to oxidized Pb, as a result of oxygen doping. The higher binding energy component found in C 1s at 288 eV after ligand exchange is likely due to the oxygenated species due to oxygen doping. In fact, there is no C=O in the EDT (unlike MPA) which can appear at this binding energy. We have discussed about this particular component in C 1s in detail elsewhere.⁴

Table S2. Summary of XPS on CQD solids ligand exchanged with [EDT]

Atomic ratio					
[EDT]	Pb/S				
0	1.43				
10-2	0.91				



Figure S15. Histograms for (a) J_{SC} , (b) V_{OC} , (c) FF, and (d) PCE for *n-i-p* solar cells fabricated using some of the key [EDT] conditions.

References in SI

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