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

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ABSTRACT. Progress in chalcogenide and perovskite CQD optoelectronics has relied in significant part on solid-state ligand exchanges (SSEs): the replacement of initial insulating ligands with shorter conducting linkers on CQD surfaces. Herein we develop a mechanistic model of SSE employing 3-mercaptopropionic acid (MPA) and 1,2-ethanedithiol (EDT) as the linkers. The model suggests that optimal linker concentrations lead to efficient exchange resulting in ca. 200 – 300 exchanged ligands per CQD, a 50% thickness reduction of the initial film, decreased interdot spacing, a 15 nm red-shift in the excitonic absorption peak and a 10x reduction in carrier lifetime. It is a combined effect of these physico-chemical changes that have traditionally made 1% MPA and 10⁻²% EDT (v:v) the concentrations of choice for efficient CQD optoelectronics.

TOC GRAPHICS
INTRODUCTION

Colloidal quantum dots (CQDs) have been explored extensively in the past decade for applications in low-cost thin-film photovoltaics, photodetectors, light-emitting diodes, lasers and transistors.\textsuperscript{1-8} Bandgap tunability and the ease of solution-processability makes these novel nanomaterials highly promising for widespread scalability in the above-said applications. In particular, owing to their strong optical absorption, large dielectric constant and small exciton binding energies, lead sulfide (PbS) CQDs have been chiefly pursued as absorbers in solar cells.

PbS CQDs are initially capped with long-chain insulating ligands (such as oleic acid, OA) which impart dispersion and steric stability in organic solvents. After the colloidal ink is transformed into a thin solid film via spin, blade or spray coating,\textsuperscript{7, 9-10} the CQDs are exchanged by replacing the insulating ligands with shorter conductive linkers (such as thiols and halides) employing solid-state ligand exchange (SSE). The process brings the CQDs closer enhancing charge transport and leading to a dense solid with increased optical absorption and electrical conductivity.\textsuperscript{11-12} This process is repeated in a layer-by-layer (LbL) fashion until the desired film thickness is achieved.\textsuperscript{13}

To date, 3-mercaptopropionic acid (MPA) has been employed as a routine monodentate linker in SSE.\textsuperscript{9, 11, 14-20} Briefly treating the OA-capped PbS (OA-PbS) CQD film with a 1\% solution of MPA (by volume) in methanol, MeOH, has been the standard recipe for carrying out the exchange process, resulting in efficient MPA-based PbS CQD solar cells.\textsuperscript{11, 21} Although the $n$-$i$-$p$ device architecture, employing a solution-phase ligand exchanged (SolEx) PbS CQD absorber, has defined the latest trend in CQD PV, SSE with 1,2-ethandithiol (EDT) is still necessary to fabricate the $p$-type hole-transporting layer in this new architecture.\textsuperscript{8, 22-27} Furthermore, the latest high-performing colloidal perovskite QD solar cells also require a SSE LbL build-up of the active layer.\textsuperscript{2, 28} In general, the effect of linker concentration in SSE on the various physical and chemical
attributes of the CQD solids has not been explored in detail resulting in a largely trial-and-error based optimization approach to the process.

Herein, we sought to systematically explore and optimize the SSE process. We selected the two most commonly-used linkers, MPA and EDT. First, we performed ligand exchange on OA-PbS CQD films with a variety of MPA concentrations in MeOH ([MPA], in volume:volume %), carefully tuning [MPA] from $10^{-6}$% to 10% (v:v) in steps. This allowed us to tune the linker-CQD interaction and, therefore, the number of MPA ligands delivered to the CQD surface. We identified two contrasting [MPA] regimes: concentrations above $10^{-2}$% represent a linker-dominated regime and lead to exchanged, densely packed films with enhanced absorption resulting in state-of-the-art solar cells; concentrations below $10^{-4}$% leave the films unexchanged, indicating a solvent-dominated regime, and lead to poorly performing solar cells. A phase transition-like sudden change was observed between these two regimes. We successfully translated the lessons learned from MPA-exchange optimization and achieved our best-performing devices of 10.7% power conversion efficiency (PCE) with an optimized EDT-exchange in $n$-$i$-$p$ architecture devices.

**EXPERIMENTAL SECTION**

*CQD synthesis:* PbS CQDs synthesis was carried out using a modification of a literature method,\textsuperscript{29} employing an in-synthesis halide treatment.\textsuperscript{30} This involved addition of CdCl\textsubscript{2} (dissolved in a mixture of tetradecylphosphonic acid (TDPA) and oleylamine) in solution-phase after the nucleation and growth of the PbS CQDs, as reported previously.\textsuperscript{30} The function of CdCl\textsubscript{2} is to replace the loosely-bound OA ligands and passivate the surface sites that can otherwise be source to dangling bonds and act as trap states. CQDs used for the HTL in $n$-$i$-$p$ architecture devices did not employ a halide treatment. CQDs used in this study are ca. 3.2 nm in size.
Device fabrication: For the fabrication of n-p architecture devices OA-PbS CQDs were spin-coated on a TiO$_2$ nanoparticle-based electrode on ITO-coated glass substrate using a layer-by-layer deposition approach. A solution of 50 mg mL$^{-1}$ OA-PbS CQDs in octane was spin-coated under ambient conditions at 2500 rpm. This was followed by a ligand exchange step which employed a desired concentration of MPA in MeOH solvent, as described in the paper. The OA-PbS CQD solid was soaked in the MPA/MeOH solution for 3 s followed by spinning and rinsing twice with MeOH solvent to remove any residual MPA and OA ligands. The process resulted in a layer with the thickness of approximately 30 nm.\textsuperscript{11} The process was repeated 9 times until the desired thickness was achieved. The top electrodes, comprising of 40 nm MoO$_3$ and 120 nm Au, were thermally evaporated at the rates of 0.2 Å s$^{-1}$ and 1 Å s$^{-1}$ respectively, at the pressure of $1 \times 10^{-6}$ mbar.

For the fabrication of n-i-p architecture devices, solution-phase ligand exchange was carried out as per reported protocol.\textsuperscript{8} A precursor solution (0.1 M PbI$_2$, 0.02 M PbBr$_2$, 0.04 M ammonium acetate) was first made in 5 mL DMF solvent. 5 mL of OA-PbS CQDs (10 mg mL$^{-1}$) were then added to the vial and vortexed for 5 min. The resulting solution-phase ligand exchanged CQDs were washed thrice with octane, followed by precipitation in toluene and a subsequent centrifugation (6000 rpm, 2 min). The centrifuged vials were left under vacuum for drying for 1 hour. The powder was then redispersed in a butylamine-amylamine-hexylamine (10:3:2) solvent mixture to obtain a colloidal ink of 200 mg mL$^{-1}$ concentration. 40 µL of this colloidal ink was spun at 2500 rpm for 15s atop a ZnO nanoparticle-based electron transporting layer on ITO-coated glass substrate. This was followed by deposition of the EDT-PbS HTL. OA-PbS CQDs were spun atop the active layer and soaked for 30s in an EDT/ACN solution of a desired concentration as discussed in the paper. The solution was subsequently spun and the exchanged solid was rinsed.
twice with ACN. This was repeated one more time ensuring a total HTL thickness of ca. 50 nm. Finally, the top electrode comprising of 80 nm Au was thermally evaporated at a rate of 1.0 \( \text{Å s}^{-1} \). After completion of electrode evaporation, the devices were taken out of the nitrogen glove box housing the evaporator and stored for a day in a dry box environment (0% RH) to ensure oxygen doping of the HTL.

**Time-resolved PL measurements:** TRPL measurements were carried out using a Horiba Fluorolog Time Correlated Single Photon Counter (TCSPC) system, using a 635 nm laser diode as the pump emitting pulses with 60 ps widths and peak powers of 300 mW. Emission was measured with a Hamamatsu infrared detector. Measurements were performed at room temperature.

**J–V characterization:** \( J-V \) characterization was performed using a Keithley 2400 source-meter at ambient temperature, in a nitrogen glove box. The solar spectrum at AM1.5 was simulated to within class A specifications (less than 25% spectral mismatch) with a xenon lamp and filters (ScienceTech; measured intensity of 100 mW cm\(^{-2}\)). A circular aperture of 0.049 cm\(^2\) defined the active area of the \( n-p \) devices. For the \( n-i-p \) solar cells, an active area of 0.1 cm\(^2\) was used.

**XPS measurements:** XPS was measured in an ultrahigh vacuum (UHV) Omicron chamber equipped with a SPHERA U7 hemispherical energy analyzer. The spectra were obtained using X-ray photons having an incident kinetic energy of 1486.6 eV from a monochromated Al K\( \alpha \) X-ray source with a total energy resolution of 0.1 eV. The measurements were done on CQD films spin-coated on pre-cleaned ITO substrates (non-patterned, 0.5 x 0.5 cm\(^2\)), at chamber base pressures of \( < 5 \times 10^{-9} \text{ mbar} \) at room temperature.

**VASE measurements:** An M-2000XI, J. A. Woollam Co., Inc. ellipsometer (400 – 1700 cm\(^{-1}\)) was used to study the variation in film thickness and optical properties following ligand exchange.
of the CQD film spin-coated on a thermally oxidized Si substrate. The spectra were obtained at incidence angles in the range 45°-75° with discrete increments of 5°. The film properties were modelled assuming a B-Spline dispersion relation in the absorption region using the EASE and WVASE32 software packages from J. A. Woollam Co., Inc.

**GISAXS:** Measurements were carried out at the D-line of the Cornell High Energy Synchrotron Source (CHESS) (Cornell University). A beam with a wavelength of 1.15 Å was used, obtained from a wide bandpass (1.47%) double-bounce multilayer monochromator. The angle of incidence was varied discretely from 0.04° to 0.25° with respect to the plane of the substrate. Measurements were performed on CQD films spin-coated on thermally oxidized Si substrates.

**QCM-D measurements:** QCM-D measurements were carried out as per reported protocol. Ultrasonically cleaned and UV-ozone treated AT-cut quartz crystals (5 MHz resonance frequency) were coated with OA-PbS CQDs by spinning and loaded into a QCM-D open module (E4 model, QSense, Biolin Scientific) maintained at room temperature (25°C). MPA/ACN solutions (150 µL) of desired concentrations were individually dropped on the sensor surface. Changes to the frequency were followed for 10 min each.

**RESULTS and DISCUSSION**

Ligand exchange is expected to drastically change the physical and chemical properties of the CQD film at the micro- and nanoscales. OA-PbS CQD thin films (ca. 80 nm) were treated with a series of [MPA]. The treatment was limited to ~3 s in accordance with the standard active layer fabrication protocol. We have previously reported that the MPA ligand exchange is complete within the first ~3 s of treatment with MPA solution (Figure S1). This was confirmed by monitoring the C-H stretching vibrations of OA for various MPA treatment times. The vibrational
intensity was found to be negligible after ~3 s of treatment suggesting that any remnant OA ligands beyond this point are below the resolution limit. This is further confirmed by the QCM-D data shown in Figure S2. The frequency change shown on the Y-axis represents mass loss of the CQD film for various [MPA] scenarios. It is clear that the mass loss (signifying ligand exchange) is complete with in the first few seconds and no change in mass is detected over the next several minutes. On the basis of these findings, we have assumed for the rest of this study that a ‘complete’ ligand exchange refers to replacement of all of the OA ligands with MPA.

In order to track the efficacy of exchange, we probed the film thickness, refractive index and optical absorption using variable-angle spectroscopic ellipsometry (VASE), interdot spacing using grazing incidence small angle X-ray scattering (GISAXS), carrier lifetime using time-resolved photoluminescence (TRPL) and the number of exchanged ligands was deduced using quartz crystal microbalance with dissipation (QCM-D) capability. Results are shown in Figure 1.
Figure 1. Solvent- vs. linker-dominated regimes: OA-PbS CQD films were ligand exchanged with a series of [MPA] in MeOH solvent. The various film properties, (a) thickness, (b) refractive index, (c) excitonic peak, and (d) interdot spacing were found to follow a similar trend. (e) Carrier lifetime and (f) ligand exchanged per CQD were also tracked using TRPL and QCM-D, respectively. Blue lines are drawn as a guide to the eye. Lower concentration exchanges are not found to affect the films considerably leaving the final films similar to the unexchanged control (the data points in black circles). The film properties show a sudden drastic change in the concentration range of $10^{-4}$ to $10^{-2}$ (white shaded regions), whereafter the changes are found to relatively saturate. Blue lines are drawn as guide to eye.
Lower concentrations do not have any noticeable effect on the film thickness (Figure 1a) where the thicknesses resemble the untreated baseline. As [MPA] is increased, a sudden transition is observed above $10^{-4}$ %. The film thickness is found to reduce to ca. 50% of the initial thickness for $10^{-2}$ %. Films treated with higher [MPA] do not show any further thickness decrease. The OA-PbS CQD film is expected to show thickness reduction upon ligand exchange as the bulkier OA ligands are replaced by the shorter MPA molecules.\textsuperscript{11} We find the film density to follow a similar trend. The refractive index ($n_{1200}$) measured at a wavelength of 1200 nm increases significantly for [MPA] $\geq 10^{-4}$ % indicating film densification, as shown in Figure 1b. This densification is accompanied by an enhanced absorption (Figure S3). We also find that the excitonic peak, $\lambda_{\text{peak}}$, red-shifts upon ligand exchange. The exchange-induced red-shift in CQD films is well-known for thiol ligands and has been previously ascribed to a combination of enhanced electronic coupling between the CQDs and the increased film disorder.\textsuperscript{31-32} The red-shift has also been reported when halides, hybrid perovskites and metal chalcogenides have been used to passivate the surface of PbS CQDs.\textsuperscript{33-35} The $\lambda_{\text{peak}}$ peak red-shift, therefore, is another important indicator to efficient ligand exchange. We find that the red-shifts increase and saturate for MPA $\geq 10^{-2}$% (Figure 1c). We were also interested in studying the effect of [MPA] on interdot spacing, $d$. Ligand exchange is known to bring CQDs closer leading to better coupling and enhanced delocalization of carrier wavefunctions. Further understanding and modifications to the solid-state exchange process have recently improved wavefunction delocalization leading to high mobilities in HgSe CQDs and possible band-like charge transport in HgTe CQD solids, that are important for application in mid-infrared photodetection.\textsuperscript{36-40} Figure 1d shows a similar variation of $d$ as a function of [MPA]. Lower [MPA] are ineffective in bringing the CQDs closer while higher [MPA] ($\geq 10^{-2}$ %) lead to a closely packed CQD solid with an average $d$-spacing of ca. 3.5 nm.
The above trends reveal an important insight into the nature of SSE. The lower [MPA] regime is dominated by the solvent, MeOH, and is incapable of exchanging the OA ligands while the higher [MPA] regime is dominated by MPA and leads to efficient ligand exchange. The various film properties are found to saturate for these concentrations. The intermediate concentrations, $10^{-4} \leq [\text{MPA}] \leq 10^{-2}$, represent a transition regime. As a generalization to the above-observed trend, we have carried out this experimental investigation for another commonly employed solvent, acetonitrile (ACN). ACN is known to be a better and less disruptive process solvent when longer SSE times are required, for example, when exchanging a thicker OA-PbS CQD absorber layer,\textsuperscript{11} due its high dipole moment and aprotic nature.\textsuperscript{41} The results are similar to the case of MeOH and are shown in Figure S4. Earlier, we have explored the interaction of neat MeOH and ACN with CdCl\textsubscript{2}-passivated OA-PbS CQDs.\textsuperscript{11} Although, the aprotic solvent, ACN does not interact with OA, it was found that being a protic solvent, MeOH interacts with the CQDs and, over an extended time ($\sim$10 mins), removes OA and leaches off Cl resulting in surface traps. Supporting data can be found in Figure S5-S7 and suggests that for shorter times ($\sim$3 s), there is no noticeable interaction between MeOH and the CQDs. It is for this reason that, in the present study, the ligand exchanges were limited to $\sim$3 s. This was done to limit the interaction of MeOH with OA-PbS CQDs. Therefore, in the solvent-dominated regime, MeOH-interaction with the CQDs for 3 s leaves them essentially unaffected.

Transient PL measurements (Figure 1e) revealed an order of magnitude reduction in carrier lifetime from 300 ns in solvent-dominated regime to 30 ns in the linker-dominated regime, suggesting significantly improved charge extraction in exchanged CQD solids. Although ligand exchange also creates traps, it improves carrier diffusion lengths which are much larger than the dimensions of a single CQD.\textsuperscript{42} Therefore, the reduction in carrier lifetime observed upon exchange
is primarily indicative of more efficient exciton dissociation and subsequent non-radiative recombination at a trap in the film, rather than of quenching inside the CQD. We also monitored the linker-CQD interactions using QCM-D. QCM-D uses a quartz crystal substrate vibrating at a resonance frequency. Subtle changes in mass and viscoelastic properties of the rigid film coated atop the crystal can be tracked in terms of changes to the vibration frequency. Since ligand exchange involves a mass change equivalent to the difference in masses of OA and MPA, we were able to approximate the number of ligands exchanged per CQD from the overall mass changes observed. Importantly, since these measurements required an extended interaction of the MPA solution with OA-PbS CQD solids, we preferred to use ACN as the carrier for MPA. As has been shown earlier, ACN minimizes solvent-CQD interactions and does not lead to any ligand loss on its own.\textsuperscript{11, 41} We assumed random packing of CQDs, given the harsh and invasive nature of the SSE,\textsuperscript{30, 43} and used interdot spacings from Figure 1d to quantify the ligand exchange. The data is shown in Figure 1f and confirms that linker-CQD interactions dominate at higher [MPA] leading to exchange of ca. 200 – 300 MPA ligands (see Figure S2 frequency change vs time trends and further discussion).

X-ray photoelectron spectroscopy (XPS) suggests higher [MPA] result in a complete exchange as highlighted by the atomic ratio of cations to anions approaching 1.0, a condition necessary to suppress surface traps (Figure S8-S11 Table S1).\textsuperscript{44-45} Any change in position of the Fermi level (doping) with respect to the valence band corresponds to a shift in core level positions. This is likely being observed here for MPA-treated PbS CQDs. As an example, the S 2p\textsubscript{1/2} component (S\textsubscript{QD}) located at 162.2 eV for the OA-capped CQDs in S4a shifts to 161.6 eV for 10% [MPA] in S4b. A roughly similar shift to lower binding energies is observed for all the other core level peaks (S8-S11), and is due to the \textit{p}-doping induced by ligand exchange.
Scheme 1. Mechanistic model of SSE. Schematic representation of the SSE model as discerned from the findings reported above. Solvent- and linker-dominated regimes are separated by a transition regime residing in intermediate values of [MPA]. Green region: linker-dominated regime, red region: solvent-dominated regime, white region: transition regime.

Scheme 1 summarizes our proposed qualitative model of SSE based on the findings presented above. As the linker concentration is increased above the solvent-dominated regime, $10^{-4}$% for the case of MPA, the CQD solid undergoes a phase transition-like sudden change in properties, marking the onset of ligand exchange. A further increase in the linker concentration saturates the changes resulting in a completely exchanged film. Apparently, a critical number of linkers (ca. 200 – 300 MPA molecules) is necessary to be delivered to the CQD solid in order to enable a sudden and complete exchange, as discussed below. 3.2 nm PbS CQDs have been suggested to have $\sim$220 OA surface ligands. If we are to assume a 1:1 exchange, then our number of $\sim$200-300 ligands exchanged per CQD is in line with this expectation.
Figure 2. *n-p architecture devices.* (a) Schematic of the device architecture. (b) *J-V* curves of solar cells fabricated by employing various [MPA] in the SSE. (c) *J_SC, V_OC,* and (d) FF, PCE as a function of [MPA].

Table 1. Device parameters for solar cells fabricated in various [MPA] regimes. [MPA] is the units of volume concentration in MeOH (v:v). ± denotes one standard deviation over the mean. Values in brackets represent parameters of the best-performing device in each category.

<table>
<thead>
<tr>
<th>[MPA] (v:v)</th>
<th><em>J_SC</em> (mA.cm⁻²)</th>
<th><em>V_OC</em> (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th><em>R_S</em> (Ω.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>13.31 ± 0.60 (13.99)</td>
<td>0.57 ± 0.00 (0.57)</td>
<td>63.1 ± 0.5 (63.1)</td>
<td>4.8 ± 0.2 (5.1)</td>
<td>5.3 ± 0.3 (5.1)</td>
</tr>
<tr>
<td>10⁻¹</td>
<td>15.02 ± 0.02 (15.02)</td>
<td>0.49 ± 0.00 (0.49)</td>
<td>56.1 ± 0.7 (57.1)</td>
<td>4.2 ± 0.1 (4.2)</td>
<td>6.6 ± 0.2 (6.4)</td>
</tr>
<tr>
<td>10⁻²</td>
<td>14.02 ± 0.08 (14.24)</td>
<td>0.49 ± 0.01 (0.49)</td>
<td>53.2 ± 0.8 (55.9)</td>
<td>3.6 ± 0.1 (3.9)</td>
<td>8.6 ± 0.4 (7.8)</td>
</tr>
<tr>
<td>10⁻³</td>
<td>5.58 ± 0.81 (6.82)</td>
<td>0.48 ± 0.00 (0.48)</td>
<td>23.4 ± 2.1 (26.8)</td>
<td>0.6 ± 0.1 (0.9)</td>
<td>129.5 ± 38.8 (71.8)</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>4.57 ± 0.06 (4.64)</td>
<td>0.45 ± 0.00 (0.45)</td>
<td>37.4 ± 1.5 (39.9)</td>
<td>0.8 ± 0.0 (0.8)</td>
<td>57.9 ± 3.8 (55.4)</td>
</tr>
</tbody>
</table>
Sharp order-disorder transitions for ligand exchange in solution-phase have recently been reported.\textsuperscript{47-48} The authors found that the sharpness of transition is associated with a strong ligand-ligand coupling. A favorable ligand-ligand interaction was found to reduce the energy needed for succeeding ligand exchange, evident from equilibrium constant that changed during the exchange.

However, we believe that our case of solid-state exchange is much more complex. First, there are limited degrees of freedom in the solid state (film) compared to solution-phase. Second, the thiols ligands are being delivered via solvents (MeOH and ACN) which, due to solvophobic interactions with OA-PbS CQDs, inhibit easy access of thiols to the CQD surface, although OA is relatively more soluble in MeOH than ACN. Finally, ligand exchange is expected to be further hindered due to steric hindrance effects felt by the short thiols from the longer OA ligands. Due to a combination of these factors, once a critical number of thiols (~200) is supplied to the OA-capped CQDs, strong ligand-ligand coupling leads to a change in equilibrium constant and a favorable condition for exchange to proceed. This results in the sharp phase-transition observed around 10\textsuperscript{-3}\% ligand concentration.

Curious to know if the qualitative model predicts CQD solar cells performances, we made devices employing PbS CQDs as the absorber layer in an \textit{n-p} device configuration. Results are shown in Figure 2 and Table 1 and suggest that the solar cells indeed follow the trend. This is expected since the various physical and chemical attributes of the CQD absorber layer peak and saturate for the higher [MPA] range resulting in a complete exchange. Although devices fabricated for [MPA]<10\textsuperscript{-4}\% did not perform due to roughness and film dissolution during the LbL, we found that [MPA]>10\textsuperscript{-2}\% resulted in solar cells that started to perform significantly better, with concurrent increases in the various device parameters. Peak performances were obtained for [MPA] = 1\%, a concentration condition that has been routinely used in the CQD device literature.
It was not possible to fabricate working devices with [MPA] >1% due to cracks and delamination of the QD layers during the LbL buildup, as depicted in Figure S12.

To demonstrate generality of the model, we also made solar cells that use EDT-based SSE. EDT-PbS CQD solids are used as the HTL in $n$-$i$-$p$ architecture devices which utilize a halide or perovskite ligand-capped single step-deposited active layer. The general practice for the HTL deposition is to soak the OA-PbS CQD solid for a duration of 30s in a 10^{-2} % v:v EDT/ACN solution. Using the lessons from the MPA-exchange above, we anticipated a similar trend for the EDT-exchange. We fabricated $n$-$i$-$p$ solar cells (Figure 3a) using single-step deposited PbX$_2$-PbS (X = I, Br) CQD solid as the active layer while, for the HTL, we successively varied the [EDT] from 10^{-3}% to 1% in steps. For [EDT] below 10^{-3}%, the cells did not operate due to unexchanged/poorly exchanged HTL.
Figure 3. *n-i-p architecture devices.* (a) Schematic of the device architecture. (b) $J-V$ curves for a few selected [EDT]. (c) PCEs as a function of [EDT]. Blue line is drawn as a guide to eye.

Variation of PCE with [EDT] is shown in Figure 3c where the phase transition-like behavior is evident. The average device parameters are summarized in Table 2 and demonstrate that [EDT] = $10^{-20}\%$ results in the best-performing solar cells, with the hero device yielding 10.7\% PCE.
Table 2. Device parameters for n-i-p architecture solar cells fabricated employing different [EDT] in the HTL. [EDT] is in the units of volume concentration (v:v) in ACN. Statistics represent averages over 15-20 devices per category. ± denotes standard error of the mean. Values in brackets represent parameters of the best-performing device in each category.

<table>
<thead>
<tr>
<th>[EDT] (v:v)</th>
<th>( J_{SC} ) (mA.cm(^{-2}))</th>
<th>( V_{OC} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
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<tr>
<td>1</td>
<td>25.26 ± 0.34 (25.06)</td>
<td>0.65 ± 0.01 (0.65)</td>
<td>60.2 ± 2.1 (62.7)</td>
<td>9.9 ± 0.5 (10.3)</td>
</tr>
<tr>
<td>10(^{-1})</td>
<td>25.33 ± 0.47 (24.59)</td>
<td>0.65 ± 0.01 (0.66)</td>
<td>60.5 ± 1.5 (60.9)</td>
<td>9.9 ± 0.3 (10.3)</td>
</tr>
<tr>
<td>10(^{-2})</td>
<td><strong>25.01 ± 1.12 (26.51)</strong></td>
<td><strong>0.64 ± 0.01 (0.64)</strong></td>
<td><strong>62.7 ± 3.0 (62.6)</strong></td>
<td><strong>10.1 ± 0.5 (10.7)</strong></td>
</tr>
<tr>
<td>5x10(^{-3})</td>
<td>24.86 ± 0.22 (24.9)</td>
<td>0.63 ± 0.00 (0.63)</td>
<td>59.7 ± 0.6 (60.6)</td>
<td>9.3 ± 0.1 (9.5)</td>
</tr>
<tr>
<td>3x10(^{-3})</td>
<td>25.28 ± 0.31 (25.57)</td>
<td>0.62 ± 0.02 (0.64)</td>
<td>56.9 ± 3.3 (58.3)</td>
<td>9.0 ± 0.7 (9.5)</td>
</tr>
<tr>
<td>10(^{-3})</td>
<td>7.46 ± 3.46 (13.76)</td>
<td>0.61 ± 0.01 (0.61)</td>
<td>45.4 ± 1.7 (46.9)</td>
<td>2.1 ± 1.0 (4.0)</td>
</tr>
</tbody>
</table>

10\(^{-2}\)% [EDT] results in a cation:anion ratio approaching 1.0 pointing toward completion of ligand exchange (Figure S13-S14, Table S2).\(^{44-45}\) High resolution XPS data for Pb 4f, S 2p, O 1s and C 1s shows that the core levels shift to lower binding energies upon exchange, as expected from a Fermi level due to exchange-induced p-doping. We note that, for [EDT]>10\(^{-2}\)%, PCEs saturate although the FF shows a slight decline. We argue this happens because higher [EDT] likely harm the underlying PbX\(_2\)-PbS CQD active layer, in accordance with a recent finding.\(^{50}\) Higher [EDT] increase p-character of the HTL evident from a slight enhancement of the \( V_{OC} \), yet damage to the underlying absorber harms the FF, limiting the overall PCE. These subtle but statistically significant changes in device parameters between [EDT] = 1.0%, 10\(^{-1}\)% and 10\(^{-2}\)% are highlighted in the histograms shown in Figure S15. This explains as to why 10\(^{-2}\)% [EDT] has been the standard choice for n-i-p CQD solar cell fabrication.
CONCLUSIONS

In summary, we have explored SSE of CQD solids in an attempt to understand the various factors that lead to complete optimization of the exchange process, and to move past the trial-and-error optimization approach. We find that the linker-CQD interactions play a defining role in modifying the various physical and chemical attributes of the CQD solids. We present a qualitative mechanistic model of SSE which suggests that the CQD solids undergo a phase transition-like sharp change in properties once a critical number of linker molecules are supplied, resulting in complete exchange of the CQDs. Below this transition point, the solid remains unexchanged and, therefore, behaves as an inefficient photovoltaic material. We successfully apply this model to fabricate n-p and n-i-p architecture solar cells resulting in a hero device of 10.7% PCE.

Supporting Information: IR-VASE data, QCM-D data, effect of ACN on OA-PbS CQDs, effect of neat MeOH on OA-PbS CQDs, XPS core level peaks for [MPA] and [EDT] exchanges, histogram for device statistics shown in Table 2.

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REFERENCES


A mechanistic model for solid-state ligand exchange of PbS CQDs is reported. The model explains the various physico-chemical changes that are required to optimize exchange for efficient CQD optoelectronics.