

Supporting Information

Comparing Halide Ligands in PbS Colloidal Quantum Dots for Field-Effect Transistors and Solar Cells

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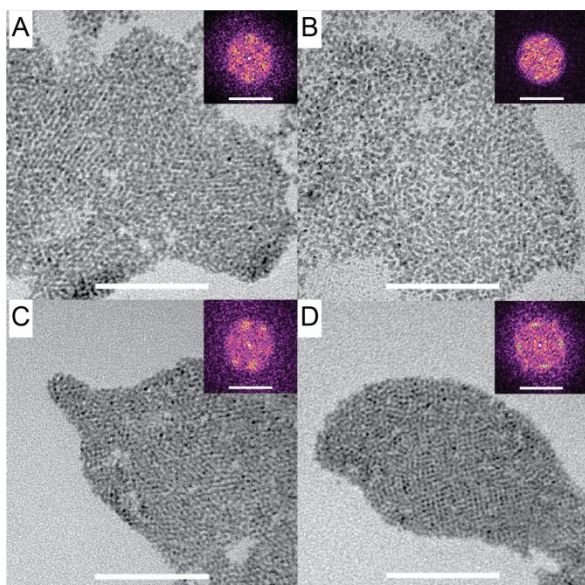


Figure S1 TEM micrographs of the 3.5 nm PbS CQDs treated with TMAF (A), TBACl (B), TBABr (C) and TBAI (D). The scale bar is 100 nm. Insets: Fourier-transformed TEM images of single domains with $500 \mu\text{m}^{-1}$ scale bar.

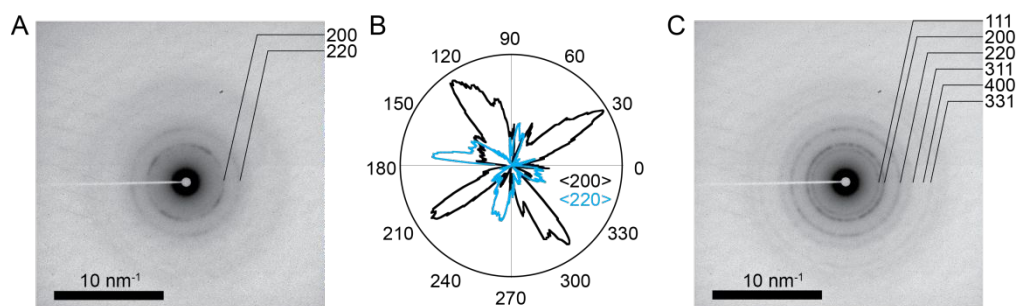


Figure S2 Electron diffraction of the PbS CQDs treated with TBAI (A) and TMAF (C). Radial distribution of the electron diffraction pattern intensity across the diffraction ring for the PbS-TBAI sample (B).

PbS CQDs have a cubic rock salt structure. The electron diffraction pattern of the TBAI-treated PbS CQDs (Figure S2A) display features that are assigned to the 200 and 220 atomic planes, indicating a preferential orientation relative to the substrate. Figure S2B shows a profile plot of the intensities around the diffraction circles for the same sample. The angle between the $\langle 200 \rangle$ and $\langle 220 \rangle$ directions is close to 45° , which is consistent with the rock salt structure; the presence of peaks superimposed on

a circular pattern suggests in-plane disorder with a preferential common orientation of the individual CQDs. Epitaxial necking has been shown to cause such alignment.¹ The diffraction pattern measured for the fluoride-treated sample are shown in Figure S2C; the assignment shows the absence of a preferential out-of-plane orientation, and the complete circular patterns shows the lack of in-plane supercrystalline order on the atomic scale.

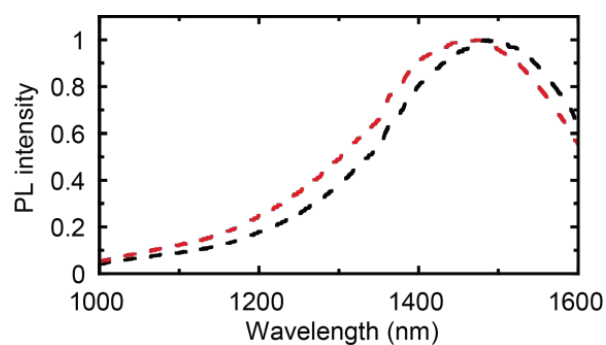


Figure S3. PL spectra of the fluoride-treated PbS CQD film taken at different spots. The difference of the peak position indicates the inhomogeneity of the film. The particle size in this case was 3.0 nm.

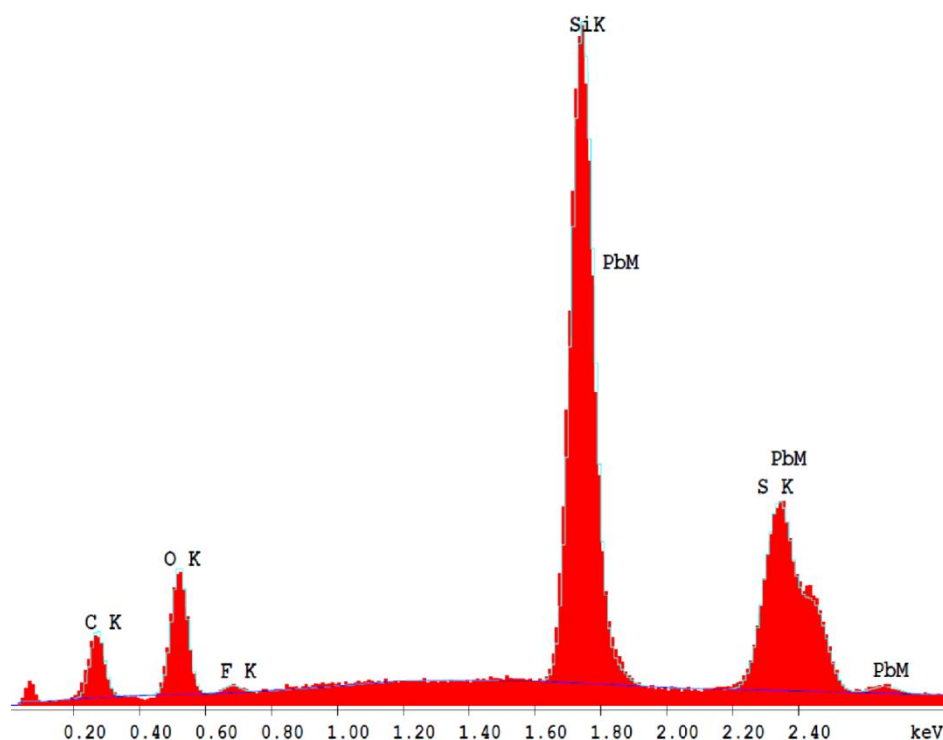


Figure S4. EDX spectrum of the fluoride-treated PbS CQD solid. The peak around 0.68 eV indicates the presence of fluorine in the film. The strong peaks from Si and O arise from the quartz substrate.

The quantification of the amount of light atoms such as fluorine is a challenging task with standard techniques as EDX or XPS. Our samples contain lead and sulfur and are processed from solution with many chemical treatments. Therefore, the samples also display typically carbon and oxygen as contaminants and may not be giving clean and easy to interpret data in particular when an extremely surface sensitive technique as XPS is used. Hence we only report qualitative EDX data.

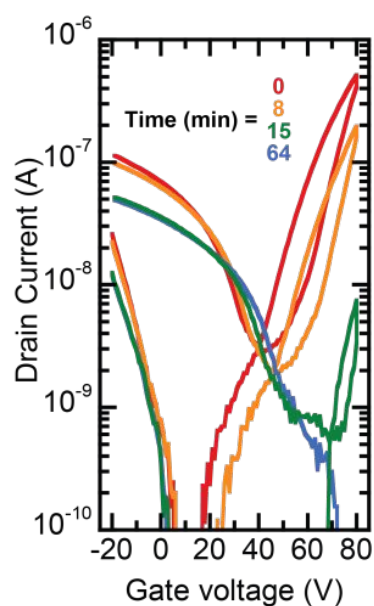


Figure S5. Transfer characteristics of a representative PbS-F CQD FET showing decreasing current after few minutes inside a nitrogen-filled glovebox.

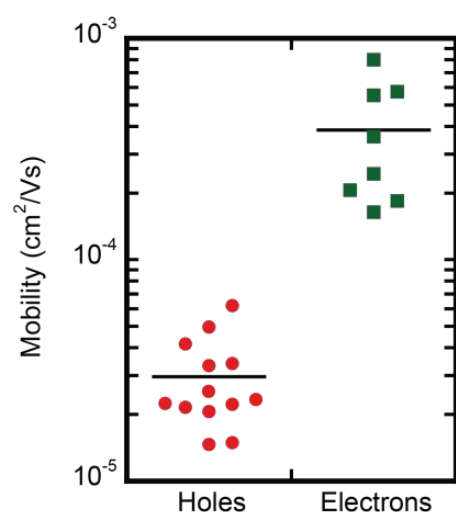


Figure S6. Charge carrier mobility values for PbS-F FETs, as extracted from the transfer curves. The horizontal black lines represent the mean values. The lower amount of data points for the electron mobility is the result of the electron current fading during the measurements.

Table S1 Performance parameters of colloidal quantum dot solar cells. First are reported the best values obtained, the average and standard deviation are given in brackets.

| L | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | PCE (%) |
|-------|--------------------------------|---------------|---------------|-------------|
| TMAF | 28.8 | 0.51 | 0.50 | 7.4 |
| | (28.2 ± 0.7) | (0.51 ± 0.01) | (0.50 ± 0.01) | (7.3 ± 0.1) |
| TBACl | 27.3 | 0.51 | 0.53 | 7.3 |
| | (27.1 ± 0.1) | (0.50 ± 0.01) | (0.50 ± 0.01) | (7.0 ± 0.2) |
| EDT | 25.6 | 0.55 | 0.51 | 7.2 |
| | (25.4 ± 0.3) | (0.54 ± 0.01) | (0.52 ± 0.01) | (7.1 ± 0.1) |

References:

- (1) Balazs, D. M.; Dirin, D. N.; Fang, H.-H.; Protesescu, L.; ten Brink, G. H.; Kooi, B. J.; Kovalenko, M. V.; Loi, M. A. Counterion-Mediated Ligand Exchange for PbS Colloidal Quantum Dot Superlattices. *ACS Nano* **2015**, *9*, 11951–11959.