Supplementary information for

Hybrid oleate-iodide ligand shell for air-stable PbSe nanocrystals and superstructures.

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S1. Two air stable PbSe NCs synthesized by two different methods.

![Absorbance spectra](image)

Figure S1. Two examples of oxygen protection after exposure to normal atmosphere. The red and blue curve are of PbSe NCs synthesized by the Campos et al.\(^1\) method, while the purple and green line are synthesized by the Steckel et al.\(^2\) method. The red and purple line are both not exposed to oxygen while the blue line is exposed for 4 days and the green line for 2 days. The peak position of the samples which are exposed to oxygen didn’t blue shift, which illustrate the effectiveness of this method.

S2. TEM images of original and air-stable PbSe NCs.

![TEM images](image)

Figure S2. TEM images of the original PbSe NCs (a) and the NCs treated with NaI and Pb(oleate)\(_2\) (b). There is no noticeable size- or shape change visible. The oleate density of the air-stable NCs is slightly smaller (2.5 oleates/nm\(^2\)) compared to the pristine NCs (2.9 oleates/nm\(^2\)). This results in a somewhat shorter NC-NC distance in (b).
S3. EDX spectrum of air-stable PbSe NC.

Figure S3. EDX spectrum on PbSe NC washed with NaI and Pb(oleate)$_2$. The peak of iodide is clearly present in the spectra, while the peak of sodium (at 1.040 keV) (in between the copper and selenium) is not visible.

S4. XPS survey and I 3d core level spectra of air-stable PbSe NCs.

Figure S4. XPS survey (a) and I 3d core level (b) spectra of air-stable PbSe NCs. (a) Shows the XPS survey spectrum of the air-stable NCs. Only a very small peak is detected for sodium as remainder from the NaI precursor. (b) I 3d core level XPS spectrum of air-stable NCs. The observed I 3d$_{5/2}$ and I 3d$_{3/2}$ binding energies match those of PbI$_2$.
Figure S5. FT-IR spectrum of Pb(oleate)$_2$ used for the XPS. Besides the typical features for oleate, it also shows an acid impurity, due to the peak around 1710 cm$^{-1}$. The inset shows the symmetric (v1) and asymmetric (v2) carboxylic stretch vibrations. The carboxylic asymmetric (v2) stretch shows a typical doublet where the higher energy part belongs to a bridging carboxylic coordination$^{2,3}$, typical for free Pb(oleate)$_2$. 

S5. FT-IR spectrum of Pb(oleate)$_2$. 

![FT-IR spectrum](image)
S6. FT-IR spectra zoomed on possible hydroxide contamination.

![FT-IR spectra](image)

Figure S6. FT-IR spectra of the untreated NCs (blue) and the treated NCs (red). A peak at 3475 cm\(^{-1}\) was previously assigned to bound hydroxide, but this peak is not present in our PbSe NCs\(^4\).

S7. Oriented attachment of air-stable PbSe NCs in ambient conditions.

![Oriented attachment](image)

Figure S7. Oriented attachment of air-stable PbSe NCs in ambient conditions. Although the self-assembly is not periodic, it shows enormous improvement in stability of these NCs in ambient conditions. The same experiment in ambient results in big nanocrystal agglomerates, visible by eye, but not suited for TEM analysis. It also shows that the NCs can attach via their (100) facets, even with the presence of PbI\(_2\) ligands. This suggests the absence of PbI\(_2\) on many of the (100) facets. The NCs self-assemble in linear structures.
S8. Square superstructure synthesized from air-stable NCs inside a nitrogen filled glovebox.

Figure S8. Square superstructure synthesized from air-stable NCs inside a nitrogen filled glovebox.

Figure S9. Square superstructure after treatment.

Figure S9. An example of a square structure after treatment with Pb(oleate)$_2$ in toluene and NaI in methanol. No structural changes are detected, however PbI$_2$ crystals might form if excessive amounts are added.

Table S1. Summary of the absorption peak shifts after treatment with several salts. All experiments were performed with the same batch of nanocrystals made via the method of Campos et al. which
had an absorption peak position at 0.79 eV. The experiment setup was similar as in the main text except that for some salts, no Pb(oleate)$_2$ was added in the toluene and the molar ratio added halide/ligand was only 0.33. Fluoride doesn’t protect the PbSe NCs and iodide seems to give the best protection.

<table>
<thead>
<tr>
<th>Type of salt used</th>
<th>Pb(oleate)$_2$ added to toluene</th>
<th>Peak position after exposure (eV)</th>
<th>Photoluminescence detected</th>
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<tbody>
<tr>
<td>None</td>
<td>No</td>
<td>0.83</td>
<td>No</td>
</tr>
<tr>
<td>NH$_4$F</td>
<td>Yes</td>
<td>0.83</td>
<td>No</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
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<td>0.82</td>
<td>Yes</td>
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<tr>
<td>NH$_4$Br</td>
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<td>0.81</td>
<td>Yes</td>
</tr>
<tr>
<td>NH$_4$I</td>
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<td>Yes</td>
</tr>
<tr>
<td>CdF$_2$</td>
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<tr>
<td>CdBr$_2$</td>
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<tr>
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<td>No</td>
</tr>
<tr>
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<tr>
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<td>Yes</td>
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</tbody>
</table>
Figure S10. TEM images of the superstructure made from PbSe NCs stabilized by NH₄I (a-b) and CdI₂ (c-d). Patches of a periodic square structure are visible in (a-b), whereas only unattached NCs are observed for NCs stabilized by CdI₂. This suggests that CdI₂ forms a layer on top of the NCs surface, or causes cation exchange, which can both impede oriented attachment.
S11. Fitting of the asymmetric and symmetric carboxylic stretch.

Figure S11. The FT-IR spectra of the air-stable (top) and original NCs (bottom). The spectra of the symmetric (right) and asymmetric (left) carboxylic stretch vibrations are fitted with two Gaussians (purple). The combination of the two Gaussians is displayed in green. Since the symmetric and asymmetric carboxylate stretch vibration are too broad for a single coordination, this means that there are most likely two coordinations. Due to the strong overlap, it is (especially for the asymmetric vibration) hard to know with certainty if the peaks and widths are perfectly defined. The general trend is that PbSe NCs with a hybrid ligand shell show a smaller energy difference between the symmetric and asymmetric vibration peak. See below the difference outer (bridging coordination) and inner (chelating coordination) in the last two columns.
Table S2. Summary of all peak positions, corresponding FWHM and peak shifts of the carboxylate stretch vibration for both NCs.

<table>
<thead>
<tr>
<th></th>
<th>Symmetric carboxylic vibration [cm(^{-1})]</th>
<th>Asymmetric carboxylic vibration [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>peak v(_{1b})</td>
<td>FWHM v(_{1b})</td>
</tr>
<tr>
<td>Original PbSe</td>
<td>1403</td>
<td>20</td>
</tr>
<tr>
<td>Hybrid ligand shell</td>
<td>1403</td>
<td>26</td>
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</tbody>
</table>

S12. NMR spectra of the untreated NCs and the air-stable NCs.

Figure S12. \(^1\)H-NMR spectra of the untreated NCs (blue) and the air-stable NCs (red). § Originates from the three methyl hydrogen atoms at the end of the oleate chain. The peaks † and ‡ correspond to the other hydrogen atoms in the oleate chain. ¥ originated from ferrocene which is added in a known concentration as internal standard, # originates from the vinyl peak and * from chloroform. There are no sharp peaks visible demonstrating that all Pb\(\text{oleate})_2\) is bound to the NC surface. The increased broadening of the peaks of the air-stable NCs sample indicate better solvated ligands\(^5\).

References.
