Low-Dimensional Hybrid Perovskites Containing an Organic Cation with an Extended Conjugated System: Tuning the Excitonic Absorption Features

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Abstract: Low-dimensional hybrid perovskites are receiving increased attention. One of the advantages of the low-dimensional hybrids over their 3D counterparts is their greater structural flexibility towards the incorporation of bigger, more complex, organic cations. In this communication, we introduce a pyrene derivative as an organic cation containing an extended π-system for use in a variety of low-dimensional hybrids. We show that materials with different excitonic absorption features can be obtained by tuning the iodide/lead ratio in the precursor solutions, using the same pyrene cation. In this way, hybrids with optical characteristics corresponding to 2D, 1D and 0D hybrid perovskites are obtained. The formation and thermal stability of the different hybrids is analysed and compared.

Hybrid organic-inorganic perovskites have received a lot of attention in recent years, mainly related to their use in solar cells. Due to the high efficiency of their solar cells, the focus of this field is primarily directed towards 3D hybrid perovskites. More recently interest in lower dimensional hybrids is increasing for a multitude of applications.[1] The versatility of the organic-inorganic hybrids allows for the formation of materials with a dimensionality of 3D, 2D, 1D and 0D.[2] It is important to note here that the 3D, 2D, 1D and 0D classification is solely related to the dimensionality of the inorganic (lead halide) framework, not to that of the hybrid material as a whole (which remains 3D).[3] Materials with different dimensionalities have different optical and electronic properties and therefore different envisaged applications.[4] For example, the extent of the quantum confinement in these hybrids can be tuned by changing their dimensionality. 2D, 1D, and 0D hybrids are bulk quantum materials,[14] that can respectively be considered as bulk assemblies of 2D quantum wells, 1D quantum wires, and 0D quantum dots (as isolated metal halide clusters).[15] Especially the 1D and 0D hybrids remain underexplored, with a huge parameter space still open to be investigated.[14]

In this study, we use a pyrene derivative as an organic cation to obtain organic-inorganic hybrids. We show that next to 2D layered perovskites, also organic-inorganic hybrids with excitonic absorption features matching with those of 1D and 0D hybrid perovskites can be obtained using PyrC4NH3+ by tuning the I/Pb ratio of the precursor solutions.

Pyrene derivatives have found different uses in hybrid perovskite-related literature. Pyrene-CH2NH3+ has been used as an emitting chromophore in chloride, bromide and iodide based 2D hybrid perovskites.20 In the recent work of Passarelli et al.[15] pyrene derivatives (pyrene-C6H4–NH2) were used in 2D layered perovskites to improve the out-of-plane conductivity of these materials. In literature, there is a move away from the use of ‘simple’ alkylic (e.g. butylammonium) or benzylic (e.g. phenethylammonium) cations towards more complex cations with more extended π-systems.[3–4] We use a pyrene derivative as an example of such a type of molecule.

Using PyrC4NH3I, we obtain hybrids with excitonic absorption peak energies of 3.27 eV ([PyrC4NH3]PbI3), 3.0 eV ([PyrC4NH3]2PbI4) and 2.54 eV ([PyrC4NH3]2PbI4) depending on the stoichiometry used in the precursor solution. This shows that this system is highly versatile.

Films of the hybrids formed using PyrC4NH3I and PbI2 in different ratios show characteristic excitonic peaks in their absorption spectra (Figure 1 and Table 1). This indicates that in all cases low-dimensional excitonic materials are obtained. We classify these obtained hybrids based on their characteristic

| Table 1. Excitonic absorption peak energies for different PyrC4NH3+ containing hybrids. |
|-----------------|-----------------|
| Hybrid | Excitonic absorption peak energy (eV/nm) |
| [PyrC4NH3]PbI3 (0D) | 3.27/379 |
| [PyrC4NH3]2PbI4 (1D; LT) | 3.01/412 |
| [PyrC4NH3]2PbI4 (1D; HT) | 2.90/428 |
| [PyrC4NH3]2PbI4 (2D; LT) | 2.48/499 |
| [PyrC4NH3]2PbI4 (2D; HT) | 2.53/490 |

LT = low-temperature phase, HT = high-temperature phase. As described in the text, the transition temperature between the LT and HT phases is not the same for the 1D and 2D phases.
The excitonic absorption peak energy for the "0D" pyrene-based hybrid matches very well with the excitonic peak positions for known 0D hybrids, such as (Et₄N)PbI₃ (at 384 nm) and (CH₃NH₃)₄PbI₆·2H₂O (at 372 nm). The peak position for our "1D" hybrid (in its low-temperature phase; at room temperature) also matches very well with that of the 1D hybrid possessing a different stoichiometry. A hybrid with a APb₂I₅ stoichiometry supported by the crystal structure obtained from single crystals (vide infra) was based on the nominal compositions (i.e. molar ratios as added to the precursor solutions). For the 2D hybrid perovskite, (PyrC₄NH₃)₂PbI₄, the structural formula is further supported by the crystal structure obtained from single crystals (vide infra).

The excitonic absorption peak energy for our "0D" pyrene-based hybrid matches very well with the excitonic peak positions for known 0D hybrids, such as (Et₄N)PbI₃ (at 384 nm) and (CH₃NH₃)₄PbI₆·2H₂O (at 372 nm). The peak position for our "1D" hybrid (in its low-temperature phase; at room temperature) also matches very well with that of the 1D hybrid (piperidinium)PbI₂ (at 413 nm) although our hybrid possesses a different stoichiometry. A hybrid with a APb₂I₅ stoichiometry has been obtained with a TTF-* radical cation. However, since this TTF-* cation does not contain an ammonium group its structure is expected to be significantly different.

The excitonic absorption peak energy for the 2D layered perovskite (PyrC₄NH₃)₂PbI₄ is dependent on the annealing temperature (~499 nm for a film annealed at 110°C and ~490 nm for a film annealed at 150°C). This is due to a phase transition in between these temperatures. An endothermic signal at ~110°C is indeed present in differential scanning calorimetry for crystals of this material (Figure S6), pointing to a phase transition. Also, it can be seen that at 100°C two sets of ordered reflections (each set is typical for a 2D layered perovskite) are present in the XRD pattern of a film of this material, only one set of which remains at higher temperatures (Figure S7). The presence of two sets of reflections at 100°C points to the presence of a certain amount of both 2D perovskite phases at this temperature. Temperature-controlled UV-Vis absorption experiments also support the presence of a phase transition for this 2D perovskite (vide infra). It has been shown that the distortion of the Pb-I lattice (e.g. the Pb-I-Pb angle between adjacent PbI₆ octahedra) influences the excitonic absorption peak position. Hence, this phase transition likely induces a distortion of the Pb-I lattice.

For the 2D layered hybrid perovskite containing the pyrene derivative, we were able to obtain single crystals using an antisolvent vapor-assisted crystallization approach (details on the method can be found in the supporting information). As expected based on the excitonic peak position, the XRD pattern (vide infra) and the stoichiometry, the crystal structure does indeed match with that of a 2D layered perovskite with the pyrene molecules forming a bi-layer between layers of corner-sharing PbI₆ octahedra (Figure S8). For the other stoichiometries we have not yet been able to obtain single crystals due to the propensity of the 2D layered phase to crystallize preferentially. However, the excitonic peak positions in the absorption spectra can clearly be linked to distinct materials based on the provided stoichiometries.

Further tuning of the quantum confinement of hybrids containing the pyrene derivative can be achieved by moving from 2D layered (n = 1) to multi-layered (quasi-2D) perovskites. Where instead of one inorganic layer, multiple inorganic layers (n > 1) containing an additional small organic cation (e.g. methylammonium) are separated by the organic bilayers of pyrene cations. The thicker inorganic layers result in reduced quantum confinement of the excitons. As shown in the supporting information (Figure S9), n = 2 (2.21 eV excitonic peak) and n = 3 (2.08 eV excitonic peak) multi-layered perovskites can be obtained with PyrC₄NH₃I, methylammonium iodide (MAI) and PbI₂.

In order to study the formation and degradation of different hybrids as a function of temperature, in-situ temperature-controlled (T-ctrl) UV-Vis measurements were carried out. In these measurements, the formation and degradation of the hybrids can be followed on the basis of the appearance and disappearance of their characteristic excitonic absorption peaks. For the 2D layered perovskite also a T-ctrl XRD experiment was carried out to complement the UV-Vis measurements, in order to elucidate the more complex nature of its formation, phase transition and degradation.

Figure 2 shows the absorption spectra of a film of the 2D layered hybrid perovskite (PyrC₄NH₃)₂PbI₄) at selected temperatures. Figure 3a and Figure 3b show the absorbance of the film at respectively 490 nm and 430 nm, as a function of temperature. For the 2D hybrid, a small excitonic peak is already present after deposition at room temperature (located at ~500 nm), indicating that the perovskite structure is already partially formed. Starting at ~100°C, the excitonic peak starts to shift towards ~490 nm (Figure 2). The high-temperature phase with this excitonic peak position is fully formed at ~160°C (Figure 3a). At higher temperatures, the 2D layered perovskite starts to degrade concomitant with the formation of a new phase with an excitonic absorption peak located at ~430 nm (Figure 2 and Figure 3b). Since the excitonic absorp-
tion peak of this new phase is shifted to significantly higher energy compared to the 2D layered perovskite, it is expected that this new phase has a reduced dimensionality. It can be seen from T-ctrl XRD measurements (Figure 4) that this new phase also has a reduced interlayer spacing (~21.7 Å; see Figure S13 for the full pattern) compared to the 2D layered perovskite phase (~26.6 Å; see Figure S14 for the full pattern) since the reflections are shifted to higher diffraction angles (2θ).

Comparing with XRD measurements of films of the 1D hybrid (vide infra; Figure S16), it is clear that this degradation phase of the 2D layered perovskite corresponds to our 1D hybrid phase (PyrC4NH3)Pb2I5. Hence, the 2D layered perovskite degrades into the 1D hybrid before complete degradation of the system into lead iodide. In summary, the 2D layered perovskite (PyrC4NH3)2PbI4 undergoes the following changes as a function of temperature (with approximate starting temperatures indicated above the arrows):

\[
\begin{align*}
\text{PyrC}_4\text{NH}_3^2\text{PbI}_4 \text{ (LT)} & \xrightarrow{140 \degree \text{C}} \text{PyrC}_4\text{NH}_3^2\text{PbI}_4 \text{ (HT)} \xrightarrow{190 \degree \text{C}} \text{PyrC}_4\text{NH}_3\text{Pb}_2\text{I}_5 \xrightarrow{240 \degree \text{C}} \text{PbI}_2
\end{align*}
\]

The 1D hybrid ((PyrC4NH3)Pb2I5) with a room-temperature excitonic absorption peak at ~412 nm, is fully formed at ~100 °C and then slowly degrades until ~170 °C (Figures 5 and 6). As can be seen in Figure 5, at temperatures >170 °C the excitonic peak starts to shift to higher wavelength. Before final degradation to lead iodide a shoulder at ~430 nm is present, corresponding to the excitonic peak that was also seen in T-ctrl UV-Vis measurements of the 2D hybrid (Figure 2; 194 °C) where the 1D phase is a degradation product. Therefore, we surmise that the 1D hybrid undergoes a phase transition to a high-temperature phase with an excitonic peak at ~430 nm.

We have indications that the formation of 1D hybrids with an APbI3 stoichiometry is not limited to this specific pyrene derivative. We recently showed that 2D and multi-layered (quasi-2D) hybrid perovskites can be obtained using a carbazole derivative, carbazole-C4H9-NH-I (CA-C4NH-I).[13] Here we show that, like for pyrene, a hybrid with a APbI3 stoichiometry can
also be obtained with this carbazole cation. The absorption spectrum and the X-ray diffraction pattern of a film of \((\text{CA-C}_{4}\text{NH}_{3})\text{Pb}_{2}\text{I}_{5}\) are shown in Figure S17. The excitonic absorption peak value for the carbazole containing hybrid is located at \(~409\) nm (3.03 eV), which is indeed very close to the \(~412\) nm of the \((\text{PyrC}_{4}\text{NH}_{3})\text{Pb}_{2}\text{I}_{5}\) hybrid. The reflections in XRD are shifted to a slightly higher angle \((2\theta)\) with the carbazole, showing that the interlayer spacing of the structure is reduced compared to the corresponding pyrene hybrid. Since the carbazole core is less bulky than the pyrene core, this is consistent with expectations.

The 0D hybrid \((\text{PyrC}_{4}\text{NH}_{3})\text{PbI}_{3}\) appears to be very difficult to obtain in thin films without the concomitant formation of a certain (small) amount of the 2D layered perovskite phase and/or the 1D hybrid. Hence, a small amount of the 2D perovskite phase was already present in the film used for the T-ctrl UV-Vis experiment obtained using a precursor solution with \(\text{APbI}_{3}\) stoichiometry. \(\text{APbI}_{3}\) stoichiometry for 0D perovskite hybrids. \([7a,8]\)

The 0D phase \((\text{PyrC}_{4}\text{NH}_{3})\text{PbI}_{3}\) already starts to degrade at \(~100\) °C. This phase clearly degrades into a combination of the 1D phase \((\text{PyrC}_{4}\text{NH}_{3})\text{Pb}_{2}\text{I}_{5}\), with an excitonic peak at \(~412\) nm, and \((\text{PyrC}_{4}\text{NH}_{3})_{2}\text{PbI}_{4}\) with an excitonic peak at \(~498\) nm (at that temperature). This indicates that the phase is unstable towards thermal degradation into a combination of the 2D and 1D crystal phases. We suggest the following degradation reaction:

\[
3 \, (\text{PyrC}_{4}\text{NH}_{3})\text{PbI}_{3} \rightarrow (\text{PyrC}_{4}\text{NH}_{3})\text{Pb}_{2}\text{I}_{5} + (\text{PyrC}_{4}\text{NH}_{3})_{2}\text{PbI}_{4}
\]

As can already be expected from Figure 7, a cross section of the absorption spectra as a function of temperature taken at the excitonic peak position (384 nm) is complex and much less insightful than for the 2D and 1D hybrids because multiple components absorb at such a low wavelength (i.e. there is significant overlap with the sub-bandgap absorption of the 1D and 2D hybrids that start to form as a function of temperature). The degradation of the 0D hybrid can nonetheless clearly be followed indirectly by observing the formation of the 2D and 1D hybrids out of the 0D hybrid (Figure 8). The absorbance at both 424 nm and 500 nm starts to increase simultaneously at \(~100\) °C, when the 0D hybrid starts degrading into the 1D and 2D hybrids. Starting at \(~170\) °C the 2D hybrid that was formed...
In conclusion, we showed that a variety of organic-inorganic hybrids with different optical properties can be obtained by using a single organic cation, PyrC4NH3+, by tuning the I/Pb ratio. This work shows that our pyrene derivative and similar derivatives such as the carbazole derivative are versatile templates for the formation of different organic-inorganic hybrids. In this regard, this work makes a contribution of a fundamental nature to the field of low-dimensional lead iodide hybrids. The temperature stability and interconversion of the different pyrene hybrids was analysed in detail. We expect that the elucidated compositions of the identified hybrids and their characteristic excitonic peak positions will prove useful characterization tools in the field of low-dimensional hybrids. Further work includes the optimization of such hybrids towards specific applications.

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Conflict of Interest

The authors declare no conflict of interest.

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