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Towards 2D layered hybrid perovskites with enhanced functionality: introducing charge-transfer complexes via self-assembly

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This study broadens the family of 2D layered perovskites by demonstrating that it is possible to self-assemble organic charge-transfer complexes in their organic layer. Organic charge-transfer complexes, formed by combining charge-donating and charge-accepting molecules, are a diverse class of materials that can possess exceptional optical and electronic properties.

The pioneering work of D.B. Mitzi[1–3], G.C. Papavassiliou[4,5] and N. Mercier[6,7], combined with more recent work[8–14] has shown that 2D layered hybrid perovskites are a versatile class of materials, with interesting optoelectronic properties. Currently, interest towards the use of functional organic molecules for 2D layered perovskites is increasing.[15–20] For example, organic molecules with fluorescent properties can be incorporated.[21,22] Such 2D layered perovskites could have potential in LEDs.[23] Very recent work by Passarelli *et al*.[20] showed convincingly that the use of conjugated organic molecules as cations in 2D layered perovskites significantly improves the photovoltaic properties of these materials. The structural constraints on the organic cation are much more limited for 2D layered perovskites compared to their 3D counterparts[3] and a large variety of possible molecules remains unexplored. However, the organic cations that can be used for 2D layered perovskites are still limited, mainly by their bulkiness.[3] This potentially excludes a variety of organic semi-conductors with, as for example, low band gaps due to their extended chromophores.

Such limitations could potentially be overcome by means of intercalation. Mitzi *et al*., intercalated benzene or hexafluorobenzene molecules into respectively 2,3,4,5,6-pentafluorophenethylammonium or phenethylammonium based layered perovskites using the fluoroaryl-aryl interactions.[2] More recently Smith *et al*. intercalated molecular iodine (I_2) into hexylammonium and 6-iodohexan-1-aminium based layered perovskites in order to decrease the electronic confinement in the layered perovskite.[8]

Organic charge-transfer complexes (CTCs) are formed by combining charge-donating and charge-accepting molecules. The resulting complex has optical and electronic properties differing from the separate donor and acceptor molecules.[24]

Their properties can include ambipolar charge transport, metallicity, photoconductivity, ferroelectricity or even (low temperature) superconductivity.[25,26] Due to this variety of interesting properties, charge-transfer complexes have been studied extensively over the past decades and interest in these materials remains high.[24,26–27]

In this study, we combine the field of hybrid perovskites with the field of charge-transfer complexes. A combination of two different organic molecules (a donor and an acceptor) is used in the organic layer of the layered perovskite, of which only one has a tethering group. The molecules without tethering group (the acceptors) self-assemble together with the donor molecules in a charge-transfer complex. In this way optoelectronic properties may be obtained that can generally only be obtained using organic molecules with an extended conjugated system, whilst bypassing the structural constraints. Different combinations of donor and acceptor molecules can be used to tune the optoelectronic properties of the perovskite.

As a proof-of-concept we analyse first examples of 2D layered hybrid perovskites containing charge-transfer complexes. We introduce the combination of pyrene-butylammonium (Pyrene-C_4H_8-NH_3^+; abbreviated as "$PyrC_4$") as a donor molecule with the strong acceptor molecules tetracyanoquinodimethane (TCNQ) and tetracyanobenzene (TCNB). Pyrene is known to form a 1:1 mixed-stack charge-transfer complex with TCNQ[28–31] and with TCNB[32].

Pyrene-based cations have already been applied in layered perovskites. Pyrene-CH_2-NH_3^+ has been used as an emitting chromophore in chloride, bromide and iodide based 2D layered hybrid perovskites.[33] In the recent work of Passarelli *et al.*[20], pyrene derivatives (pyrene-O-C_n-NH_3) were used in 2D layered perovskites to improve the out-of-plane conductivity of these materials. We recently studied the variety of hybrids that can be obtained using different ratios of $PyrC_4$ and PbI_2.[34] For the current study, pyrene was mainly chosen for its role of donor in charge-transfer complexes.

Through self-assembly from a precursor solution containing all the components in the stoichiometric ratios, we obtain films after annealing of 2D layered perovskites containing CTCs as organic layer denoted as $(PyrC_4\text{:TCNQ } 1{:}1)_2PbI_4$ and $(PyrC_4\text{:TCNB } 1{:}1)_2PbI_4$. Note that the stoichiometry indicated by the formulas $(PyrC_4\text{:TCNQ } 1{:}1)_2PbI_4$ and $(PyrC_4\text{:TCNB } 1{:}1)_2PbI_4$ is based on the nominal composition (i.e. the molar ratios as added to the precursor solutions). The absorption/emission properties and the thermal degradation of these materials are discussed and compared to the 2D layered perovskite $(PyrC_4)_2PbI_4$. A detailed study of the photophysics and the (opto)electronic properties of these materials is the subject of a follow-up paper.

Pyrene is a moderately strong donor molecule, with a relatively low ionization potential of ~ 7.47 eV.[28] TCNQ and TCNB are strong acceptors, with high and moderately high electron affinities of respectively ~ 2.88 eV and ~ 2.30 eV.[28] Upon addition of TCNQ or TCNB to a solution of $PyrC_4$ there is indeed a clear colour change from colourless to respectively brown-black and brown-red, indicative of the formation of charge-transfer complexes in the solution. Deposited as a thin film, the $PyrC_4$:TCNQ charge-transfer complex exhibits multiple charge-transfer bands. A weaker band at ~ 870 nm and a stronger band with a maximum at ~ 593 nm (**Fig. S4**). In solution a charge-transfer band is located at ~ 570 nm (**Fig. S5**). These results are in line with literature reports on the charge-transfer complex of the unsubstituted pyrene with TCNQ.[31] The strongest charge-transfer absorption band of the $PyrC_4$:TCNB charge-transfer complex in film (**Fig. S6**) partially overlaps with the absorption of the $PyrC_4$ donor and the TCNB acceptor and is blue shifted compared to the corresponding $PyrC_4$:TCNQ CT absorption band. In solution (**Fig. S7**), the charge-transfer absorption band for $PyrC_4$:TCNB has a maximum at ~ 470 nm. The shift of this CT absorption band to higher energy for TCNB is expected due to the lower electron affinity when compared to TCNQ.[35]

Films of the $(PyrC_4)_2PbI_4$ layered perovskite (annealed at 150 °C) exhibit an excitonic absorption peak at ~ 490 nm (2.53 eV) and a corresponding excitonic emission peak at ~ 499 nm (2.48 eV) (**Fig. 1a** and **2**). The excitonic peak positions are in the range expected for such a 2D layered lead iodide perovskite.[20,36] In the photoluminescence emission spectrum also a broad emission feature from ~ 550 nm till ~ 830 nm is present. Determining the exact nature of this broad emission band is beyond the scope of this communication. Similar features have been ascribed in literature to fluorescence emission from trapped excitons[37,38] or to emission due to interstitial iodide and other Frenkel defects[39].

The diffraction pattern (**Fig. 3**) of a film of $(PyrC_4)_2PbI_4$ consists of a series of reflections (0 0 l) characteristic for a n = 1 layered 2D perovskite with preferential growth such that the organic layers are oriented parallel to the substrate.[11] An interplanar spacing (d_{00l}) of ~ 26.6 Å is obtained. The 2D perovskite crystal structure of this material was confirmed through single-crystal x-ray diffraction (**Fig. S8**).

Upon incorporation of TCNQ molecules in a 1:1 ratio with $PyrC_4$, to form $(PyrC_4{:}TCNQ\ 1{:}1)_2PbI_4$, a novel 2D layered perovskite containing CTCs, significant changes in the absorption and emission spectra are apparent. The excitonic absorption peak shifts from ~ 490 nm (2.53 eV) to ~ 532 nm (2.33 eV) and the excitonic emission peak shifts from ~ 499 nm (2.48 eV) to ~ 540 nm (2.3 eV)

(**Fig. 1a** and **2**). Such a shift in excitonic peak position points to a significant change in the Pb-I-Pb angle and/or the Pb-I bond length of the inorganic framework.[2,3,36,40] In the absorption spectrum of $(PyrC_4:TCNQ\ 1:1)_2PbI_4$, also charge-transfer absorption bands are clearly present. The first band is located at ~ 870 nm and the second band (from ~ 450 nm to ~ 700 nm) partially overlaps with the excitonic absorption peak of the material. Both bands are located at almost the same positions as in a film of the separate $PyrC_4$:TCNQ 1:1 charge-transfer complex (**Fig. S4**). In the emission spectrum, the broad feature at lower energy that was present for $(PyrC_4)_2PbI_4$ is no longer present after the incorporation of TCNQ. Also, no emission from the $PyrC_4$:TCNQ charge-transfer complex could be observed in the spectrum of $(PyrC_4:TCNQ\ 1:1)_2PbI_4$ in the region expected for charge-transfer emission[31]. However, the emission spectrum of a film of the separate $PyrC_4$:TCNQ 1:1 charge-transfer complex (**Fig. S9**) also does not contain a clear charge-transfer emission band. This is contrary to $(PyrC_4:TCNB\ 1:1)_2PbI_4$ (*vide infra*). For the convenience of the reader, the absorption and emission spectra of all the components contained in the described perovskites are overlaid with the spectra of the perovskites in the supporting information (**Fig. S4-S7 and S9-S13**).

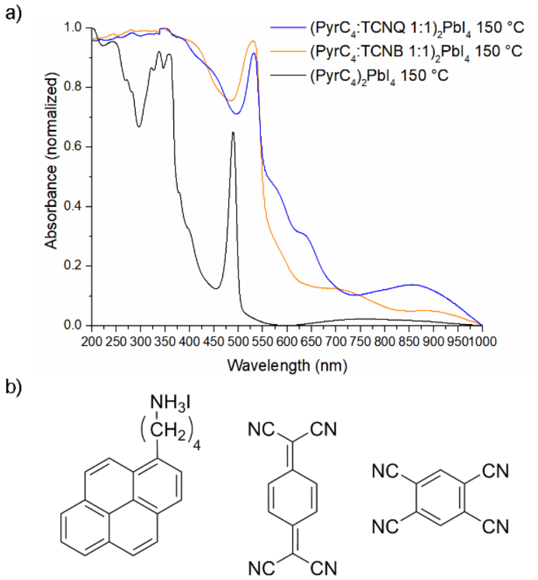

Fig. 1 a) Absorption spectra of $(PyrC_4)_2PbI_4$ (black), $(PyrC_4:TCNQ\ 1:1)_2PbI_4$ (blue) and $(PyrC_4:TCNB\ 1:1)_2PbI_4$ (orange) films annealed at 150 °C for 15 min. b) Chemical structures of pyrene-butylammonium ($PyrC_4$), tetracyanoquinodimethane (TCNQ) and tetracyanobenzene (TCNB).

The diffraction pattern of $(PyrC_4:TCNQ\ 1:1)_2PbI_4$ films (**Fig. 3**) shows a similar series of $(0\ 0\ l)$ reflections as $(PyrC_4)_2PbI_4$, however shifted towards lower diffraction angles indicating an increased interplanar spacing (d_{00l}) of ~30 Å due to incorporation of the TCNQ molecules in the structure.

With TCNB, the excitonic absorption peak shifts to ~ 529 nm (~ 2.34 eV) and the excitonic emission peak shifts to ~ 542 nm (~ 2.29 eV) (**Fig. 1a** and **2**). In the emission spectrum of (PyrC$_4$:TCNB 1:1)$_2$PbI$_4$, a charge-transfer emission band is apparent at ~ 611 nm (at approximately the same position as in the emission spectrum of the PyrC$_4$:TCNB 1:1 charge-transfer complex; **Fig. S9**). From the XRD pattern (**Fig. 3**) an interplanar spacing (d_{00l}) of ~ 28.7 Å is obtained for (PyrC$_4$:TCNB 1:1)$_2$PbI$_4$. From the XRD patterns and the excitonic peak positions, it is clear that a similar structure is obtained with TCNQ and TCNB. In both cases, the characteristic pattern[11,20] of ordered (00*l*) reflections shows that the 2D perovskite structure is retained upon incorporation of the CT complex.

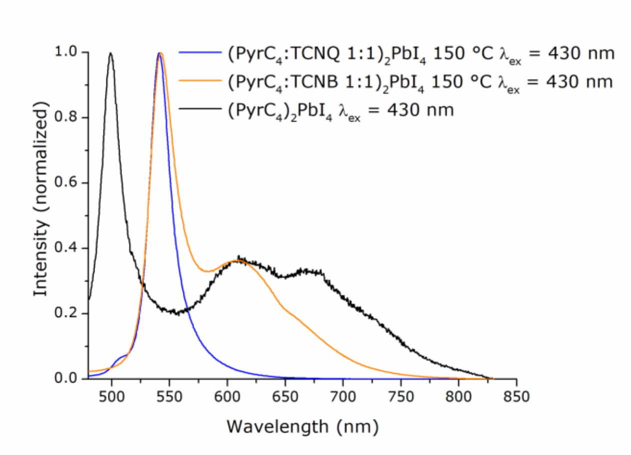

Fig. 2 Emission spectra of (PyrC$_4$)$_2$PbI$_4$ (black), (PyrC$_4$:TCNQ 1:1)$_2$PbI$_4$ (blue) and (PyrC$_4$:TCNB 1:1)$_2$PbI$_4$ (orange) films annealed at 150 °C for 15 min.

When a different PyrC$_4$:TCNQ or PyrC$_4$:TCNB ratio is attempted (e.g. a 2:1 donor:acceptor ratio, while keeping the PyrC$_4$:PbI$_2$ ratio constant), the absorption (**Fig. S10** and **S11**) and emission (**Fig. S12** and **S13**) spectra and the diffraction patterns (**Fig. S14** and **S15**) show clear signs of two phases being present. These spectra show that a mixture of the regular 2D perovskite (PyrC$_4$)$_2$PbI$_4$ and the 2D perovskite containing the CT complex is formed. Since less TCNQ or TCNB is added, not all of the PyrC$_4$ molecules are complexed with the acceptor molecules and hence 2D perovskite containing only PyrC$_4$ molecules is also formed in the films. This indicates that the 1:1 donor:acceptor ratio is indeed necessary for the formation of the desired crystal structure, as expected based on literature reports on the 1:1 ratio of pyrene:TCNQ and pyrene:TCNB charge-transfer complexes.[28–32]

The thermal stability of the different perovskites was analysed using temperature-controlled X-ray diffraction. For (PyrC$_4$)$_2$PbI$_4$, it can be seen that at high temperatures (~ 200 °C) a different crystal phase with a decreased interplanar spacing (~ 21.7 Å) is formed before further degradation into lead iodide occurs (**Fig. S16a**). For (PyrC$_4$:TCNQ 1:1)$_2$PbI$_4$ (**Fig. S16b**; see **Fig. S17** for a zoom of the patterns between 150 °C and 200 °C) the reflections of the (PyrC$_4$)$_2$PbI$_4$ crystal phase start to appear at 150 °C concomitant with a decrease in the reflections corresponding to the (PyrC$_4$:TCNQ 1:1)$_2$PbI$_4$ crystal phase. At 175 °C, the reflections of the (PyrC$_4$:TCNQ 1:1)$_2$PbI$_4$ crystal phase have disappeared from the pattern. This indicates that the PyrC$_4$:TCNQ charge-transfer complex in the structure dissociates and TCNQ leaves the system leading to the formation of (PyrC$_4$)$_2$PbI$_4$. Further degradation at higher temperatures follows the same pathway as for (PyrC$_4$)$_2$PbI$_4$. The thermal degradation of (PyrC$_4$:TCNB 1:1)$_2$PbI$_4$ (**Fig. S16c**) is very similar to that of the (PyrC$_4$:TCNQ 1:1)$_2$PbI$_4$ system. Temperature-controlled absorption spectroscopy experiments corroborate these XRD results. For (PyrC$_4$)$_2$PbI$_4$ (without acceptor) no significant changes occur between 120 °C and 180 °C (**Fig. S18; left)**. While for (PyrC$_4$:TCNQ 1:1)$_2$PbI$_4$ (**Fig. S18; right** and **S19**) the excitonic peak belonging to the crystal phase containing the CT complex and also the CT absorption band disappear and the excitonic peak of (PyrC$_4$)$_2$PbI$_4$ starts to appear. For the thin films with the fluoroaryl-aryl system described by Mitzi et al., full deintercalation happened already at 60 °C.[2] It is expected that the interaction between the donor and acceptor in our systems is much stronger compared to the fluoroaryl-aryl interaction between benzene and hexafluorobenzene. This could account for the improved thermal stability of our intercalated system compared to that system.

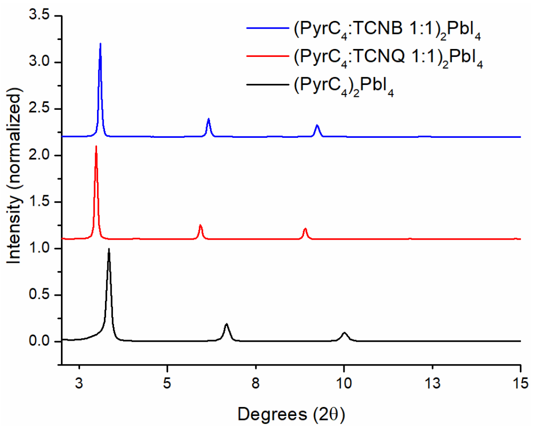

Fig. 3 X-ray diffraction pattern of (PyrC$_4$)$_2$PbI$_4$ (black), (PyrC$_4$:TCNQ 1:1)$_2$PbI$_4$ (blue) and (PyrC$_4$:TCNB 1:1)$_2$PbI$_4$ (orange) films annealed at 150 °C for 15 min from 2° till 15° 2θ. The full diffraction patterns (2° - 60° 2θ) can be found in the supporting information **Fig. S20-S22**.

We have shown that charge-transfer complexes of a $PyrC_4$ donor and TCNQ or TCNB acceptors can be formed in the organic layer of 2D layered perovskites. The material with TCNQ as an acceptor was compared with the material containing TCNB. In contrast to the intercalated structures studied by Mitzi, where only slight changes in the visible wavelength range were seen[2], we show that the incorporation of charge-transfer complexes has a significant influence on the absorption in the visible wavelength region.

This work opens up a new avenue towards 2D layered hybrid perovskites containing a functional organic layer. Many different combinations of donors and acceptors are known to form charge-transfer complexes, with widely different optical and electronic properties.[24-27] Therefore, combinations of donors and acceptors could be targeted to obtain layered perovskites where the organic and inorganic layer have synergistic properties. Future work will include a systematic study of different donor-acceptor combinations incorporated into layered perovskites. Next to this, the concept will be broadened from single-layer 2D perovskites towards multi-layered perovskites such that the properties of the materials can be further tuned by changing the number of inorganic layers in the structure.

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Conflicts of interest

There are no conflicts to declare.

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