# **Supporting Information**

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

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#### **Experimental and methods**

#### Chemicals and reagents

7,7,8,8-Tetracyanoquinodimethane (TCNQ, > 98.0%) was bought from TCI and 1,2,4,5-Tetracyanobenzene (TCNB, 99%) and potassium phthalimide salt (95%) were obtained from Fluorochem. Lead iodide (PbI<sub>2</sub>, 99.999%) was obtained from Lumtec. 1-Pyrenebutyric acid (95%) was purchased from Combi-Blocks, Inc. Lithium aluminium hydride (LiAlH<sub>4</sub>, 95%), carbon tetrabromide (CBr<sub>4</sub>, 98%), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 99+%), magnesium sulfate (MgSO<sub>4</sub>, 99%), ammonium chloride (NH<sub>4</sub>Cl, 99+%), triphenylphosphine (Ph<sub>3</sub>P, 99%), hydrazine monohydrate (65%) and hydriodic acid (57 wt.% aqueous solution) were bought from Fisher Scientific. All chemicals were used without further purification. The dry dimethylformamide (DMF) that was used to make the precursor solutions, and dry tetrahydrofuran (THF) which was used for the reactions, was obtained from our in-house solvent-purification system (MBRAUN SPS-800). Chloroform (CHCl<sub>3</sub>), dichloromethane (DCM) and ethyl acetate (EtOAc) were laboratory grade solvents (+99%) purchased from Fisher Scientific. Petroleum ether (PE), methanol (MeOH), ethanol (EtOH) and diethylether were technical solvents purchased from VWR. Synthesis of 1-Pyrenebutamine, hydriodide (PyrC<sub>4</sub>)



Fig. S1. Synthesis pathway of the PyrC<sub>4</sub>NH<sub>3</sub>I salt.

1-Pyrenebutanol (II): LiAlH<sub>4</sub> (2.0 g, 52 mmol) was dispersed in dry THF (15 mL) under N<sub>2</sub> atmosphere. The dispersion was heated to 85 °C (or until refluxing). A solution of 1-pyrenebutyric acid (I, 10 g, 35 mmol) in THF (15 mL) was added to the refluxing dispersion of LiAlH<sub>4</sub> in THF. The reaction was followed with thin layer chromatography (TLC). After the reaction was completed, after approximately 1h, a satured solution of K<sub>2</sub>CO<sub>3</sub> was added slowly to the reaction mixture. Next, the reaction mixture was extracted with 1M HCl (50 mL) and EtOAc (3 × 50 mL). Then, the organic layer was dried with magnesium sulfate, filtered and the solvent was removed by vacuum elimination. The residue was purified by flash chromatography (DCM), to obtain II as an off-white solid (8.8 g, 93%). <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  8.28 (d, J = 9.3 Hz, 1H), 8.19 – 8.16 (m, 1H), 8.15 (d, J = 2.5 Hz, 1H), 8.12 (d, J = 2.0 Hz, 1H), 8.10 (d, J = 3.4 Hz, 1H), 8.07 – 7.96 (m, 3H), 7.87 (d, J = 7.8 Hz, 1H), 3.71 (t, J = 6.5 Hz, 2H), 3.43 – 3.34 (m, 2H), 1.94 (m, 2H), 1.81 – 1.69 (m, 2H).

1-(Bromobutyl)pyrene (III): CBr<sub>4</sub> (13.3 g, 40.1 mmol), K<sub>2</sub>CO<sub>3</sub> (6.7 g, 48.1 mmol) and II (8.80 g, 32.1 mmol) were dissolved in DCM (120 mL) under a N<sub>2</sub> atmosphere and cooled to 0 °C. A solution of Ph<sub>3</sub>P (10.5 g, 40.1 mmol) in DCM (50 mL) was added to the former solution and the reaction mixture was allowed to warm up to room temperature, and stirred for 10 h. Afterwards, the reaction mixture was filtered and the filtrate was concentrated. The residue was purified by flash chromatography (8:1 PE:EtOAc), to obtain III as an off-white solid (10.8 g, 99.8%). <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  8.27 (d, J = 9.3 Hz, 1H), 8.20 – 8.17 (m, 1H), 8.16 (d, J = 2.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), 8.09 – 7.97 (m, 3H), 7.86 (d, J = 7.8 Hz, 1H), 3.52 – 3.43 (m, 2H), 3.41 – 3.34 (m, 2H), 2.09 – 1.98 (m, 4H).

1H-Isoindole-1,3(2H)-dione, 2-[4-(1-pyrenyl)butyl]- (IV): potassium 1,3-dioxoisoindolin-2-ide (7.42 g, 40.1 mmol) and III (10.8 g, 32.0 mmol) were dissolved in DMF (50 mL), heated to 80 °C and stirred for 6 h. After the reaction was completed, aqueous NH<sub>4</sub>Cl was added and the reaction mixture was extracted with CHCl<sub>3</sub> (3x 100 mL). Then, the organic layer was dried with magnesium sulfate, filtered and the solvent was removed by vacuum elimination. The residue was recrystallized from MeOH to obtain IV as an off-white solid (11.7 g, 90.4%). <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  8.26 (d, J = 9.3 Hz, 1H), 8.16 (d, J = 1.4 Hz, 1H), 8.14 (d, J = 1.8 Hz, 1H), 8.12 – 8.06

(m, 2H), 8.05 – 7.95 (m, 3H), 7.86 (d, J = 7.8 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.68 – 7.62 (m, 2H), 3.76 (t, J = 6.8 Hz, 2H), 3.39 (t, J = 7.2 Hz, 2H), 2.01 – 1.81 (m, 4H).

1-Pyrenebutamine (V): Hydrazine monohydrate (65 wt. % in H<sub>2</sub>O, 49 mL, 1.01 mol) was added to a refluxing solution of IV (11.7 g, 29.0 mmol) in EtOH (250 mL) and reacted overnight. Over the course of the reaction, large white crystals precipitate. After the reaction was completed, the reaction mixture was allowed to cool down to room temperature and the precipitate was filtered off and the solvent was removed by vacuum elimination. Next, the residue was dissolved in chloroform and again filtered. The filtrate was concentrated by rotary evaporation. Afterwards, an extraction was performed with basic water (pH = 12, 50 mL) and CHCl<sub>3</sub> (3 × 50 mL). Then, the organic layer was dried with magnesium sulfate, filtered and the solvent was removed by vacuum elimination to obtain V (7.48 g, 94.4%). <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  8.28 (d, J = 9.2 Hz, 1H), 8.17 (d, J = 2.5 Hz, 1H), 8.15 (d, J = 3.0 Hz, 1H), 8.12 (d, J = 2.5 Hz, 1H), 8.06 – 7.95 (m, 3H), 7.87 (d, J = 7.8 Hz, 1H), 3.40 – 3.29 (m, 2H), 2.76 (t, J = 7.1 Hz, 2H), 1.89 (tt, J = 9.4, 6.9 Hz, 2H), 1.72 – 1.53 (m, 2H).

1-Pyrenebutamine, hydriodide (VI): Hydrogen iodide was generated *in situ* and added to a solution of V in ethanol at room temperature.<sup>1</sup> Afterwards, the solvent was evaporated. Next, the residue was redissolved in ethanol and precipitated in a large amount of cooled diethylether. The residue was further purified by recrystallization in ethanol to obtain VI as a white solid (10.7 g, quantitative yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.37 (d, J = 9.3 Hz, 1H), 8.28 (td, J = 8.0, 1.2 Hz, 2H), 8.25 – 8.21 (m, 2H), 8.17 – 8.11 (m, 2H), 8.06 (t, J = 7.6 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.60 (s, 3H), 3.46 – 3.20 (m, 4H), 3.01 – 2.73 (m, 2H), 1.84 (tt, J = 8.6, 6.2 Hz, 2H), 1.67 (tt, J = 8.9, 6.4 Hz, 2H).



Fig. S2. Liquid-state <sup>1</sup>H-NMR spectrum of the PyrC<sub>4</sub>NH<sub>3</sub>I salt in DMSO-d<sub>6</sub>.



Fig. S3. Liquid-state <sup>13</sup>C-NMR spectrum of the PyrC<sub>4</sub>NH<sub>3</sub>I salt in DMSO-d<sub>6</sub>.

# Preparing the precursor solutions

The compounds were dissolved together (Table S1) in dry DMF by stirring at 50 °C for 15 min, after which the solutions were allowed to cool down to room temperature. The solutions were filtered before use using a syringe filter (0.45  $\mu$ m pore size).

**Table S1** Concentration of chemicals used in precursor solutions for the preparation of films.

Composition	PyrC <sub>4</sub> concentration (mol/l)	Pbl <sub>2</sub> concentration (mol/l)	TCNQ concentration (mol/l)	TCNB concentration (mol/l)
(PyrC <sub>4</sub> ) <sub>2</sub> PbI <sub>4</sub>	0.6	0.3	0	0
(PyrC4:TCNQ 1:1)2Pbl4	0.6	0.3	0.6	0
(PyrC4:TCNB 1:1)2PbI4	0.6	0.3	0	0.6
(PyrC4:TCNQ 2:1)2Pbl4	0.6	0.3	0.3	0
(PyrC4:TCNB 2:1)2PbI4	0.6	0.3	0	0.3

#### Deposition and annealing

Quartz substrates were cleaned by sonication in consecutively detergent water, deionized water, acetone and isopropanol. Prior to spin-coating, the substrates were further cleaned using a UV-ozone treatment for 15 minutes. The spin-coating was carried out in a glovebox (< 0.1 ppm  $O_2$ , < 0.1 ppm  $H_2O$ ), the settings used were 2000 rpm, 2000 rpm/s, 20 s. The annealing of the films was performed on a hotplate in the glovebox, the films were annealed for 15 min at different temperatures. The annealing temperature that was used to obtain a certain sample is indicated in the relevant Figure captions.

# Synthesis of single crystals of (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub>

The single crystals were grown using an antisolvent vapor-assisted crystallization approach<sup>2</sup> in which the components are dissolved together in a good solvent (y-butyrolactone; GBL) and dichloromethane (DCM) anti-solvent slowly diffuses into the GBL solution through the vapor phase. Specifically,  $PyrC_4NH_3I$  and  $PbI_2$  were dissolved together in GBL by stirring at 50 °C for 15 min (Table S2). The precursor solution was filtered through a syringe filter (0.45 µm). The precursor solution (0.5 ml) was transferred to a small glass vial. The small vial (5 ml volume) was capped off with aluminum foil. A small hole was made in the aluminum foil. The small vial with the aluminum foil was put in a larger glass vial (20 ml volume). An amount of DCM (2 ml) was injected in the gap between the two vials and the larger vial was capped off with a plastic cap and parafilm. The vials were left undisturbed at room temperature. After 1 week light orange crystals suitable for single-crystal X-ray diffraction were harvested. These crystals were washed three times with dry dichloromethane and were subsequently dried under reduced pressure at room temperature.

Composition	PyrC <sub>4</sub>	Pbl <sub>2</sub>	
	concentration	concentration	
	(mol/l)	(mol/l)	
(PyrC <sub>4</sub> ) <sub>2</sub> PbI <sub>4</sub>	0.216	0.108	

**Table S2** Concentration of chemicals used in precursor solutions for the preparation of singlecrystals.

# Characterization

X-ray diffraction measurements were performed at room temperature in ambient air on a Bruker D8 Discover diffractometer with  $CuK_{\alpha}$  radiation. Temperature-controlled XRD measurements were performed on the same instrument with a temperature cell, under nitrogen flow.

Absorption spectra were measured on a Cary 5000 UV-Vis-NIR spectrophotometer from Agilent Technologies, a cleaned quartz substrate was used as calibration background.

Photoluminesence emission spectra were taken with a Horiba-Jobin Yvon Fluorolog-3 spectrofluorometer, equipped with double-grating excitation and emission monochromators and a 450 W Xe lamp as a light source. An excitation wavelength of either 300 nm or 430 nm was used (as indicated in the corresponding Figure captions).

For temperature-controlled UV-Vis, the precursor solution was spin coated onto a cleaned quartz disk and transferred to a temperature-controlled cell (custom made by Harrick Scientific Products, New York). The temperature was controlled using a temperature-controller from Watlow<sup>®</sup>. The temperature of the film is measured with a thermocouple touching the film. A heating ramp of 1 °C/min was used for the measurements. After the heating ramp, the system is left to cool down naturally to room temperature. The measurements were conducted under a nitrogen gas flow.

#### Single crystal X-ray diffraction

For the structure of the  $(PyrC_4)_2PbI_4$  2D layered hybrid perovskite, X-ray intensity data were collected at 100 K, on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using  $\omega$  scans and MoK $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro.<sup>3</sup> Using Olex2<sup>4</sup>, the structure was solved by direct methods using the ShelXT structure solution program and refined by full-matrix least-squares on F<sup>2</sup> using the ShelXL program package.<sup>5,6</sup> Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms.

Crystal data for compound (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> 2D layered hybrid perovskite. C<sub>40</sub>H<sub>40</sub>I<sub>4</sub>N<sub>2</sub>Pb, M = 1263.54, monoclinic, space group P2<sub>1</sub>/c (No. 14), a = 25.0798(3) Å, b = 8.70360(10) Å, c = 8.76250(10) Å,  $\theta = 92.6530(10)^{\circ}$ , V = 1910.67(4) Å<sup>3</sup>, Z = 2, T = 100 K,  $\rho_{calc} = 2.196$  g cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 7.677 mm<sup>-1</sup>, F(000) = 1176, 49790 reflections measured, 5140 unique ( $R_{int} = 0.0453$ ) which were used in all calculations. The final R1 was 0.0211 ( $I > 2\sigma(I)$ ) and wR2 was 0.0451 (all data).

CCDC 1876191 contains the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or <u>deposit@ccdc.cam.ac.uk</u>).

#### **Supporting Figures**



Fig. S4. Absorption spectrum of a film of the PyrC₄:TCNQ 1:1 charge-transfer complex dried at 50 °C for 15 min (orange), a film of TCNQ dried at 110 °C for 5 min (blue) and a film of PyrC₄ dried at 110 °C for 5 min (black).



Fig. S5. (left) Absorption spectrum of a PyrC<sub>4</sub>:TCNQ 1:1 complex in DMF. (right) Overlay of absorption spectra of a PyrC<sub>4</sub>:TCNQ 1:1 complex in DMF (blue), TCNQ in DMF (orange) and PyrC<sub>4</sub> in DMF (black). The absorption peaks at ~ 850 nm and ~ 750 nm are assigned to a TCNQ radical anion<sup>7</sup> formed in DMF<sup>8</sup>. The two sharp peaks at ~ 344 nm and ~ 328 nm are assigned to

 $PyrC_4$ . The broad absorption band with a maximum at ~ 570 nm is not present for TCNQ or  $PyrC_4$  separately and is assigned to charge-transfer absorption of the  $PyrC_4$ :TCNQ 1:1 complex in solution.



Fig. S6. Absorption spectrum of a thin film of the PyrC<sub>4</sub>:TCNB 1:1 charge-transfer complex dried at 50 °C for 15 min (orange), a film of TCNB dried at 110 °C for 5 min (blue) and a film of PyrC<sub>4</sub> dried at 110 °C for 5 min (black).



Fig. S7. (left) Absorption spectrum of a PyrC<sub>4</sub>:TCNB 1:1 complex in DMF. (right) Overlay of absorption spectra of a PyrC<sub>4</sub>:TCNB 1:1 complex in DMF (blue), TCNB in DMF (orange) and PyrC<sub>4</sub> in DMF (black). charge-transfer absorption band starts at~ 620 nm with a maximum at ~ 470 nm. Absorption below ~ 400 nm is related to TCNB and PyrC<sub>4</sub>.



Fig. S8. (left) Unit cell of the (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> 2D layered hybrid perovskite. (right) View along the aaxis. Visualization is performed using the VESTA package.<sup>9</sup> The lead atoms are colored bright grey, the iodine atoms dark purple, the nitrogen atoms light blue, the hydrogen atoms light pink and the carbon atoms dark orange.



Fig. S9. (Left) Photoluminescence emission spectra of PyrC<sub>4</sub>:TCNQ 1:1 (black) and PyrC<sub>4</sub>:TCNB 1:1 (blue) films dried at 50 °C (absolute intensity). (Right) Photoluminescence emission spectrum of a (PyrC<sub>4</sub>:TCNB 1:1)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C for 15 min (black) and a PyrC<sub>4</sub>:TCNB 1:1 film dried at 50 °C (blue). All samples were excited at 430 nm.



Fig. S10. Absorption spectrum of a (PyrC<sub>4</sub>:TCNB 2:1)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C for 15 min (orange), of a (PyrC<sub>4</sub>:TCNB 1:1)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C for 15 min (black) and of a (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C for 15 min (blue). Two excitonic peaks are clearly present in the spectrum of (PyrC<sub>4</sub>:TCNB 2:1)<sub>2</sub>PbI<sub>4</sub>, belonging to (PyrC<sub>4</sub>:TCNB 1:1)<sub>2</sub>PbI<sub>4</sub> and (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub>.



Fig. S11. Absorption spectrum of a (PyrC4:TCNQ 2:1)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C for 15 min (orange), of a (PyrC4:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C for 15 min (black) and of a (PyrC4)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C for 15 min (blue). In the spectrum of (PyrC4:TCNQ 2:1)<sub>2</sub>PbI<sub>4</sub>, the main excitonic peak corresponds to (PyrC4:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> while a shoulder at lower wavelength corresponds to (PyrC4)<sub>2</sub>PbI<sub>4</sub>. Note also that for (PyrC4:TCNQ 2:1)<sub>2</sub>PbI<sub>4</sub> the chargetransfer absorption between 550 nm and 700 nm is much less pronounced than for (PyrC4:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub>.



Fig. S12. Emission spectrum of a (PyrC4:TCNB 2:1)<sub>2</sub>Pbl<sub>4</sub> film annealed at 150 °C for 15 min (orange), of a (PyrC4:TCNB 1:1)<sub>2</sub>Pbl<sub>4</sub> film annealed at 150 °C for 15 min (black) and of a (PyrC4)<sub>2</sub>Pbl<sub>4</sub> film annealed at 150 °C for 15 min (blue). An excitation wavelength of 430 nm was used for all films. For (PyrC4:TCNB 2:1)<sub>2</sub>Pbl<sub>4</sub> an excitonic emission peak belonging to (PyrC4)<sub>2</sub>Pbl<sub>4</sub> is present at ~ 500 nm.



Fig. S13. Emission spectrum of a (PyrC4:TCNQ 2:1)<sub>2</sub>Pbl<sub>4</sub> film annealed at 150 °C for 15 min (orange), of a (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>Pbl<sub>4</sub> film annealed at 150 °C for 15 min (black) and of a (PyrC<sub>4</sub>)<sub>2</sub>Pbl<sub>4</sub> film annealed at 150 °C for 15 min (blue). An excitation wavelength of 430 nm was used. For (PyrC<sub>4</sub>:TCNQ 2:1)<sub>2</sub>Pbl<sub>4</sub> a clear excitonic emission peak belonging to (PyrC<sub>4</sub>)<sub>2</sub>Pbl<sub>4</sub> is present at ~ 500 nm. Note that in the (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>Pbl<sub>4</sub> film (black curve) made for this experiment there is also some small amount of (PyrC<sub>4</sub>)<sub>2</sub>Pbl<sub>4</sub> present as indicated by the presence of a small shoulder at ~ 500 nm, likely related to a slight off-stoichiometry. All films were excited at 430 nm.



Fig. S14. X-ray diffraction pattern of a (PyrC<sub>4</sub>:TCNB 2:1)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C.



Fig. S15. X-ray diffraction pattern of a (PyrC<sub>4</sub>:TCNQ 2:1)<sub>2</sub>PbI<sub>4</sub> film annealed at 150 °C.



Fig. S16. Temperature-controlled XRD of: a) a film of (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> that was annealed at 110 °C for 15 min before the temperature-controlled experiment. b) a film of (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> that was annealed at 150 °C for 15 min before the temperature-controlled experiment. c) a film of (PyrC<sub>4</sub>:TCNB 1:1)<sub>2</sub>PbI<sub>4</sub> that was annealed at 150 °C for 15 min before the temperature-controlled experiment.



Fig. S17. Selected XRD patterns from the temperature-controlled XRD experiment of a (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> film showing, with increasing temperature, the disappearance of the reflections belonging to (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub>, the appearance of reflections belonging to (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> and finally formation of a new phase with decreased interplanar spacing formed out of the to (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> phase.



Fig. S18. (left) Absorption spectra as a function of temperature for a film of (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> (right) absorption spectra as a function of temperature for a film of (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub>.



Fig. S19. Absorbance at 530 nm - the excitonic peak of (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> - and at 496 nm – the excitonic peak of (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> – as a function of temperature. These plots are a cross-section of a temperature-controlled UV-Vis experiment carried out with a (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> film (Fig. S18; right). The (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> phase (peak at ~ 530 nm) is converted into (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> (peak at ~ 496 nm).



Fig. S20. Full diffraction pattern of a film of (PyrC<sub>4</sub>)<sub>2</sub>PbI<sub>4</sub> annealed at 150 °C.



Fig. S21. Full diffraction pattern of a film of (PyrC<sub>4</sub>:TCNQ 1:1)<sub>2</sub>PbI<sub>4</sub> annealed at 150 °C.



Fig. S22. Full diffraction pattern of a film of (PyrC<sub>4</sub>:TCNB 1:1)<sub>2</sub>PbI<sub>4</sub> annealed at 150 °C.



#### Additional supporting figures not directly referred to in the article

Fig. S21. Liquid-state <sup>1</sup>H-NMR spectrum of (PyrC<sub>4</sub>:TCNB 1:1)<sub>2</sub>PbI<sub>4</sub> in d<sub>6</sub>-DMSO. The water peak is located under a signal belonging to PyrC<sub>4</sub> at 3.37 ppm.



Fig. S22. Liquid-state <sup>1</sup>H-NMR spectrum of TCNB in d<sub>6</sub>-DMSO.



Fig. S23. Photoluminescence emission spectrum of  $PyrC_4$  salt deposited as a thin-film dried at 110 °C for 5 min, with excitation at 300 nm.



Fig. S24. Photoluminescence emission spectrum of PyrC<sub>4</sub> salt deposited as a thin-film dried at 110 °C for 5 min, with excitation at 430 nm.



Fig. S25. Photoluminescence emission spectrum of TCNQ deposited as a thin-film dried at 110 °C for 5 min, with excitation at 300 nm.



Fig. S26. Photoluminescence emission spectrum of TCNQ deposited as a thin-film dried at 110 °C for 5 min, with excitation at 430 nm.



Fig. S27. Photoluminescence emission spectrum of TCNB deposited as a thin-film dried at 110 °C for 5 min, with excitation at 300 nm.



Fig. S28. Photoluminescence emission spectrum of PbI<sub>2</sub> deposited as a thin-film annealed at 150 °C, with excitation at 300 nm.

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