Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

# Supporting information

# 2D layered perovskite containing functionalised benzothienobenzothiophene molecules: formation, degradation, optical properties and photoconductivity

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## *Chemicals and reagents*

Lead iodide ($PbI_2$, 99.999%) was obtained from Lumtec. Hydroiodic acid (HI, 57 % w/w aq., distilled, stabilized), sodium hydrosulfide hydrate ($NaSH.xH_2O$), 3-chloropropanoyl chloride, aluminum trichloride ($AlCl_3$) and lithium aluminum hydride ($LiAlH_4$) were purchased from Acros Organics and used as received. Hydrazine monohydrate (65%) and 2-chlorobenzaldehyde (99%) were purchased from Fisher Scientific. Potassium 1,3-dioxoisoindolin-2-ide (95%) was purchased from Fluorochem. HCl (37%) was purchased from VWR. All solvents and reagents were used as received. The dry DMF that was used to make the precursor solutions, dichloromethane (DCM), toluene and diethyl ether ($Et_2O$) were obtained from a solvent purification system (MBRAUN SPS-800). All other solvents (reagent grade) were purchased from Fisher Scientific.

## *Synthesis of the BTBT derivative*

The benzothieno[3,2-*b*]benzothiophene core (BTBT, **II**) was synthesized *via* a one-pot procedure consisting of a nucleophilic aromatic substitution followed by intramolecular dehydration and cyclization, as described in literature.[1] In five following steps, a monofunctionalised BTBT derivative was prepared, as displayed in Figure S1. After obtaining the building block, BTBT was functionalised *via* a Friedel-Crafts acylation to attain **III**, on the 2-position of the phenyl group.[2] The ketone was reduced with $LiAlH_4$ and $AlCl_3$ to obtain **IV**. Next, a Gabriel synthesis was used to synthesize the corresponding amine **VI**, which was converted to an ammonium iodide salt **VII** with hydroiodic acid.

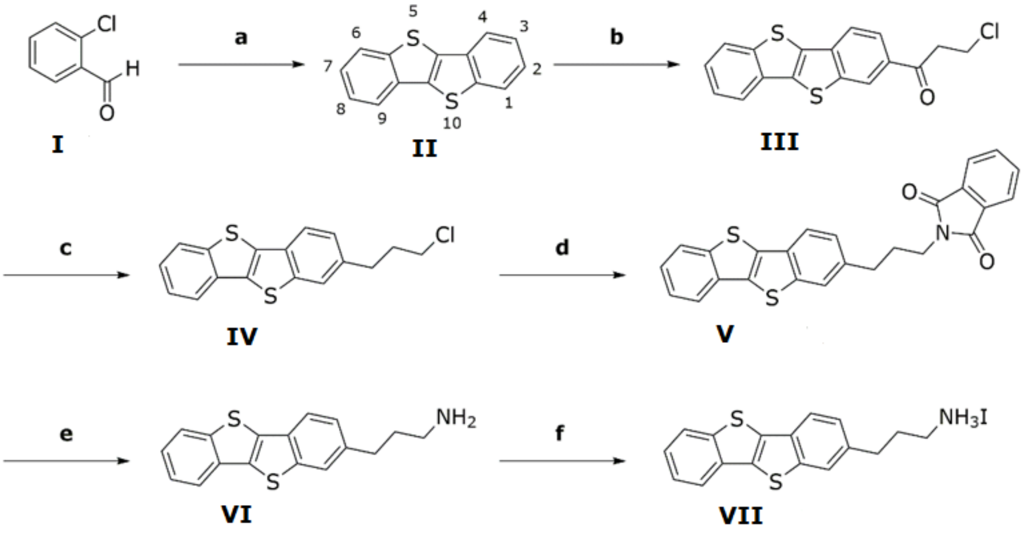


Figure S1. Synthetic pathway to obtain BTBT-$C_3$. a) NaSH.x$H_2O$, NMP, 80 °C → 180 °C, overnight. b) 3-chloropropanoyl chloride, $AlCl_3$, DCM, -78 °C → RT, 4 h. c) $LiAlH_4$, $AlCl_3$, $Et_2O$, DCM, RT, overnight. d) Potassium phthalimide, DMF, 80 °C, 6 h. e) Hydrazine monohydrate (65%), EtOH, 100 °C, 2 h. f) HI, $CHCl_3$, RT, 1 h.

Benzothieno[3,2-b]benzothiophene (**II**): A solution of 2-chlorobenzaldehyde (16.03 mL, 142.3 mmol) in NMP (40 mL) was heated to 80 °C and sodium hydrosulfide hydrate (23.81 g, 284.6 mmol) was added. The reaction mixture was stirred for 1 h, then heated to 180 °C and stirred further overnight. Afterwards, the reaction mixture is poured into a saturated $NH_4Cl$ solution (200 mL) at 0 °C. The precipitate was filtered off and washed with water and acetone. The crude product was purified by recrystallization from toluene to obtain **II** as an off-white solid (4.00 g, 12 %). $^1H$ NMR (400 MHz, Chloroform-*d*) δ 7.93 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 2H), 7.89 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.41 (ddd, *J* = 8.0, 7.2, 1.4 Hz, 2H).

2-Benzothienobenzothiophene-3-chloro-1-propanone (**III**): **II** (3.653 g, 15.20 mmol) was dissolved in dry DCM (500 mL) under a $N_2$ atmosphere and cooled to -10 °C. Then, the reaction mixture was cooled to -78 °C and $AlCl_3$ (2.027 g, 15.20 mmol) was added. Next, 3-chloropropanoyl chloride (1.45 mL, 15.20 mmol) was added drop-wise and the mixture was stirred for 4 h and allowed to warm up till room temperature.. The reaction was then quenched with ice water and diluted with MeOH, causing the precipitation of the product. The product was filtered off, washed with water (2 x 50 mL) and MeOH (2 x 50 mL) and dried under vacuum. The residue was purified by flash chromatography (PE:$CHCl_3$ 80:20), to obtain **III** as an off-white solid (3.87 g, 77 %). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.56 (dd, *J* = 1.5, 0.7 Hz, 1H), 8.06 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.99 – 7.90 (m, 3H), 7.56 – 7.43 (m, 2H), 3.99 (t, *J* = 6.8 Hz, 2H), 3.58 (t, *J* = 6.8 Hz, 2H).

2-(3-Chloropropyl)-benzothienobenzothiophene (**IV**): $AlCl_3$ (3.900 g, 29.25 mmol) was suspended in dry $Et_2O$ (100 mL) under a $N_2$ atmosphere and a suspension of $LiAlH_4$ (1.110 g, 29.25 mmol) in dry DCM (25 mL) was added drop-wise. **III** (3.870 g, 11.70 mmol) in dry DCM (400 mL) was added drop-wise and the reaction was stirred overnight. Afterwards, the reaction was cooled to 0 °C and quenched by adding a solution of 2 M HCl until pH = 2 was obtained. The mixture was extracted with $CHCl_3$ (3 x 100 mL). Then, the organic layers were combined and dried with magnesium sulphate, filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (PE:$CHCl_3$ 10:1), to obtain **IV** as an off-white solid (2.23 g, 60 %). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.88 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1H), 7.81 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.75 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.50 –

7.43 (m, 1H), 7.42 – 7.36 (m, 1H), 7.30 (dd, *J* = 8.1, 1.5 Hz, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.26 – 2.12 (m, 2H).

2-(3-Phthalimidepropyl)-benzothienobenzothiophene (**V**): Potassium 1,3-dioxoisoindolin-2-ide (1.963 g, 10.60 mmol) and **IV** (2.240 g, 7.07 mmol) were dissolved in DMF (10 mL), heated to 80 °C and stirred for 6 h. After the reaction was completed, aqueous $NH_4Cl$ was added and the reaction mixture was extracted with $CHCl_3$ (3x 50 mL). Then, the organic layers were combined and dried with magnesium sulphate, filtered and the solvent was evaporated under reduced pressure. The residue was recrystallized from MeOH to obtain **V** as an off-white solid (2.10 g, 70 %). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.90 (ddd, *J* = 7.9, 1.2, 0.6 Hz, 1H), 7.86 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.64 – 7.53 (m, 2H), 7.48 – 7.42 (m, 1H), 7.39 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H), 7.28 (dd, *J* = 8.1, 1.6 Hz, 1H), 3.80 (t, *J* = 7.0 Hz, 2H), 3.14 – 2.63 (m, 2H), 2.30 – 1.91 (m, 2H).

2-(3-Aminopropyl)-benzothienobenzothiophene (**VI**): Hydrazine monohydrate (65 wt. % in $H_2O$, 8.2 mL, 171.73 mmol) was added to a refluxing solution of **V** (2.099 g, 4.91 mmol) in EtOH (150 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 evaporated under reduced pressure. Next, the residue was dissolved in $CHCl_3$ and again filtered. The filtrate was concentrated by rotary evaporation. Afterwards, basic water (pH = 12, 50 mL) and $CHCl_3$ were added and the mixture was extracted with $CHCl_3$ (3 × 50 mL). Then, the organic layer was dried with magnesium sulphate, filtered and the solvent was evaporated under reduced pressure to obtain **VI** as an off-white solid (1.356 g, 93 %). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.21 – 8.08 (m, 1H), 8.01 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.37 (dd, *J* = 8.2, 1.5 Hz, 1H), 2.89 – 2.71 (m, 2H), 2.57 (t, *J* = 6.8 Hz, 2H), 1.83 – 1.63 (m, 2H).

2-(3-propylamine)benzothieno[3,2-b]benzothiophene, hydroiodide (**VII**): Hydroiodic acid (HI, 57 % w/w) was added to a solution of **VI** (500.0 mg, 1.68 mmol) in $CHCl_3$ at room temperature. The salt precipitates from the reaction mixture. Afterwards, the precipitate was filtered. Next, the precipitate was redissolved in EtOH and precipitated in a large amount of cooled ether. The precipitate was further purified by recrystallization in EtOH to obtain **VII** as an off-white solid (695.0 mg, quantitative yield). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.19 – 8.11 (m, 1H), 8.07 – 7.95 (m, 3H), 7.67 (s, 3H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.4 Hz, 1H), 2.83 (t, *J* = 7.6 Hz, 4H), 2.03 – 1.85 (m, 2H).

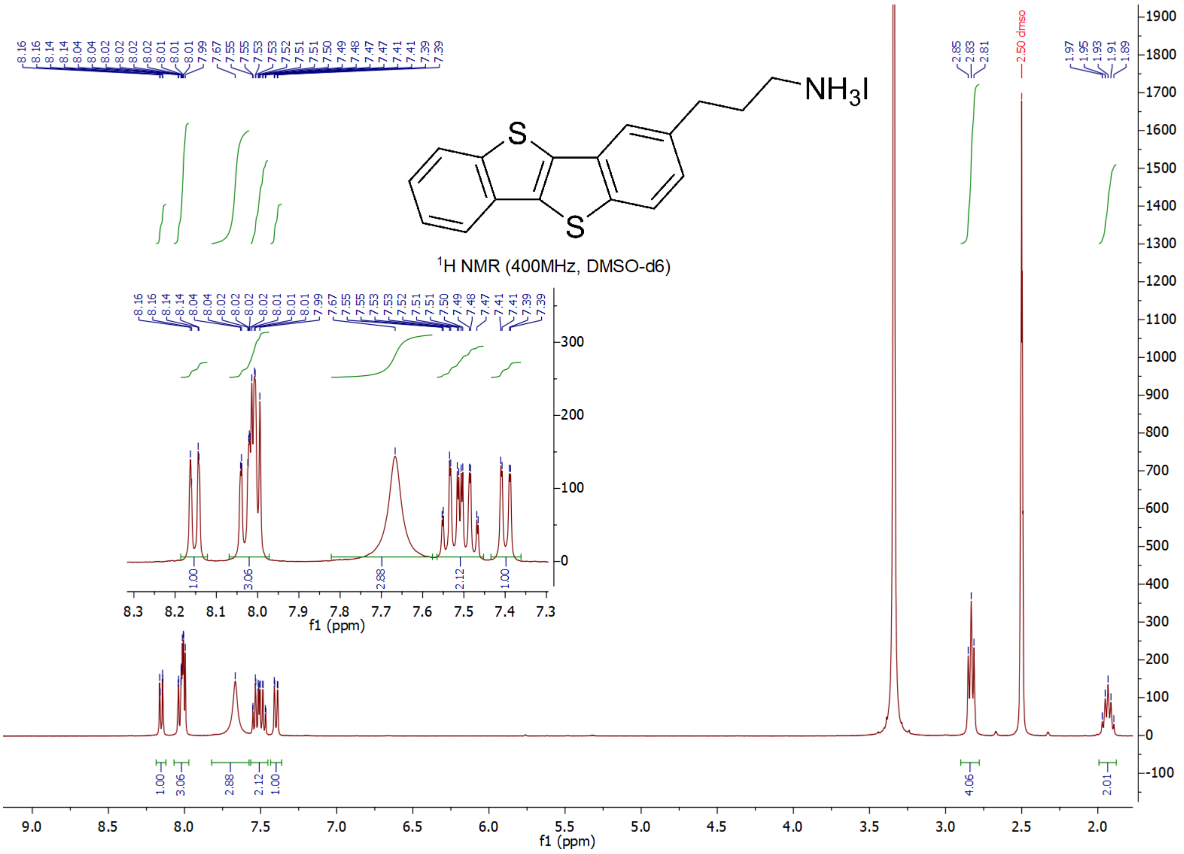


**Figure S2**. $^1$H-NMR spectrum of BTBT-$C_3H_6$-$NH_3$I (VII) in DMSO-$d_6$.

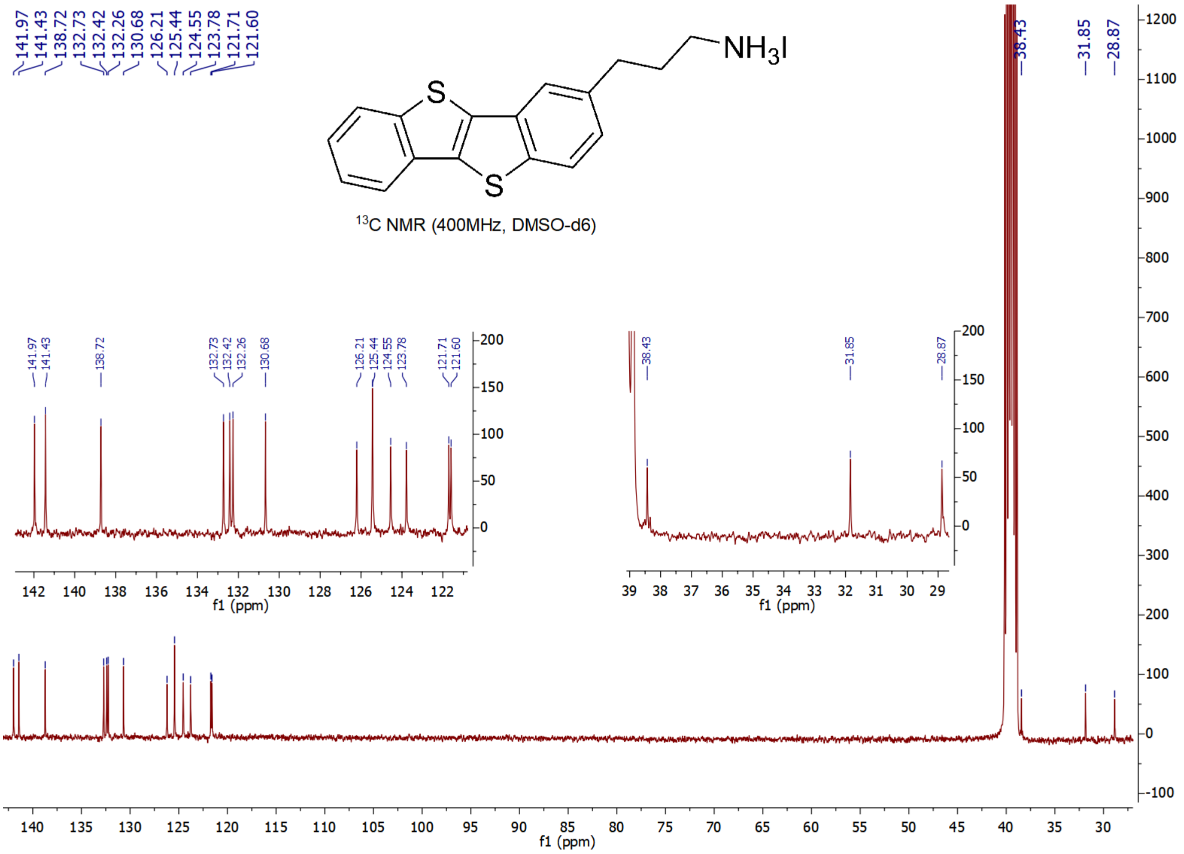


**Figure S3**. $^{13}$C-NMR spectrum of BTBT-$C_3H_6$-$NH_3$I (VII) in DMSO-$d_6$.

### *Thin film deposition and annealing*

Precursor solutions were prepared by dissolving stoichiometric amounts of BTBT-$C_3$ (0.6 mol/l) and $PbI_2$ (0.3 mol/l) in dry dimethylformamide (DMF) at 50 °C for 30 min under constant stirring. The resulting clear solutions were filtered through a syringe filter (0.45 µm pore size) before use. Quartz substrates were cleaned through consecutive sonication steps in a series of solvents (detergent water, deionized water, acetone, isopropanol) for 15 min each, followed by a UV-ozone treatment for 30 min.

Films for optical measurements and XRD analysis were deposited on quartz substrates using spin coating in a glovebox with nitrogen atmosphere (< 1 ppm $O_2$, < 1 ppm $H_2O$) at 2000 rpm, 2000 rpm/s for 20 s. Annealing was performed by post-annealing on a hot plate in the glovebox unless *in-situ* temperature-controlled XRD or UV-Vis was used. For some of the films, a solvent vapor annealing method was used. In this method, a drop of DMSO (20 µl) was put on a hot plate (at a certain temperature), the spin-coated film was put next to the drop and a petri dish was used to immediately cover both the film as well as the drop. The DMSO drop evaporates and generates an atmosphere containing DMSO for the film during thermal annealing. After the desired annealing time, the petri dish was removed and the film was taken from the hot plate. The annealing temperature differs for different films and is indicated in the relevant figure captions. Prepared samples were kept in a glovebox and were only removed for analysis.

### *Single-crystal synthesis*

For the growth of the single-crystals of phase 3 with an empirical formula of (BTBT-$C_3)_4Pb_3I_{10}$, a quartz substrate covered with a spin-coated film of (BTBT-$C_3)_2PbI_4$ that was solvent vapor annealed at 150 °C for 15 min was put partially into a solution containing BTBT-$C_3$ salt (0.21 mol/l) and $PbI_2$ (0.11 mol/l) in dry dimethylformamide (DMF). The substrate together with the solution (in a small vial) were put inside a bigger vial containing dry dichloromethane (DCM) as an anti-solvent. Over time, the DCM vaporizes and mixes with the DMF solution. This causes the liquid level in the vial to rise such that it covers the spin-coated film on the substrate. After 4 days, the substrate was removed and small needle-like crystals that had grown on top of the spin-coated film were selected using tweezers.

For the growth of crystals with an empirical formula of (BTBT-$C_3$)$PbI_3$·(GBL) an anti-solvent vapour crystallization approach[3] was used. BTBT-$C_3$ salt (0.075 mol/l) was dissolved together with $PbI_2$ (0.038 mol/l) in gamma-butyrolactone (GBL) by stirring at 50 °C for 15 min. The precursor solution was then filtered through a syringe filter (0.45 µm). The precursor solution (0.25 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 dichloromethane (1.5 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, 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.

### *Single-crystal X-ray diffraction*

For the structure of (BTBT-$C_3$)$_4$$Pb_3I_{10}$ (phase 3) (code = dvdz011), 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 CuKα ($\lambda$ = 1.54184 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro.[4] Using Olex2[5], the structure was solved by direct methods using the ShelXS structure solution program and refined by full-matrix least-squares on $F^2$ using the ShelXL program package[6, 7]. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms.

*Crystal data for compound (BTBT-C$_3$)$_4$Pb$_3$I$_{10}$.* $C_{68}H_{64}I_{10}N_4Pb_3S_8$, $M$ = 3084.28, monoclinic, space group $P$bca (No. 61), $a$ = 21.7102(2) Å, $b$ = 8.53560(10) Å, $c$ = 45.5345(4) Å, $V$ = 8437.98(15) Å$^3$, $Z$ = 4, $T$ = 100 K, $\rho_{calc}$ = 2.428 g cm$^{-3}$, $\mu$(Cu-Kα) = 42.333 mm$^{-1}$, $F$(000) = 5616, 75572 reflections measured, 8475 unique ($R_{int}$ = 0.0850) which were used in all calculations. The final $R$1 was 0.0698 ($I > 2\sigma(I)$) and $wR$2 was 0.1725 (all data).

For the structure of (BTBT-C$_3$)PbI$_3$·(GBL) (code = dvdz007), X-ray intensity data was 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 MoKα ($\lambda$ = 0.71073 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro.[4] Using Olex2[5], the structures were solved by direct methods using the ShelXS structure solution program and refined by full-matrix least-squares on $F^2$ using the ShelXL program package.[6, 7] 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 (BTBT-C$_3$)PbI$_3$·(GBL).* $C_{21}H_{22}I_3NO_2PbS_2$, $M$ = 972.42, monoclinic, space group $P2_1$/c (No. 14), $a$ = 8.61360(10) Å, $b$ = 37.1171(7) Å, $c$ = 8.01050(10) Å, $\beta$ = 91.825(2)°, $V$ = 2559.75(7) Å$^3$, $Z$ = 4, $T$ = 100 K, $\rho_{calc}$ = 2.523 g cm$^{-3}$, $\mu$(Mo-Kα) = 10.391 mm$^{-1}$, $F$(000) = 1776, 29003 reflections measured, 6474 unique ($R_{\mathrm{int}}$ = 0.0342) which were used in all calculations. The final $R1$ was 0.0305 ($I > 2\sigma(I)$) and $wR2$ was 0.0600 (all data).

CCDC 1914880 and 1985268 contain 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 deposit@ccdc.cam.ac.uk).

### *Characterization*

X-ray diffraction measurements on thin films were performed at room temperature in ambient atmosphere on a Bruker D8 Discover diffractometer with a parallel beam geometry using a Göbel mirror and $\mathrm{CuK}_{\alpha}$ radiation, with an energy-dispersive one-dimensional detector (Lynxeye). Temperature-controlled XRD measurements were performed on the same instrument with a temperature cell under a nitrogen flow. Patterns were measured at temperatures separated by 10 °C, starting at 30 °C till 210 °C. A heating ramp of 1°C/min was used, followed by an isothermal period of 10 min to measure each pattern.

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

Photoluminescence emission spectra were taken with a Horiba-Jobin Yvon Fluorolog-3 spectrofluorometer, equipped with double-grating excitation and emission monochromators and a 450 W xenon lamp as a light source. An excitation wavelength of 430 nm was used.

SEM measurements were performed on a FEI Quanta 200F.

For temperature-controlled UV-Vis, precursor solutions were 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®. 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 (only data points during the ramping period were used). The measurements were conducted under a nitrogen gas flow.

Devices were made by spin-coating films of a $(BTBT\text{-}C_3)_2PbI_4$ precursor solution (prepared as described above) on quartz substrates, followed by either thermal annealing or solvent vapor annealing. On top of the resulting film, 80 nm of Au was evaporated through a shadow mask to obtain electrodes with interdigitating finger structures as described in the text (Figure S3). Next, silver paste was applied to the edges of the substrate to make electrical contact between the evaporated Au electrode and the pins of the measuring cell. The active area was 4 cm², using a mask. The devices were measured from – 10 V till + 10 V in steps of 0.5 V, either in the dark or under 1 sun A.M 1.5G illumination.

Laser induced time-resolved microwave conductivity (TRMC) measurements were performed on thin films deposited on quartz substrates and placed in a sealed resonant cavity inside a nitrogen-filled glovebox. Photoconductivity TRMC measurements quantify the change in conductivity [microwave (8−9 GHz) power] upon pulsed excitation (repetition rate 10 Hz) due to free mobile charge carriers. The change of microwave power is related to the change in conductivity before and during the photo-conductance measurements, the samples were kept in an inert nitrogen environment to prevent degradation by exposure to moisture. The films were excited at the excitonic peak (~490 nm – 500 nm). The fluence intensities required in order to obtain conductivity signals from these compounds were in the order of 2x$10^{11}$ ph/cm$^2$ to 1x$10^{15}$ ph/cm$^2$ (which results in concentrations of ~ $10^{13}$ cm$^{-3}$ to ~ $10^{17}$ cm$^{-3}$, depending on the thickness of the film).

# Supporting figures

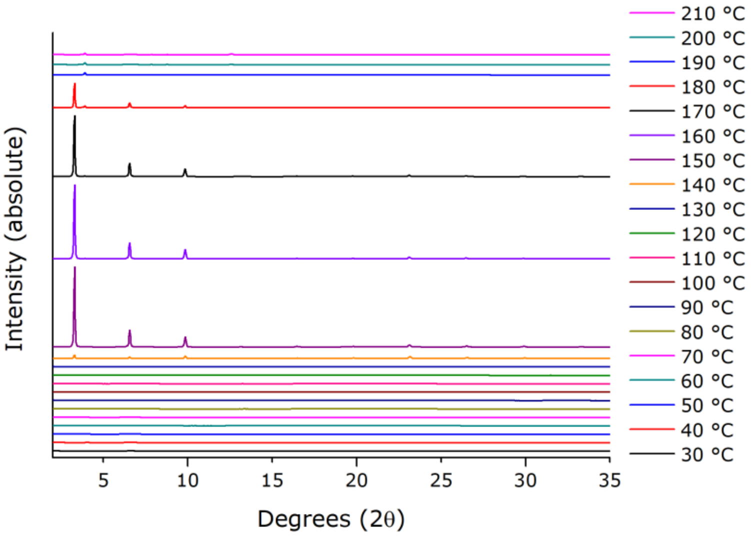


**Figure S4.** X-ray diffraction patterns (absolute) as a function of temperature starting from a spin-coated film of (BTBT-C$_3$)$_2$PbI$_4$ that was dried at 50 °C for 5 min before the in-situ experiment.

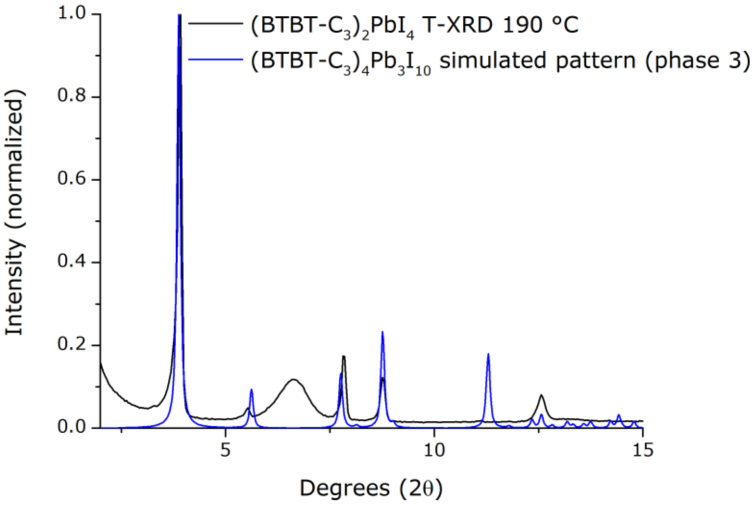


**Figure S5.** Simulated X-ray diffraction pattern of phase 3 (Figure 10 in the main manuscript) in blue compared to the experimental X-ray diffraction pattern in black from an *in-situ* temperature-controlled XRD experiment at 190 °C starting from a (BTBT-C$_3$)$_2$PbI$_4$ film that was annealed at 50 °C for 5 min before the temperature program (this is a trace from Figure 8 in the main manuscript). The broad peak at ~ 6.6° 2ϑ in the experimental pattern is due to Kapton from the temperature chamber of the XRD.

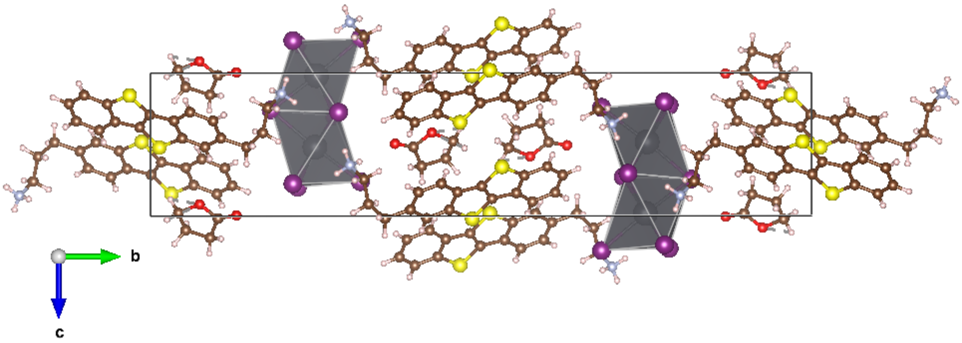


**Figure S6.** Unit cell of (BTBT-C₃)PbI₃·(GBL). The lead atoms are coloured bright grey, the iodine atoms dark purple, the nitrogen atoms light blue, the hydrogen atoms light pink, the carbon atoms dark orange, the sulfur atoms yellow and the oxygen atoms red. This figure was made using VESTA.

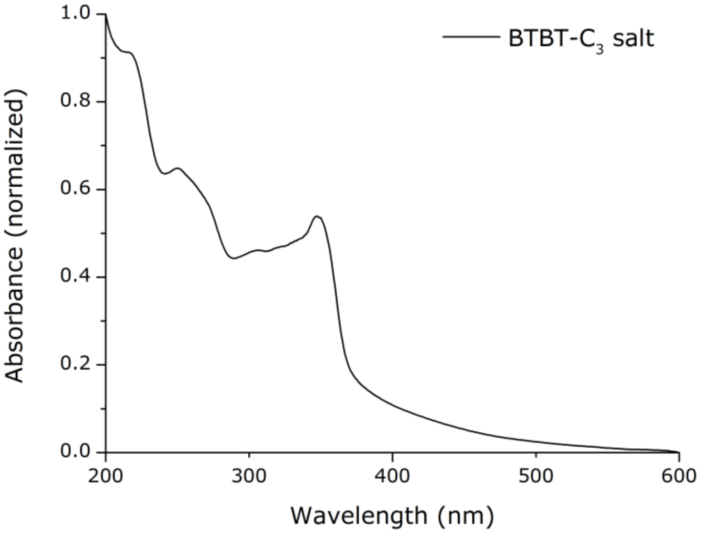


**Figure S7.** Absorption spectrum of a film of BTBT-$C_3$ salt.

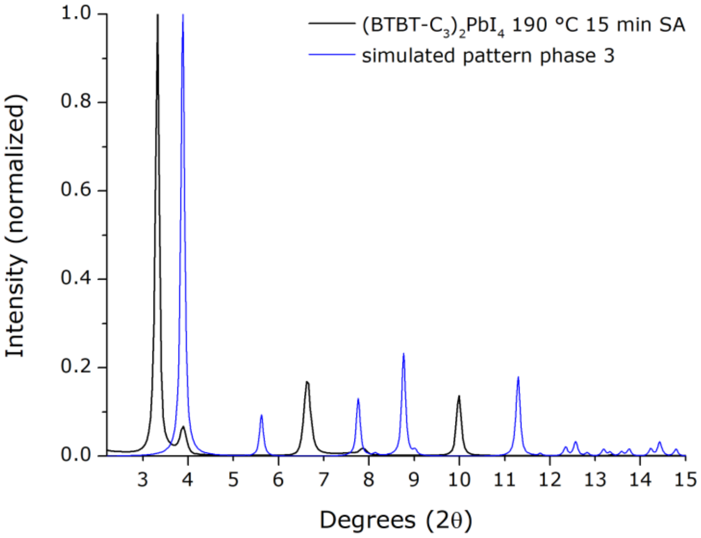


**Figure S8.** Experimental XRD pattern of a film of $(BTBT-C_3)_2PbI_4$ solvent vapour annealed at 190 °C for 15 min (black) compared to a simulate pattern of phase 3 (blue).

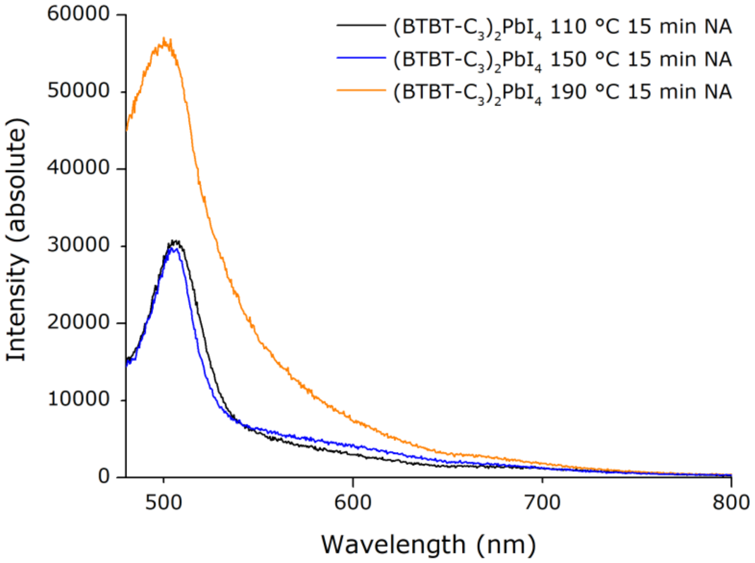


**Figure S9.** Emission spectra (absolute) of films of $(BTBT\text{-}C_3)_2PbI_4$ that were thermally annealed (NA) for 15 min at different temperatures. The films were excited at 430 nm.

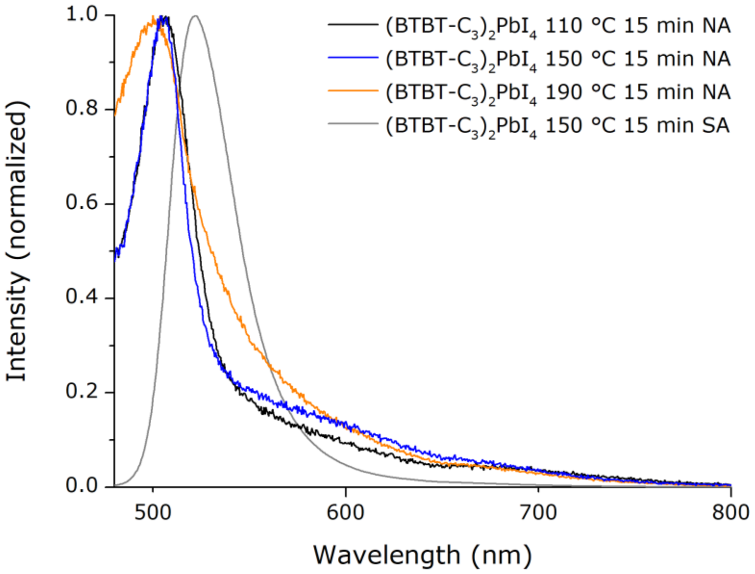


**Figure S10.** Emission spectra (normalized) of films of $(BTBT\text{-}C_3)_2PbI_4$ that were thermally annealed for 15 min at different temperatures (NA) and a film that was solvent vapour annealed at 150 °C for 15 min (SA). The films were excited at 430 nm.

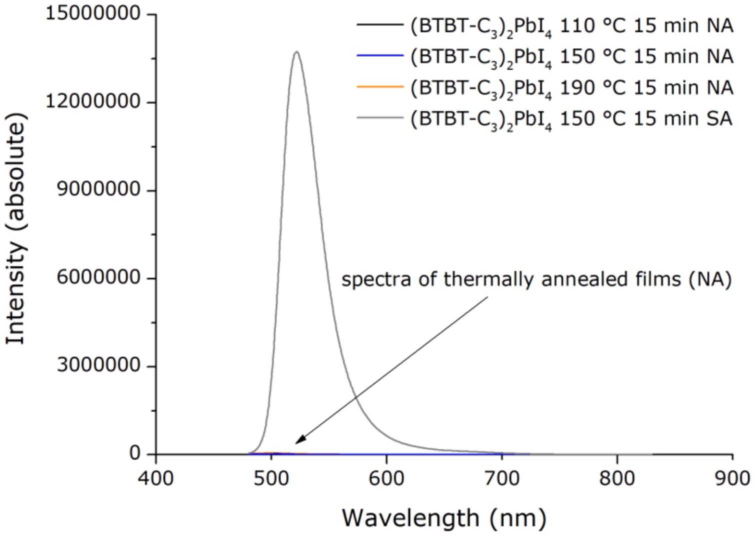
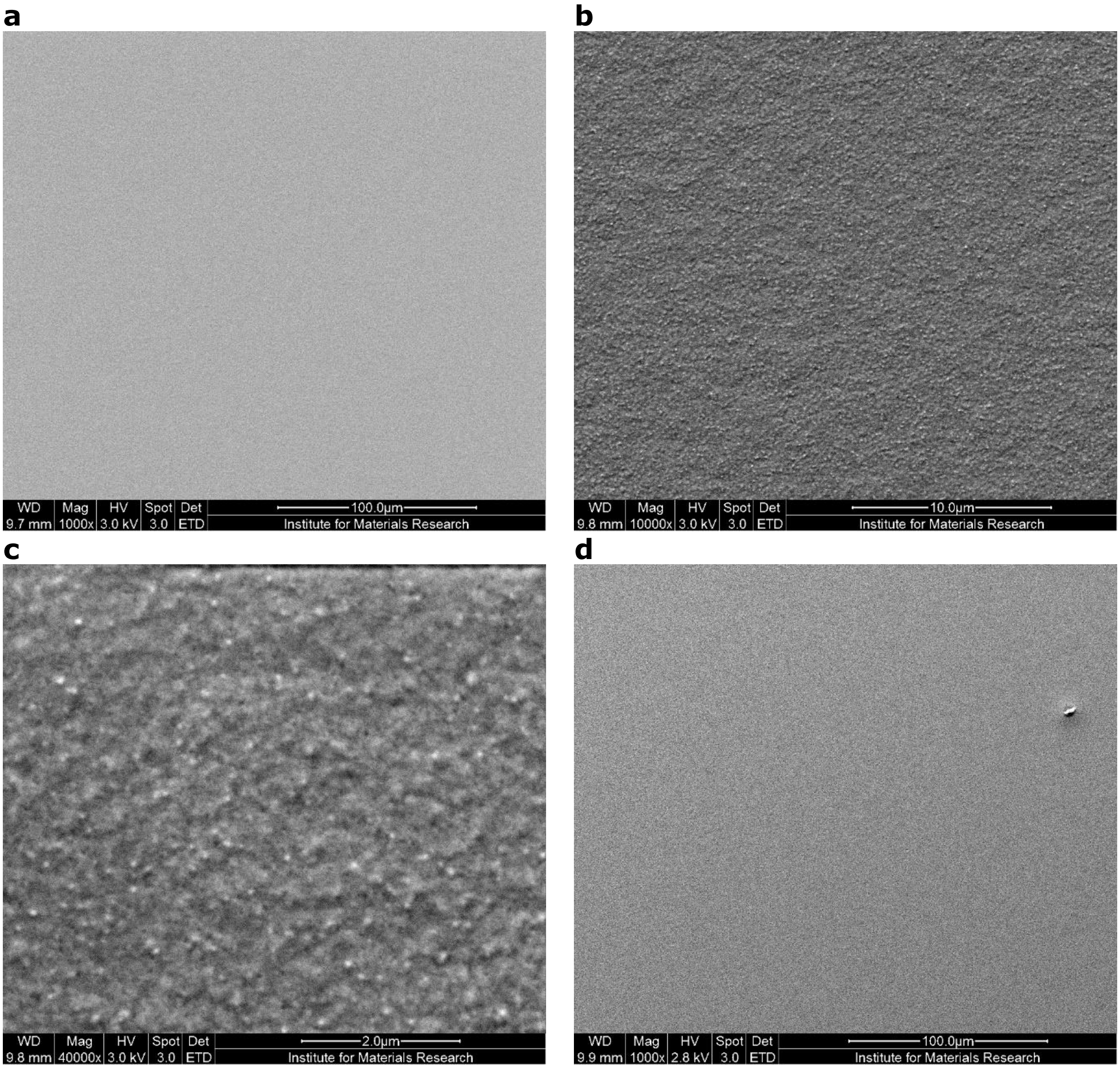


**Figure S11.** Emission spectra (absolute) of films of (BTBT-$C_3$)$_2$Pb$I_4$ that were thermally annealed for 15 min at different temperatures (NA) and a film that was solvent vapour annealed at 150 °C for 15 min (SA). The films were excited at 430 nm. Note that the intensity of the emission peak for the thermally annealed films is much lower than for the solvent annealed film.



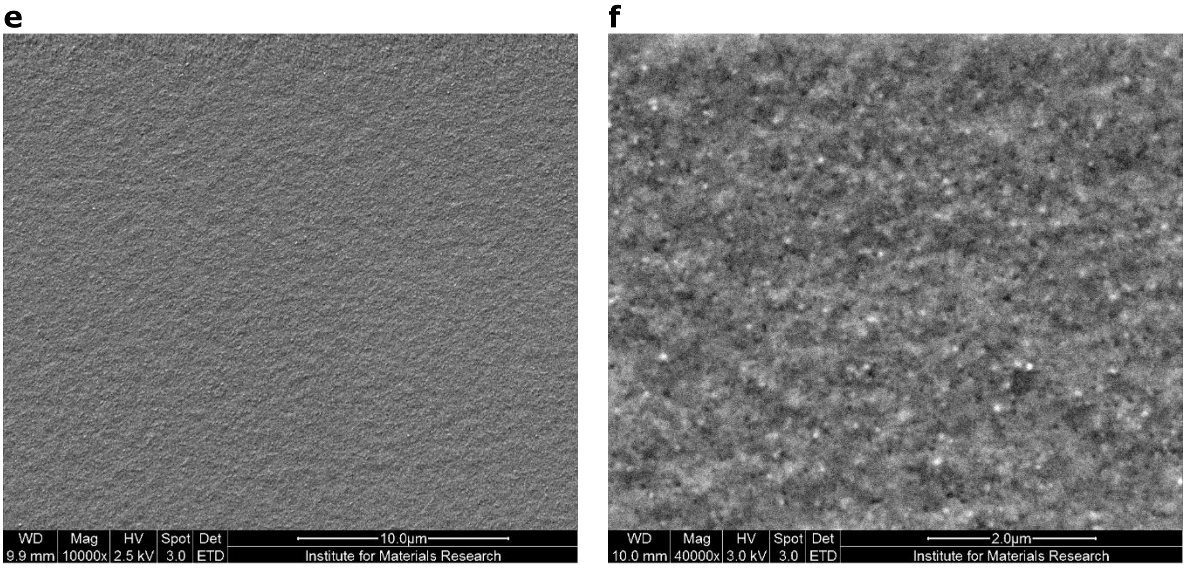


**Figure S12.** SEM images of films of (BTBT-C$_3$)$_2$PbI$_4$ thermally annealed at 150 °C for 15 min (a-c) or solvent annealed at 150 °C for 15 min (d-f).

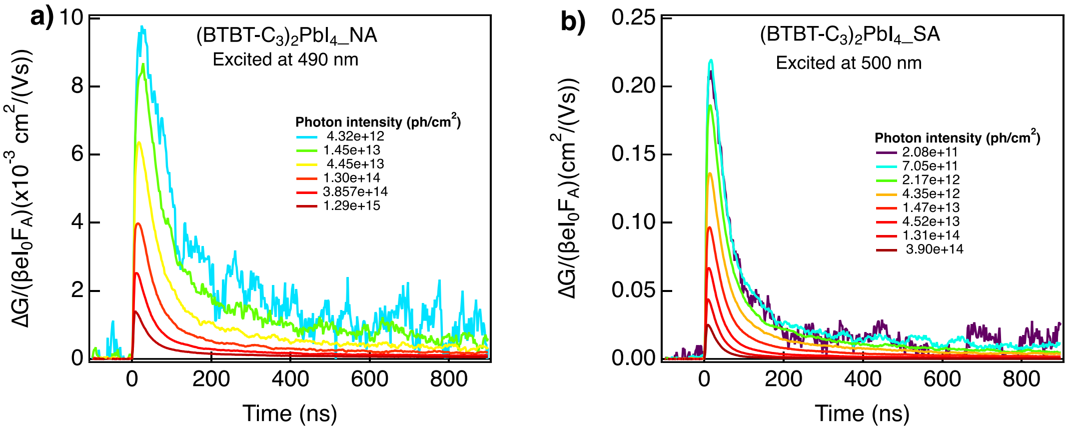


**Figure S13.** Photoconductivity TRMC as a function of photon intensity of (BTBT-C$_3$)$_2$PbI$_4$ films. a) thermal evaporation (NA). b) Solvent vapour annealing (SA). Notice that the y-axis for films prepared by thermal annealing is three orders of magnitude lower. The photon intensity was varied from 2x10$^{11}$ ph/cm$^2$ to 1x10$^{15}$ ph/cm$^2$ (which results in concentrations of ~ 10$^{13}$ cm$^{-3}$ to ~ 10$^{17}$ cm$^{-3}$).

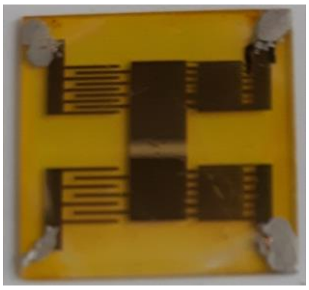


**Figure S14.** Picture of a device of (BTBT-C3)$_2$PbI$_4$ with an electrode consisting of interdigitating finger structures.

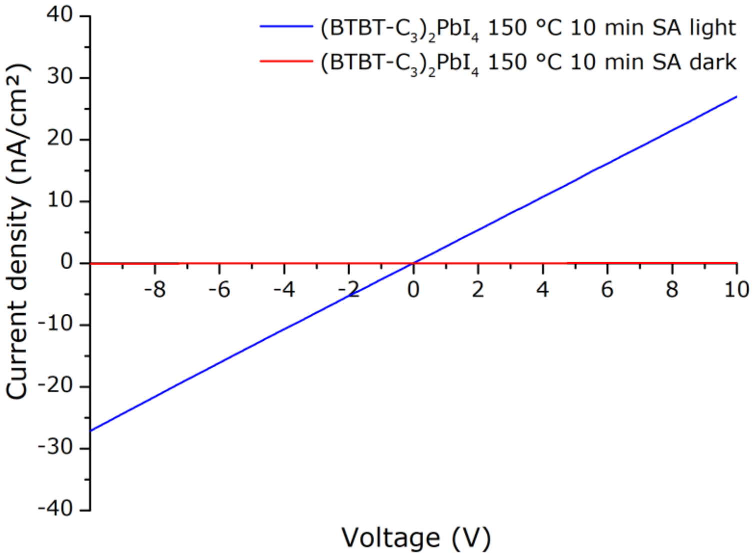


**Figure S15.** Dark current density (red) compared to light current density (blue) for a device containing a (BTBT-C$_3$)$_2$PbI$_4$ film solvent vapour annealed at 150 °C for 10 min.

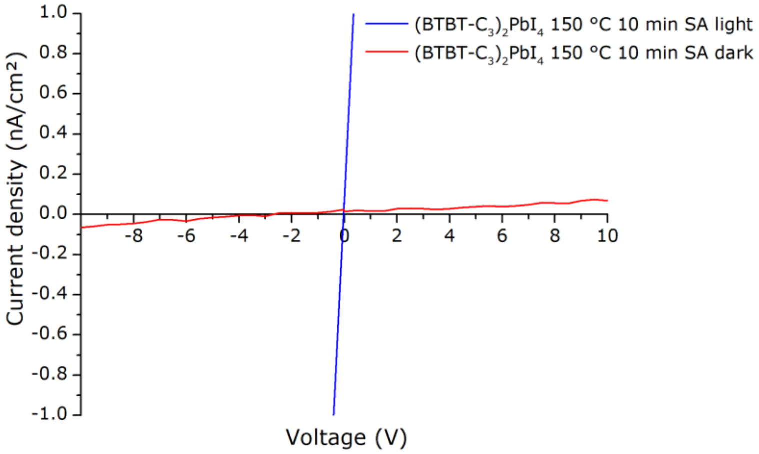


**Figure S16.** Dark current density (red) compared to light current density (blue) for a device containing a (BTBT-C$_3$)$_2$PbI$_4$ film solvent vapour annealed at 150 °C for 10 min. This is a zoomed in version of Figure S8 (note the difference in the scale of the y-axis).

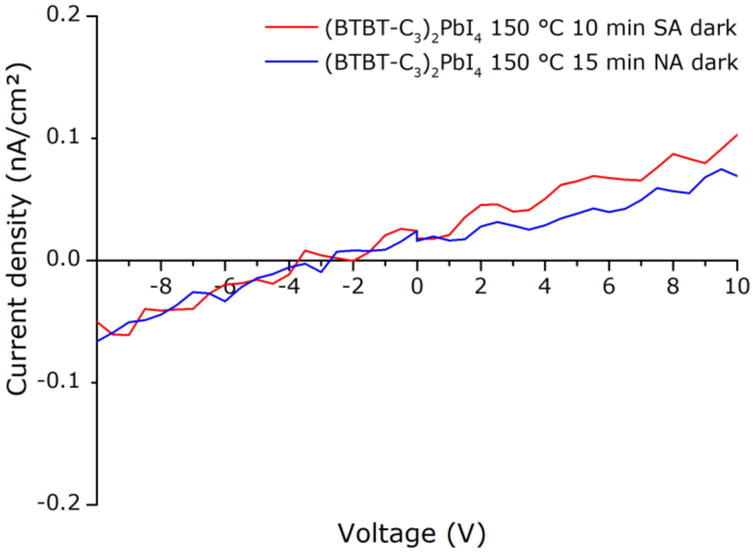


**Figure S17.** Dark current compared between a device containing a (BTBT-C$_3$)$_2$PbI$_4$ film solvent vapour annealed at 150 °C for 10 min (red) and a device containing a (BTBT-C$_3$)$_2$PbI$_4$ film thermally annealed at 150 °C for 15 min (blue).

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