Metal-organic framework nanosheets for enhanced performance of organic photovoltaic cells

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Supplementary information

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1. General experimental procedures

Commercial solvents and reagents were used without further purification. Synthesis of organic ligands was carried out in dry glassware with a nitrogen overpressure. Solvothermal synthesis of metal-organic frameworks was undertaken using borosilicate vials with Teflon faced rubber lined caps.

NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer. Chemical shifts for ¹H are reported in ppm on the \square scale; ¹H chemical shifts were referenced to the residual solvent peak. All coupling constants are reported in Hz. Mass spectra were collected using a Bruker Reflex III MALDI-TOF spectrometer. Elemental analyses were obtained on a vario MICRO CHNS elemental analyzer equipped with a thermal conductivity detector. X-Ray powder diffraction patterns were collected using a Bruker D8 Advance powder diffractometer equipped with a copper K_{α} source (λ =1.5418 Å) operating at 40 kV and 40 mA. The instrument was fitted with an energy-dispersive LYNXEYE detector. Measurements were carried out using a fixed goniometer stage with a rotating flat plate sample holder. IR spectroscopy was performed on a Perkin-Elmer Pyris TGA from 30-600°C at 10°C min⁻¹, under a 20 mL min⁻¹ nitrogen flow. UV-Vis absorption spectra were collected on a Cary 5000 UV-Vis-NIR instrument using a 1 cm internal length quartz cuvette. PL spectra were recorded using a Horiba FluoroMax spectrofluorometer using 500 nm excitation. The fluorescence emission was corrected for sample absorption at the excitation wavelength to produce an emission spectrum proportional to the fluorescence quantum efficiency.

Nanoscopic characterisation was performed using a Bruker Multimode 5 AFM, operating in soft-tapping mode under ambient conditions. Bruker OTESPA-R3 cantilever were used, with a drive amplitude and nominal resonance frequency of 20.4 mV and 290 kHz, respectively. Images were processed using standard techniques with free Gwyddion software. TEM images were obtained using a JEOL-2010F TEM operated at an accelerated voltage of 200 kV.

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2. Syntheses

2.1 Synthesis of meso-tetracarboxyphenyl porphyrin (TCPP) ligand

10 mL of pyrrole (98%, light brown solution) was distilled under vacuum at 80°C to give 5 mL of a clear solution. 4-formylbenzoic acid (3.0 g, 20 mmol) was dissolved in propionic acid (100 mL) and freshly distilled pyrrole (1.4 mL, 20 mmol) was added by syringe. The solution immediately darkened and was refluxed for 15 hours. The mixture was chilled in a fridge for 10 hours before collection of the solid by vacuum filtration. The solid was washed with hot water (2 x 20 mL) and dried under vacuum to give the product as a black powder (3.23 g, 4.0 mmol, 80 %). Elemental Analysis calculated for $C_{48}H_{30}N_4O_8$: Expected: C, 72.91; H, 3.82; N, 7.09. Found: C, 72.95; H, 4.08; N, 6.82

 $λ_{max}$ (nm): 420 (π- $π^*$)

¹H-NMR (d₆-DMSO) δ/ppm: 8.85 (8H, s, β-pyrrolic H), 8.38 (8H, d, *J* = 8.0, Ar-H), 8.32 (8H, d, *J* = 8.0, Ar-H), -2.95 (2H, s, internal pyrrole NH).

MALDI-TOF: m/z 791.2 ([MH]⁺)

2.2 Synthesis of bulk Zn₂(Zn-TCPP)(DMF)

 H_2 TCPP (7.9 mg, 0.03 mmol), Zn(NO₃)₂.3H₂O (8.9 mg, 0.09 mmol), DMF (1.5 mL) and ethanol (0.5 mL) were mixed at room temperature and heated at 80°C for 24 hours. Purple crystals were collected by centrifugation at 4500 RPM for 10 minutes and repeatedly washed in ethanol until the supernatant became clear (Yield 87%)

Elemental analysis C₄₈H₂₄N₄O₈Zn₃(H₂O)₄(DMF)₃: Expected C, 53.57; H, 4.50; N, 8.33 Found C, 52.76; H, 4.77; N, 8.88.

A slight excess of Zn around the edge of the MOF and possible nitrate counter ions could be the reason for lower carbon content and higher nitrogen.

2.3 Exfoliation of MOF into MONs

20 mg of Zn₂(ZnTCPP) MOF was added to a 10 mL glass vial along with 4 mL of the desired solvent. The sample was mixed in a vortex mixer for 30 seconds to disperse the sediment. The samples were sonicated using a Fisherbrand Elmasonic P 30H ultrasonic bath (2.75 L, 380/350

W, UNSPSC 42281712) filled with water. Samples were sonicated for 60 min at a frequency of 80 kHz with 100% power and the temperature was thermostatically maintained at 16-20°C using a steel cooling coil. Sonication was applied using a sweep mode and samples were rotated through the water using an overhead stirrer to minimise variation due to ultrasound "hot-spots". Following sonication, the vials were transferred to centrifuge tubes and centrifuged at 1500 RPM for 10 minutes to remove non-exfoliated particles.

3. Structural characterisations



Figure S1 Powder diffraction pattern for as-synthesized Zn₂(ZnTCPP) MON in comparison with the synthesized bulk MOF. The diffraction patterns are in accordance with the previous reports¹



Figure S2 Thermo-gravimetric analysis of Zn₂(ZnTCPP)(H₂O)₄(DMF)₃ MOF

Loss of solvent (Calculated 22.89%; Experimental: 22.74%)





The tyndall scattering observed in the supernatant containing the MONs confirms their colloidal nature.



Figure S4. Tyndall scattering observed in a MON suspension

4. Morphological characterisations

4.1 AFM

AFM samples of the nanosheets were prepared through dropping aliquots (typically 2 x 5 μ L drops) of a suspension onto freshly cleaved Mica, which had been stuck to a magnetic, stainless steel Agar scanning probe microscopy specimen disc for loading into the instrument.



Figure S5 AFM topographical images of the nanosheets and the corresponding height profile.

Prior to TEM characterisation, the suspension (10uL) of the nanosheets was dropcast onto holey C-coated Cu grid and allowed for evaporation of the solvent.



Figure S6. HRTEM and corresponding FFT (b) pattern of the MONs; c. Electron energy loss spectroscopy

5. Opto-electronic characterisation

5.1 UV-Vis in solution state





5.2 Cyclic voltammetry

The CV analysis was conducted in an acetonitrile solution containing tetrabutylammonium perchlorate electrolyte with Ag/Ag⁺ as the reference electrode and Pt wire as the counter electrode. The nanosheets were dropcast as films onto the glassy carbon working electrode

and the measurements were performed under an inert atmosphere of Argon with a scan rate of 100 mVs⁻¹.



Figure S8 HOMO-LUMO level determination from the CV scan of $Zn_2(ZnTCPP)$ MONs

5.3 Thin film UV-Vis for optical band gap evaluation



Figure S9. Thin film UV-vis spectra obtained by dropcasting a 5mg/ml suspension of MON in ethanol onto a quartz substrate, followed by evaporation of solvent resulting in a 40nm thin film (dektak).

5.4 Photoluminescence spectroscopy



Figure S10 The fluorescence emission of a 0.1 μ M suspension of the MONs (concentration adjusted for Absorbance <0.1 OD) is quenched upon gradual addition of PCBM (1 μ M) indicating charge transfer between them. The addition of the PCBM solution was done in increments of 20 μ L (20 μ l, <u>40 μ l</u>, <u>60 μ l</u>, <u>80 μ l</u>, 100 μ l). Excitation wavelength= 430nm





5.5 Thin film PL





P3HT (10mg/ml) was spin-coated onto Quartz slides (2000rpm, 60 s) and dried for solvent evaporation. Similarly P3HT:ZnTCPP precursor solutions were prepared for the required weight ratios and spin coated (1500rpm, 60s), dried prior to PL measurements.

The PL intensity of P3HT is quenched by 70% upon addition of 1:0.5 weight ratio of the MONs and any further addition does not cause more quenching of the signal.

6. Casting of films

6.1 Optimization of spin parameters



Figure S13 Calibration curve of thickness of the spin-coated films as a function of spin speed (t=60 seconds). Concentration of spin coat precursor solutions are: P3HT- 10 mg/ml; P3HT-Zn₂(ZnTCPP)- 10 mg/ml (1:0.5); P3HT:PCBM- 10 mg/ml (1:1); P3HT-Zn₂(ZnTCPP)-PCBM-10mg/ml (1:0.5:1)

6.2 AFM analysis of spin coated Pure P3HT and P3HT-Zn₂(ZnTCPP) films on Quartz substrate



Figure S14 AFM topographical images of spin coated films

a) Pure P3HT on quartz substrate; b) P3HT-Zn₂(ZnTCPP) (1:0.5) on quartz substrate; c) As-cast P3HT-PCBM on ITO coated glass substrate; d) As-cast P3HT- Zn₂(ZnTCPP)-PCBM (1:0.5:1) on ITO coated glass substrate

7. Fabrication of devices

7.1 Preparation of substrates

Pre-patterned ITO Glass substrates (20 mm x 15 mm) of 20 ohm/square resistance (Ossila) were cleaned via hellmenex (1-3vol%) in boiling DI water (10-minute sonication), followed by further washing in boiling DI water (10-minute sonication) and finally 5-10 minutes sonication in isopropyl alcohol. The substrates were dried with a nitrogen gun and placed in a UV-Ozone cleaner for 10 minutes to ensure removal of any surface particulates.

7.2 Deposition of PEDOT:PSS

PEDOT:PSS solution (Al4083, Ossila) was brought to room temperature, filtered through a 0.45 μ m PVDF filter into an amber vial and dynamically spin-coated (45 μ L) onto room-temp substrates at 6000 rpm, to achieve a film ~25 nm. The PEDOT:PSS coated substrates were placed on a hotplate at 110 °C for 15 minutes. This was followed by further annealing in the glovebox at 110 °C for 15 minutes to remove any surface moisture. After 15 minutes annealing in the glovebox, the ITO/PEDOT samples were cooled to room temperature before active layer deposition.

7.3 Active layer deposition

P3HT (Sigma Aldrich) and PCBM (99% purity, supplied by Ossila) were used as received. P3HT (10mg/mL) was dissolved in chlorobenzene (CB) solvent. After heating at 60 °C for 10 minutes followed by cooling towards room temperature, the solution was filtered through a 0.45 um PTFE filter. The P3HT solution in chlorobenzene was then mixed with 5mg ZnTCPP MONs (1:0.5 wt/wt ratio of P3HT:ZnTCPP)) and stirred at 60 °C for an hour. Then 10 mg of PCBM was added and the final P3HT:ZnTCPP:PCBM (1:0.5:1 wt/wt ratio) was heated at 70°C for an hour and cooled to room temperature prior to spin coating. The solutions were then spin-cast onto ITO/PEDOT at 1000 rpm under a nitrogen atmosphere in a glove box, forming films of ~150 nm as determined by dektak. For control devices, 1:1(wt/wt) (P3HT:PCBM) were spin cast at 2000 rpm in the same method as above to give films of ~150nm. Solvent-vapour annealing of the films was carried out by placing the coated substrates in a sealed metal container containing 20uL of solvent chlorobenzene) for 5 minutes.

7.4 Top contact deposition and encapsulation

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The ITO/PEDOT:PSS/Active layer substrates were placed under a vacuum of <2E-6 mBar before thermally evaporating BCP (5nm) and Silver (100nm) layers using a shadow mask. The devices were encapsulated using an epoxy resin (Ossila, E131).

7.5 Device testing

Device performance was determined under ambient conditions by measuring *J*–*V* curves using a Newport 92251A-1000 solar simulator, with devices illuminated through a 0.0256 cm² aperture mask. Before each set of measurements, the intensity was calibrated to 100 mW cm⁻² using an NREL certified silicon reference cell. The applied bias was swept from 0.0 to +1.2 V and back again at a scan speed of 0.4 V s⁻¹ using a Keithley 237 source measure unit.

External quantum efficiencies were measured using a white light source that was monochromated using a Spectral Products DK240 monochromator that was then imaged on the PSC active area. The intensity of the monochromated light was determined using a calibrated silicon photodiode having a known spectral response. The external quantum efficiency was measured in the spectral range 400-700 nm using an Xtralien X100 (Ossila) source measure unit to determine the PSC photocurrent.

Laser beam induced current (LBIC) mapping was performed on the ternary blend devices. The system comprised a mechanically chopped laser that was passed through a spatial filter before being focused to a spot size of ~1 μ m onto the sample via a 50x Mitutoyo infinity-corrected long working distance objective. The sample was mounted on a computer controlled XY-stage, and moved in a sawtooth pattern in steps of 1 μ m. A blue 3mW, 405 nm diode laser (power density of 27 W/cm²) used to generate photocurrent. Photocurrent was measured using a Stanford Research Systems SR830 lock-in amplifier referenced to the chopped laser.

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Figure S15a Current-density-voltage curves of P3HT-Zn₂(ZnTCPP)-PCBM devices.



Figure S15b- Current-density-voltage curves of P3HT-PCBM devices

Table S1 Device performance metrics corresponding to the different blend ratios and processing conditions used in this work for optimization. All the results shown here are averaged values of data obtained from a set of 35 devices each.

| | Active layer | J _{sc} | V _{oc} | FF | PCE | PCE (%) |
|-------------------------------------|-------------------------------|-----------------------|-----------------|------------|-----------|----------|
| | (P3HT:Zn ₂ ZnTCPP: | (mA/cm ²) | (V) | (%) | (%) | Champion |
| | PCBM) | | | | | device |
| Varying composition of active layer | | | | | | |
| а | 1:0:1 | 5.25±0.31 | 0.64±0.06 | 49.21±2.50 | 1.94±0.14 | 2.02 |
| b | 1:0.25:1 | 6.34±0.21 | 0.64±0.02 | 50.26±1.40 | 2.27±0.23 | 2.50 |
| С | 1:0.5:1 | 8.42±0.20 | 0.69±0.05 | 59.17±1.27 | 3.24±0.35 | 3.60 |
| d | 1:1:1 | 7.23±0.12 | 0.66±0.07 | 35.87±3.20 | 1.87±0.02 | 1.90 |
| Thermal annealing | | | | | | |
| e | 1:0:1 | 6.11±0.40 | 0.66±0.05 | 51.64±2.74 | 2.04±0.04 | 2.09 |
| f | 1:0.5:1 | 8.72±0.32 | 0.70±0.04 | 60.12±0.85 | 3.63±0.15 | 3.96 |
| Solvent vapour annealed | | | | | | |
| g | 1:0:1 | 6.50±0.23 | 0.65±0.03 | 53.21±1.70 | 2.25±0.23 | 2.46 |
| h | 1:0.5:1 | 9.51±0.31 | 0.70±0.05 | 62.70±0.72 | 4.06±0.10 | 4.21 |
| Solvent + thermal annealed | | | | | | |
| i | 1:0:1 | 7.09±0.15 | 0.66±0.02 | 57.44±2.20 | 2.67±0.01 | 2.67 |
| j | 1:0.5:1 | 10.54±0.2 | 0.70±0.03 | 63.12±0.15 | 4.65±0.30 | 5.20 |

7.6 Analysis of device data reported in literature.

Scifinder search yielded 65 literature results containing the search keywords "P3HT", "PCBM" and "BCP". Out of these reports, devices with plasmon modified hybrid systems, with <1% power conversion efficiencies or which were only reported as a patent were excluded. The remaining 38 device results from 18 papers are shown in figure S2 and used in for the statistical analysis given in Figure 3.

Table S2. The configuration and performance parameters of the devices used for statisticalanalysis in Figure 3

| Configuration | | Voc | FF | PCE |
|--|-------|-------|-------|------|
| P3HT-PC71BM/BCP/Al ² | 14.21 | 0.58 | 57.8 | 4.79 |
| P3HT-PCBM/BCP/Ag/Wox ³ | 6.33 | 0.54 | 60.2 | 2.07 |
| P3HT-PCBM/Yb/BCP/Ag/Wox ³ | 6.68 | 0.55 | 65.4 | 2.42 |
| P3HT-PCBM/BCP/AI ^₄ | 11.74 | 0.59 | 62.29 | 4.31 |
| | 9.76 | 0.63 | 60 | 3.72 |
| P3HT-PCBM/BCP/AI ^₅ | 9.55 | 0.65 | 57 | 3.52 |
| | 9.38 | 0.64 | 56 | 3.36 |
| | 10.02 | 0.64 | 41 | 2.61 |
| | 9.41 | 0.63 | 62.73 | 3.74 |
| | 10.22 | 0.64 | 63 | 4.11 |
| P3HT-PCBM-PMMA/BCP/Al ⁶ | 5.41 | 0.61 | 52.6 | 1.65 |
| | 4.18 | 0.61 | 45.5 | 1.16 |
| P3HT-PCBM/BCP/Al ⁶ | 4.35 | 0.59 | 52.2 | 1.34 |
| | 4.51 | 0.59 | 51.1 | 1.36 |
| P3HT-PCBM/BCP/AI ⁷ | 10 | 0.64 | 60 | 3 |
| P3HT-PCBM/BCP/Al ⁸ | 6.28 | 0.61 | 38 | 2.66 |
| P3HT-PCBM/BCP/LiF/Al ⁹ | 12.31 | 0.645 | 44.5 | 3.54 |
| P3HT-PCBM/MoO3/ ZnPc/C60/BCP/LiF- | 4.76 | 0.457 | 56.6 | 1.21 |
| Al ¹⁰ | 4.23 | 0.57 | 58.3 | 1.42 |
| | 5.68 | 0.48 | 56.0 | 1.53 |
| P3HT-PCBM/Ca-Al/Subpc/C60/BCP/Ag ¹¹ | 8 | 0.55 | 60 | 3.00 |
| P3HT-PCBM-BCP/LIF-Al ¹² | 8.88 | 0.59 | 39.1 | 2.05 |
| P3HT-PCBM/BCP/Al ¹³ | 9.64 | 0.63 | 61.2 | 3.72 |
| P3HT-PCBM/BCP/LiF/Al ¹⁴ | 10.83 | 0.56 | 65.2 | 3.74 |
| P3HT-PCBM/BCP/Ag ¹⁵ | 8 | 0.6 | 60 | 3.5 |
| P3HT-PCBM/BCP/Al ¹⁶ | 11.06 | 0.59 | 40 | 2.64 |
| P3HT-PCBM/BCP-LiQ ¹⁶ | 11.30 | 0.66 | 58 | 4.29 |
| ZnO/BCP/P3HT-PCBM/MoO3/Al ¹⁷ | 9.23 | 0.61 | 62 | 3.49 |
| | 8.53 | 0.50 | 35 | 1.50 |
| | 8.85 | 0.58 | 60 | 3.08 |
| | 8.68 | 0.59 | 55 | 2.82 |
| CsCl/BCP/P3HT-PCBM/MoO3/Al ¹⁸ | 9.43 | 0.59 | 54.1 | 3.00 |
| | 9.49 | 0.60 | 58.6 | 3.31 |
| BCP/P3HT-PCBM/MoO3/Al ¹⁸ | 9.24 | 0.53 | 50.1 | 2.50 |
| P3HT-PCBM/BCP/Al ¹⁹ | 4.51 | 0.65 | 42 | 1.24 |
| | 6.29 | 0.61 | 52 | 1.99 |
| P3HT-PCBM/BCP-LiF/Al ²⁰ | 4.58 | 0.66 | 41 | 1.25 |
| | 6.12 | 0.61 | 49 | 1.85 |



Figure S16. J-V curve of P3HT/TCPP-ligand/PCBM ternary device.

8. Transient absorption and Kinetics

We recorded transient absorption (TA) spectra for P3HT-PCBM and P3HT/Zn₂(ZnTCPP)/PCBM samples using broadband probe pulses spanning both NIR (850nm-1300nm) and UV-visible (350nm-750nm) regions (see methods). During the UV-visible measurement, both samples were observed to degrade slightly over the course of several sweeps. The data presented in this section is taken from the first sweep only. Note that Figure 5c in the main text displays data averaged over 5 sweeps, hence the signal magnitude is slightly weaker.

The following transient absorption features were observed and assigned by reference to previous reports:^{21–24}

- 1. Ground state bleach (GSB) at 470-530nm
- 2. Polaron pair photoinduced absorption (PIA) at 600-700nm (charge-pairs in P3HT or charge transfer states at theP3HT/PCBM interface)
- Polaron photoinduced absorption (PIA) at 900-1000nm (free charges in P3HT overlapped with the singlet PIA at times < 10ps)
- 4. Singlet exciton photoinduced absorption (PIA) 1000-1400nm (photogenerated singlet exciton in P3HT).

No obvious new TA features were observed when Zn₂(ZnTCPP) was added to the blend. However, the TA signal for the sample with Zn₂(ZnTCPP) added is roughly twice that of the sample without (Figure S17a-b). This gives evidence of enhanced light absorption in the blend with the nanosheets, corresponding to higher current density in the solar cell performance. Of all the TA features, the singlet PIA feature around 1300nm increased less than the other features when Zn₂(ZnTCPP) is added. Evaluation of kinetics of the P3HT-PCBM and P3HT-Zn₂(ZnTCPP)-PCBM blends show no real change in the excited state dynamics upon addition of Zn₂(ZnTCPP), at least on timescales ranging from 1ps to 1ns (Figure S18a). Addition of Zn₂(ZnTCPP) seems to cause a large relative increase (more than twofold) in the population of charges in P3HT (Figure S18b).



Figure S17. Transient absorption spectra of a. P3HT-PCBM film and b. P3HT-ZnTCPP-PCBM film.



Figure S18a: Comparison of kinetics of the blends (normalized). No significant change in the excited state dynamics is observed upon addition of Zn₂(ZnTCPP), at least on timescales ranging from 1ps to several ns.



Figure S18b: Dynamics of excitons and charges in P3HT-PCBM blends with and without addition of Zn₂(ZnTCPP). Here, the signal from PIA associated with charges (red and blue) has been normalised to the maximum (i.e. initial value) of the PIA associated with singlet excitons (black). It appears that the film with Zn₂(ZnTCPP) has a much higher population of charge pairs (red) as a proportion of the photoexcited singlet exciton population. However, this doesn't seem to be replicated for the free-charge population (blue).

Methods for TA studies: For transient absorption (TA) measurements, a Ti:sapphire regenerative amplifier (Spitfire ACE PA-40, Spectra-Physics) providing 800nm pulses (40fs FWHM, 10kHz, 1.2mJ) was used to generate both the pump and probe beams. Narrowband pump pulses at 500nm were generated in an optical parameteric amplifier (TOPAS Prime, Light Conversion). Probe pulses spanning the ranges 350-750nm and 850-1300nm were generated by focussing a portion of the 800nm beam through a continuously translating calcium fluoride or sapphire crystal, respectively. Pump-probe delay was controlled using a motorized linear stage. Detection was carried out using a commercial instrument (Helios, Ultrafast Systems) equipped with CMOS and InGaAs detectors for the UV-visible and NIR probe regions respectively. The pump and probe polarizations were set to magic angle. The pump beam spot size was measured at the sample position using a CCD beam profiler (Thorlabs). The pump pulse energy was approximately 130µJcm⁻². Data processing (background correction, correlated noise removal and chirp correction) were performed using a custom-made MATLAB programme.

9. SCLC devices for charge carrier mobility measurement

The investigation of space-charge limited electron-only or hole-only devices for extraction of mobility values is a well-known and reliable method. Space-charge limited currents were tested in hole only devices with the configuration ITO:PEDOT/PSS:active layer:MoO₃:Ag and a well-established protocol from literature was used for data fitting and analysis²⁵. The hole mobility was determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility based on Mott-Gurney law (Figure S19a-S22b, ESI). Electron only devices were fabricated with the configuration ITO:ZnO:Active layer:BCP:Ag to extract the electron mobility.

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Table S3 Hole mobility and electron mobility extracted from SCLC holes only and electrons only

 devices for different thicknesses of active layer; Number of devices tested for each thickness=3.

| Device | Active layer | μ_h | μ _e |
|------------------------------------|--------------|------------------------------|------------------------------|
| configuration | (nm) | (cm²/Vs) | (cm²/Vs) |
| РЗНТ-РСВМ | 100 | (6.06±0.50)x10 ⁻⁴ | (3.77±0.71)x10 ⁻³ |
| | 150 | (1.13±0.17)×10 ⁻⁴ | (1.35±0.07)x10 ⁻³ |
| | | | |
| P3HT-Zn ₂ (ZnTCPP)-PCBM | 100 | (3.20±0.48)x10 ⁻³ | (2.14±0.46)x10 ⁻³ |
| | 150 | (2.12±0.34)x10 ⁻³ | (2.13±0.14)x10 ⁻³ |
| | | | |

Figure S19(a)-S22(b): The J–V characteristics of electron and hole only devices in different structures and active layer thickness. The bias is corrected for built-in voltage , arising from difference in the work function of the contacts, and the voltage drop due to substrate series resistance.





Good fit at this electric field



Good fit at this electric field











The devices were prepared following the same procedure described in the experimental section for photovoltaic devices, except that of the metal electrode. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility²⁵, which is described as

J= [(9 $\varepsilon_r \varepsilon_0 \mu_0 V^2)/8L^3$] exp($\beta \sqrt{V}/L$)

Where, J is the current, μ_0 is the zero-field mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, V is the effective voltage, and L is the thickness of the active layer.

10. GI-WAXS

The GIWAXS thin film measurements were performed with a Xeuss 2.0 system (Xenons, France). The Sheffield machine is fitted with a MetalJet (Excillum, Sweden) liquid gallium X-ray source, providing a 9.24 keV X-ray beam collimated to a beam spot of 400 µm laterally at the sample position, measuring the full sample length. X-ray diffraction patterns were acquired with a Pilatus3R 1M 2D detector (Dectris, Switzerland). The sample to detector distance was calibrated using a silver behenate calibrant standard in transmission geometry. Samples were measured in GI-WAXS geometry near the critical angle (calculated to probe the entire film thickness) and under vacuum atmosphere to minimise the background scatter.



Figure S23. GI-WAXS 2-D detector images of a. Pristine P3HT film; b. P3HT-ZnTCPP blend film. The corresponding 1-D cross sections are shown in Figure 4.



Figure S24. GI-WAXS 2-D detector images of a. Thermal annealed, b. Solvent annealed, and c. Solvent+thermal annealed P3HT-Zn₂(ZnTCPP)-PCBM device active layers.

Table S4. Scherrer analysis and calculation of crystallite sizes from the 100 and 010 P3HTpeaks.

| Sample | B _f ^{hkl} | D, nm | |
|------------------------------------|-------------------------------|--------------------------------|------------|
| | 100, 2θ ₁₀₀ = 5.4° | 010, 20 ₁₀₀ = 24.0° | |
| | | | |
| РЗНТ | 0.012 | 0.013 | 10.96± 0.7 |
| P3HT-Zn ₂ (ZnTCPP) | 0.013 | 0.014 | 11.39±0.8 |
| P3HT-Zn ₂ (ZnTCPP)-PCBM | 0.011 | 0.012 | 13.59±0.7 |

11. AFM – Morphological investigation of the device active layers

11.1 P3HT-Zn₂(ZnTCPP)-PCBM active layers and the corresponding Fourier transformations used to extract the domain length scale



Figure S25. Investigation of changes in the morphology of the device active layer during the different annealing procedures followed for performance optimisation: a. P3HT-Zn₂(ZnTCPP)-PCBM film: thermal annealed at 120°C for 10 minutes; b: solvent vapour annealed in a column saturated with chlorobenzene vapour at 120°C for 5 minutes; c: solvent annealed like in (b) for 10 minutes followed by thermal annealing at 120°C for 5 minutes;

11.2 P3HT-PCBM active layers and the corresponding Fourier transformations used to extract the domain length scale



Figure S26. Investigation of changes in the morphology of the device active layer during the different annealing procedures followed for performance optimisation: a. P3HT-PCBM film: thermal annealed at 120°C for 10 minutes; b: solvent vapour annealed in a column saturated with chlorobenzene vapour at 120°C for 5 minutes; c: solvent annealed like in (b) for 10 minutes followed by thermal annealing at 120°C for 5 minutes;

12. Spectroscopic ellipsometry

For fitting of the data, J. A. Woollam WVASE32 Software was used. During the fitting, reasonable boundaries were set for model parameters to restrict them to physically meaningful values. Fitting in the range of 700–900 nm was performed first using a Cauchy model and the thickness value determined by a step-profiler as the initial guess to obtain a good estimate of film thickness. Then, a B-spline model incorporating a Kramers Kronig model was used to fit the *n* and *k* were fitted in the desired wavelength range with the thickness fixed. Finally, both thickness and optical functions were allowed to vary in the last fitting run to verify that a reasonable solution has been obtained.



Figure S27. The extinction coefficient spectra and wavelength dependant refractive index plots of P3HT and P3HT-Zn₂(ZnTCPP) extracted using spectroscopic ellipsometry;



Figure S28. The optical properties of the device active layer as a function of annealing conditions extracted using spectroscopic ellipsometry

13. References

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