

Supporting Information

One Step Facile Synthesis of Novel Anthanthrone Dye Based, Dopant-Free Hole Transporting Material for Efficient and Stable Perovskite Solar Cells

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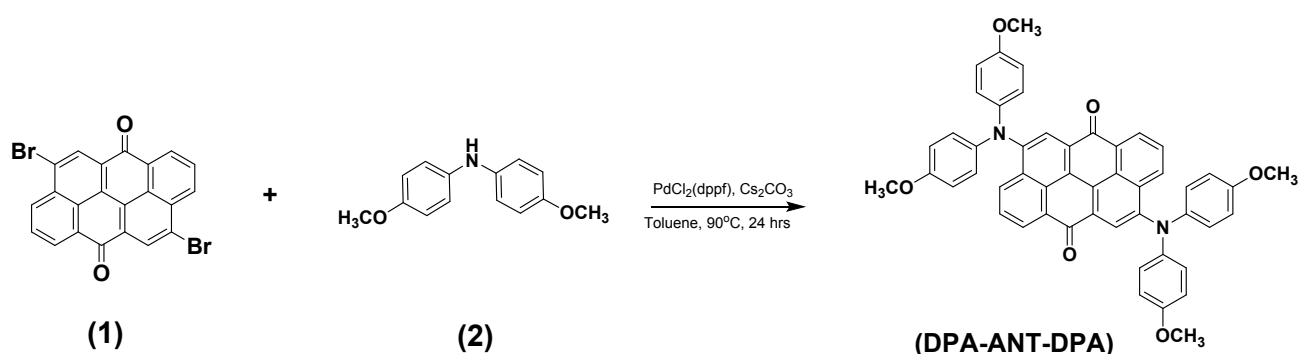
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Experimental details

1. Materials and instruments

All chemicals and reagents were purchased from commercial vendors and used directly without any further purification. Synthesized compounds were characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy using Bruker 600 MHz spectrometer. High-resolution mass spectra were acquired on an LTQ Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with an electrospray ionisation (ESI) source, operating in the positive ion mode at a resolution of 120,000 (at m/z 400). Reserpine ($[\text{M}+\text{H}]^+$, m/z 609.28066) was used as a lock mass calibrant to increase the measurement accuracy. Thermal analysis was performed using a Pegasus Q500TGA thermogravimetric analyzer under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) was conducted under nitrogen using a Chimaera instrument Q100 DSC. The sample was heated at $10\text{ }^\circ\text{C}/\text{min}$ from $30\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$. Absorption spectra were recorded on a Shimadzu UV-1800 spectrometer. Photoelectron spectroscopy in air (PESA) measurements were conducted using on an AC-2 photoelectron spectrometer (Riken-Keiki Co.). The cyclic voltammetry (CV) was performed by a Potentiostat Galvanostat with a three electrode cell in a solution of Bu_4NPF_6 (0.1M) in freshly distilled DCM at a scan rate of 100 mV/s . The counter electrode was a Pt wire, the working electrode was glassy carbon and a Ag/Ag^+ electrode was used as the reference electrode.

2. Synthesis



Scheme S1. The synthetic route of DPA-ANT-DPA.

Synthesis of 4,10-bis(bis(4-methoxyphenyl)amino)naphtho[7,8,1,2,3-nopqr]tetraphene-6,12-dione (DPA-ANT-DPA)

A mixture of compound 1 (1 g, 2.16 mmol), PdCl₂(dppf) (150 mg, 0.21 mmol), Cs₂CO₃ (2.5 g, 7.67 mmol), and compound 2 (1.5 g, 6.55 mmol) was added into a flask and degassed by argon for 30 min. Then dry toluene (50 mL) was added. After doing vacuum and degas for 30 min, it was stirred at 90 °C for 24 hours under the flow of argon. The cooled mixture was extracted by using CH₂Cl₂ and filtered on a silica gel column (Hexane as the eluent). The crude product was recrystallized by using hot MeOH to obtain product as a green solid (1.35 g, 80%).

¹H NMR (600 MHz, CDCl₃): δ 8.56 (d, *J* = 7.2 Hz, 2H), 8.31 (d, *J* = 7.8 Hz, 2H), 8.00 (s, 2H), 7.55 (t, 2H), 6.93 (d, *J* = 6.6 Hz, 8H), 6.74 (d, *J* = 9 Hz, 8H), 3.72 (s, 12H). ¹³C NMR (120 MHz, CDCl₃): δ 183.35, 169.19, 155.67, 142.67, 132.61, 131.65, 130.71, 130.38, 129.95, 129.53, 128.29, 124.89, 124.50, 114.86, 55.52. ESI-MS: C₅₀H₃₆N₂O₆⁺⁺ *m/z* 760.50 (calculated *m/z* 760.26).

3. Fabrication of Organic Thin Film Transistor (OFET) Devices:

3.1. Device Fabrication

Bottom-gate top-contact organic thin-film transistors were fabricated as follows. Glass substrates (700 μm thick) were cleaned in an ultrasonic bath with ultra-pure water, acetone, and 2-propanol, sequentially. Gold gate electrodes (50 nm thick) were deposited in vacuum through a metal shadow mask. Then, a polymer dielectric layer of parylene (diX-SR, 315 nm thick) was deposited by vapour polymerization. DPA-ANT-DPA was dissolved in toluene and chlorobenzene, respectively, at a same concentration of 0.1 wt%. The semiconductor layer of each ink was fabricated by edge cast method.¹ Finally, Gold source and drain electrodes (50 nm thick) were deposited in vacuum through a metal shadow mask.

3.2. Device Characterization

Fig. S6(a) shows the optical microscope images of the DPA-ANT-DPA film. Small semiconductor crystals in sizes between a few and a hundred micrometers were grown on the substrates. Since semiconductor film did not completely cover the channel area because of the low concentration of the solution, the effective channel width is smaller than the nominal channel length of 1400 μm. The transfer characteristics of the DPA-ANT-DPA thin-film transistors are displayed in Fig. S6(b). DPA-ANT-DPA exhibited p-type transistor characteristics in air. The field-effect mobility and threshold voltage in the saturation regime were estimated at 2.6×10^{-4} cm²/Vs and -49 V, calculated with the nominal channel width of 1400 μm. The high threshold voltage is most probably due to the deep HOMO level of the semiconductor material.

4. Perovskite Solar Cell Fabrication

4.1. Substrates Preparation: A patterned FTO-coated glass ($13 \Omega \text{ sq}^{-1}$, Aldrich) was etched by Zn powder and 2 M HCl diluted in deionized water. Subsequently, the substrates were cleaned with detergent diluted in deionized water, rinsed with deionized water, acetone and ethanol, and dried with clean dry air. A compact blocking layer of TiO_2 (40 nm, c- TiO_2) was deposited on the fluorine doped SnO_2 (FTO, Pilkington, TEC8) substrate by spray pyrolysis using a 20 mM titanium di-isopropoxide bis(acetylacetonate) solution (Aldrich) at 500°C for 30 minutes.² To deposit the mesoporous TiO_2 layer, Dyesol DSL 30 NR-D paste is dissolved in anhydrous isopropanol and kept for sonication for 1 hours. Once the solution is homogeneous it is ready to deposit on FTO/Compact TiO_2 substrate by spin coating at 3000 rpm for 30 second followed by annealing at 550°C estimated to give ~ 400 nm thick layer.³

4.2. Fabrication of Perovskite Solar Cell Devices: The PSCs were prepared by one step spin coating of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution. The solution was prepared in DMF/DMSO = 6:4 by mixing $\text{CH}_3\text{NH}_3\text{I}$ (0.199 gm) and PbI_2 (0.600 gm). The solution was heated at 60°C for 3 hours for mixing. Then the solution was spin coated using Chlorobenzene as antisolvent at rpm of 4000 for 30 s, and annealed for 30 minutes at 100°C on a hotplate. The absorber perovskite material with electrode (FTO/Compact- TiO_2 /Mesoporous TiO_2) is ready after the above annealing procedure. The electrodes with the absorber material were allowed to cool down to room temperature. A solution containing 2-7,7-tetrakis(N,N-di-*p*-methoxyphenylamine)-9,9-17-spirobifluorene (Spiro-OMe-TAD) in chlorobenzene and additives ($10 \mu\text{l ml}^{-1}$ tBP, $32 \mu\text{l ml}^{-1}$ Li-TFSI solution: 600 Mm in acetonitrile) was spin coated onto the perovskite film at 5000 rpm, for 30 second. Finally, 80 nm thick silver contacts were evaporated at 10^{-4} torr.

Similarly, DPA-ANT-DPA were dissolved in 60 mg in 1 ml chlorobenzene and kept for sonication for 30 minutes. The solution was filtered (0.45 μ) before use and spin coated on top of perovskite absorber at 5000 rpm for 30 seconds.

4.3. Power Conversion Efficiency and Incident Photon to Current Conversion Efficiency (IPCE) or External quantum efficiency (EQE) : Masked devices (0.100 cm^2) were tested under a class AAA solar simulator (Newport Oriel Sol3A) at AM1.5 and 100 mW cm^{-2} illumination conditions calibrated against a KG5 filtered silicon reference cell (Newport Oriel 91150-KG5) using a Keithley 2400 source meter. Current–voltage sweeps were performed from forward-to-reverse bias at a rate of 0.1 V s^{-1} .

4.4. Stability Measurements: Stability tests on optimized champion devices without encapsulation for different hole transporting material were performed. The solar cells were kept in relative humidity of >57% at room temperature in the dark, where the humidity level is constantly maintained throughout the measurements. The simple setup is shown in Fig. S8.

5. Perovskite Solar Cell Characterisation:

5.1. Scanning Electron Microscopy (SEM): Scanning electron microscopy images of films were collected using a Jeol JSM-7800F field emission gun electron microscope with a 5 kV beam, 9 μ A at approximately 10 mm working distance.

5.2. Photoluminescence Measurements: Steady state emission measurements were done on the Horiba Fluoromax-4 spectrofluorometer equipped with double-grating at the excitation wavelength of 550 nm on the 3-layer assembly Glass/CH₃NH₃PbI₃/HTM with different HTMs (DPA-ANT-DPA, and Spiro-OMeTAD). Front face illumination with respect to the incident beam was used to minimize the inner filter effects.

5.3. Contact Angle Measurements: Contact angle measurements were performed using a simple home built instrument. High resolution images of water droplets on the surface of hole transport layers deposited on the perovskite sample were collected using Nikon DSL90 camera.

5.4. Time Correlated Single Photon Counting (TCSPC)

Time Correlated Single Photon Counting measurements were performed on Horiba Jobin Yvon Fluorolog system. Steady state photoluminescence measurements were done on perovskite and hole transport layers with < 200 ps pulses of 635 nm excitation from a picosecond diode laser (NanoLED source). The laser pulse excitation density was 2.3×10^{14} cm⁻³, Rep.rate:1MHz. Measurements were done in reverse mode at 1 MHz rep. rate. A cutoff filter (OG575) was used to block the stray excitation light. To increase the sensitivity of measurements, all wavelengths transmitted by cutoff filter were collected without the use of any monochromator.

5.5 Hole Transport Measurements: Space Charge Limited Current (SCLC) Method

PEDOT: PSS (Poly(3,4-ethylenedioxythiophene)–poly (styrene sulfonate)) was spin-coated onto indium tin oxide substrate (ITO) and dried at 130 °C for 20 minutes in vacuum. The purpose of PEDOT: PSS layer (40 nm) was to reduce the roughness of ITO as well as to improve the work function, achieving enhanced hole-only device properties. The HTMs were spin coated onto PEDOT: PSS from chloroform solution (30 mg/mL) in a nitrogen atmosphere. Finally, Au contacts (400 nm thick) were applied via thermal evaporation through a shadow mask in 2

$\times 10^{-6}$ Torr vacuum. The work function of Au and ITO are close to the HOMO energy level of the HTM as well as far below the LUMO energy level. Therefore, the electron injection barrier is higher than the corresponding hole injection barrier. As a result, the transport is dominated by holes. The J–V characteristics of the sample was measured with a Keithley 2420 source meter unit at room temperature. The device configuration and equations to extract mobility has been reported by us previously.³

6. Supporting Figures:

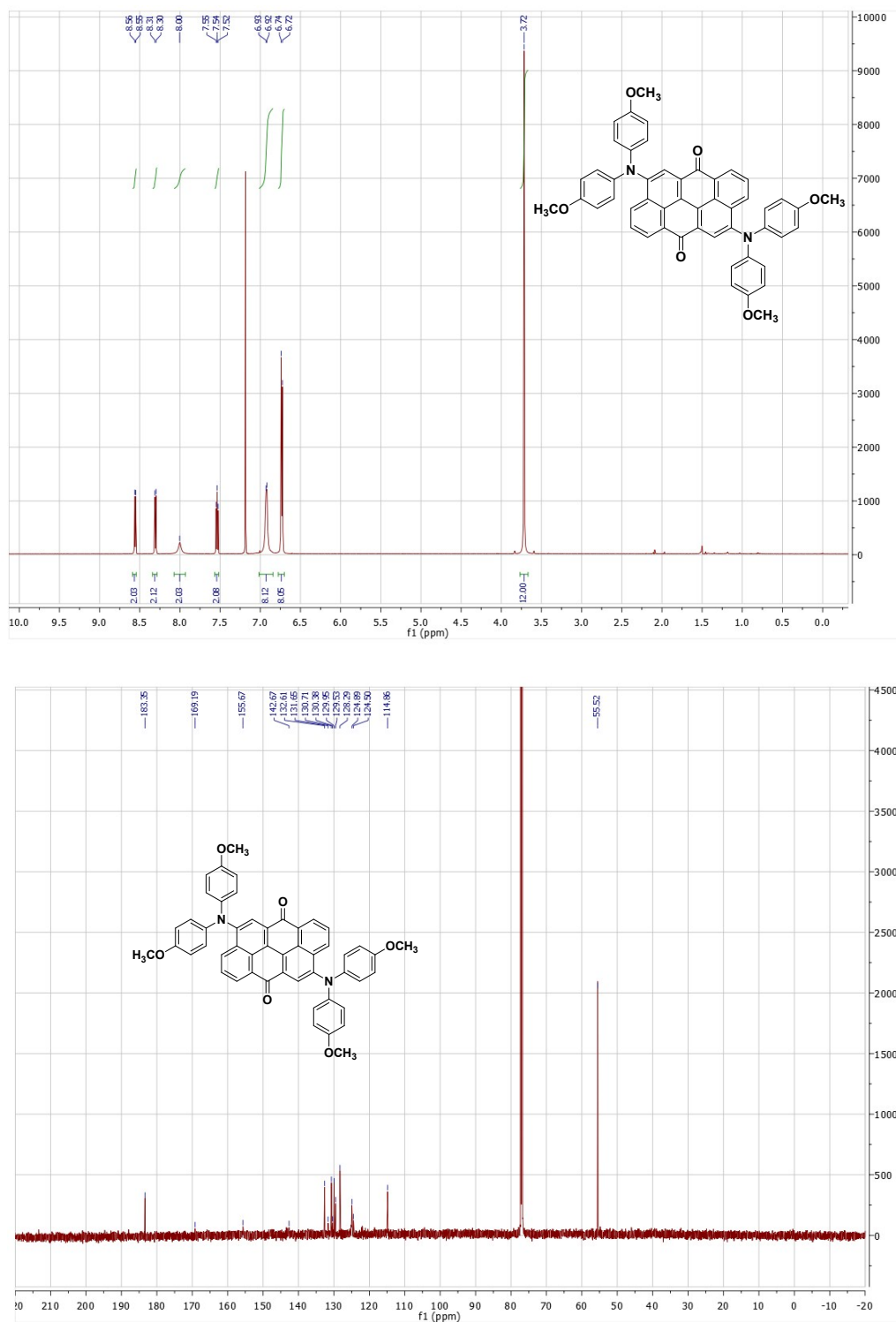


Fig. S

Fig. S1 ¹H and ¹³C NMR (CDCl₃) spectrum of DPA-ANT-DPA.

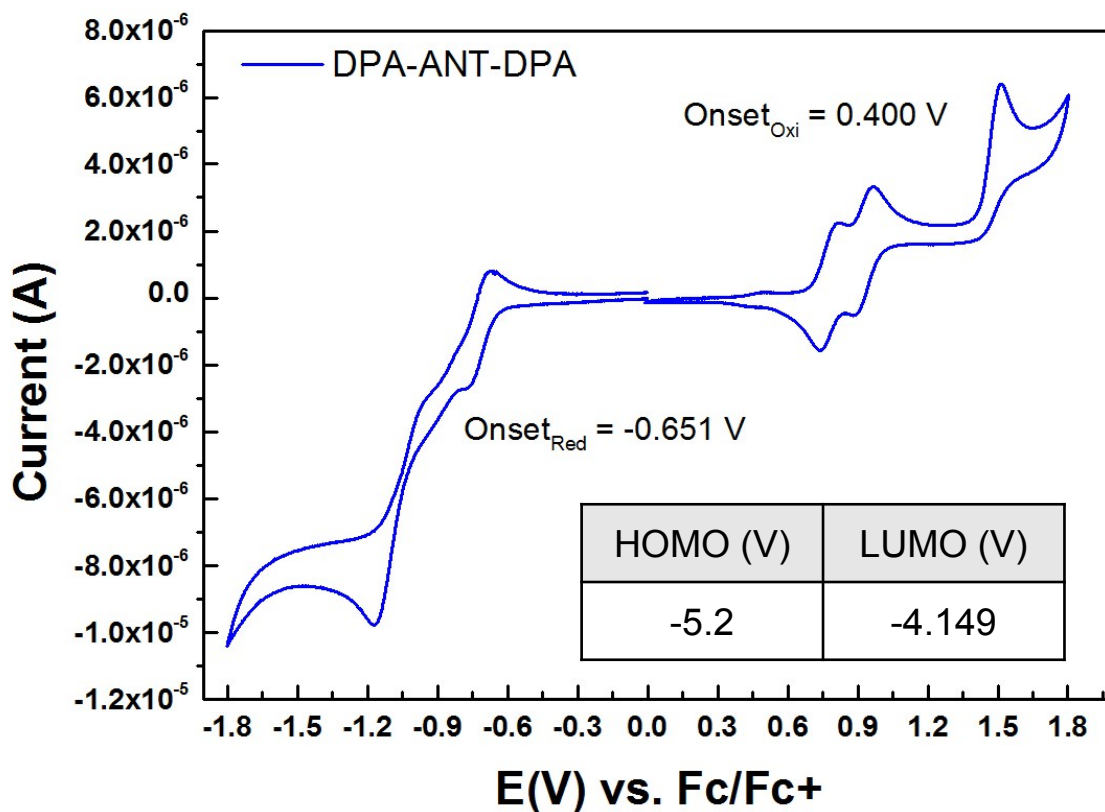


Fig. S2 Cyclic voltammograms of DPA-ANT-DPA. The oxidation and reduction were measured in DCM/0.1M Bu₄NPF₆ at a scan rate of 100 mV/s.

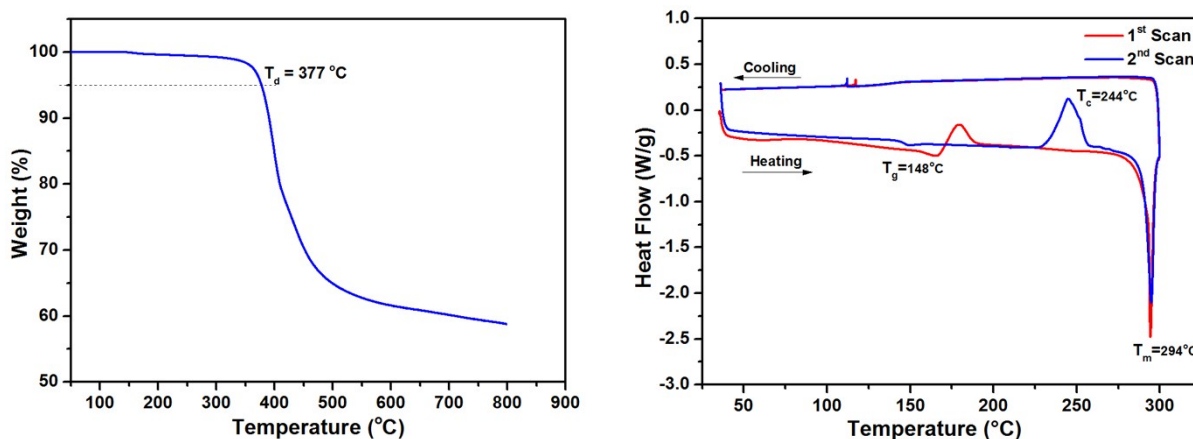


Fig. S3 (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) curve of DPA-ANT-DPA.



Fig. S4 Crystallization test of DPA-ANT-DPA. The sample is prepared by dropping the chloroform solution into the glass tube and then observed the formation of crystal needles during the solvent drying process.

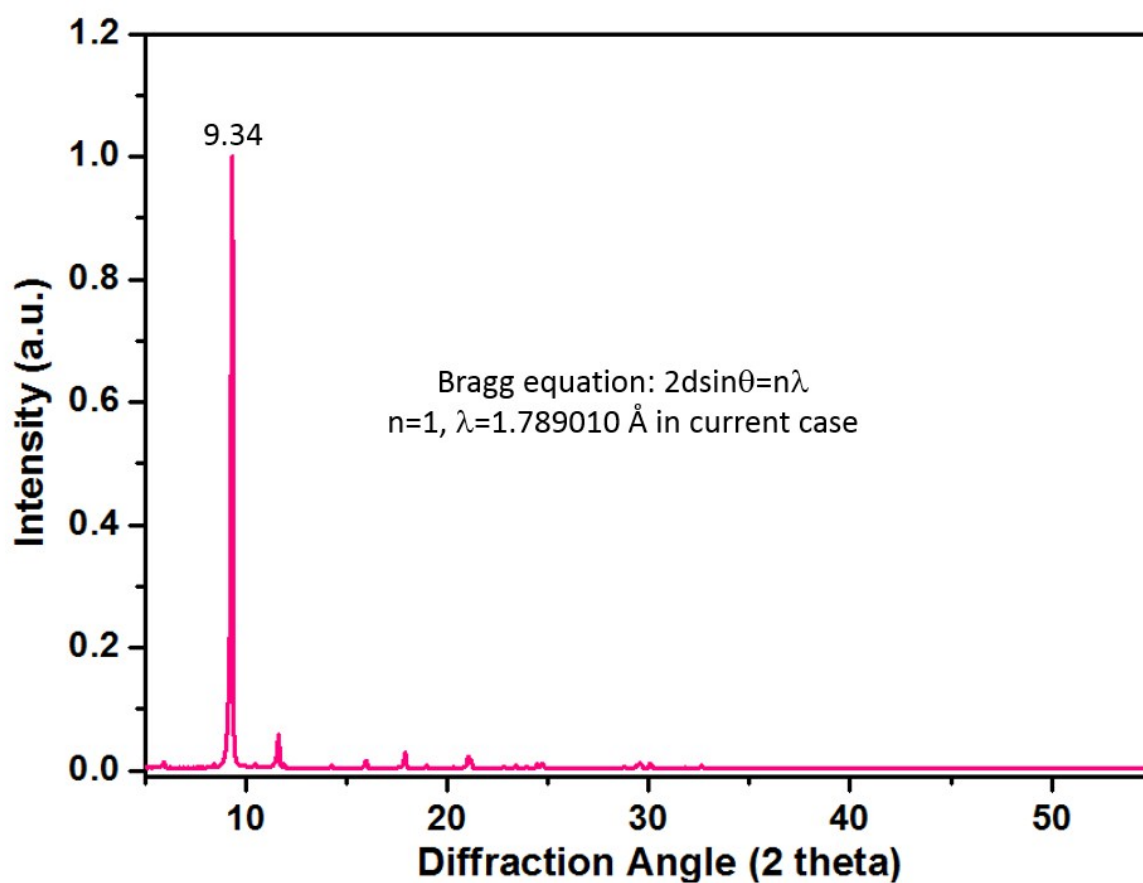


Fig. S5 XRD pattern of DPA-ANT-DPA.

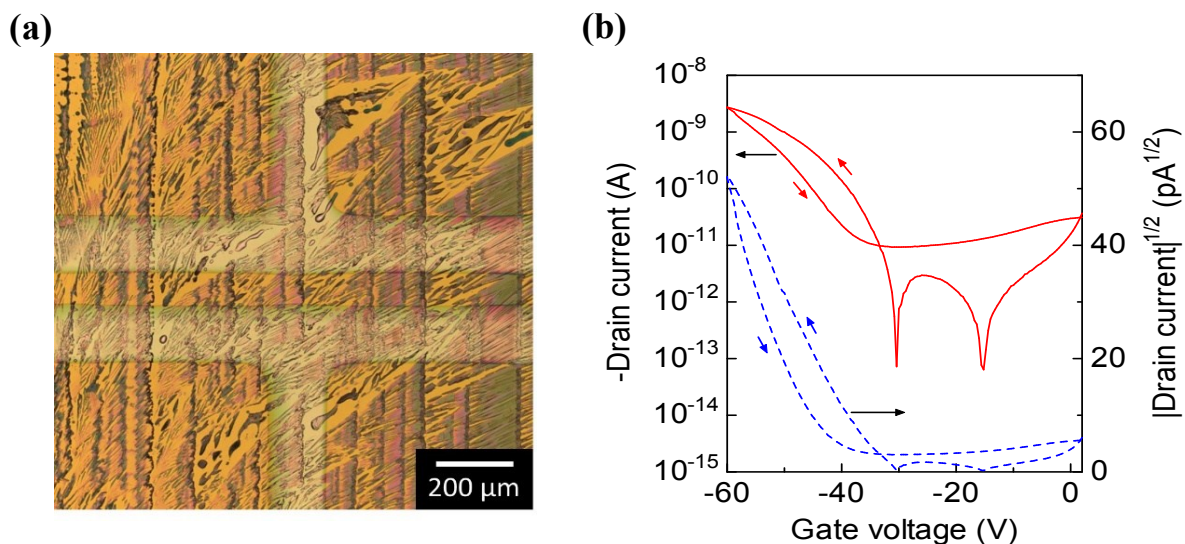


Fig. S6 (a) Optical microscope images of the DPA-ANT-DPA film with gold source and drain electrodes; (b) Transfer characteristics of DPA-ANT-DPA thin-film transistors at a drain voltage of -60 V. Channel length and width were 90 μm and 1400 μm , respectively.

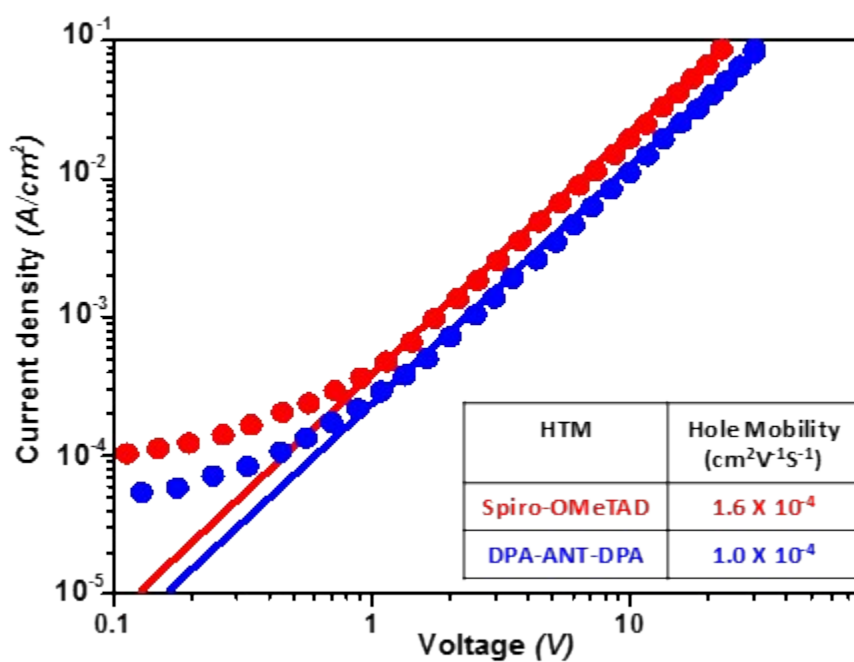


Fig. S7 J-V data for space charge limited current (SCLC) method of hole-mobility determination. The resulting mobilities of DPA-ANT-DPA (blue line) and Spiro-OMeTAD (red line) were found 1×10^{-4} and $1.6 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively.

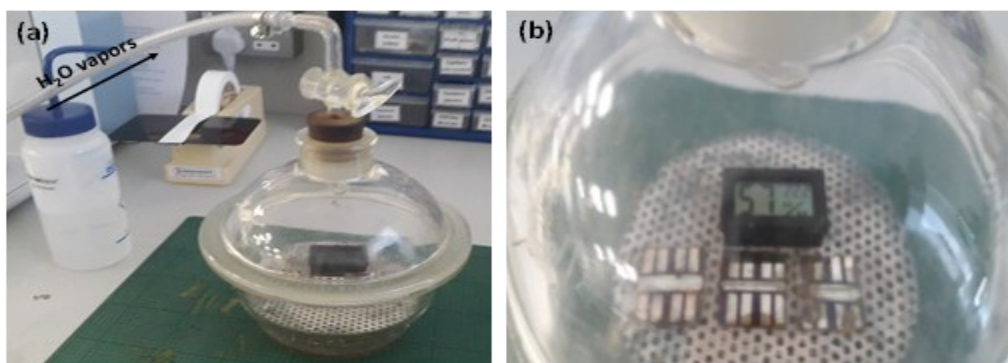


Fig. S8 (a) and (b) Simple stability measurement setup in a humidified desiccator for aging of PSCs at constant 57% relative humidity (RH) maintained during the measurement.

References

1. T. Uemura, Y. Hirose, M. Uno, K. Takimiya and J. Takeya, *Appl. Phys. Express*, 2009, **2**.
2. S. M. Jain, Z. Qiu, L. Häggman, M. Mirmohades, M. B. Johansson, T. Edvinsson and G. Boschloo, *Energy Environ. Sci.*, 2016, **9**, 3770-3782.
3. S. M. Jain, B. Philippe, E. M. J. Johansson, B.-w. Park, H. Rensmo, T. Edvinsson and G. Boschloo, *J. Mater. Chem. A*, 2016, **4**, 2630-2642.