**Supporting information: High Mobility, Hole Transport Materials for Highly Efficient PEDOT:PSS Replacement in Inverted Perovskite Solar Cells**

Materials. All reagents from commercial sources were used without further purification. Solvents were dried and purified using standard techniques. Compounds were characterized by ^{1}H NMR (400MHz), ^{13}C NMR (101MHz) on a Bruker Avance III Ultrashield 600 Plus instrument and at room temperature. High-resolution mass spectrometry (HRMS) data was recorded using a Thermo Scientific – LTQ Velos Orbitrap MS in positive atmospheric pressure photoionisation (+APPI) mode. Thermogravimetric analysis (TGA) was performed using Bruker TGA-IR TG209F1 using 10°C/min scanning rate. Differential Scanning Calorimetry (DSC) was performed on DSC-204F1 using 10°C/min scanning rate.
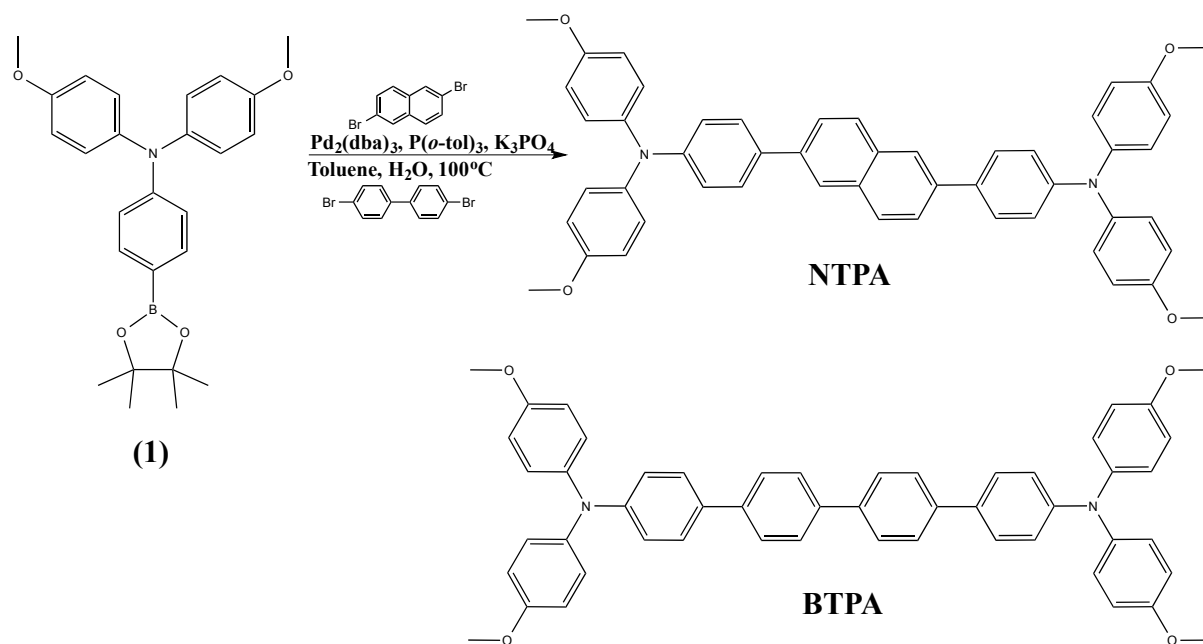
Scheme 1. Synthesis of NTPA and BTPA.

The synthesis of 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1) was conducted according to a modified literature procedure[1] where the crude product was recrystallized from ethanol to afford the product as a white solid. Yield (1.06g, 64%).

4,4'-(Naphthalene-2,6-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) (NTPA). Compound (1) (0.33g, 0.77mmol), 2,6-dibromonaphthalene (0.11g, 0.35mmol), Pd$_2$(dba)$_3$ (0.014g, 0.015mmol) and tri(*o*-tolyl)phosphine (0.013g, 0.042mmol)

were dissolved in degassed toluene. To this an aqueous solution of K_3PO_4 (0.37g, 1.75mmol) was added and the mixture stirred at 100°C overnight. The reaction mixture was dried with anhydrous sodium sulfate, filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with hexane:dichloromethane (3:1) as eluent. The product was washed with methanol, resulting in a yellow solid. Yield: 0.20g (78%)

¹H NMR (400MHz, d6-acetone) δ = 8.18 - 8.09 (m, 2H, ArH), 8.05 - 7.96 (m, 2H, ArH), 7.90 - 7.78 (m, 2H, ArH), 7.72 - 7.65 (m, 4H, ArH), 7.18 - 7.08 (m, 8H, ArH), 7.01 - 6.93 (m, 12H, ArH), 3.82 (s, 12H, OCH_3).

¹³C NMR (101MHz, CD_2Cl_2) δ = 156.1, 148.3, 140.7, 137.7, 132.6, 132.4, 128.4, 127.5, 126.7, 125.4, 124.1, 120.5, 114.7, 55.4

HMRS: found: 735.3196, calcd. for $C_{50}H_{42}N_2O_4$ ([M+H]$^+$): 735.9079.

$N^4,N^4,N^{4'''},N^{4'''}$-tetrakis(4-methoxyphenyl)-[1,1':4',1'':4'',1'''-quaterphenyl]-4,4'''-diamine (BTPA).

Compound (1) (0.50g, 1.16mmol), 4,4'-dibromo-1,1'-biphenyl (0.14g, 0.46mmol), $Pd_2(dba)_3$ (0.04g, 0.02mmol) and tri(o-tolyl)phosphine (0.017g, 0.06mmol) were dissolved in degassed toluene (6ml). To this an aqueous solution of K_3PO_4 (0.59g, 2.76mmol) was added and the mixture stirred at 100°C overnight. The reaction mixture was dried with anhydrous sodium sulfate, filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with hexane:ethyl acetate (10:1) as eluent. The product was subsequently recrystallized from ethanol, resulting in a yellow solid. Yield: 0.17g (48%)

¹H NMR (400MHz , d6-acetone) δ = 7.80 - 7.68 (m, 8 H, ArH), 7.60 - 7.53 (m, 4 H, ArH), 7.14 - 7.05 (m, 8 H, ArH), 6.93 (d, J = 8.8 Hz, 12 H, ArH), 3.80 (s, 12 H, OCH_3).

¹³C NMR (101MHz, CD_2Cl_2) δ = 156.1, 148.4, 140.7, 139.5, 138.6, 132.1, 127.2, 127.1, 126.7, 126.6, 120.4, 114.7, 55.4

HMRS: found: 761.3355, calcd. for $C_{52}H_{44}N_2O_4$ ([M+H]$^+$): 761.9379.

1. Yu, L.; Xi, J.; Chan, H. T.; Su, T.; Antrobus, L. J.; Tong, B.; Dong, Y.; Chan, W. K.; Phillips, D. L., Novel Organic D-π-2A Sensitizer for Dye Sensitized Solar Cells and Its Electron Transfer Kinetics on TiO2 Surface. *The Journal of Physical Chemistry C* **2013,** *117* (5), 2041-2052.

Device fabrication

Patterned indium doped tin oxide (ITO) coated glass substrates (15 Ω cm^{-1}) were cleaned in an ultrasonic bath with acetone and isopropanol consecutively. Subsequently these substrates were dried with pressurised pure N_2 gas and treated in UV-Ozone plasma for 20 min. HTMs (10 mg/mL in 1:1 chlorobenzene (CB):ortho-dichlorobenzene (o-DCB)) were spin coated between 1000 rpm and 5000 rpm for 30 seconds and annealed at temperatures between 80˚C and 160˚C for times ranging between 0 and 20 min.

A $CH_3NH_3PbI_3$ perovskite solution was made at a concentration of 620 mg/mL; synthesis was carried out by mixing 1:1 equimolar ratios of methyl-ammonium iodide (CH_3NH_3I) purchased from DyeSol and lead (II) iodide (PbI_2) purchased from Alfa Aesar, in γ-butyrolactone and dimethyl sulphoxide (DMSO) in 6:4 ratio at 60˚C, the solution was left to stir until fully dissolved. The perovskite layer was spin coated at 1000 rpm for 10 seconds followed by 4000 rpm for 40 seconds with CB addition to induce fast crystallisation. The substrate was subsequently left to dry in a N_2 environment for 1 hour before annealing at 80˚C for 10 minutes. After annealing deposition of the $PC_{70}BM$ ([6,6]-Phenyl-C71-butyric acid methyl ester) (16 mg/mL in CB) occurred, spin coating was carried out at spin speeds varying from 1200 rpm to 2250 rpm. Devices were further annealed for 2 minutes.

Subsequently 100nm of silver were thermally evaporated onto the substrates under 1x10^{-6} Torr vacuum pressure. An active area of 10mm^2 was determined by a shadow mask under evaporation conditions.

J/V device characterisation of the solar cells was preformed using a solar simulator with Xenon lamp (Oriel Instruments) calibrated to 100mW/cm^2, AM1.5G, with KG-5 silicon reference cell in a N_2 environment with computerised Keithley 2400 SourceMeter. External quantum efficiency (EQE) was performed by illumination of the device with Xenon arc lamp; providing monochromatic light when in combination with a dual-grating monochromator. The incident photon number was calibrated using silicon photodiode by NIST across each wavelength.

Film Characterisation

Absorption:

UV-Vis absorption spectra were obtained using a Varian Cary 5000. Photo-Electron Spectroscopy in Air (PESA) measurements were carried out at room temperature using a Riken Instruments AC-2 model to determine the ionisation potential of the HTMs. Scanning electron microscopy (SEM) images were taken at 5 V accelerating voltage and beam aperture of 30 μm, using a Zeiss Auriga microscope equipped with an in-lens detector.

Space Charge Limited Current:

In order to determine charge carrier mobility for the NTPA and BTPA, hole-only devices were fabricated with structure ITO/HTL/MoOx/Ag. Solutions of HTM were prepared in 1:1 ratios of CB:*o*-DCB at concentrations of 10 mg/mL and heated to 70˚C. The solutions were spin coated at varying spin speeds from 1000-5000 rpm. 8 nm of molybdenum oxide was thermally evaporated as an electron blocking layer, with a further 100 nm of silver subsequently evaporated as a cathode at 1×10^{-6} Torr vacuum pressure. An active area of 10mm^2 was determined by a shadow mask under evaporation conditions.

Hole mobilities were extracted using the modified Mott-Gurney equation below:

$$J_{SCLC} = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V_{in}^2}{L^3}e^{\left(\frac{0.89\beta}{\sqrt{L}}\sqrt{V_{in}}\right)}$$

where J_{SCLC} is the measured current density, ε_0 and ε_r are defined as the vacuum permittivity and material dielectric constant respectively, L is the film thickness, μ the hole mobility, and β is the field activation parameter.
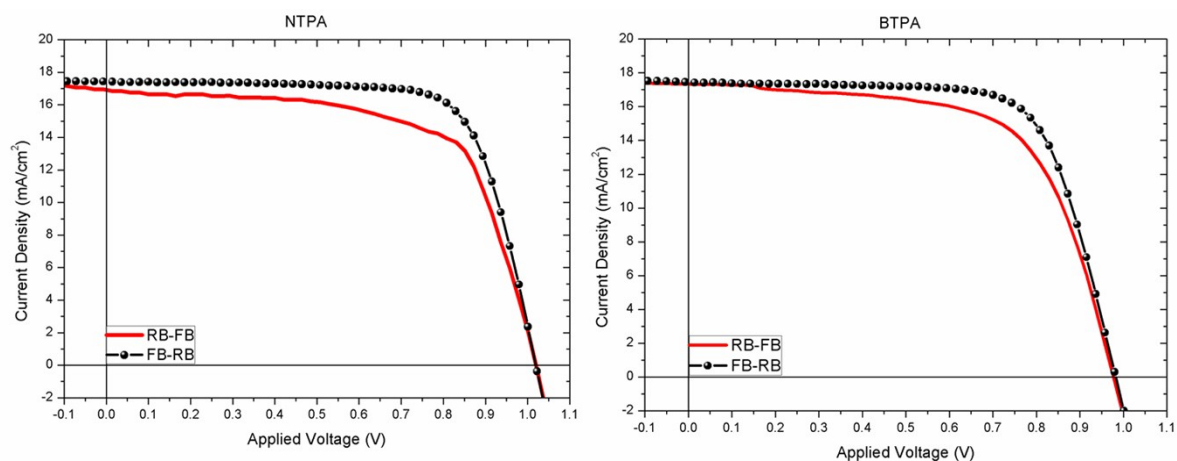
Hysteresis

Figure S1: J/V characteristics of perovskite devices with NTPA and BTPA measured in both Reverse-Forward Bias (RB-FB) and Forward-Reverse (FB-RB).
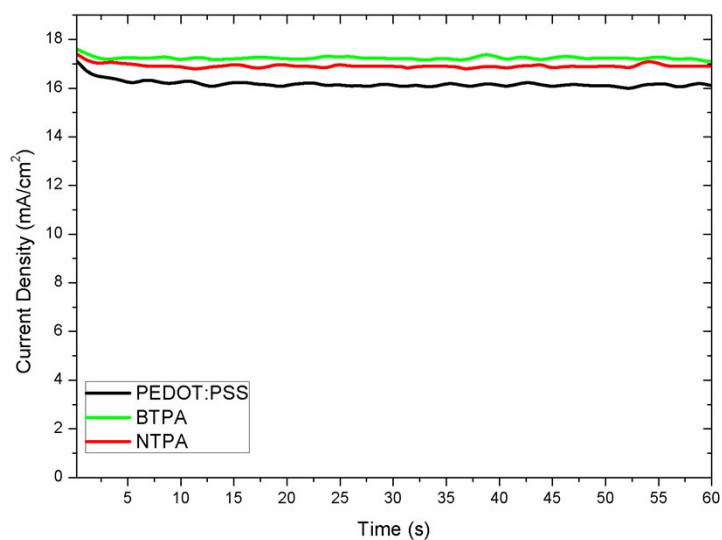
Device statistics

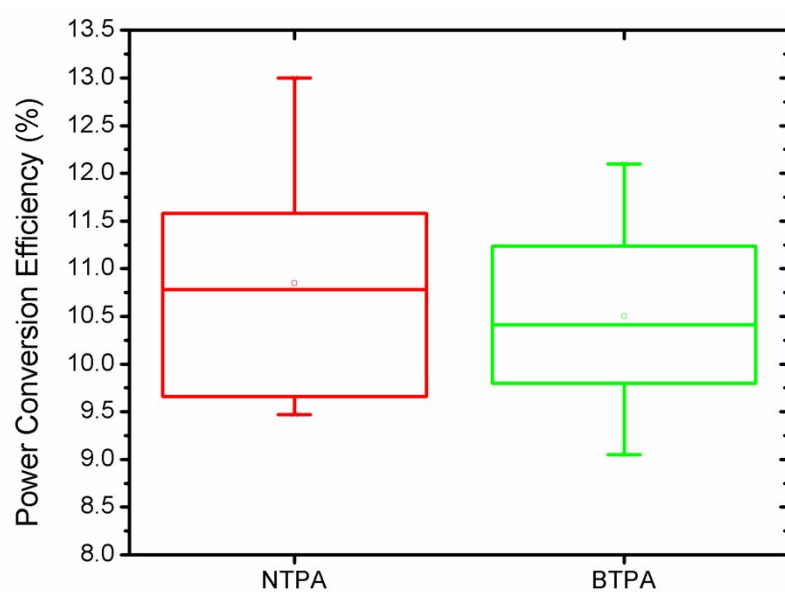Figure S2: Current stability over time at Maximum Power Point (M_{PP}).
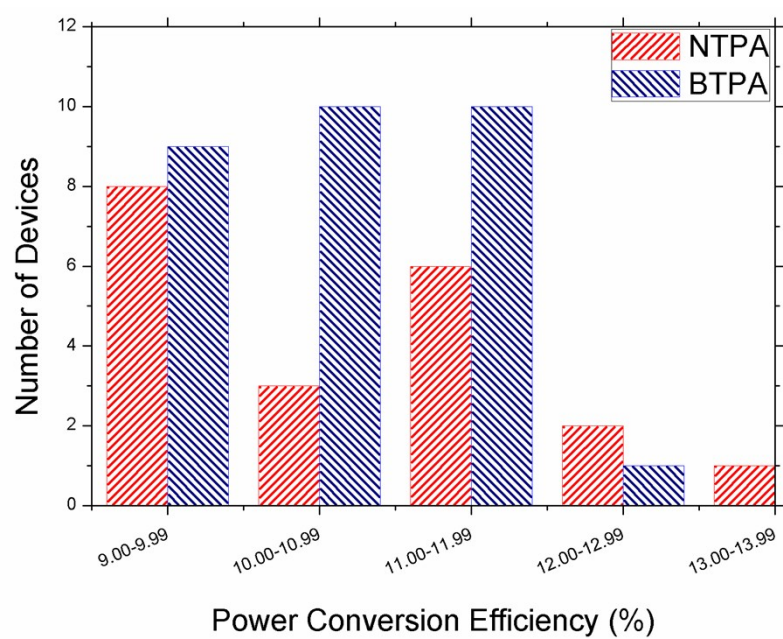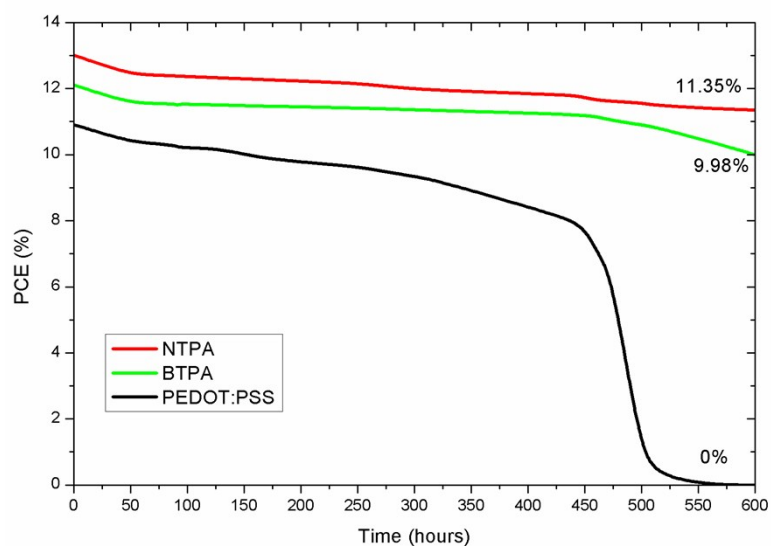
Figure S3(a), (b): Device statistics.
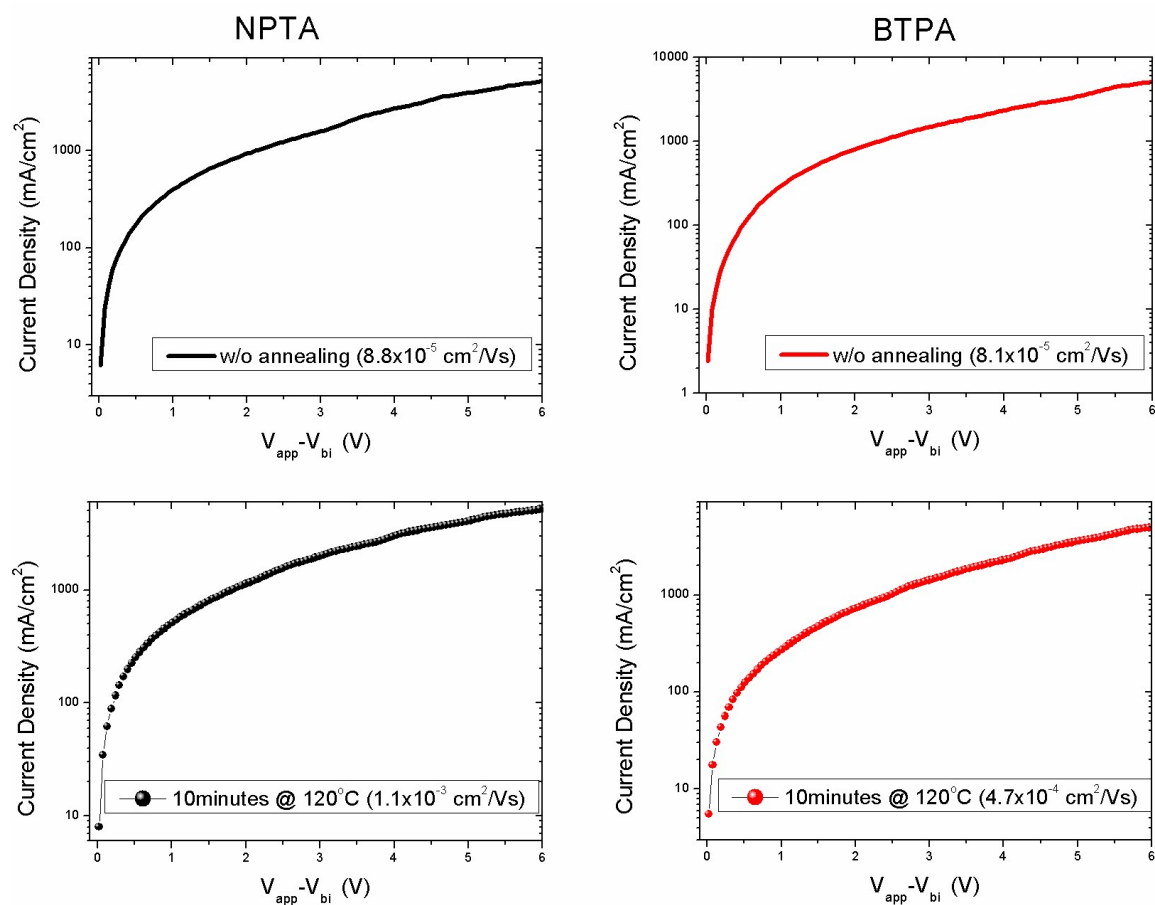
Figure S4: Lifetime measurements and PCE evolution.

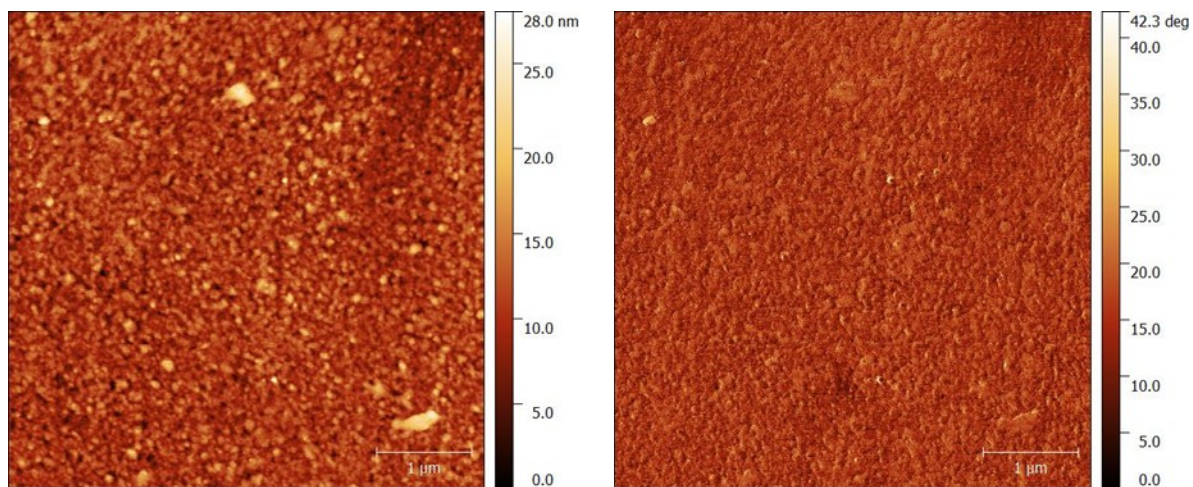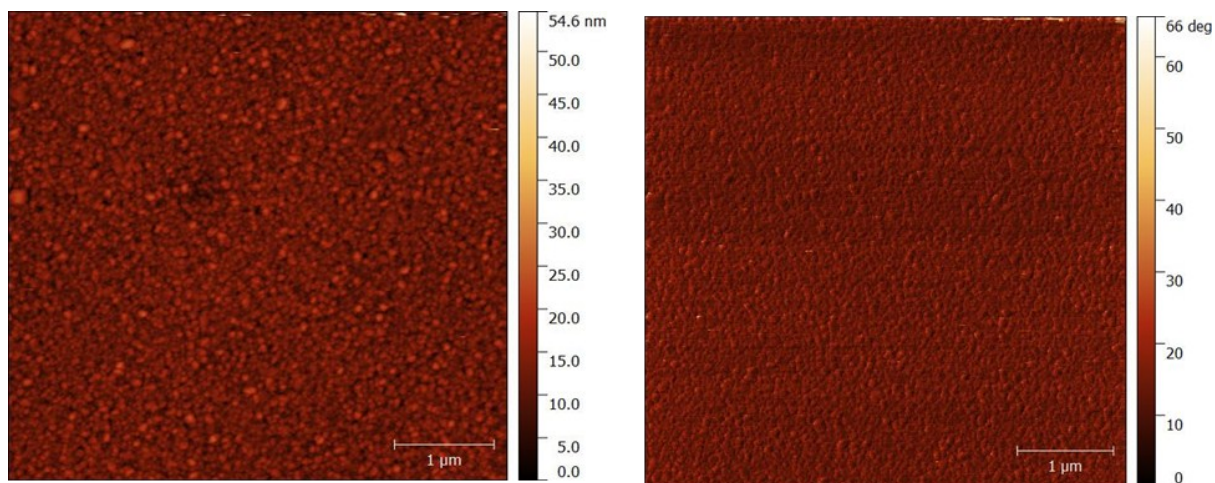Figure S5: SCLC mobility measurements for NTPA and BTPA.

BTPA.

NTPA.

Figure S6: AFM of NTPA and BTPA layers showing height and phase of annealed devices.
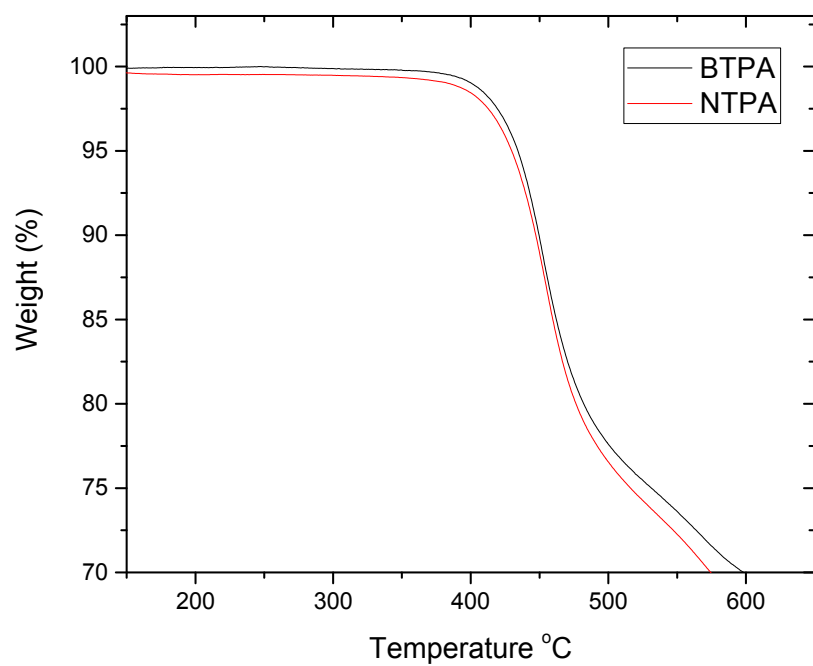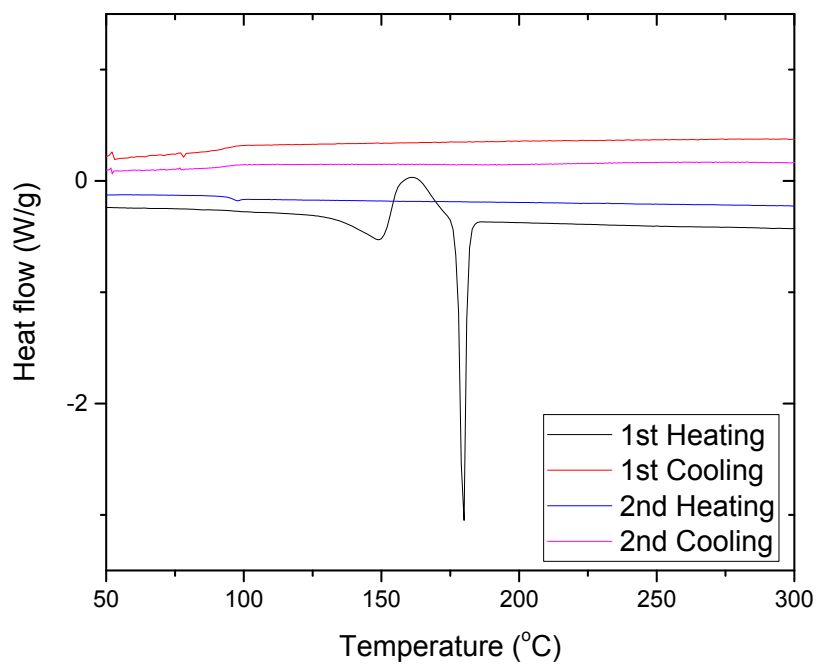
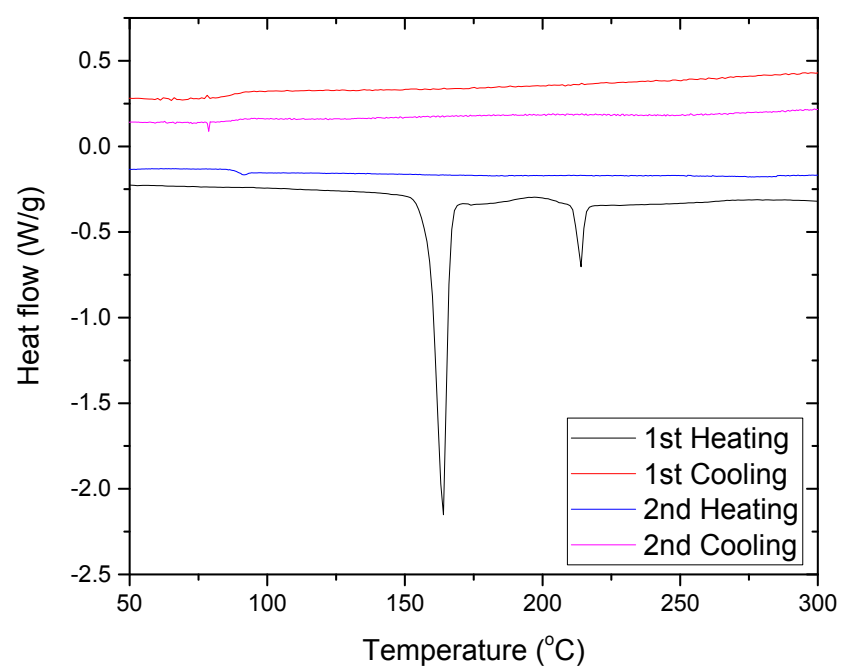Figure S7: TGA curves of NTPA and BTPA.

Figure S8: DSC curves of NTPA.

Figure S9: DSC curves of BTPA.
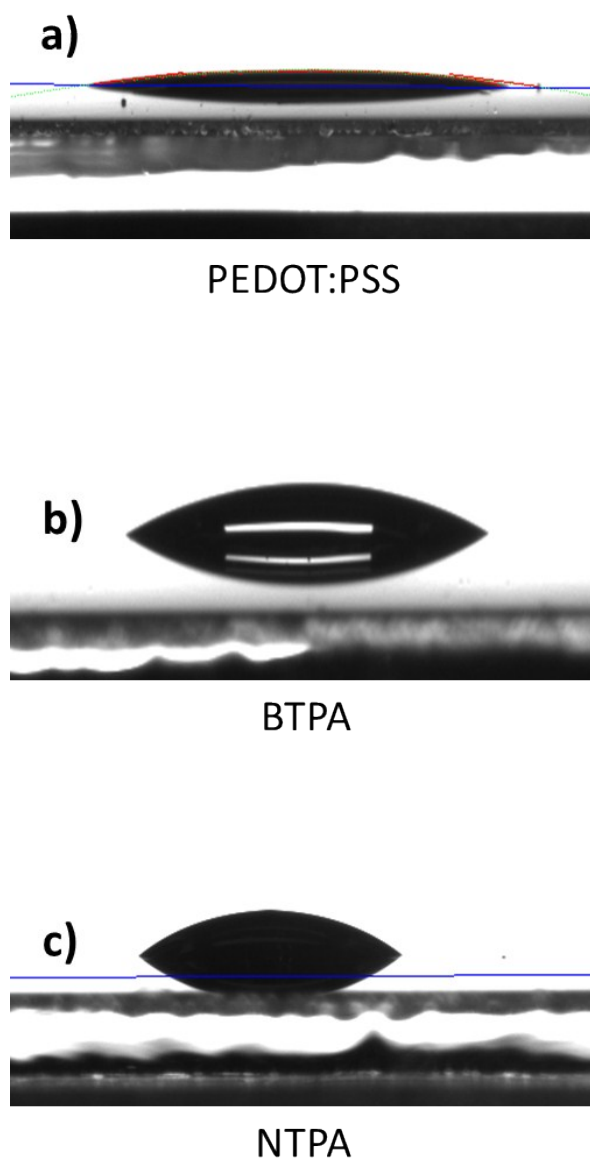
a)

PEDOT:PSS

b)

BTPA

c)

NTPA

Figure S10. Contact angle of perovskite droplets on top of a) PEDOT:PSS, b) BTPA and c) NTPA with measured angles 5.6°, 17.9° and 45.5° respectively.
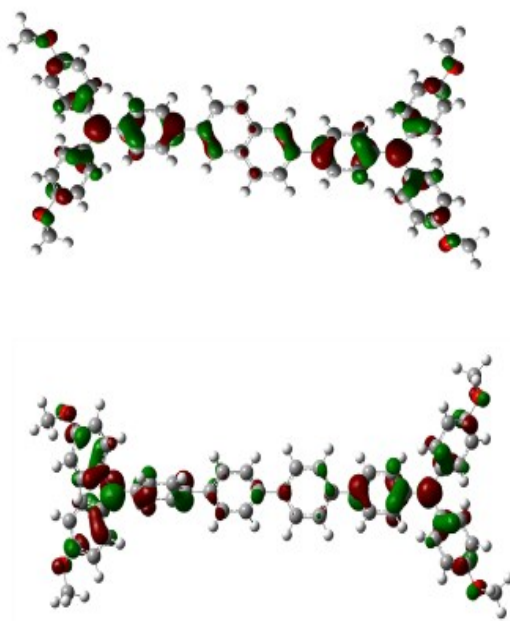
DFT calculations

Figure S11. DFT calculations for the in-use molecules

Density functional theory (DFT) calculations were carried out with Gaussian at the B3LYP/6-31g* level of theory in gas phase to determine the energy-minimized molecular conformations and to visualize the HOMO and LUMO spatial distributions. Images were generated with the GaussView software package.