Supporting information

# Two anthracene-based copolymers as the hole transporting materials for high-performance inverted (*p-i-n*) perovskite solar cells

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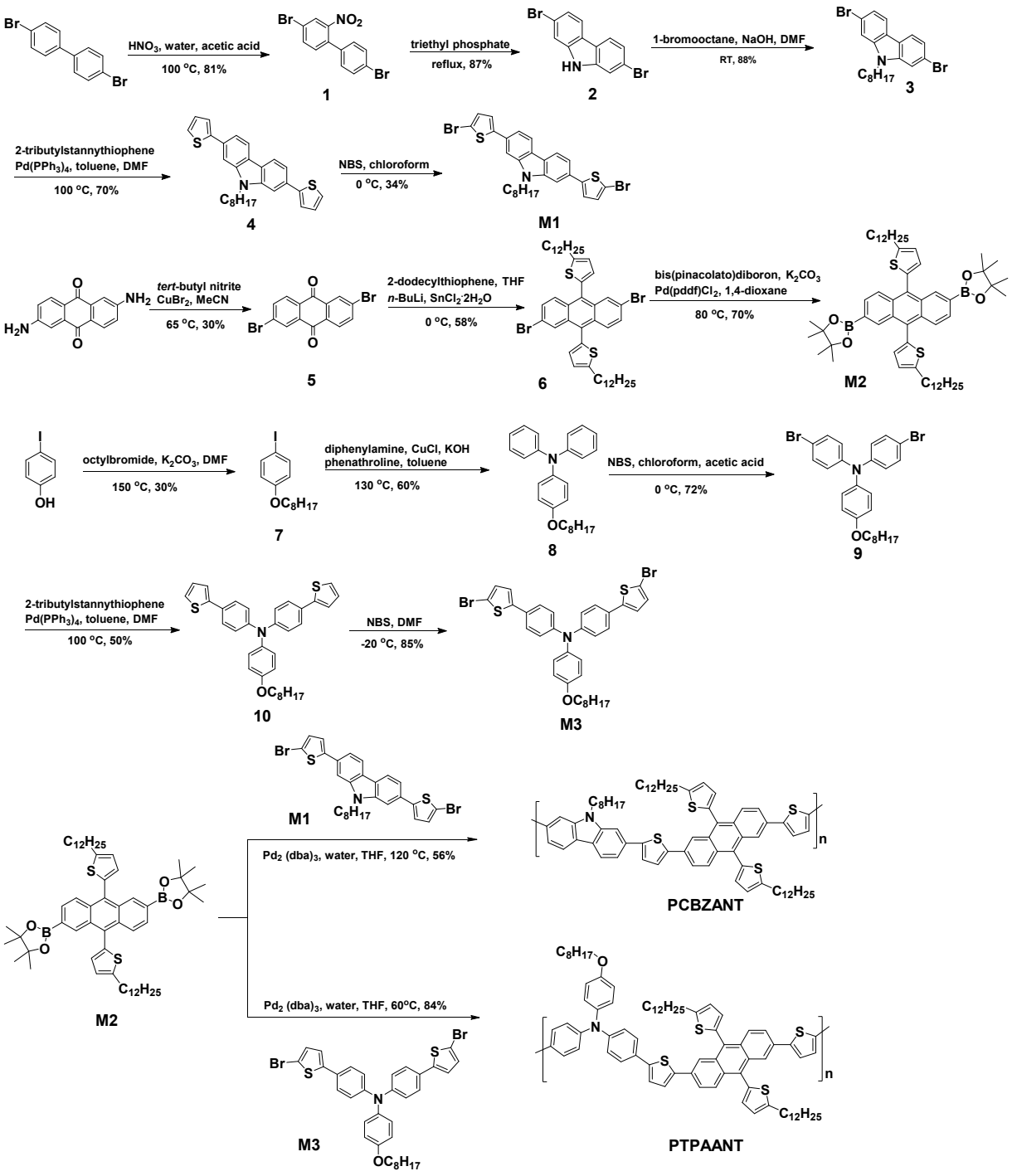
**Materials.** All reagents and chemicals for chemical synthesis of the monomers and polymers were purchased from commercial suppliers without further purification, unless otherwise stated. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) (Clevious PVP AI 4083) was obtained from Heraeus-(Precious Metals GmbH & Co. KG) Inc. Fullerene ($C_{60}$, purity ≥ 99.5%), bathocuproine (BCP, purity ≥ 98.0%), methylammonium iodide ($CH_3NH_3I$, purity ≥ 99.5%) and lead iodide ($PbI_2$, purity ≥ 99.999%) were obtained from Alfa Aesar. Phenyl-C61-butyric acid methyl ester ($PC_{61}BM$, purity ≥ 99.5%) was purchased from Nichem-(Fine Technology Co. Itd), Inc. 4,4',4''-Tris(N-3-methylphenyl-N-phenylamino)triphenylamine (m-MTDATA) was obtained from Sigma-Aldrich.

**Characterization.** Nuclear magnetic resonance ($^1$H NMR and $^{13}$C NMR) spectra were conducted on Bruker Avance 400 and III 600 instrument. APCI mass spectra were conducted on a Bruker Daltronik micrOTOF system (KrF*-Laser ATLEX-SI, ATL Wermelskirchen), MALDI-TOF mass spectra were collected on a Bruker Reflex TOF, and field desorption (FD) mass spectra were collected on a VG Instruments ZAB2-SE-FPD. Thermogravimetric analysis (TGA) measurements and differential scanning calorimetry (DSC) were conducted under argon flow on a Mettler Toledo TGA/DSC1 STAR System. Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted on a multichamber UHV system with a base pressure of $5\times10^{-10}$ mbar. The spectrometer is equipped with an Omicron hemispherical analyzer (EA 125), a helium discharge lamp (Leybold-Hereaus UVS10/35). Current density-voltage (J-V) measurements were acquired from Keithley 2400 source-meter unit controlled by computer. All the devices were measured under Newport 6279 NS solar simulator (450 W) AM 1.5G light source with 100 mW/cm$^2$. Atomic force microscopy (AFM, Park, XE-70) was used to learn the surface condition of different substrates.

X-ray diffraction (XRD, Smartlab 3KW) measurements with Cu Kα beam and scanning electron microscopy (SEM, JSM-7800F) were used to study the crystal condition of perovskite on different hole-transporting layers (HTLs). The ultraviolet (UV, SHIMADZU UV-1750) and photoluminescence (PL, F-4600) measurements were conducted at the ambient atmosphere. Time-correlated single-photon counting (TCSPC, FLS980) was used to measure the lifetime of the carriers. Microscopic contact angle meter (KRUSS GmbH, DSA1005) was used to measure the contact angle of HTLs.

**Devices Fabrication.** All the components of inverted perovskite solar cells were fabricated on ITO substrate (12 × 12 $mm^2$). ITO substrates were put into ultrasonic cleaner with deionized water, acetone and isopropyl alcohol after cleaning with detergent. Then the substrates were dried with $N_2$ flow and followed with UV/Ozone cleaning for 15 min. **PCBZANT** and **PTPAANT** films doping 30% *m*-MTDATA and 20% *m*-MTDATA with different thickness were cast by spin coating their 1,2-dichlorobenzene (*o*-DCB) solution for 30 s from 2 mg/ml solution at 4500 rpm, 3 mg/ml solution at 4500 rpm, 4 mg/ml solution at 4500 rpm and then annealed at 100 °C for 20 min. PEDOT:PSS layer was prepared by spin coating process at 3500 rpm for 40 s and annealed at 120 °C for 15 min. The mixture of 462 mg/ml $PbI_2$ and 5 wt% $Pb(SCN)_2$ in DMF was stirred at 60 °C and 40 mg/ml $CH_3NH_3I$ dissolved in 2-propanol was stirred at room temperature. A hot solution of $PbI_2$:$Pb(SCN)_2$ was spin-coated onto the as-prepared layer at 3000 rpm for 40 s and $CH_3NH_3I$ solution was spin-coated onto the $PbI_2$:$Pb(SCN)_2$ layer at 3000 rpm for 40 s immediately. Then the perovskite film was annealed at 100 □ for 5 min. 2 wt% $PC_{61}BM$ dissolved in 1,2-dichlorobenzene (*o*-DCB) was spin-coated onto the as-prepared layer at 6000 rpm for 30 s. The semi-finished devices were transferred to a glove box integrated with a deposition chamber. A sequence of $C_{60}$ (20 nm),

BCP (8 nm) and Al (60 nm) were thermally evaporated through a shadow mask at a rate of 0.1 Å/s, 0.2 Å/s and 1 Å/s. The active layer of the device was calculated to be 5 $mm^2$ with shadow mask.




Scheme 1. Reaction routes of two copolymers **PCBZANT** and **PTPAANT**.

## Synthesis

**4,4'-Dibromo-2-nitro-1,1'-biphenyl (1)**

According to the literature[1], to a solution of 4,4'-dibromo-1,1'-biphenyl (10.00g, 32.00mmol) in acetic acid (Volume: 300 ml) at 100 °C was added slowly a mixture of fuming $HNO_3$ and water (Volume: 7.5 ml). After heating the reaction mixture for 30 min at 100 °C, the initially formed precipitate was dissolved again. The solution was cooled down and the resulting yellow paste was collected by filtration. Recrystallization from EtOH afforded the title compound as a yellow solid (9.30g, 81%).$^1$H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 1.3 Hz, 1H), 7.75 (m, 1H), 7.56 (d, J = 7.9 Hz, 2H), 7.28 (m, 1H), 7.16 (d, J = 7.9 Hz, 2H).

**2,7-Dibromo-9H-carbazole (2)**

A mixture of 4,4'-dibromo-2-nitro-1,1'-biphenyl (10.00 g, 28.00mmol) and triethylphosphate (Volume: 50 ml) was heated under reflux for 18 h in an inert atmosphere. The excess of triethylphosphate was distilled off and the product was purified by column chromatography (silica gel, 5% EtOAc in hexane) to provide the title compound (4.66 g, 87%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 1.6 Hz, 2H), 7.35 (dd, J = 1.6 Hz, 1.6 Hz, 2H).

**2,7-Dibromo-9-octyl-9H-carbazole (3)**

2,7-Dibromo-9H-carbazole (4.00 g, 12.31 mmol) was dissolved in DMF (Volume: 200 ml), NaOH (0.49 g, 12.31 mmol) and1-bromooctane (2.31 ml, 13.29 mmol) were added into the reaction system. The reaction mixture was stirred overnight at room temperature under $N_2$. Water was introduced to quench the reaction. The residue was extracted with chloroform and water. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane) to provide the title compound (4.73 g, 88%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 1.6

Hz, 2H), 7.35 (dd, J = 1.6 Hz, 1.6 Hz, 2H), 4.18 (t, J = 7.4 Hz, 2H), 1.83 (m, 2H), 1.31 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H).

**9-Octyl-2,7-di(thiophen-2-yl)-9H-carbazole (4)**

According to the literature[2], 9-octyl-2,7-di(thiophen-2-yl)-9H-carbazole (3.99 g, 12.16 mmol) and 2-tributylstannythiophene (9.95 g, 26.74 mmol) were dissolved in dry toluene (Volume: 56 ml) and DMF (Volume: 14 ml) under argon. Tetrakis(triphenylphosphine)palladium(0) (1.70 g, 1.49 mmol) was added, then the mixture was heated up to 100 °C. The system was refluxed overnight with stirring in the dark. After evaporating the mixture, DMF, dichloromethane and water were added and the mixture was washed with dilute HCl, saturated $NaHCO_3$ and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuum. Then the crude product was recrystallized from hexane twice (2.82 g, 70%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 0.6 Hz, 2H), 7.52 (dd, J = 1.8, 1.2 Hz, 2H), 7.42 (dd, J = 0.6, 1.1 Hz, 2H), 7.31 (dd, J = 0.6, 1.1 Hz, 2H), 7.14 (dd, J = 3.6, 3.6 Hz, 2H), 4.35 (t, J = 7.3 Hz, 2H), 1.93 (m, 2H), 1.46 (m, 2H), 1.38 (m, 2H), 1.26 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H).

**2,7-Bis(5-bromothiophen-2-yl)-9-octyl-9H-carbazole (M1)**

A mixture of 9-octyl-2,7-di(thiophen-2-yl)-9H-carbazole (2.50 g, 5.63 mmol), N-bromosuccinimide (NBS) (4.11 g, 23.10 mmol) and chloroform (Volume: 250 ml) was stirred at 0 °C for overnight in the dark. Water and $CH_2Cl_2$ were added, the organic layer was separated, the aqueous layer was extracted with $CH_2Cl_2$, and the combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The product was purified by column chromatography (silica gel, $CH_2Cl_2$: hexane = 1:4, v/v) to provide the title compound (1.25 g, 34%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 1.1 Hz, 2H), 7.41 (dd, J = 1.2, 1.8 Hz, 2H), 7.15 (d, J = 3.8 Hz, 2H),

7.08 (d, J = 4.2 Hz, 2H), 4.31 (t, J = 7.2 Hz, 2H), 1.90 (m, 2H), 1.39 (m, 4H), 1.26 (m, 6H), 0.87 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (400 MHz, $CDCl_3$): δ 145.80, 141.62, 132.36, 128.21, 124.75, 123.23, 122.36, 120.81, 118.04, 106.20, 43.20, 31.97, 29.49, 29.33, 29.11, 27.41, 22.80, 14.21. MS (APCI) m/z: calcd. for $C_{28}H_{27}Br_2NS_2$ 601.46, found 602.00 ($M^+$).

**2,6-Dibromoanthracene-9,10-dione (5)**

According to the literature[3], 2,6-diaminoanthracene-9,10-dione (5.00 g, 20.99 mmol), *tert*-butyl nitrite (6.20 ml, 52.00 mmol), copper(II) bromide (11.72 g, 52.50 mmol) and MeCN (Volume: 300 ml) were added to a one-neck flask, and the mixture was heated at 65 °C for 2 h. Afterwards the reaction was quenched by adding 20 % HCl (aq.) solution to the mixture. The resulting precipitate was filtered, washed with $CH_2Cl_2$ and brine. Then the crude product was recrystallized from 1,4-dioxane (2.44 g, 30%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 1.2 Hz, 2H), 8.17 (d, J = 5.2 Hz, 2H), 7.94 (dd, J = 1.2, 1.6 Hz, 2H).

**5,5'-(2,6-Dibromoanthracene-9,10-diyl)bis(2-dodecylthiphene) (6)**

2-Dodecylthiophene (11.06 g, 44.00 mmol) was dissolved in anhydrous THF (Volume: 100 ml) in a three-necked round bottom flask at nitrogen atmosphere. A solution of *n*-BuLi (1.6 M in hexane, 27.50 ml, 44.00 mmol) was added slowly with stirring for a period of 30 min after the mixture was cooled down to 0 °C. Then the solution was warmed up to room temperature, stirred for 30 min and heated up to 50 °C. Two hours later, 2,6-dibromo-9,10-anthraquinone (4.00 g, 11.00 mmol) was added and the mixture was stirred at 50 °C for another 1.5 h. Then the mixture was cooled to 0 °C, a solution of $SnCl_2 \cdot 2H_2O$ (22.40 g, 99.00 mmol) in HCl (10%, Volume: 50 ml) was added and stirred for another 1.5 h. When the reaction was over, all the mixture was poured into ice water and extracted with diethyl ether three times. After removing the solvent, the crude product was purified

by column chromatography (silica gel, hexane) and recrystallized from hexane to get the pure product as yellow needle (5.02 g, 58%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 1.8 Hz, 2H), 7.79 (d, J = 9.0 Hz, 2H), 7.45 (dd, J = 1.8, 1.8 Hz, 2H), 6.97 (m, 4H), 2.96 (t, J = 7.5 Hz, 4H), 1.82 (m, 4H), 1.48 (m, 4H), 1.34 (m, 32H), 0.88 (t, J = 6.9 Hz, 6H).

**2,2'-(9,10-Bis(5-dodecylthiophen-2-yl)anthracene-2,6-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M2)**

5,5'-(2,6-Dibromoanthracene-9,10-diyl)bis(2-dodecylthiphene) (1.00 g, 1.12 mmol), bis(pinacolato)diboron (1.21 g, 4.78 mmol), Pd(pddf)$Cl_2$ (0.04 g, 0.06 mmol) and $K_2CO_3$(0.74 g, 5.38 mmol) were added into a round bottom flask and then anhydrous 1,4-dioxane (Volume:80 ml) was added under the nitrogen protection. The mixture was heated up to 80 °C and stirred for overnight. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane three times. After removing the solvent, the crude product was purified by column chromatography (silica gel, hexane) to afford the pure product (0.78 g, 70%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 2H), 7.91 (dd, *J* = 0.8, 0.8 Hz, 2H), 7.71 (dd, *J* = 1.2, 1.2 Hz, 2H), 7.00 (dd, *J* = 3.6, 3.2 Hz, 4H), 2.99 (t, *J* = 7.5 Hz, 4H), 1.83 (m, 4H), 1.48 (m, 4H), 1.31 (m, 56H), 0.89 (t, J = 6.9 Hz, 6H).

**1-Iodo-4-octyloxybenzene (7)**

According to the literature[4], to a stirred mixture of 4-iodophenol (2.20 g, 0.10 mol), octylbromide (19.00 g, 0.10 mol) and DMF (Volume: 100 ml) under argon were added $K_2CO_3$ (20.70 g, 150.00 mmol). The reaction proceeded for 48 h at 150 °C and then cooled to room temperature. The resulting mixture was filtered and then extracted with chloroform. The organic layer was washed with a dilute solution of KOH and water, dried over anhydrous magnesium sulfate.

After filtration, removal of the solvent and purification with column chromatography (silica gel, hexane), the pure product was obtained as colorless oil (10.00 g, 30%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.54 (m, 2H), 6.67 (m, 2H), 3.91 (t, J = 6.4 Hz, 2H), 1.77 (m, 2H), 1.44 (m, 2H), 1.31 (m, 8H), 0.90 (t, J = 7.2 Hz, 3H).

**4-(Octyloxy)-N,N-diphenylaniline (8)**

The mixture of 1-iodo-4-octyloxybenzene (9.90 g, 30.00mmol), diphenylamine (6.00 g, 36.00 mmol), CuCl (0.20 g, 2.00mmol), phenathroline (0.26 g, 1.40 mmol), KOH (13.40 g, 24.00 mmol) and toluene (Volume: 60 ml) was reacted at 130 °C for 36 h in the dark. After cooling, the resulting mixture was poured into plenty of stirred water and extracted with chloroform. The obtained organic phase was washed several times with water, dried over magnesium sulfate, filtrated, evaporated and purified with column chromatography (silica gel, hexane). The product was got as a colorless oil (6.70 g, 60%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.21 (m, 4H), 7.05 (t, J = 8.4 Hz, 6H), 6.94 (t, J = 7.3 Hz, 2H), 6.84 (m, 2H), 3.94 (t, J = 6.5 Hz, 2H),1.78 (m, 2H), 1.47 (m, 2H), 1.36 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H).

**4-Bromo-N-(4-bromophenyl)-N-(4-(octyloxy)-phenyl)aniline (9)**

4-(Octyloxy)-N,N-diphenylaniline (3.00 g, 8.10 mmol) was dissolved in chloroform (Volume: 20 ml) and acetic acid (Volume: 20 ml), and then NBS (2.91 g, 16.35 mmol) was added and the solution was stirred for 2 h at 0 °C. Dilute aqueous sodium hydroxide was then added and the reaction mixture was stirred for a further 30 min. The reaction mixture was extracted three times using chloroform and brine; the organic layer was separated and dried with anhydrous magnesium sulfate, and then the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography (silica gel, toluene:hexane = 1:10, v/v) (3.08 g, 72%). $^1$H NMR (400

MHz, $CDCl_3$): δ 7.30 (m, 4H), 7.02 (m, 2H), 6.89 (m, 4H), 6.84 (m, 2H), 3.94 (t, J = 6.9 Hz, 2H), 1.79 (m,2H), 1.47 (m, 2H), 1.33 (m, 8H), 0.90 (t, J = 7.3 Hz, 3H).

**4-(Octyloxy)-N,N-bis(4-(thiophen-2-yl)phenyl)aniline (10)**

4-Bromo-N-(4-bromophenyl)-N-(4-(octyloxy)-phenyl)aniline (3.00 g, 5.65 mmol) and 2-(tributylstannyl)thiophene (5.41 ml, 17.04 mmol) were dissolved in dry toluene (Volume: 16 ml) and DMF (Volume: 4 ml) under argon. Tetrakis(triphenylphosphine)palladium(0) (0.79 g, 0.69mmol) was added and then the mixture was heated up to 100 °C. The mixture was refluxed overnight with stirring. After evaporating the mixture, DMF, dichloromethane, and water were added and the mixture was washed with dilute HCl, saturated $NaHCO_3$, and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuum. The crude mixture was purified by column chromatography (silica, DCM: hexane=1:4, v/v) (0.61 g, 50%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.7 Hz, 4H), 7.22 (s, 4H), 7.05 (m, 8H), 6.87 (d, J = 8.8 Hz, 2H), 3.96 (t, 2H), 1.79 (m, 2H), 1.47 (m, 2H), 1.34 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H). $^{13}$C NMR (400 MHz, $CDCl_3$): δ 151.81, 147.21, 141.61, 131.72, 131.06, 123.38, 123.31, 122.59, 121.02, 117.68, 111.29, 105.95, 43.24, 31.98, 29.47, 29.33, 29.05, 27.40, 22.78, 14.21. MS (APCI) m/z: calcd. for $C_{34}H_{35}NOS_2$ 537.78, found 538.22 ($M^+$).

**4-(5-Bromothiophen-2-yl)-N-(4-(5-bromothiophen-2-yl)phenyl)-N-(4-(octyloxy)phenyl)aniline (M3)**

4-(Octyloxy)-N,N-bis(4-(thiophen-2-yl)phenyl)aniline (1.35 g, 2.51 mmol) was cooled down to -20 °C in DMF (Volume: 50 ml), and NBS (0.98 g, 5.52 mmol) was added. Then the reaction was warmed to RT and stirred overnight. The reaction mixture was extracted three times using chloroform and brine; the organic layer was separated and dried with anhydrous magnesium sulfate,

and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography (silica gel, DCM:hexane = 1:8, v/v) (1.50 g, 85%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.1 Hz, 4H), 7.02 (m, 6H), 7.00 (d, J = 3.6 Hz, 2H), 6.94 (s, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.96 (t, 4H), 1.79 (m, 2H), 1.46 (m, 2H), 1.32 (m, 8H), 0.89 (t, J = 6.9 Hz, 3H). $^{13}$C NMR (400 MHz, $CDCl_3$): δ 147.20, 141.62, 131.71, 131.06, 124.83, 123.38, 123.31, 122.58, 121.02, 117.68, 111.29, 105.95, 43.24, 31.98, 29.48, 29.33, 29.05, 27.40, 22.78, 14.21. MS (APCI) m/z: calcd. for $C_{34}H_{33}Br_2NOS_2$ 695.57, found 696.04 ($M^+$).

**Synthesis of PCBZABT**

2,7-Bis(5-bromothiophen-2-yl)-9-octyl-9H-carbazole (**M1**) (0.50 g, 0.83 mmol), 2,2'-(9,10-bis(5-dodecylthiophen-2-yl)anthracene-2,6-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**M2**) (0.77 g, 0.83 mmol) and $Pd_2(dba)_3$ (0.05g, 0.05 mmol) were put together into a microwave tube. Then the reaction mixture were purged into argon for 30 min. Degassed water (Volume: 5 ml) and THF (Volume: 15 ml) were injected into the tube. The tube was put into the reactor and heated to 120 °C for 20 min. The crude product was purified by Soxhlet extraction method using methanol, acetone, ethyl acetate, HPLC hexane, DCM and chloroform. The chloroform fraction was evaporated to yield **PCBZANT** (0.28 g, 56%). $^{1}$H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.63 (br, 2H), 7.42 (br, 4H), 7.11 (br, 2H), 7.00 (br, 2H), 6.89 (br, 2H), 6.77 (br, 4H), 6.51 (br, 2H), 6.44 (br, 2H), 3.73 (br, 2H), 2.41 (br, 4H), 1.30 (br, 6H), 0.83 (br, 52H), 0.25 (br, 9H). GPC analysis: $M_n$ = 30400 g/mol, $M_w$ = 61900 g/mol and PDI = 2.04.

**Synthesis of PTPAANT**

4-(5-Bromothiophen-2-yl)-N-(4-(5-bromothiophen-2-yl)phenyl)-N-(4-(octyloxy)phenyl)aniline (**M3**) (0.33 g, 0.47 mmol),

2,2'-(9,10-bis(5-dodecylthiophen-2-yl)anthracene-2,6-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**M2**) (0.44 g, 0.47 mmol) and $Pd_2(dba)_3$ (0.03 g, 0.03 mmol) were put together into a microwave tube. Then the reaction mixture was purged into argon for 30 min. Degassed water (Volume: 5 ml) and THF (Volume: 15 ml) were injected into the tube. The tube was heated to 60 °C for 3 days. The crude product was purified by Soxhlet extraction method using methanol, acetone, ethyl acetate, HPLC hexane, DCM and chloroform. The DCM fraction was evaporated to yield **PTPAANT** (0.50 g, 84 %). $^1$H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.54 (br, 2H), 7.38 (br, 2H), 7.06 (br, 2H), 6.87 (br, 4H), 6.57 (br, 14H), 6.27 (br, 2H), 3.35 (br, 2H), 2.39 (br, 4H), 0.95 (br, 58H), 0.26 (br, 9H). GPC analysis: $M_n$ = 13400 g/mol, $M_w$ = 25200 g/mol and PDI = 1.89.

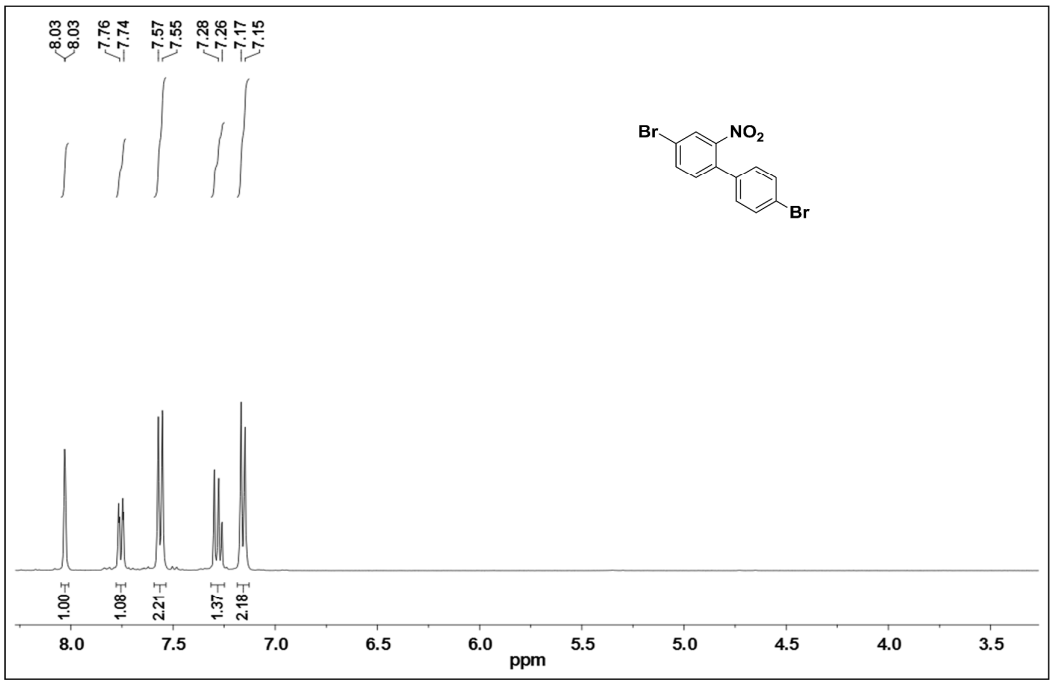



**Figure S1.** [1]H NMR of 4,4'-dibromo-2-nitro-1,1'-biphenyl

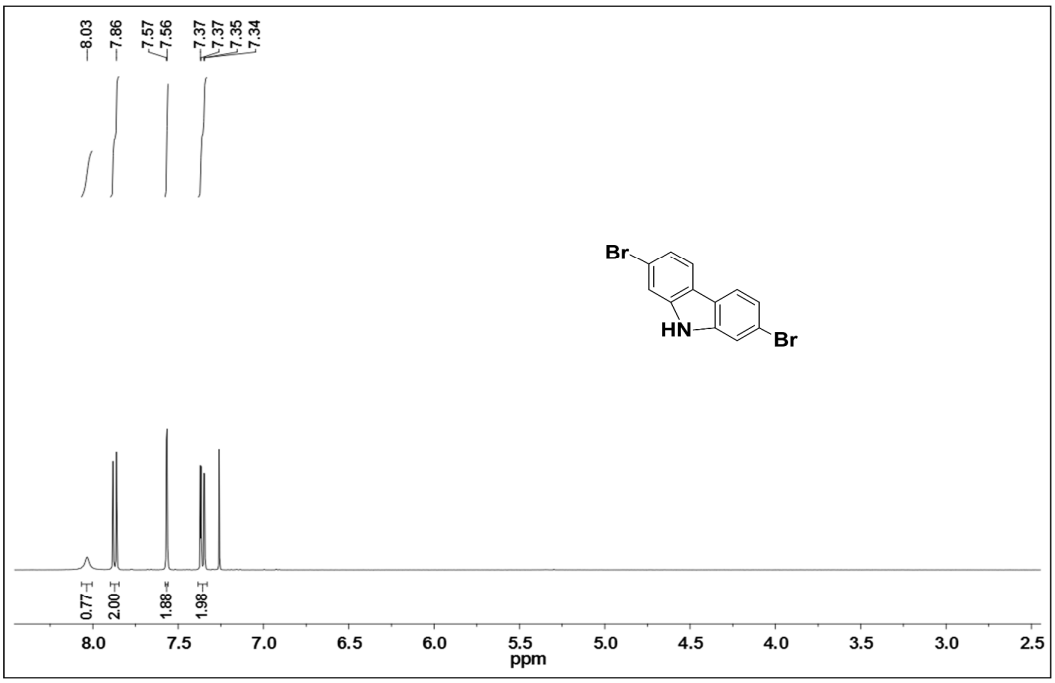



**Figure S2.** [1]H NMR of [1]H NMR of 2,7-dibromo-9H-carbazole

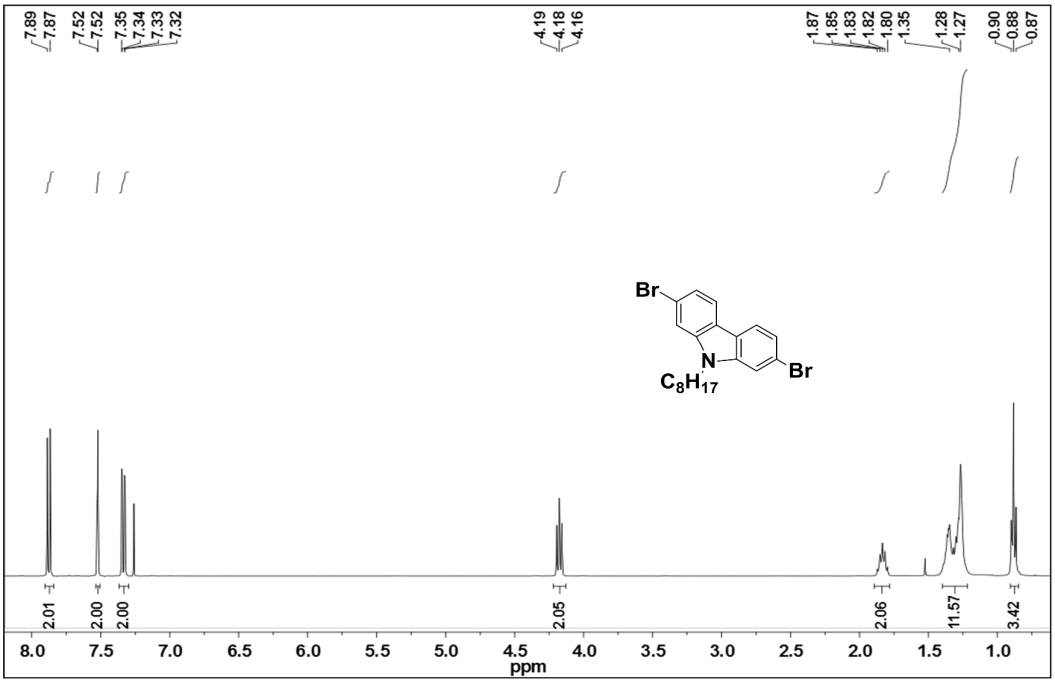



**Figure S3.** [1]H NMR of 2,7-dibromo-9-octyl-9H-carbazole

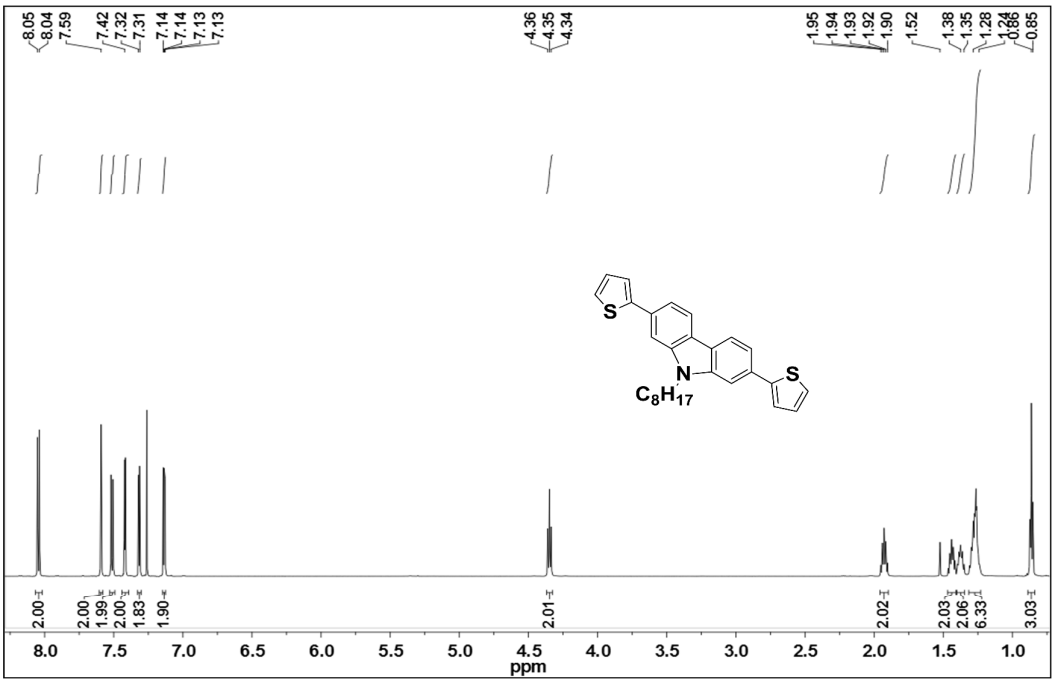



**Figure S4.** [1]H NMR of 9-octyl-2,7-di(thiophen-2-yl)-9H-carbazole

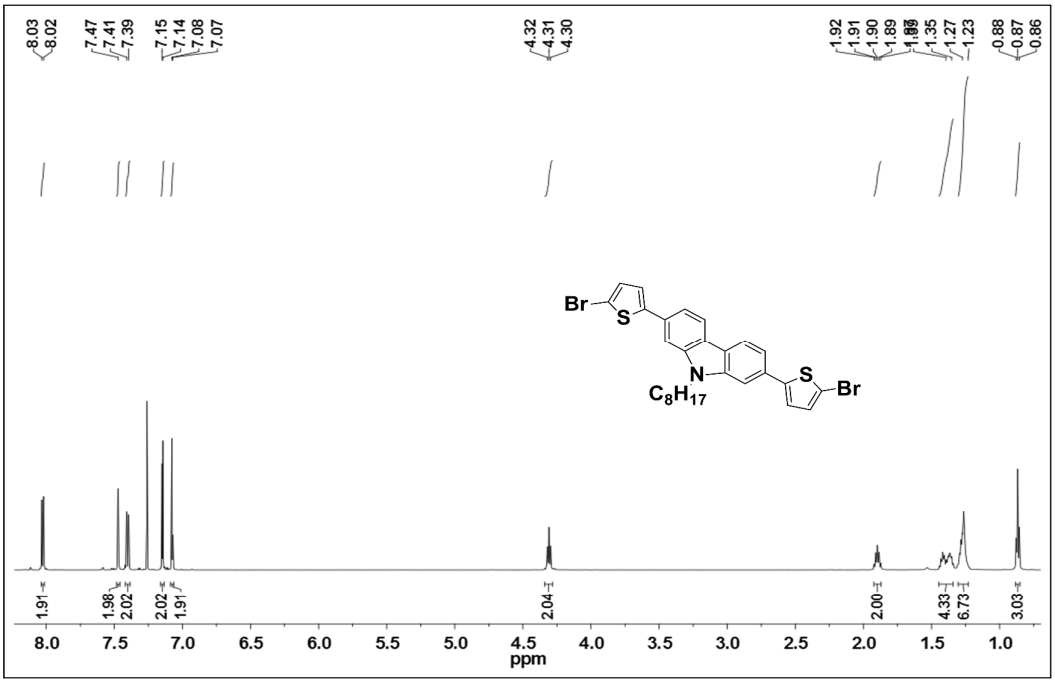



**Figure S5.** $^{1}$H NMR of **M1**

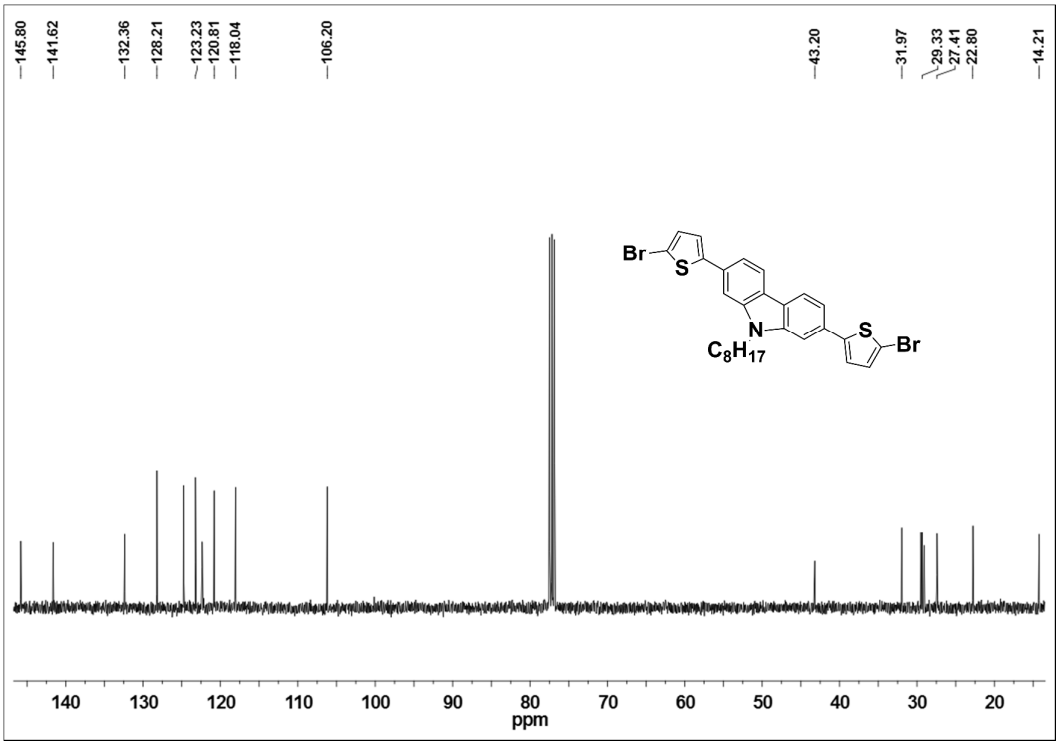



**Figure S6.** $^{13}$C NMR of **M1**

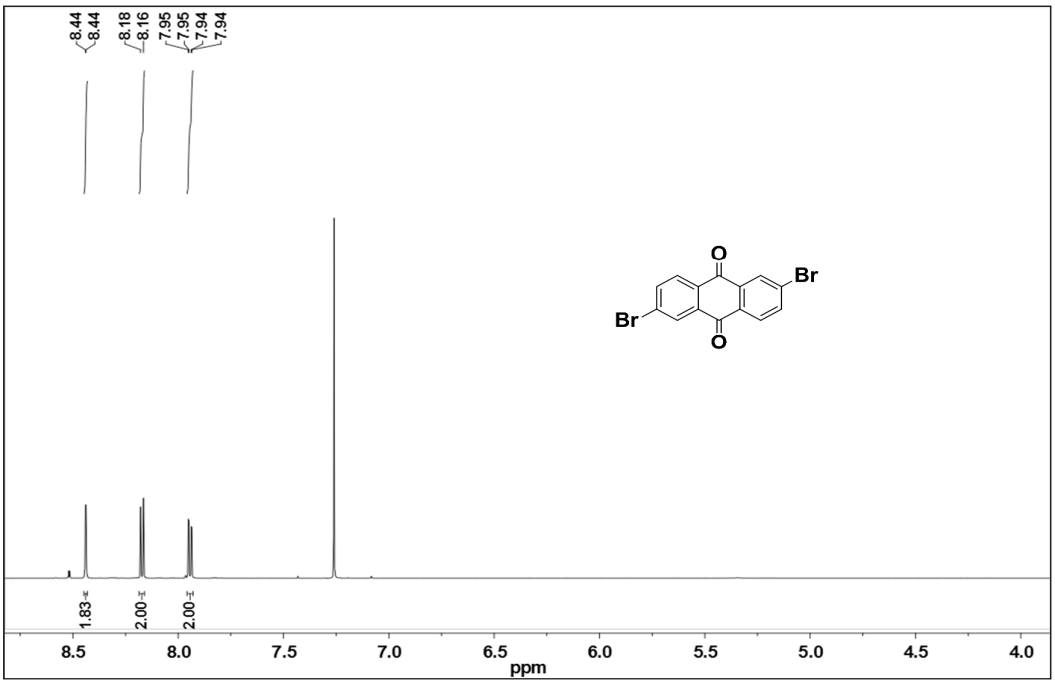



**Figure S7.** [1]H NMR of 2,6-dibromoanthracene-9,10-dione

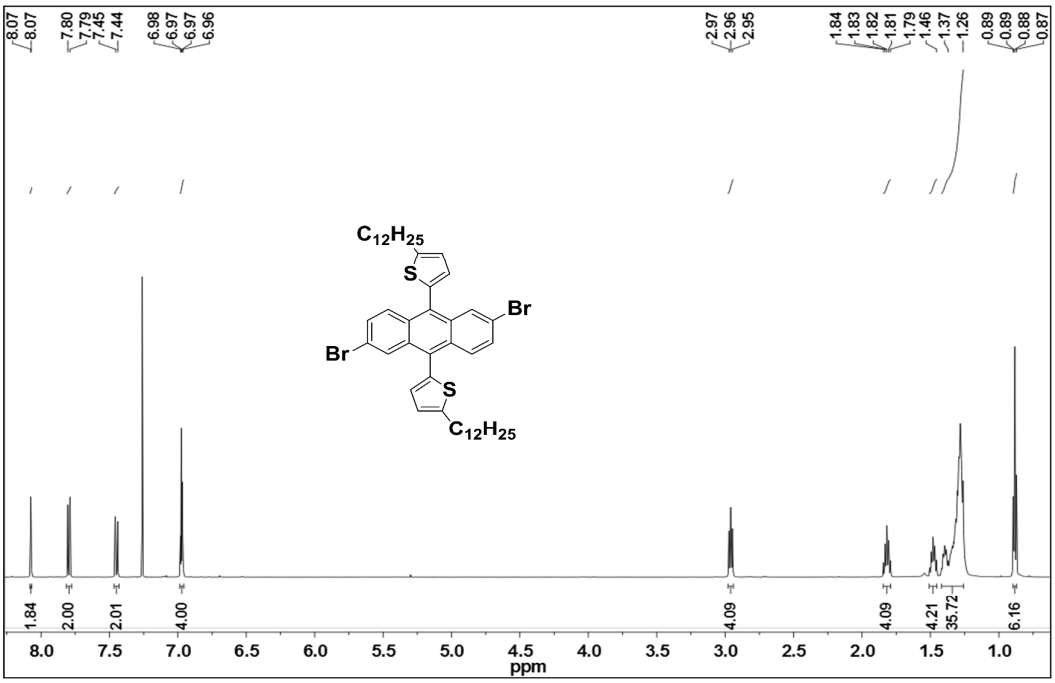



**Figure S8.** [1]H NMR of 5,5'-(2,6-dibromoanthracene-9,10-diyl)bis(2-dodecylthiphene)

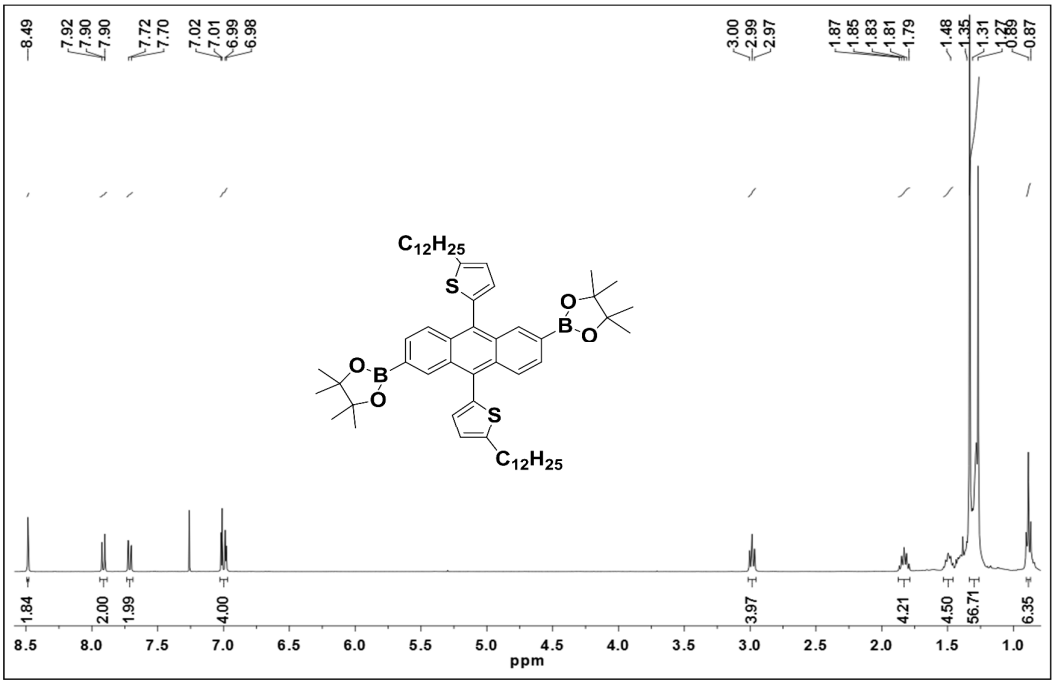



**Figure S9.** $^{1}$H NMR of **M2**

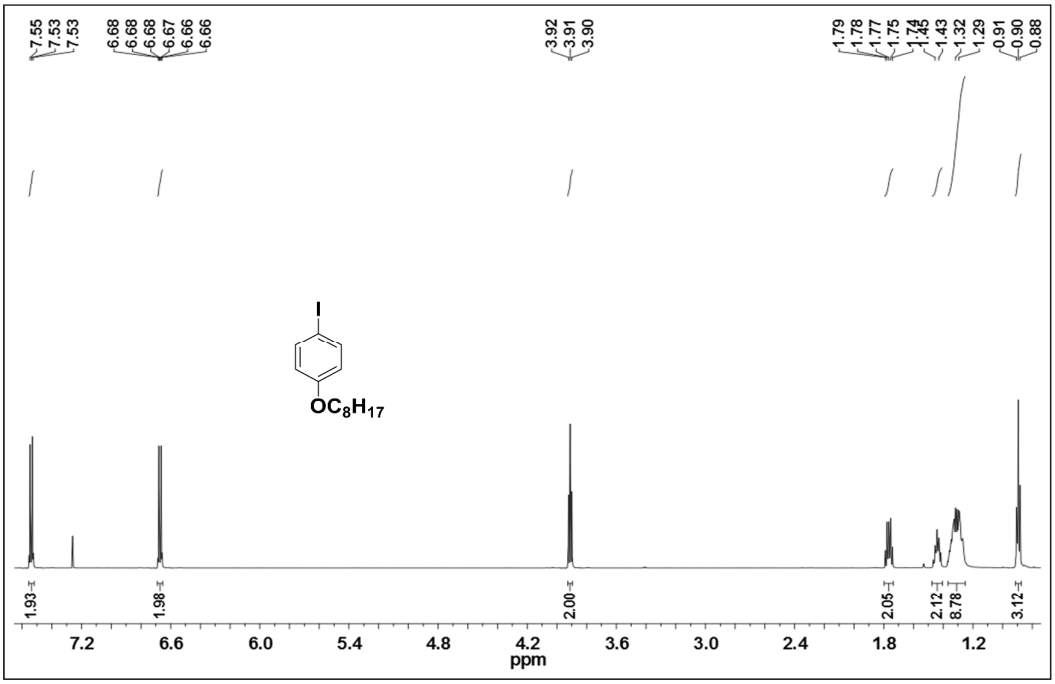



**Figure S10.** $^{1}$H NMR of 1-iodo-4-octyloxybenzene

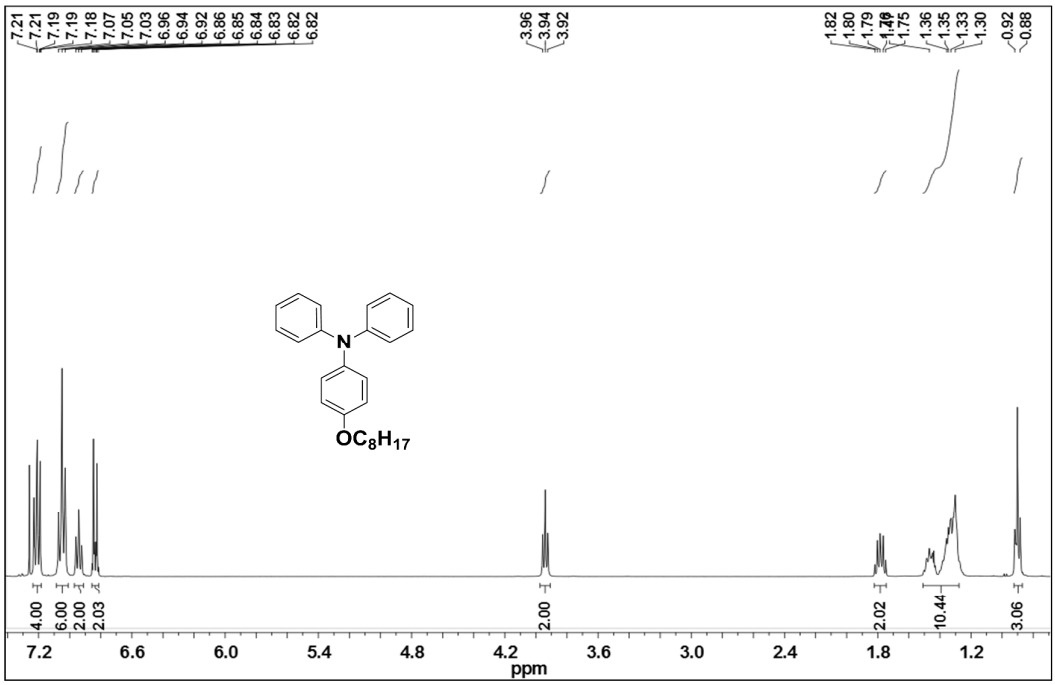



**Figure S11.** [1]H NMR of 4-(2-octyloxy phenyl) diphenylamine

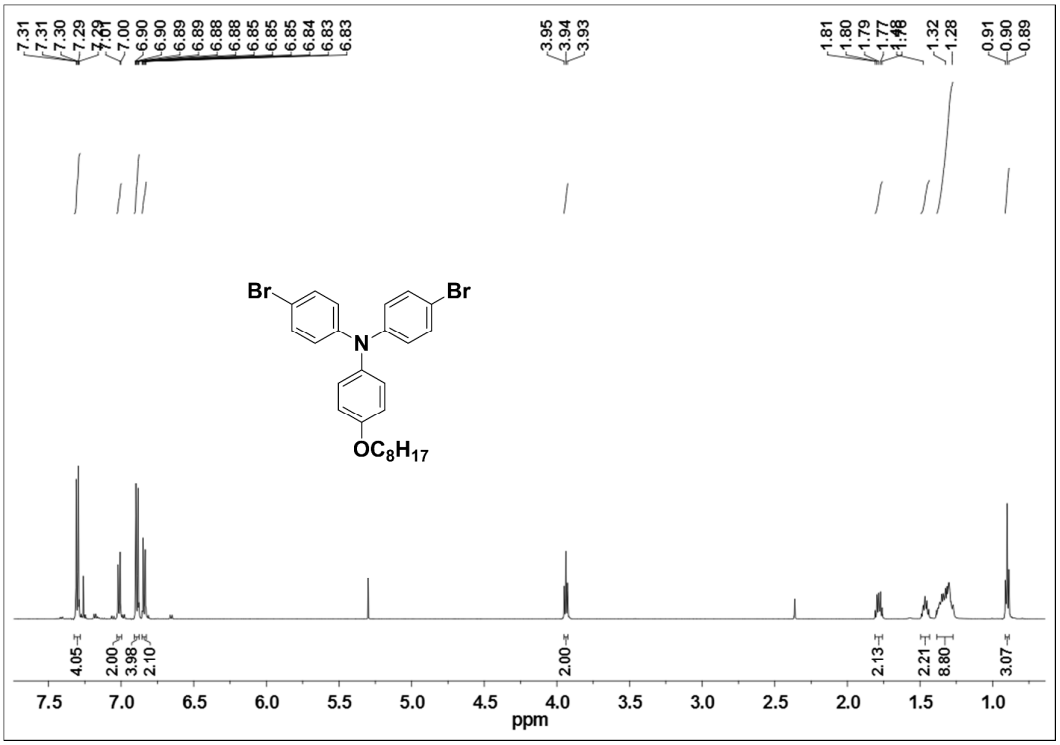



**Figure S12.** [1]H NMR of 4-bromo-N-(4-bromophenyl)-N-(4-(octyloxy)-phenyl)benzenamine

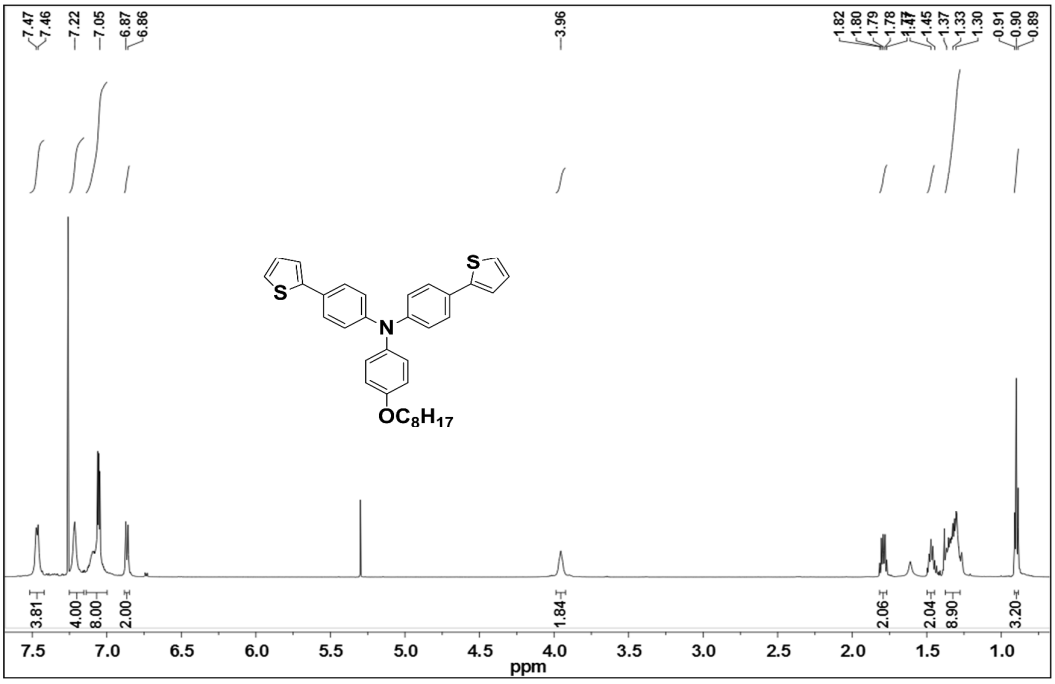



**Figure S13.** $^{1}$H NMR of 4-(octyloxy)-N,N-bis(4-(thiophen-2-yl)phenyl)aniline

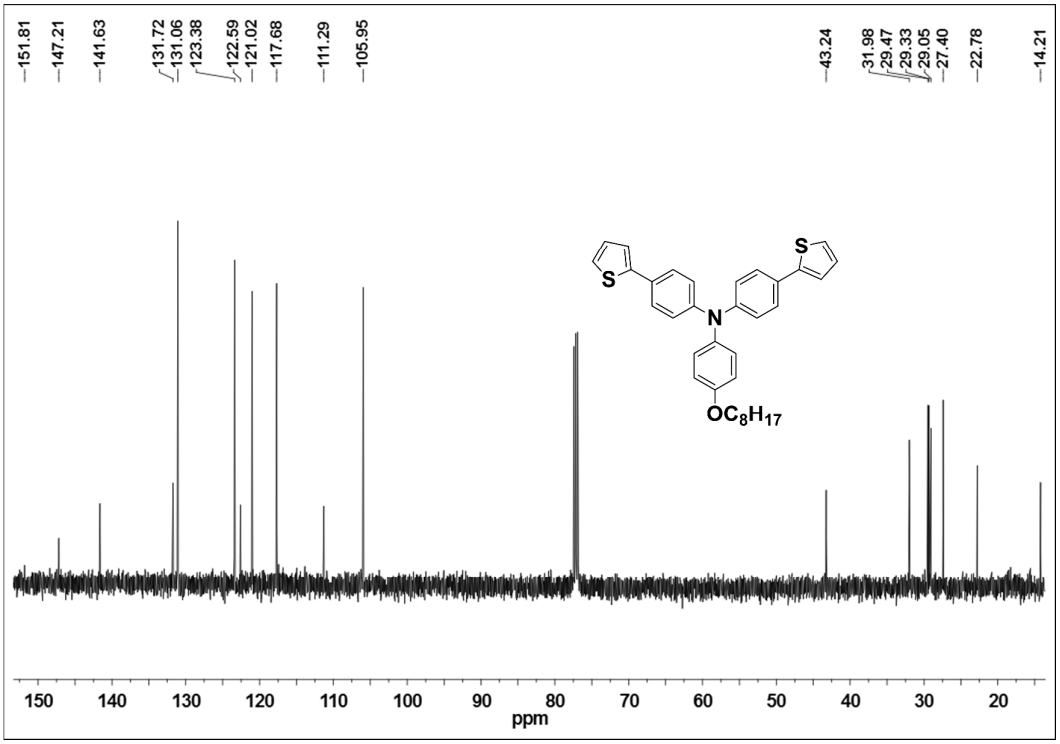



**Figure S14.** $^{13}$C NMR of 4-(octyloxy)-N,N-bis(4-(thiophen-2-yl)phenyl)aniline

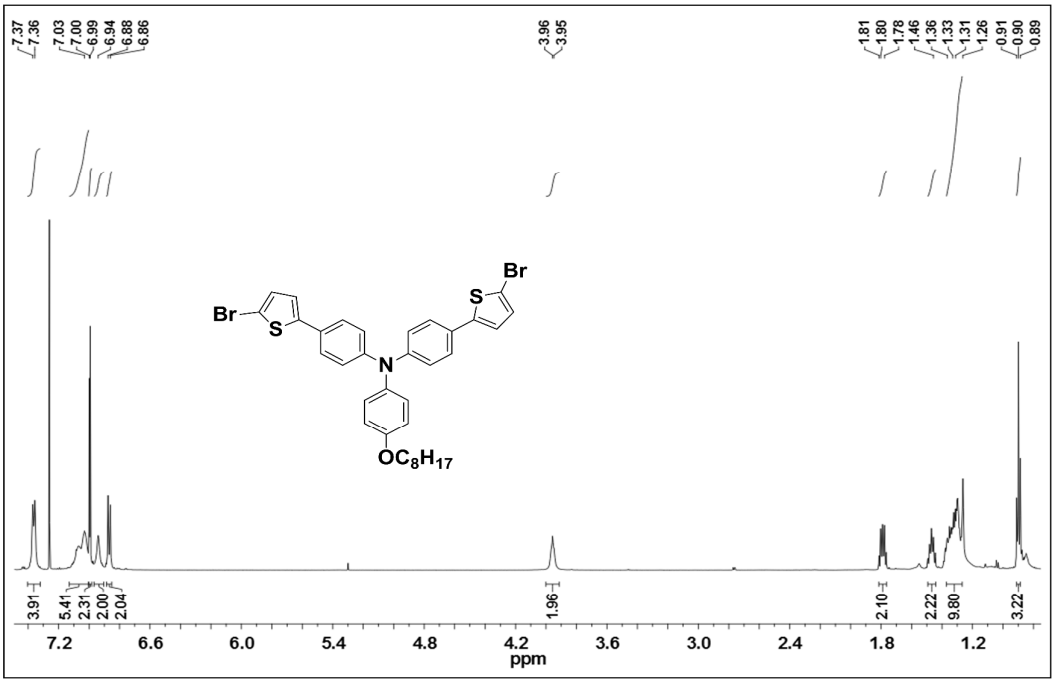



**Figure S15.** $^{1}$H NMR of **M3**

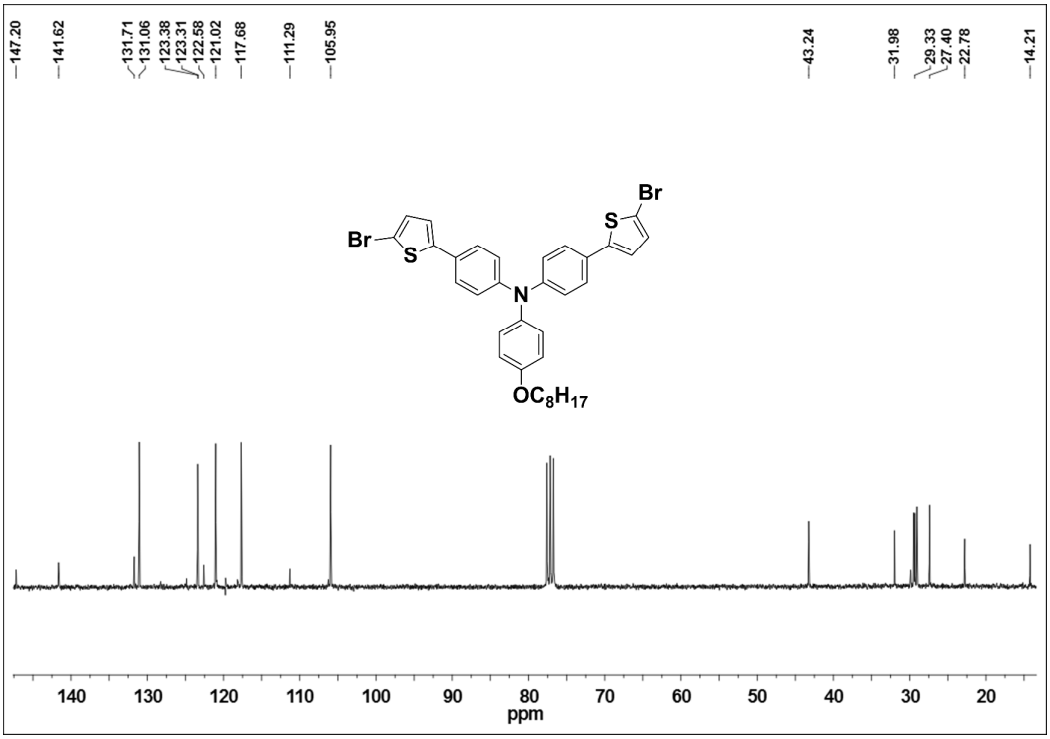



**Figure S16.** $^{13}$C NMR of **M3**

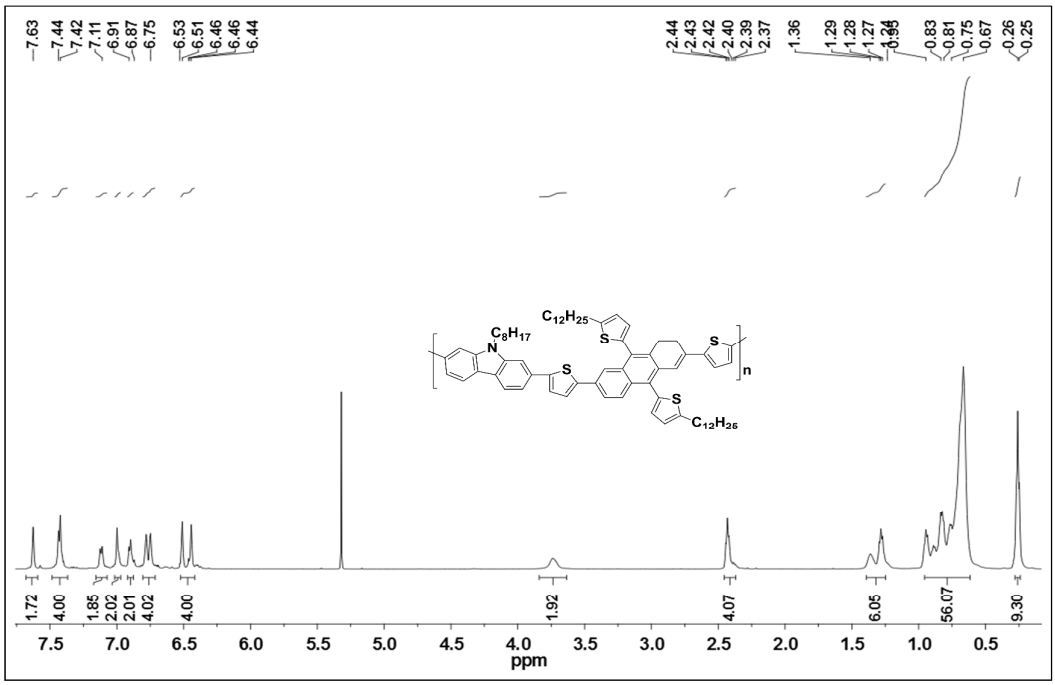



**Figure S17.** [1]H NMR of **PCBZANT**

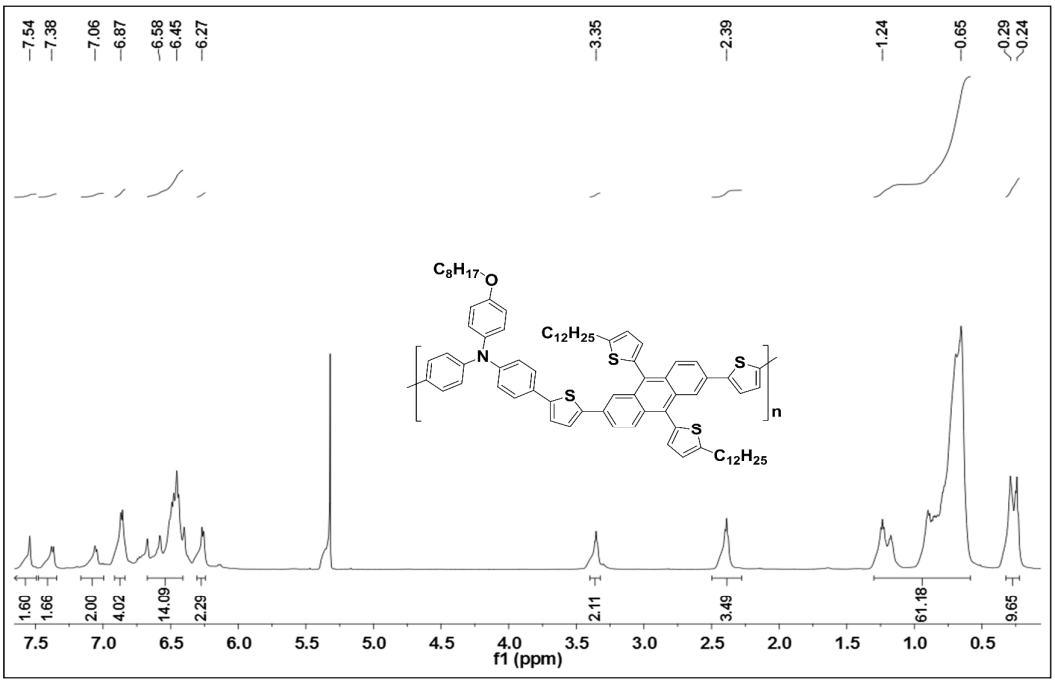



**Figure S18.** [1]H NMR of **PTPAANT**

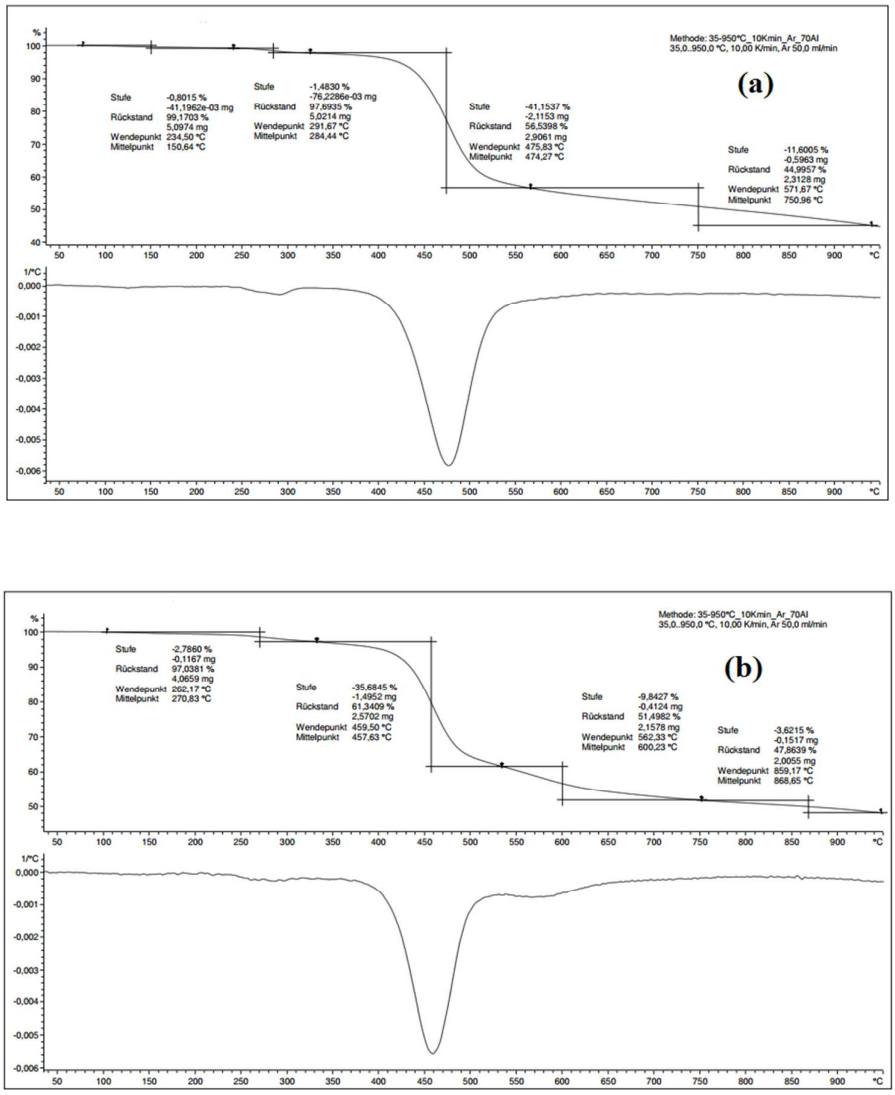






**Figure S19.** TGA curves of **PCBZANT** (a) and **PTPAANT** (b).

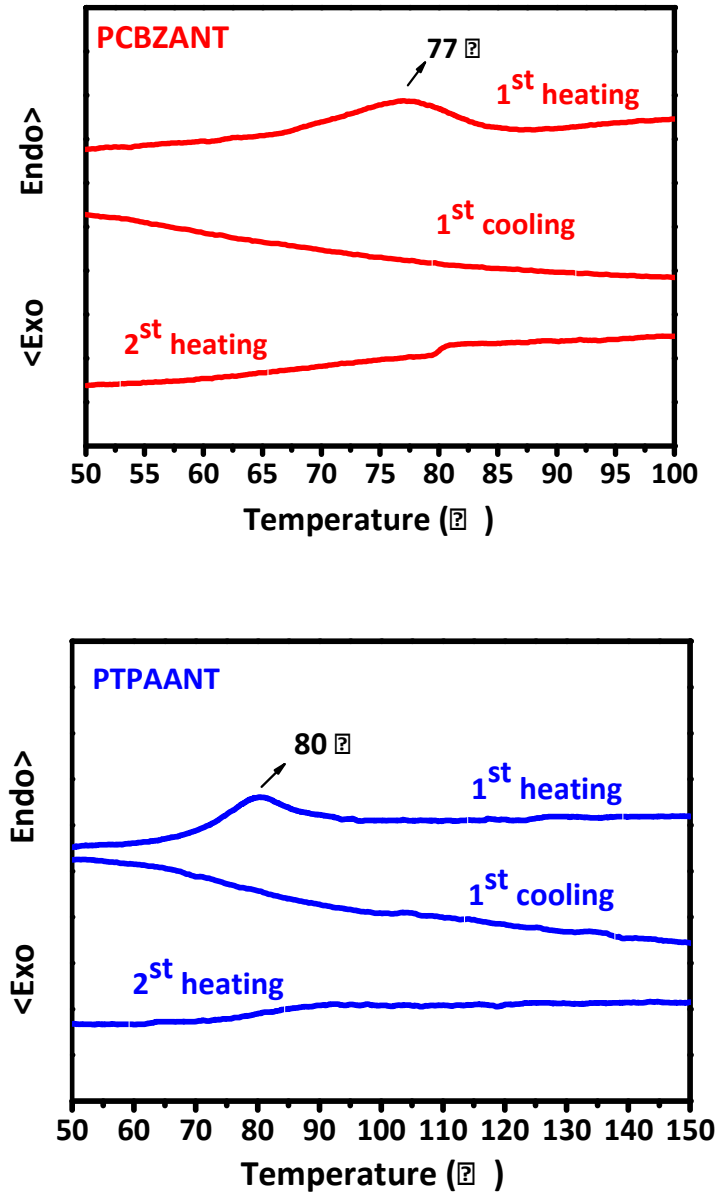



**Figure S20.** DSC (10 K/min) curves of **PCBZANT** (up) and of **PTPAANT** (down).

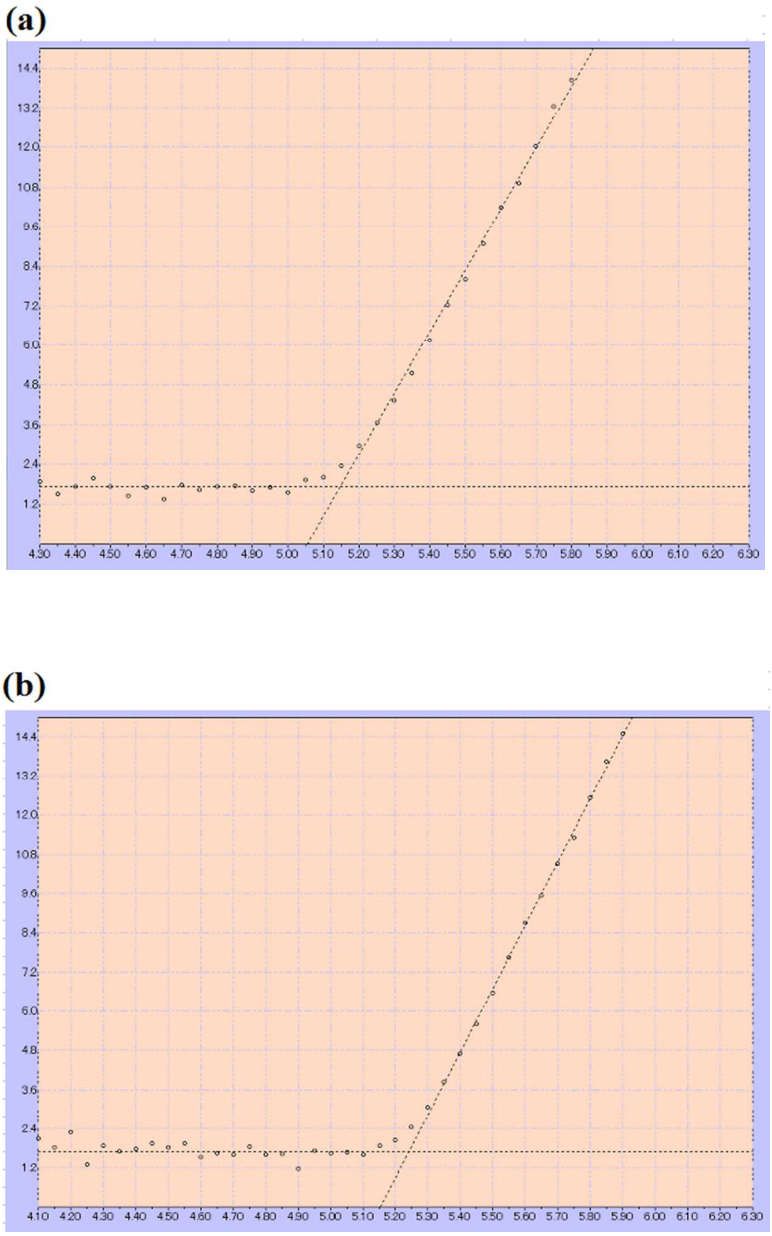



**Figure S21.** UPS characteristics of **PCBZANT** (a) and **PTPAANT** (b) for determining HOMO levels

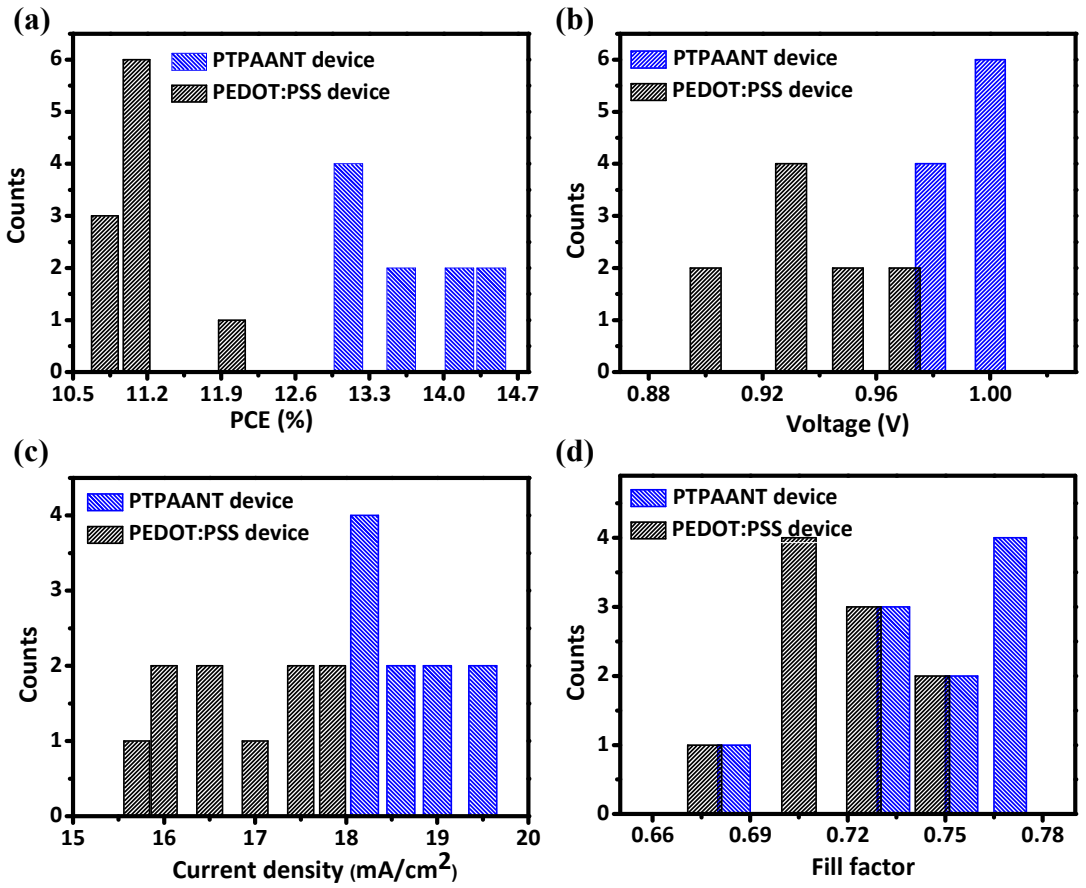



**Figure S22.** Histogram of photovoltaic parameters of **PTPAANT** versus PEDOT:PSS devices.

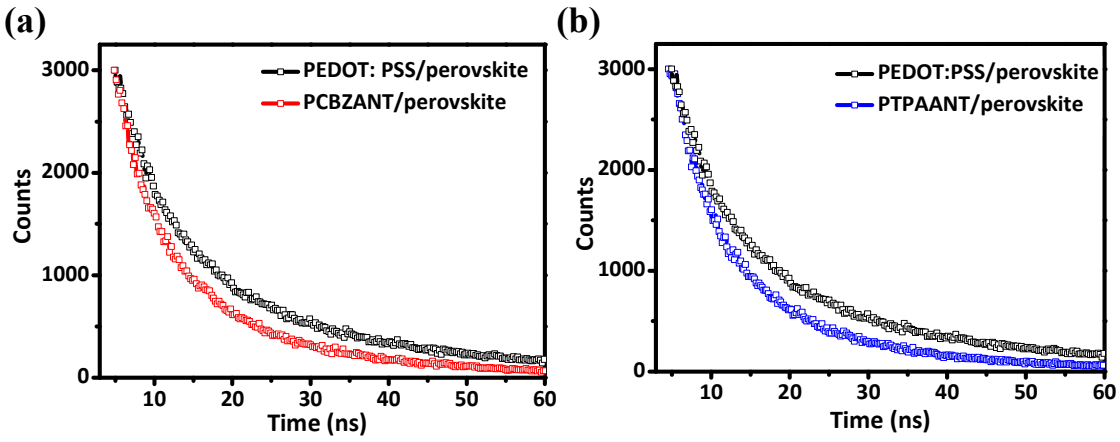



**Figure S23**. TCSPC curves of the perovskite films above **PCBZANT** layer versus above PEDOT:PSS layer (a) and those above **PTPAANT** layer versus above PEDOT:PSS layer (b).

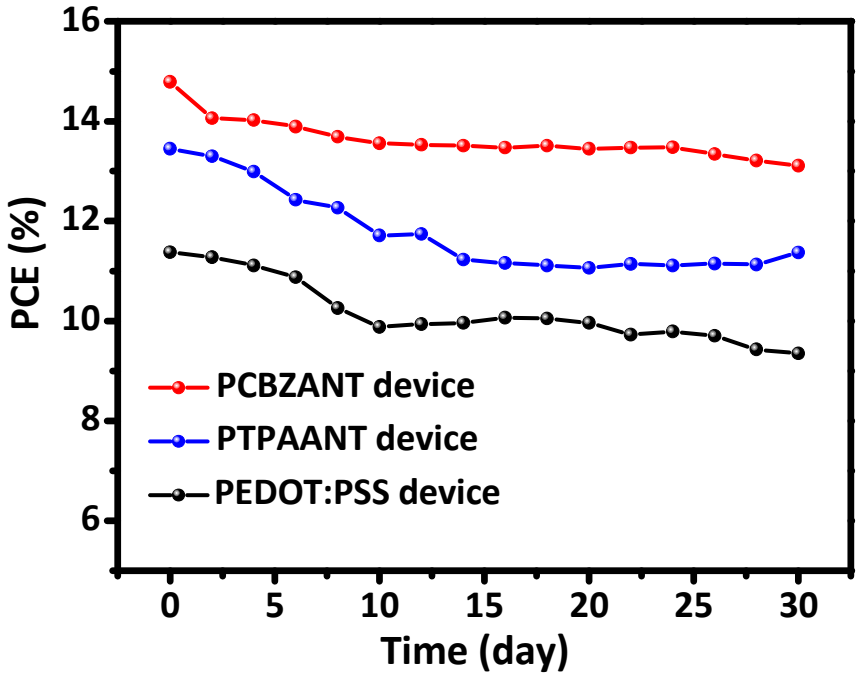



**Figure S24.** Long-term stability of the unencapsulated PSCs which were stored in a glove box.

Table S1. Photovoltaic parameters of **PCBZANT** devices with different HTM concentrations

| HTM concentration (mg ml$^{-1}$) | Sweep direction | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|---|
| 2 | forward | 0.98 | 15.48 | 58.22 | 8.87 |
| | reserve | 1.01 | 15.24 | 74.38 | 11.56 |
| 3 | forward | 0.91 | 21.40 | 58.22 | 11.36 |
| | reserve | 0.95 | 21.03 | 77.50 | 15.50 |
| 4 | forward | 0.97 | 16.83 | 60.43 | 9.88 |
| | reserve | 1.02 | 16.62 | 71.41 | 12.06 |

Table S2. Photovoltaic parameters of **PCBZANT** devices with different *m*-MTDATA concentrations

| *m*-MTDATA doping concentration (wt%) | Sweep direction | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|---|
| 20% | forward | 0.98 | 18.44 | 54.29 | 9.82 |
| | reserve | 1.02 | 18.18 | 62.37 | 11.51 |
| 30% | forward | 0.91 | 21.40 | 58.22 | 11.36 |
| | reserve | 0.95 | 21.03 | 77.50 | 15.50 |
| 40% | forward | 0.96 | 15.77 | 59.02 | 8.93 |
| | reserve | 0.99 | 15.65 | 75.33 | 11.70 |

Table S3. Photovoltaic parameters of **PTPAANT** devices with different HTM concentrations

| HTM concentration (mg ml$^{-1}$) | Sweep direction | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|---|
| 2 | forward | 0.79 | 13.86 | 46.31 | 5.07 |
| | reserve | 0.85 | 14.44 | 61.05 | 7.50 |
| 3 | forward | 0.96 | 19.22 | 56.60 | 10.48 |
| | reserve | 1.00 | 18.66 | 77.84 | 14.52 |
| 4 | forward | 0.83 | 19.83 | 53.30 | 8.75 |
| | reserve | 0.91 | 19.59 | 73.16 | 12.97 |

Table S4. Photovoltaic parameters of **PTPAANT** devices with different *m*-MTDATA concentrations

| *m*-MTDATA doping concentration (wt%) | Sweep direction | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|---|
| 10% | forward | 0.95 | 14.24 | 49.71 | 6.70 |
| | reserve | 0.97 | 14.54 | 72.54 | 10.20 |
| 20% | forward | 0.96 | 19.22 | 56.60 | 10.48 |
| | reserve | 1.00 | 18.66 | 77.84 | 14.52 |
| 30% | forward | 0.95 | 16.20 | 48.18 | 7.38 |
| | reserve | 0.97 | 16.41 | 70.41 | 11.22 |

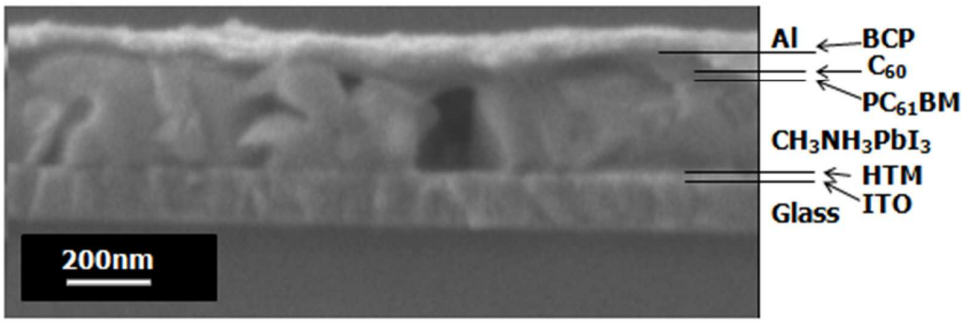



**Figure S25.** Cross-section image of the optimal device.

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[2] J. Kim, M. Hee Yun, P. Anant, S. Cho, J. Jacob, J. Y. Kimand and C. Yang, *Chem. Eur. J.* **2011**, *17*, 14681-14688.

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[4] M. X. Wan, Y. P. Zou, S. T. Tanand, Y. F. Li, *Polym. Adv. Technol.* **2010**, *21*, 256–262.