

Supporting Information

Series of Quinoidal Methyl-Dioxocyano-Pyridine Based π -Extended Narrow-Bandgap Oligomers for Solution-Processed Small-Molecule Organic Solar Cells

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Contents:

1. Experiment section.....	3
1.1 Materials.....	3
1.2 Measurements and characterizations.....	9
1.3 Fabrications and characterizations of solar cells.....	10
1.4 Tests of the hole/electron mobilities of small molecules/PC71BM.....	11
2. Supporting tables.....	12
3. Supporting figures.....	14
4. NMR figures.....	20
5. References.....	27

1. Experiment section

1.1 Materials

All reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar or TCI, and used as received. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenoneketyl under nitrogen before use. PC₇₁BM was bought from ADS (American Dye Source Inc.) and PEDOT:PSS was bought from Baytron P VP AI 4083, Germany.

3,3'-dioctyl-2,2'-bithiophene (2T(-in))

1T (275 mg, 1 mmol), 3-octyl-2-thiopheneboronic acid pinacol ester (322 mg, 1 mmol), 2.0 M aqueous K₂CO₃ solution (2 mL), and THF (15 mL) were mixed together in a flask and purged with Ar for 20 min. Then, tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄) (30 mg) was added in, and the reaction mixture was heated at 80 °C under reflux for 12 h. The mixture was extracted in CH₂Cl₂, washed with brine and dried over anhydrous MgSO₄, then the solvent was evaporated under vacuum. The crude product was purified by chromatography on silica gel (petroleum ether) to provide yellow oil (332 mg, 84.5%). ¹H NMR (400 MHz, CDCl₃, δ): 7.29-7.28 (d, *J* = 4 Hz, 2H), 6.97-6.96 (d, *J* = 4 Hz, 2H), 2.52-2.47 (t, 4H), 1.52-1.56 (m, 4H), 1.22-1.27 (m, 20H), 0.85-0.90 (m, 6H).

5,5'-diboronic acid pinacol ester-3,3'-dioctyl-2,2'-bithiophene

3,3'-dioctyl-2,2'-bithiophene (392 mg, 1 mmol) was dissolved in 10 mL dried THF and *n*-BuLi (2.5 M in THF, 1 mL, 2.50 mmol) was added by the syringe at -78 °C under the protection of Ar flow. After stirring for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mL, 2.5 mmol) was added and stirred at room temperature for 12 h. The organic solvent was removed and the residual was dissolved in ethyl acetate and washed with brine. The organic phase was dried by anhydrous MgSO₄, and then the solvent was evaporated. The crude product was used without further purification.

5,5'-dibromo-4,4'-dioctyl-2,2'-bithiophene (2Br-2T(out))

1T (1.21 g, 4.4 mmol), PdCl₂(PhCN)₂ (15.5 mg, 0.040 mmol), potassium fluoride (511 mg, 8.8 mmol), and DMSO (20 mL) were added into a 50 mL of round-bottom flask. AgNO₃ (1.49 g, 8.8 mmol) was added and heated with stirring at 60 °C for 3 h. Then, AgNO₃ (1.49 g, 8.8 mmol) and potassium fluoride (511 mg, 8.8 mmol) was added and stirred for further 3 h. The reaction mixture was purified by chromatography on silica gel (petroleum ether) to afford 964 mg of 2Br-2T(out) (82%). ¹H NMR (400 MHz, CDCl₃, δ): 6.77 (s, 2H), 2.48-2.53 (t, 4H), 1.59-1.62 (m, 4H), 1.30-1.27 (m, 20H), 0.86-0.90 (m, 6H).

3,3'-dioctyl-2,2':5,2''-terthiophene (3T)

This compound was prepared in a similar to 2T(in), using compound 2,5-bis(trimethyltin)-thiophene (0.27 mL, 0.5 mmol) instead of 3-octyl-2-thiopheneboronic acid pinacol ester. The crude product was purified by silica gel chromatography with petroleum ether, to give yellow oil (200 mg, 84.7%). ¹H NMR (400 MHz, CDCl₃, δ): 7.16-7.17 (d, *J* = 4 Hz, 2H), 7.06 (s, 2H), 6.93-6.94 (d, *J* = 4 Hz, 2H), 2.72-2.79 (t, 4H), 1.62-1.66 (m, 4H), 1.27-1.37 (m, 20H), 0.85-0.88 (m, 6H).

5,5'-bis(trimethyltin)-3,3'-dioctyl-2,2':5,2''-terthiophene

3,3'-dioctyl-2,2':5,2''-terthiophene (472 mg, 1 mmol) was dissolved in 10 mL dried THF and *n*-BuLi (2.5 M in THF, 1 mL, 2.5 mmol) was added by the syringe at -78°C under the protection of Ar flow. Then the mixture was kept stirring for 1 h. Trimethyltinchloride (1 M in THF, 2.5 mL, 2.5 mmol) was added and the reaction mixture was stirred at room temperature for 12h. The mixture was dissolved in ethyl acetate and washed with water. The organic phase was dried by anhydrous MgSO₄. The crude product was used without further purification.

4T(in)

This compound was prepared in a similar to 2T(in), using compound 5,5'-diboronic acid pinacol ester-3,3'-dioctyl-2,2'-bithiophene (185 mg, 0.5 mmol) instead of 3-octyl-2-thiopheneboronic acid pinacol ester. The crude product was purified by silica gel chromatography with petroleum ether, to give yellow oil (320mg, 81.6%). ¹H NMR (400 MHz, CDCl₃, δ): 7.16-7.15 (d, *J* = 4 Hz, 2H), 6.98 (s, 2H), 6.92-6.93 (d, *J* = 4 Hz, 2H), 2.76-2.80 (t, 4H), 2.54-2.58 (t, 4H), 1.59-1.67 (m, 8H), 1.26-1.36 (m, 40H), 0.84-0.88 (m, 12H).

4T(out)

This compound was prepared in a similar to 2T(in), using compound 2Br-2T(out) (386 mg, 0.7 mmol) instead of 1T. The crude product was purified by silica gel chromatography with petroleum ether, to give yellow oil (570 mg, 72.7%). ¹H NMR (400 MHz, CDCl₃, δ): 7.30-7.29 (d, *J* = 4 Hz, 2H), 7.02 (s, 2H), 6.96-6.97 (d, *J* = 4 Hz, 2H), 2.44-2.64 (m, 8H), 1.55-1.64 (m, 8H), 1.26-1.36 (m, 40H), 0.84-0.88 (m, 12H).

5T

This compound was prepared in a similar to 2T(in), using compound 5,5'-bis(trimethyltin)-3,3'-dioctyl-2,2':5,2''-terthiophene (798 mg, 1 mmol) instead of 3-octyl-2-thiopheneboronic acid pinacol ester. The crude product was purified by silica gel chromatography with petroleum ether, to give golden oil (650 mg, 75.6%). ¹H NMR

(400 MHz, CDCl₃, δ): 7.17-7.18 (d, J = 4 Hz, 2H), 7.08 (s, 1H), 6.95 (s, 2H), 6.92-6.93 (d, J = 4 Hz, 2H), 2.76-2.81 (m, 8H), 1.62-1.69 (m, 8H), 1.26-1.36 (m, 40H), 0.84-0.88 (m, 12H).

5-formyl-3,3'-dioctyl-2,2'-bithiophene (2T(in)-CHO)

POCl₃ (0.17 mL, 1.9 mmol) was added in DMF (10 mL) to prepare Vilsmeier reagent.

Vilsmeier reagent (0.6 mL) was added to a cold solution of 2T(in) (334 mg, 1 mmol) in 1,2-dichloroethane (10 mL) at -78 °C under Ar. After being stirred at 70 °C for 12 h, the mixture was poured into ice water (100 mL), neutralized with Na₂CO₃, and then extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over MgSO₄. The crude product was purified by silica gel chromatography with petroleum ether: DCM (4:1), to give 2T(in)-CHO (289 mg, 79.4%). ¹H NMR (400 MHz, CDCl₃, δ): 9.86 (s, 1H), 7.64 (s, 1H), 7.35-7.36 (d, J = 4 Hz, 1H), 6.99-6.98 (d, J = 4 Hz, 1H), 2.47-2.56 (t, 4H), 1.52-1.57 (m, 4H), 1.22-1.30 (m, 20H), 0.85-0.88 (m, 6H).

3T-CHO

This compound was prepared in a similar to 2T(in)-CHO, using compound 3,3'-dioctyl-2,2':5,2''-terthiophene (600 mg, 1.27 mmol) instead of 2T-in. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (3:1), to give yellow oil (478 mg, 74.6%). ¹H NMR (400 MHz, CDCl₃, δ): 9.83 (s, 1H), 7.60 (s, 1H), 7.23-7.24 (d, J = 4 Hz, 1H), 7.20-7.21 (d, J = 4 Hz, 1H), 7.09-7.10 (d, J = 8 Hz, 1H), 6.94-6.95 (d, J = 4 Hz, 1H), 2.75-2.85 (m, 4H), 1.59-1.74 (m, 4H), 1.27-1.37 (m, 20H), 0.85-0.88 (m, 6H).

4T(in)-CHO

This compound was prepared in a similar to 2T-in-CHO, using compound 4T(in) (320 mg, 0.4 mmol) instead of 2T-in. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (5:1), to give a yellow oil (240 mg, 73.8%). ¹H NMR (400 MHz, CDCl₃, δ): 9.82 (s, 1H), 7.56 (s, 1H), 7.16-7.18 (m, 2H), 6.99 (s, 1H), 6.92-6.94 (d, J = 8 Hz, 1H), 2.75-2.84 (t, 4H), 2.52-2.60 (t, 4H), 1.55-1.71 (m, 8H), 1.26-1.37 (m, 40H), 0.83-0.87 (m, 12H).

4T(out)-CHO

This compound was prepared in a similar to 2T-in-CHO, using compound 4T(out) (392 mg, 0.5 mmol) instead of 2T(in). The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (5:1), to give yellow oil (307 mg, 75.6%). ¹H NMR (400 MHz, CDCl₃, δ): 9.87 (s, 1H), 7.65 (s, 1H), 7.30-7.31 (d, J = 4 Hz, 1H), 7.04-7.05 (d, J = 4 Hz, 2H), 6.97-6.98 (d, J = 4 Hz, 2H), 2.45-2.62 (t, 8H), 1.58-1.68 (m, 8H), 1.23-1.30 (m, 40H), 0.84-0.88 (m, 12H).

5T-CHO

This compound was prepared in a similar to 2T(in)-CHO, using compound **5T** (285 mg, 0.33 mmol) instead of 2T-in. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (2:1), to give 5T-CHO (230 mg, 78.5%). ¹H NMR (400 MHz, CDCl₃, δ): 9.83 (s, 1H), 7.56 (s, 1H), 7.16-7.17 (d, *J* = 4 Hz, 1H), 7.11-7.13 (m, 3H), 6.95 (s, 1H), 6.93-6.94 (d, *J* = 4 Hz, 1H), 2.76-2.83 (t, 8H), 1.65-1.71 (m, 8H), 1.22-1.30 (m, 40H), 0.85-0.89 (m, 12H).

5-formyl-3-dioctyl-2-bromo-thiophene (*Br-1T-CHO*)

2-bromo-3-octyl-thiophene (275 mg, 1 mmol) was dissolved in 10 mL dried THF and LDA (2.5 M in THF, 0.4 mL, 1 mmol) was added by the syringe at -78°C under the protection of Ar flow. Then the mixture was kept stirring for 1 h. Dimethylformamide (DMF) (0.1 mL, 1.1 mmol) was added and the reaction mixture was stirred at room temperature for 12h. Then, water was added in this mixture and dissolved in DCM and washed with water. The organic phase was dried by anhydrous MgSO₄, and then the solvent was evaporated. The crude product was chromatographed on silica gel using dichloromethane and petroleum ether (1:10) as eluant to afford Br-1T-CHO (257 mg, 85%) as yellow oil. ¹H NMR (400 MHz, CDCl₃, δ): 9.76 (s, 1H), 7.02 (s, 1H), 7.46 (s, 1H), 2.57-2.61 (t, 2H), 1.58-1.62 (m, 2H), 1.27-1.32 (m, 10H), 0.84-0.90 (m, 3H).

5-formyl-5'-bromo-4,4'-dioctyl-2,2'-bithiophene (*Br-2T(out)-CHO*)

5,5'-dibromo-4,4'-dioctyl-2,2'-bithiophene (548 mg, 1 mmol) was dissolved in 10 mL dried THF and *n*-BuLi (2.5M in THF, 0.4 mL, 1 mmol) was added by the syringe at -78°C under the protection of Ar flow. Then the mixture was kept stirring for 2 h. Dimethylformamide (DMF) (0.1 mL, 1.1 mmol) was added and the reaction mixture was stirred at room temperature for 12h. The mixture was poured into water and extracted with dichloromethane, and washed with water. The organic phase was dried by anhydrous MgSO₄. After solvent removal, the residue was purified by column chromatography on silica gel using dichloromethane and petroleum ether (1:7) as eluant to afford Br-2T(in)-CHO (251 mg, 51%) as yellow oil. ¹H NMR (400 MHz, CDCl₃, δ): 9.98 (s, 1H), 7.02 (s, 1H), 6.97 (s, 1H), 2.88-2.94 (t, 2H), 2.52-2.57 (t, 2H), 1.59-1.70 (m, 4H), 1.25-1.31 (m, 20H), 0.84-0.90 (m, 6H).

5-formyl-5'-bromo-3,3'-dioctyl-2,2'-bithiophene (*Br-2T(in)-CHO*)

N-bromosuccinimide (196 g, 1.1 mmol) was added in small portions to a solution of 2T(in)-CHO (418 g, 1 mmol) in chloroform. After being stirred for 6 h at room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH₂Cl₂. The organic

layer was thoroughly washed with water, aqueous sodium bicarbonate, and again with water, and then dried over MgSO_4 . After removal of solvent, it was purified by column chromatography on silica gel using dichloromethane and petroleum ether (1:6) as eluant to afford Br-2T(in)-CHO (472 mg, 95%) as yellow oil. ^1H NMR (400 MHz, CDCl_3 , δ): 9.86 (s, 1H), 7.62 (s, 1H), 6.97-6.95 (s, 1H), 2.43-2.56 (t, 4H), 1.48-1.55 (m, 4H), 1.22-1.33 (m, 20H), 0.84-0.89 (m, 6H).

Br-3T-CHO

This compound was prepared in a similar to Br-2T(in)-CHO, using compound 3T-CHO (500 mg, 1mmol) instead of 2T-in-CHO. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (3:1), to give yellow oil (556 mg, 96%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.83 (s, 1H), 7.60 (s, 1H), 7.22-7.23 (d, $J = 4$ Hz, 1H), 7.04-7.05 (d, $J = 4$ Hz, 1H), 7.69 (s, 1H), 2.69-2.84 (t, 4H), 1.55-1.71 (m, 4H), 1.27-1.35 (m, 20H), 0.84-0.89 (m, 6H).

Br-4T-in-CHO

This compound was prepared in a similar to Br-2T(in)-CHO, using compound 4T(in)-CHO (807 mg, 1 mmol) instead of 2T(in)-CHO. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (5:1), to give yellow oil (842 mg, 95%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.83 (s, 1H), 7.59 (s, 1H), 7.16 (s, 1H), 6.92 (s, 1H), 6.89 (s, 1H), 2.68-2.84 (t, 4H), 2.52-2.56 (t, 4H), 1.58-1.68 (m, 8H), 1.26-1.37 (m, 40H), 0.83-0.87 (m, 12H).

Br-4T(out)-CHO

This compound was prepared in a similar to Br-2T(in)-CHO, using compound 4T(out)-CHO (807 mg, 1 mmol) instead of 2T(in)-CHO. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (5:1), to give yellow oil (820 mg, 92.5%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.86 (s, 1H), 7.65 (s, 1H), 7.02-7.03 (d, $J = 4$ Hz, 2H), 6.93 (s, 1H), 2.44-2.61 (t, 8H), 1.58-1.68 (m, 8H), 1.23-1.30 (m, 40H), 0.84-0.88 (m, 12H).

Br-5T-CHO

This compound was prepared in a similar to Br-2T(in)-CHO, using compound 5T-CHO (889 mg, 1 mmol) instead of 2T(in)-CHO. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (2:1), to give yellow oil (929 mg, 96%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.83 (s, 1H), 7.59 (s, 1H), 7.09-7.13 (m, 3H), 6.89 (s, 2H), 2.69-2.84 (t, 8H), 1.61-1.71 (m, 8H), 1.22-1.30 (m, 40H), 0.85-0.89 (m, 12H).

2,6-diethyl-4,8-bis(5-ethylhexylthiophen-2-yl)benzo-[1,2-b:4,5-b']dithiophene (BDT-CHO)

4,8-bis(5-ethylhexylthiophen-2-yl)benzo-[1,2-b:4,5-b']dithiophene (245 mg, 0.5 mmol) was dissolved in 10 mL dried THF and *n*-BuLi (2.5 M in hexane, 0.44 mL, 1.1 mmol) was added by the syringe at -78°C under the protection of Ar flow. Then the mixture was kept stirring for 1 h. Dimethylformamide (DMF) (0.11 mL, 1.5 mmol) was added and the reaction mixture was stirred at room temperature for 12h. The mixture was dissolved in water and extract with dichloromethane. The organic phase was dried by anhydrous MgSO_4 , and then the solvent was evaporated. The crude product was chromatographed on silica gel using dichloromethane and petroleum ether (3:1) as eluant to afford BDT-CHO (1.22 g, 90%) as orange solid. ^1H NMR (400 MHz, CDCl_3 , δ): 10.06 (s, 2H), 8.33 (s, 2H), 7.54 (s, 2H), 7.32 (s, 1H), 6.89-6.92 (d, 4H), 2.84-2.88 (m, 8H), 1.68-1.69 (m, 4H), 1.22-1.30 (m, 10H), 0.85-0.89 (m, 12H).

BDT-T-CHO

Under the protection of argon, Br-1T-CHO (76 mg, 0.25 mmol) and 2,6-bis(trimethyltin)-4,8-bis(5-ethylhexylthiophen-2-yl)benzo-[1,2-b:4,5-b']dithiophene (90.4 mg, 0.1 mmol) in dry toluene (20 ml), then $\text{Pd}(\text{PPh}_3)_4$ (20 mg) were added into the sealed flask. The mixture was vigorously stirred for 12 h at 110°C . After cooling to room temperature, the reaction mixture was partitioned with DCM and water. The collected organic layers were washed with water, and dried over anhydrous MgSO_4 . After filtration, the solvent was evaporated under vacuum, the crude product was purified by column chromatographically with DCM/petroleum ether (3:1), recrystallized from CHCl_3 /methanol, and dried under vacuum to afford an orange solid (86.7 mg, 85%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.85 (s, 2H), 7.82 (s, 2H), 7.61 (s, 2H), 7.33-7.34 (d, $J = 4$ Hz, 2H), 6.91-6.92 (d, $J = 4$ Hz, 2H), 2.84-2.89 (t, 8H), 1.64-1.71 (m, 6H), 1.22-1.30 (m, 36H), 0.85-0.89 (m, 18H).

BDT-2T-in-CHO

This compound was prepared in a similar to BDT-T-CHO, using compound Br-2T(in)-CHO (125 mg, 0.25 mmol) instead of Br-1T-CHO. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (3:2), to give orange oil (117 mg, 82.6%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.87 (s, 2H), 7.65 (s, 4H), 7.31-7.32 (d, $J = 4$ Hz, 2H), 7.17 (s, 2H), 6.92-6.93 (d, $J = 4$ Hz, 2H), 2.87-2.89 (m, 4H), 2.47-2.62 (m, 10H), 1.65-1.70 (m, 4H), 1.18-1.32 (m, 60H), 0.85-0.97 (m, 24H).

BDT-2T(out)-CHO

This compound was prepared in a similar to BDT-T-CHO, using compound Br-2T(out)-CHO (125 mg, 0.25 mmol) instead of Br-1T-CHO. The crude product was purified by silica gel chromatography with dichloromethane/ petroleum ether (3:2), to give orange oil (109 mg,

77.2%). ¹H NMR (400 MHz, CDCl₃, δ): 9.99 (s, 2H), 7.69 (s, 2H), 7.33-7.34 (d, *J* = 4 Hz, 2H), 7.18 (s, 2H), 7.05 (s, 2H), 6.91-6.92 (d, *J* = 4 Hz, 2H), 2.80-2.93 (m, 12H), 1.65-1.70 (m, 8H), 1.33-1.46 (m, 58H), 0.85-0.97 (m, 24H).

BDT-3T-CHO

This compound was prepared in a similar to BDT-T-CHO, using compound Br-3T-CHO (148 mg, 0.25 mmol) instead of Br-1T-CHO. The crude product was purified by silica gel chromatography with dichloromethane, to give a red solid (139 mg, 88.5%). ¹H NMR (400 MHz, CDCl₃, δ): 9.85 (s, 2H), 7.67 (s, 2H), 7.61 (s, 2H), 7.31-7.32 (d, *J* = 4 Hz, 2H), 7.22 (s, 2H), 7.19 (s, 2H), 6.92-6.93 (d, *J* = 4 Hz, 2H), 2.56-2.90 (m, 12H), 1.60-1.73 (m, 8H), 1.30-1.41 (m, 58H), 0.85-0.97 (m, 24H).

BDT-4T(in)-CHO

This compound was prepared in a similar to BDT-T-CHO, using compound Br-4T(in)-CHO (223 mg, 0.25 mmol) instead of Br-1T-CHO. The crude product was purified by silica gel chromatography with dichloromethane, to give a red solid (175 mg, 79.6%). ¹H NMR (400 MHz, CDCl₃, δ): 9.83 (s, 2H), 7.59-7.62 (d, 4H), 7.31-7.32 (d, *J* = 4 Hz, 2H), 7.17 (s, 4H), 7.12 (s, 2H), 7.03 (s, 2H), 6.93-6.94 (d, *J* = 4 Hz, 2H), 2.56-2.90 (m, 24H), 1.25-1.73 (m, 110H), 0.85-0.97 (m, 36H).

BDT-4T(out)-CHO

This compound was prepared in a similar to BDT-T-CHO, using compound Br-4T(out)-CHO (223 mg, 0.25 mmol) instead of Br-1T-CHO. The crude product was purified by silica gel chromatography with dichloromethane, to give orange oil (178 mg, 81.2%). ¹H NMR (400 MHz, CDCl₃, δ): 9.87 (s, 2H), 7.64-7.65 (s, *J* = 4 Hz, 4H), 7.31-7.32 (d, *J* = 4 Hz, 2H), 7.16 (s, 2H), 7.05 (s, 4H), 6.92-6.93 (d, *J* = 4 Hz, 2H), 2.88-2.90 (m, 4H), 2.50-2.62 (m, 16H), 1.30-1.73 (m, 114H), 0.85-0.97 (m, 36H).

BDT-5T-CHO

This compound was prepared in a similar to BDT-T-CHO, using compound Br-5T-CHO (240 mg, 0.25 mmol) instead of Br-1T-CHO. The crude product was purified by silica gel chromatography with dichloromethane, to give a red solid (186 mg, 79%). ¹H NMR (400 MHz, CDCl₃, δ): 9.83 (s, 2H), 7.62 (s, 2H), 7.59 (s, 2H), 7.31-7.32 (d, *J* = 4 Hz, 2H), 7.12-7.13 (m, 8H), 7.10 (s, 2H), 6.92-6.93 (d, *J* = 4 Hz, 2H), 2.56-2.90 (m, 20H), 1.30-1.69 (m, 114H), 0.85-0.97 (m, 36H).

1.2 Measurements and characterizations

The ^1H NMR and ^{13}C NMR spectra were performed using a Bruker AVANCE 400 MHz spectrometer and Bruker AVANCE 600 MHz spectrometer with tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Elemental analysis was contained on a flash EA1112 analyzer. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III mass spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen flow. Differential scanning calorimetry (DSC) was tested on a Diamond DSC 822e with a heating rate of 10°C/min in the temperature range of 25 to 800°C . UV-vis absorption spectrum was carried out at a Hitachi U-3010 spectrometer. The electrochemical measurements were measured under argon at a scan rate of 100mVs^{-1} at room temperature with a computer-controlled Zennium electrochemical workstation (Zahner IM6e). A glassy carbon electrode, a Pt wire, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. The samples were dissolved in chloroform with tetra-*n*-butylammoniumhexafluorophosphate (Bu_4NPF_6 , 0.1M) as electrolyte. Transmission electron microscopy (TEM) tests were performed on a JEM-2011 operated at 200 kV. The TEM specimens were prepared by transferring the spin-coated films to the 200 mesh copper grids. Grazing-incidence wide-angle X-ray scattering (GIWAXS) samples of pristine films were prepared by drop-casting of solutions on silica slides and small molecule/PC71BM blending films were spin-coated using the same conditions of the best devices on a PEDOT:PSS pre-coated Si substrate. The GIWAXS was performed at 1W1A, Beijing Synchrotron Radiation Facility. The 10 keV X-ray beam was incident at a grazing angle of 0.2° , which maximized the scattering intensity from the samples. The scattered intensity was detected with a Pilatus detector.

1.3 Fabrications and characterizations of solar cells

The solar cell devices were fabricated on the glass substrates with the normal cell architecture of indium tin oxide (ITO)/PEDOT:PSS/active layer/Ca/Al in the glove box under the protection of N_2 flow, $\text{O}_2 \leq 0.1$ ppm and $\text{H}_2\text{O} \leq 0.1$ ppm. Prior to use, ITO glass was ultrasonically cleaned with deionized water, acetone and isopropanol and treated in a Novascan PSD-ultraviolet-ozone chamber for 30 min, respectively. A thin layer of PEDOT:PSS with a thickness of 30 nm was spin-coated onto the ITO glass with a rate of 2000 rpm and then baked at 150°C for 10 min. Subsequently, the small molecule:PC71BM active layer was spin-coated on the PEDOT:PSS layer from a homogeneously blended solution (D:A=1:1.1, 10 mg/mL, prepared by dissolving the small molecule and PC₇₁BM in

chloroform). At last, the substrates were pumped down to high vacuum ($< 1 \times 10^{-4}$ Torr), and Ca/Al (ca. 20/80 nm) was thermally evaporated onto the active layer through shadow masks to define the effective cell area (6 mm^2) of the devices. The current-voltage (J - V) measurement of the devices was measured using a computer-controlled Keithley 2400 Source Measure Unit in nitrogen atmosphere in the dark and under white light illumination of simulated AM 1.5 G, 100 mW/cm^2 using a xenon-lamp-based solar simulator (AAA grade, XES-70S1). EQE measurements were measured using a 250 W Quartz Tungsten Halogen (Oriel) fitted with a monochromator (Cornerstone (CS130) 1/8m) as a monochromatic light source.

1.4 Tests of the hole/electron mobilities of small molecules/PC71BM

The hole and electron mobilities were carried out by the space-charge-limited current (SCLC) method with a hole-only device of ITO/PEDOT:PSS/active layer/Au and an electron-only device of ITO/TIPD/active layer/Al, respectively. The active layers were spin-coated under the conditions that afford the best photovoltaic results. The following equation was applied to estimate the hole and electron mobilities: ^[1-2]

$$\ln(JL^3V^2) = 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \ln(9\epsilon_0\mu_0/8) \quad (1)$$

where ϵ is the average dielectric constant of the blended film, ϵ_0 the permittivity of the vacuum, μ_0 the zero-field mobility, E_0 the characteristic field, J the current density, L the thickness of the films, and $V = V_{\text{appl}} - V_{\text{bi}}$; V_{appl} the applied potential, and V_{bi} the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{\text{bi}} = 0.2 \text{ V}$). The hole mobility of the blending films was deduced from the intercept value of $\ln(9\epsilon\epsilon_0\mu_0/8)$.

2. Supporting Tables

Table S1. Summary of current–voltage parameters of the small molecule OSCs based on based on small molecules: PC₇₁BM blends with different weight ratios.

Active layer	solvent	D/A (w/w)	PCE (%)	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)
0TBM: PC ₇₁ BM	CB	1.5:1	0.005	0.1	0.24	28.3
		1:1	0.02	0.1	0.62	31.2
		1:1.5	0.015	0.1	0.49	28.0
1TBM: PC ₇₁ BM	CB	2:1	0.33	1.48	0.77	28.5
		1:1	0.61	2.21	0.86	32.0
		1:2	0.47	1.78	0.86	30.6
2T(out)BM: PC ₇₁ BM	CF	2:1	0.18	0.86	0.81	26.1
		1:1	0.33	1.47	0.82	27.0
		1:2	0.30	1.17	0.82	31.0
2TBM: PC ₇₁ BM	CF	1.5:1	0.09	0.60	0.69	22.8
		1:1	0.071	0.47	0.66	23.1
		1:1.5	0.12	0.81	0.61	23.7
		1:2	0.20	1.27	0.65	24.2
3TBM: PC ₇₁ BM	CF	1.5:1	1.60	4.78	0.75	44.6
		1:1	2.66	5.76	0.83	55.7
		1:1.5	2.07	5.15	0.83	48.6
4T(out)BM: PC ₇₁ BM	o-DCB	1.5:1	0.16	0.89	0.76	24.3
		1:1	0.35	1.73	0.81	24.8
		1:1.5	0.24	1.23	0.76	25.6
4TBM: PC ₇₁ BM	CF	1.5:1	0.18	1.11	0.68	23.3
		1:1	0.20	1.23	0.67	24.1
		1:1.5	0.28	1.70	0.68	24.4
		1:2	0.42	2.35	0.71	25.2
5TBM: PC ₇₁ BM	CF	1.5:1	3.68	8.54	0.75	57.5
		1:1	4.07	8.69	0.79	59.2
		1:1.5	4.17	9.00	0.74	62.6

Table S2. Summary of current–voltage parameters of the OSCs based on based on small molecules: PC₇₁BM blends with different DIO ratios.

Active layer	Solvent	Spin speed (rpm)	DIO(v/v)	PCE (%)	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)
0TBM: PC ₇₁ BM	CB	2000	0.1%	0.015	0.108	0.50	27.9
			0.2%	0.02	0.11	0.60	29.6
			0.5%	0.017	0.09	0.58	31.5
1TBM: PC ₇₁ BM	CB	2000	0.1%	0.49	1.95	0.77	32.8
			0.2%	0.95	3.49	0.82	33.2
			0.5%	0.62	2.31	0.80	33.5
2T(out)BM: PC ₇₁ BM	CB	2000	0%	1.36	5.06	0.77	34.8
			0.2%	0.97	3.92	0.76	32.6
			0.5%	0.49	2.32	0.76	27.8
	110°C	2000	0%	1.56	6.33	0.81	30.4
2TBM: PC ₇₁ BM	CF	2000	0%	0.70	3.82	0.70	27.5
			0.2%	1.49	6.74	0.66	33.6
			0.5%	1.73	6.58	0.70	37.5
	CB	2000	0.5%	1.85	6.66	0.79	35.1
3TBM: PC ₇₁ BM	CF	3000	0.5%	3.74	9.38	0.77	51.8
			1%	5.34	11.59	0.81	56.8
			1.2%	5.85	12.97	0.81	55.7
	100°C	3000	1.2%	6.03	13.81	0.80	54.6
4T(out)BM: PC ₇₁ BM	o-DCB	1000	0%	0.43	2.31	0.75	25.0
			0.2%	0.38	1.96	0.78	25.1
			0.5%	0.45	2.33	0.76	25.2
4TBM: PC ₇₁ BM	CF	2000	0%	0.66	3.17	0.79	26.5
			0.2%	0.95	3.23	0.77	38.0
			0.5%	0.97	3.16	0.73	42.3
	o-DCB	1000	0.2%	1.56	5.01	0.78	40.2
5TBM: PC ₇₁ BM	CF	2000	0.15%	4.13	9.40	0.68	64.5
			0.2%	5.04	9.79	0.78	66.0
			0.5%	1.78	6.58	0.70	38.8

Table S3. Summary of the hole and electron mobilities of the optimized solar cells.

Donors	μ_h [cm ² V ⁻¹ s ⁻¹]	μ_e [cm ² V ⁻¹ s ⁻¹]
0TBM	9.06×10^{-6}	1.03×10^{-2}
1TBM	6.70×10^{-5}	1.96×10^{-5}
2TBM	2.37×10^{-5}	5.28×10^{-2}
2T(out)BM	2.37×10^{-5}	3.49×10^{-4}
3TBM	7.44×10^{-3}	2.30×10^{-2}
4TBM	1.27×10^{-5}	6.29×10^{-4}
4T(out)BM	1.27×10^{-5}	1.04×10^{-2}
5TBM	4.00×10^{-3}	1.02×10^{-1}

3. Supporting Figures

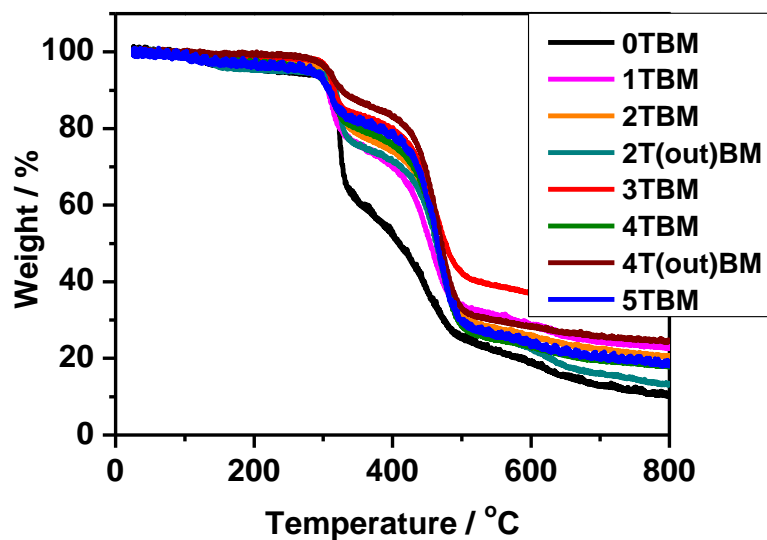


Figure S1. TGA curves of all the small molecules.

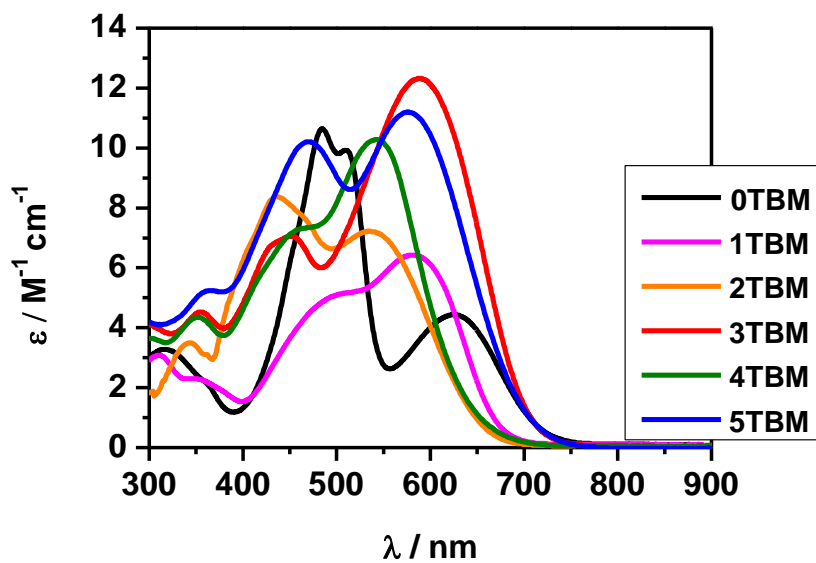


Figure S2. UV-vis absorption spectra of n TBM ($n = 0-5$) in chloroform solution.

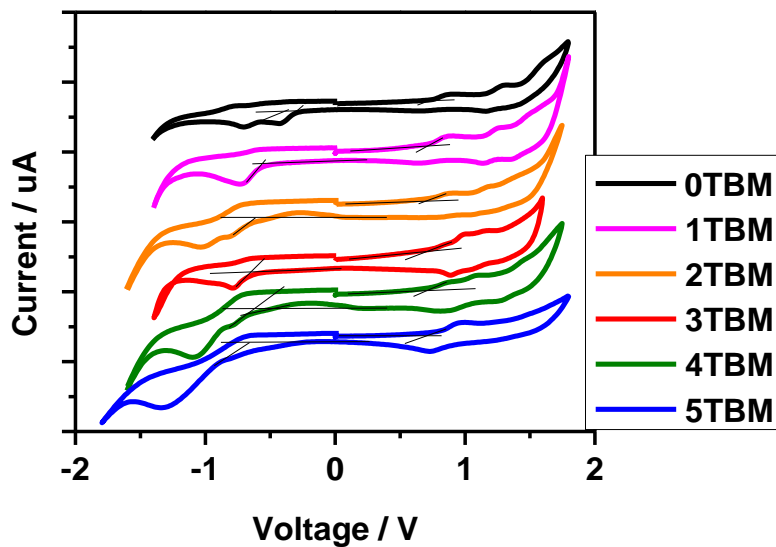


Figure S3. Cyclic voltammogram of the n TBM ($n = 0-5$) on the Pt electrode measured with 0.1m Bu₄NPF₆ in chloroform solution with Ag/AgCl as the reference electrode. The HOMO and LUMO energy levels are calculated according to the following equations: $E_{HOMO/LUMO} = -e(E_{onset(ox/red)} + 4.4)V$

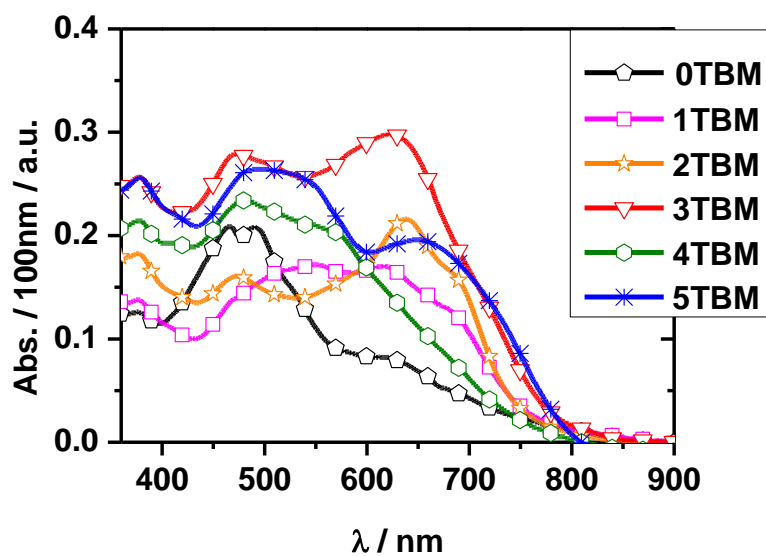


Figure S4. UV-vis absorption spectra of n TBM ($n = 0-5$): PC₇₁BM blend films.

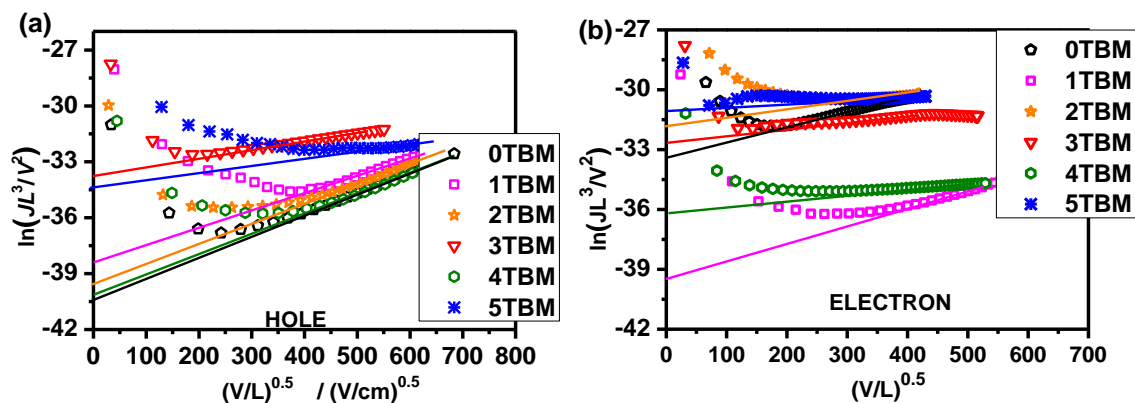


Figure S5. Plots of $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ for n TBM ($n = 0-5$) based blended films.

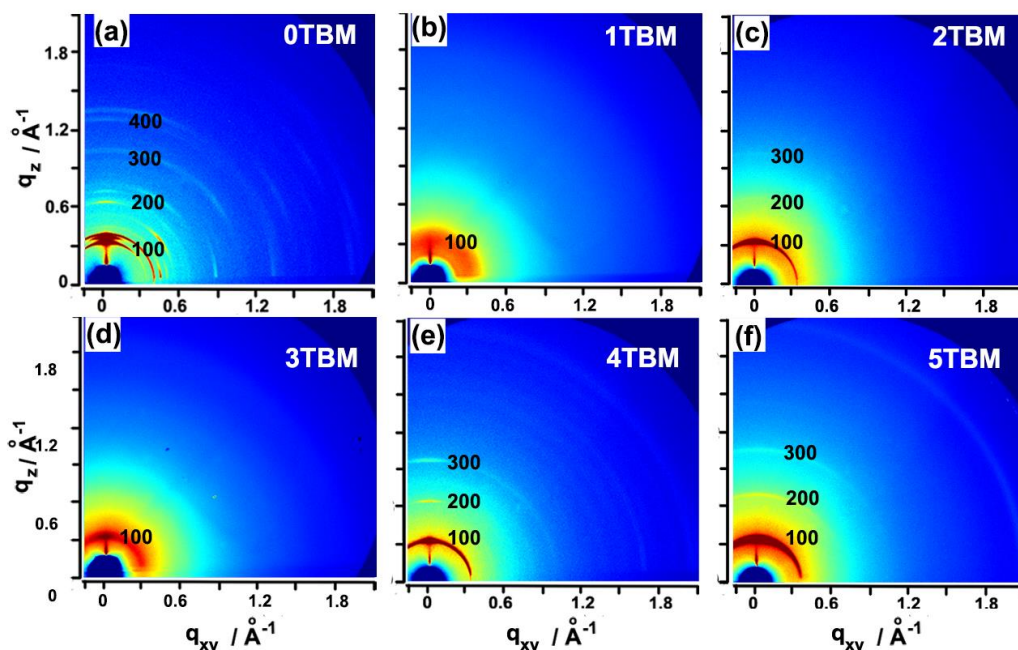


Figure S6. 2D-GIWAXS patterns of neat films for (a) 0TBM, (b) 1TBM, (c) 2TBM, (d) 3TBM, (e) 4TBM, and (f) 5TBM.

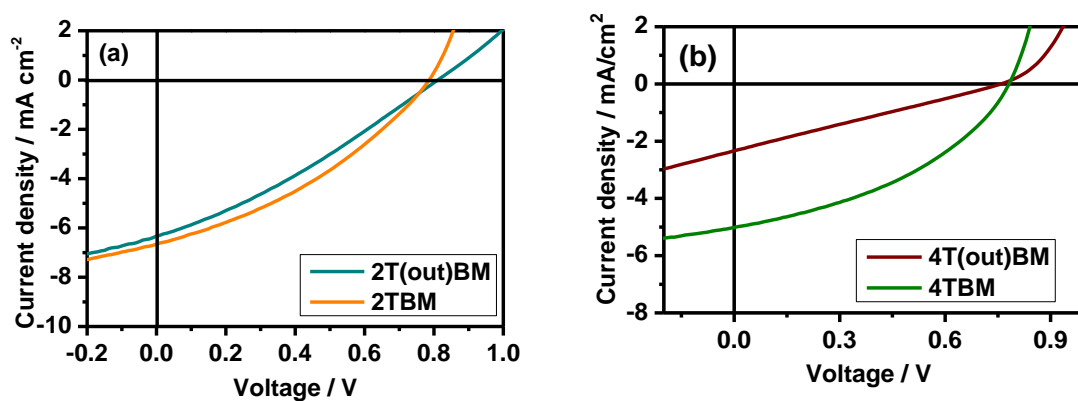


Figure S7. J - V characteristics of 2TBM (a) and 4TBM (b) based devices with “inward” and “outward” alkyl chain.

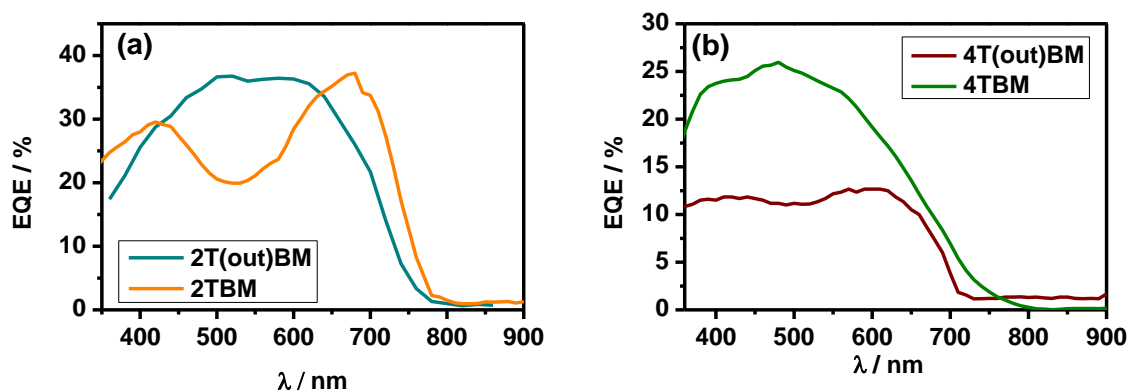


Figure S8. EQE spectra of 2TBM (a) and 4TBM (b) based devices with “inward” and “outward” alkyl chain.

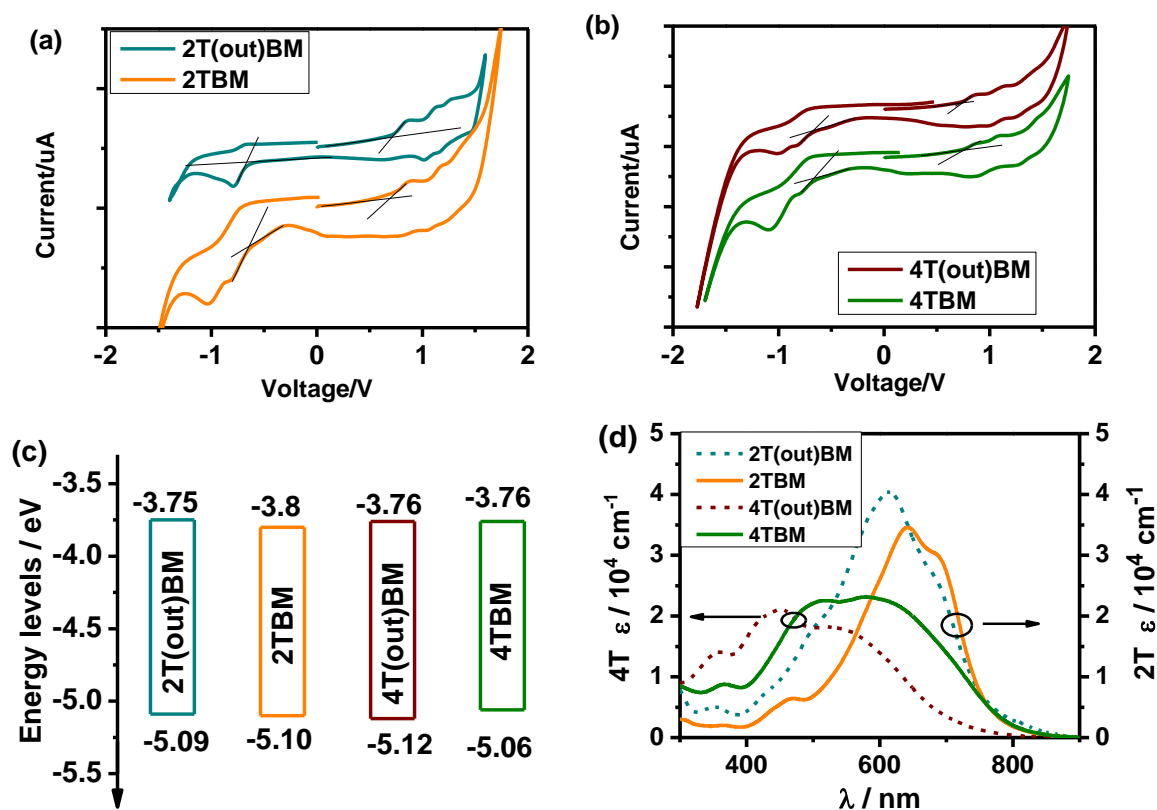


Figure S9. Cyclic voltammogram of the (a) 2T(out)BM (blue lines) and 2TBM (yellow lines) (b) 4T(out)BM (brown lines) and 4TBM (green lines) on the Pt electrode measured with 0.1m Bu_4NPF_6 in chloroform solution with Ag/AgCl as the reference electrode. The HOMO and LUMO energy levels are calculated according to the following equations: $E_{\text{HOMO/LUMO}} = -e(E_{\text{onset(ox/red)}} + 4.4)\text{V}$. (c) Diagram of the HOMO and LUMO energy levels of 2TBM and 4TBM used in the photovoltaic devices. (d) The UV-vis absorption spectra of the small molecules in as-cast solid thin films.

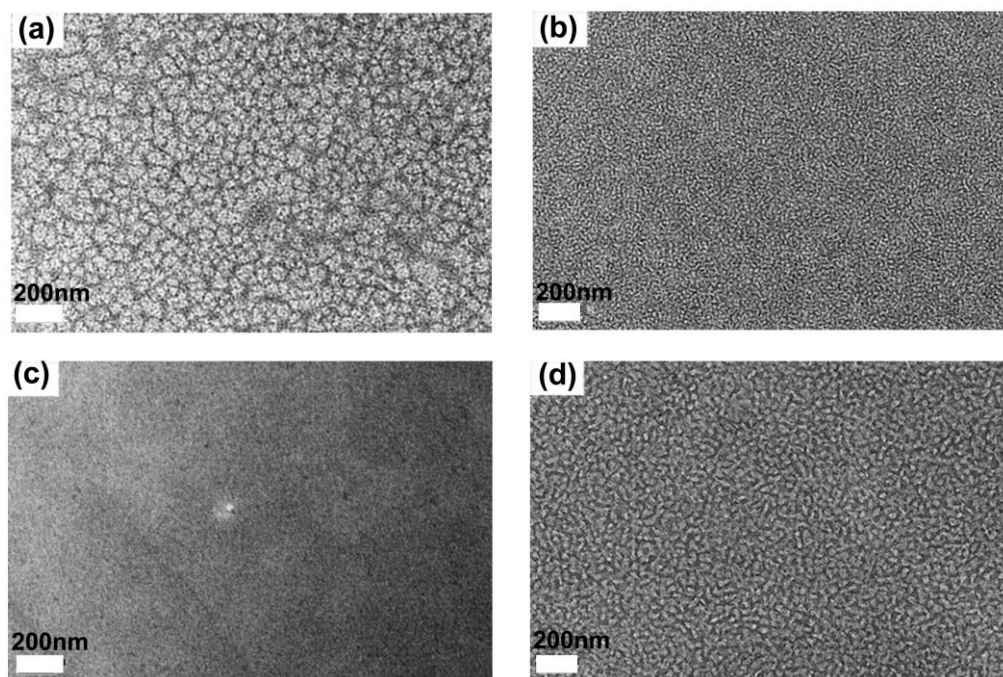


Figure S10. TEM images of the small molecules: PC71BM (1:1, w/w) blend films for (a)

2T(out)BM, (b) 2TBM, (c) 4T(out)BM, (d) 4TBM.

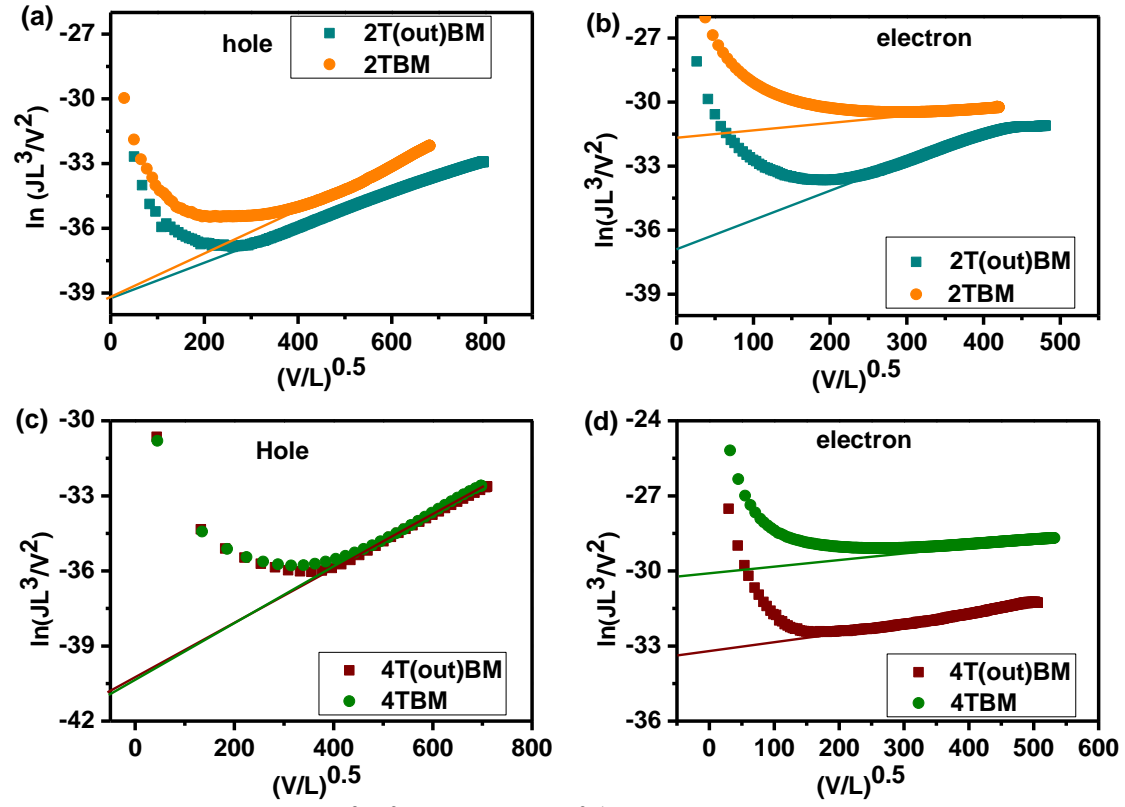


Figure S11. Plots of $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ for 2TBM and 4TBM based blended films.

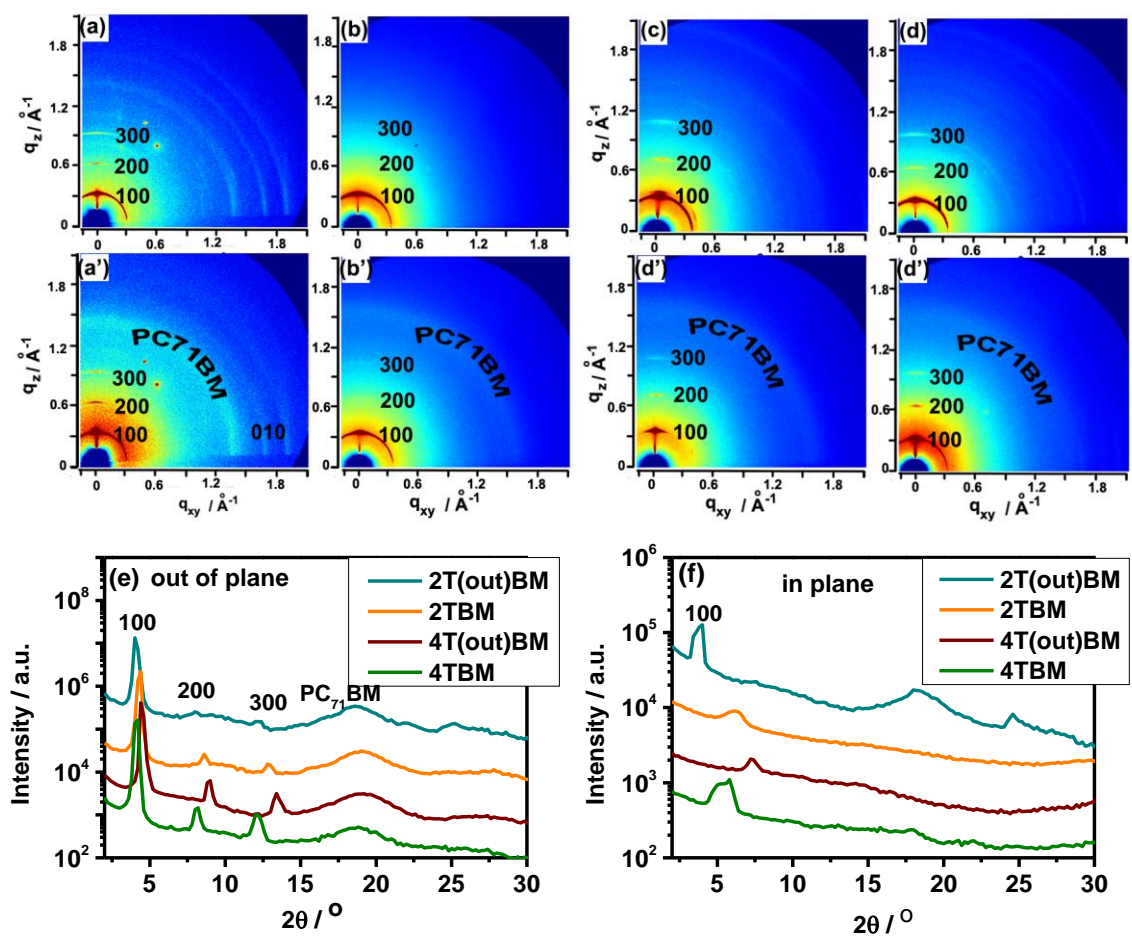
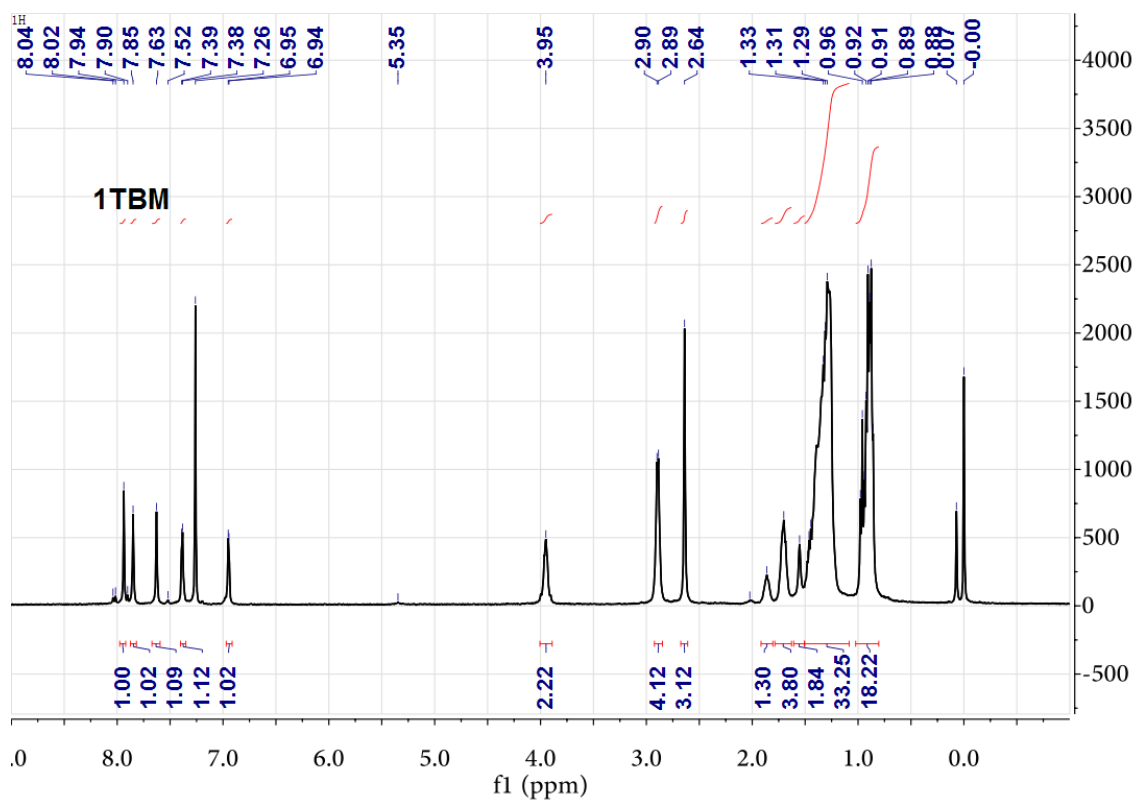
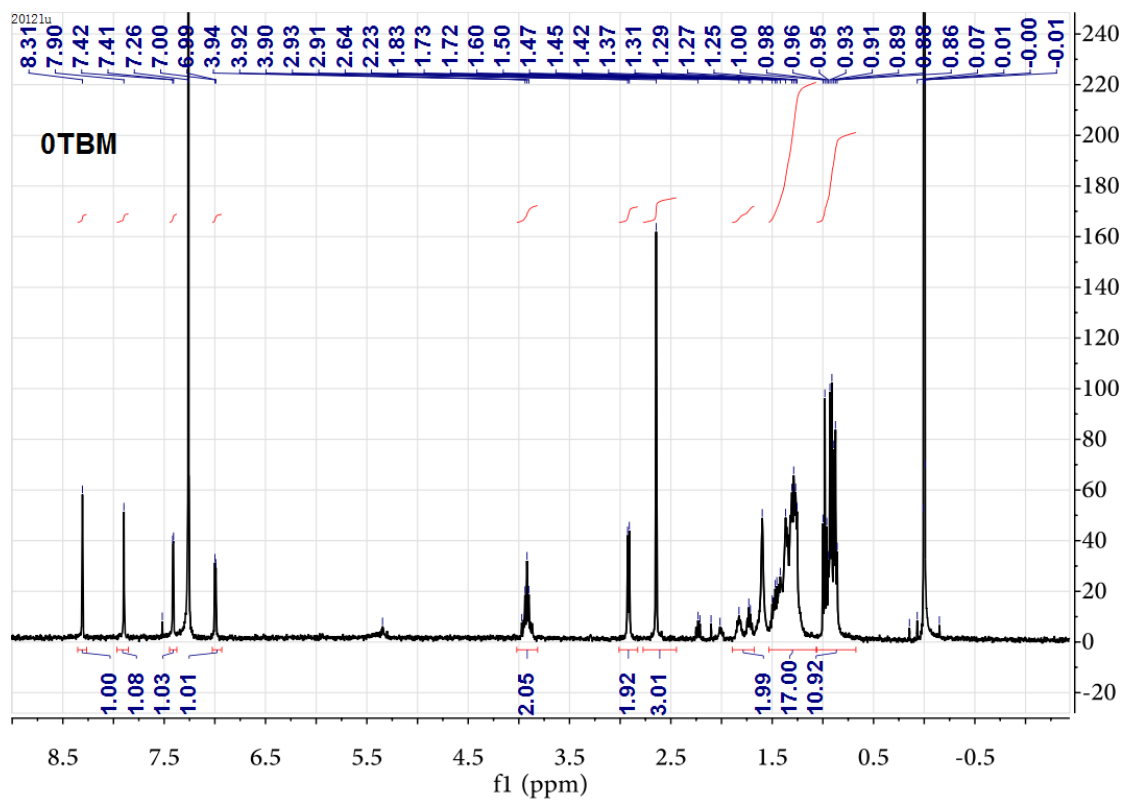
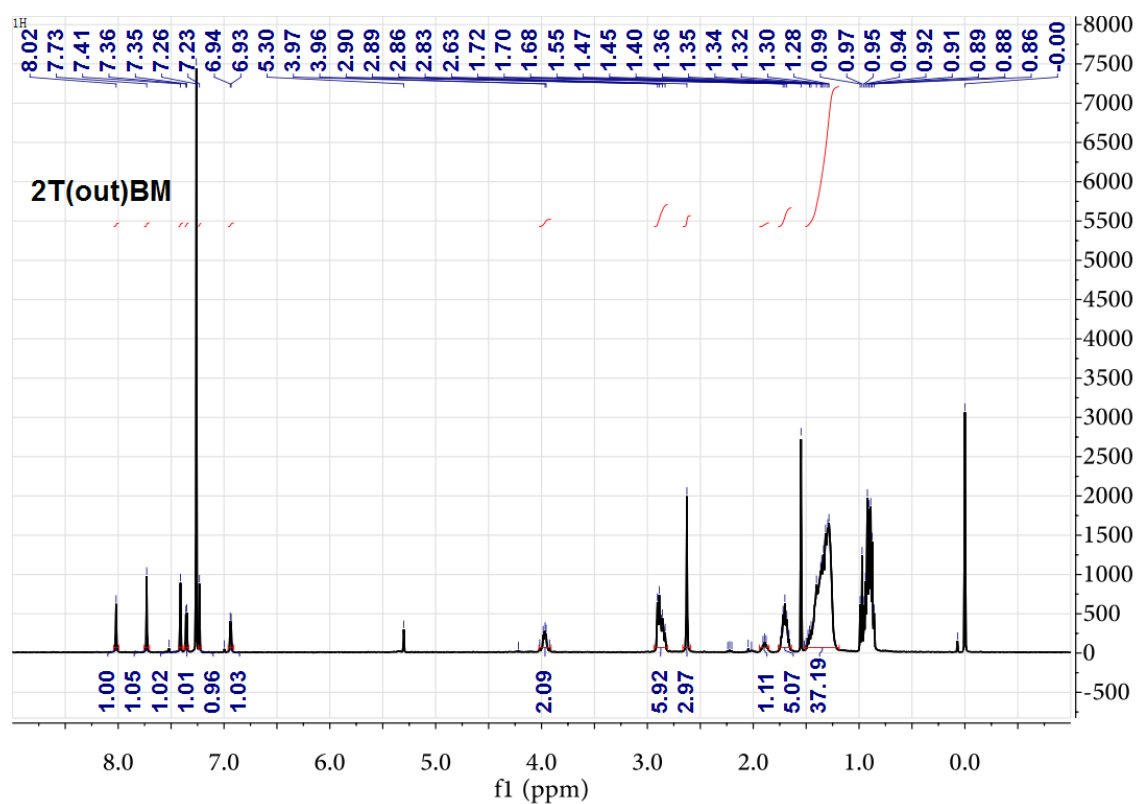
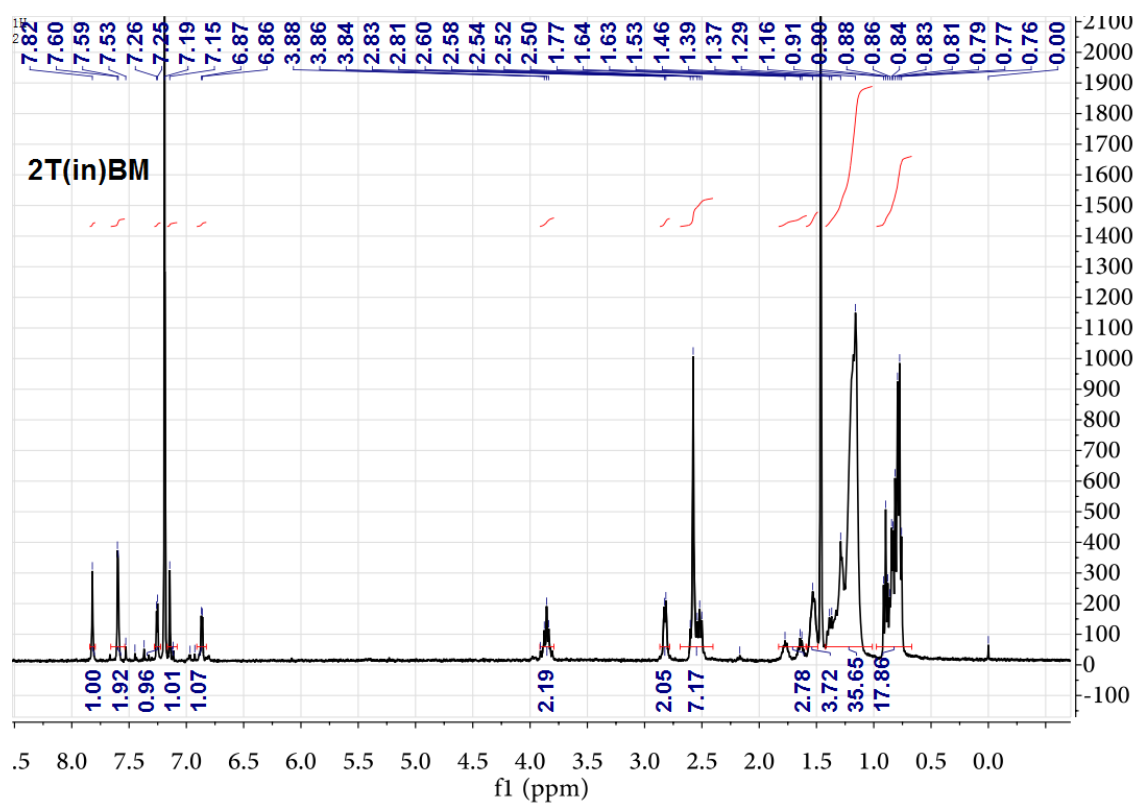
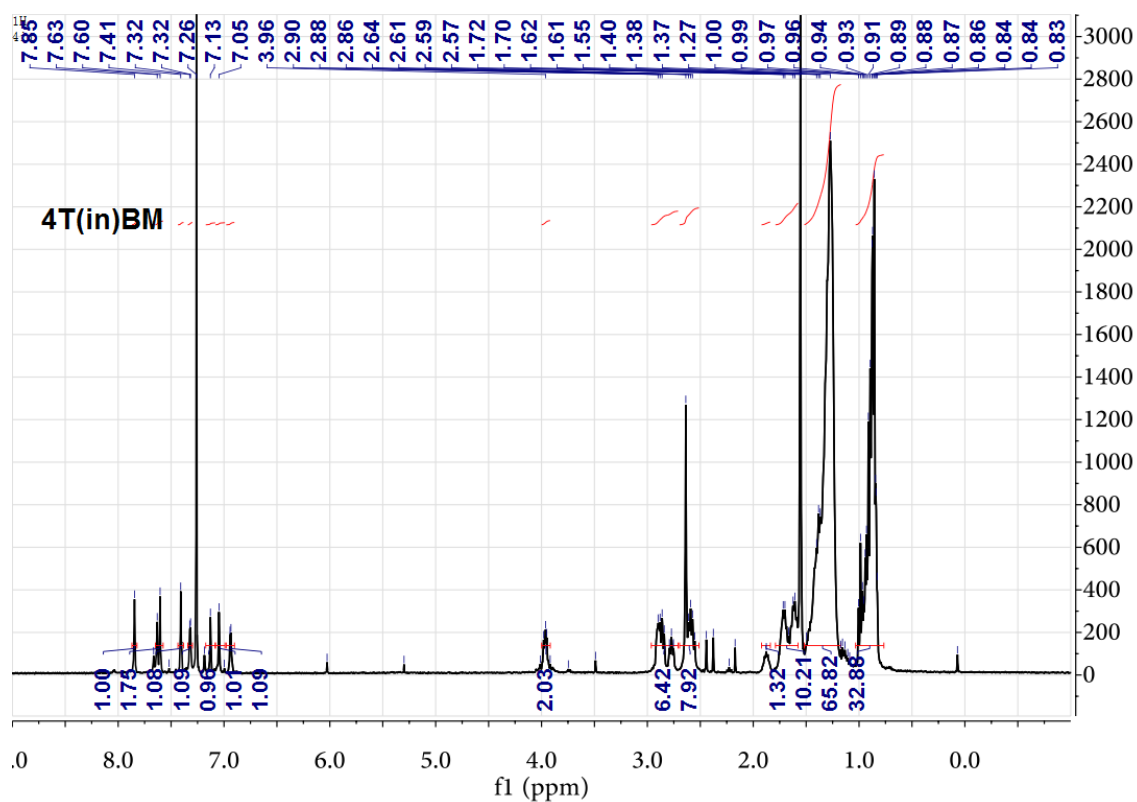
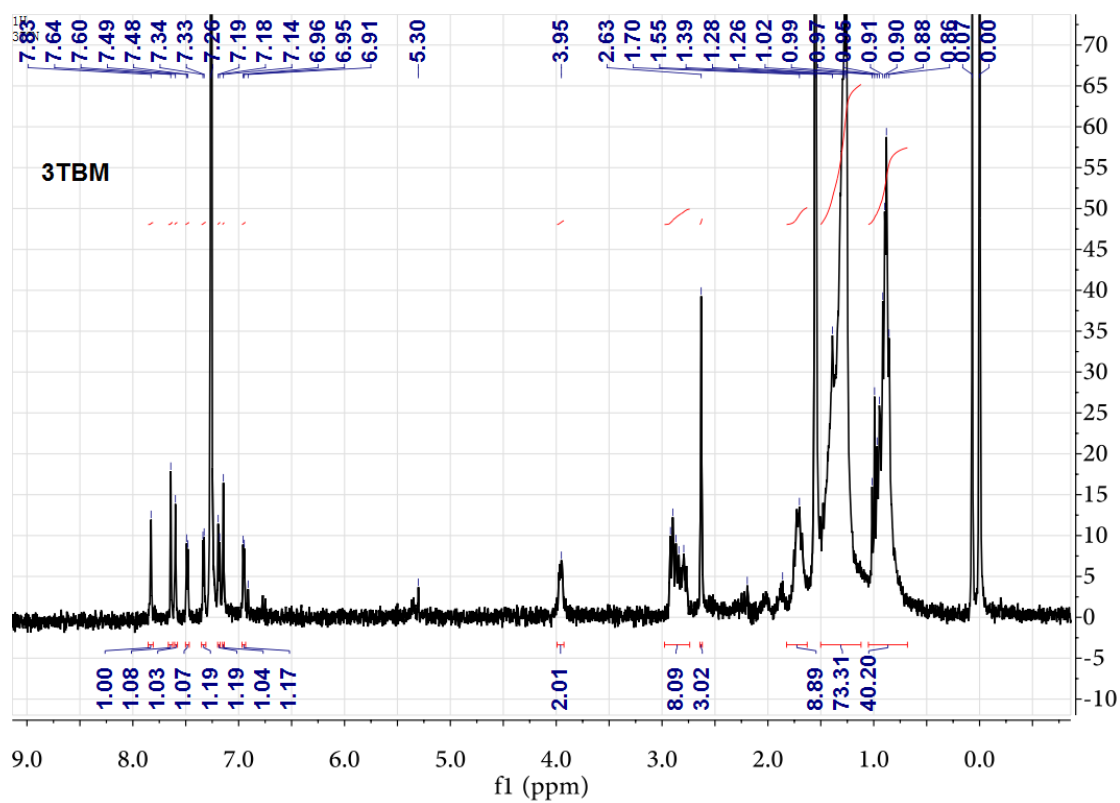


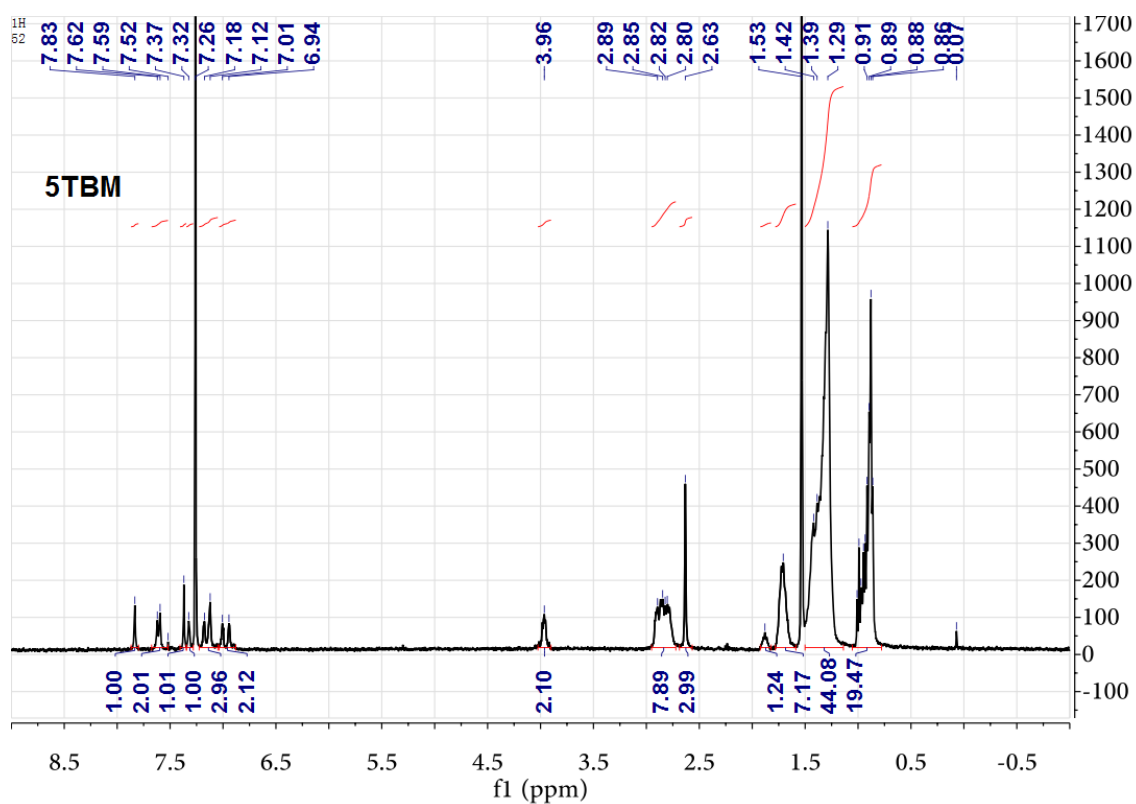
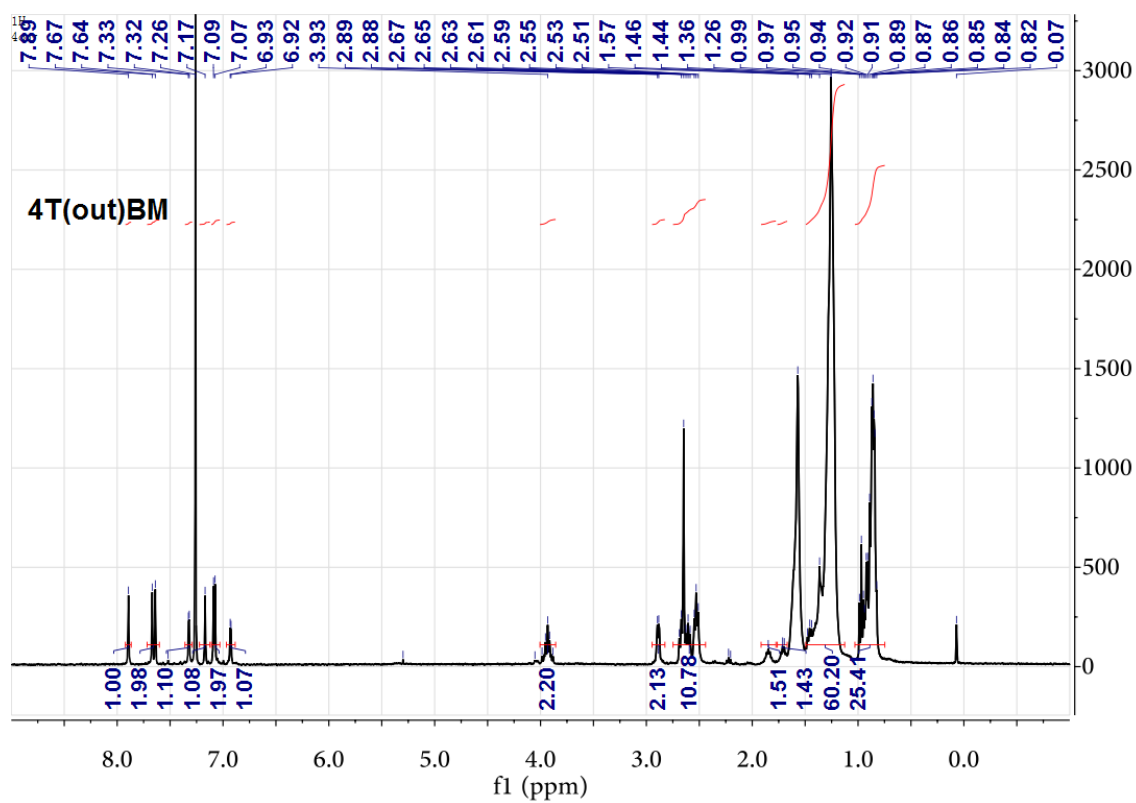
Figure S12. 2D-GIWAXS patterns of neat films for (a) 2T(out)BM, (b) 2TBM, (c) 4T(out)BM and (d) 4TBM and PC₇₁BM based blend films: (a') 2T(out)BM, (b') 2TBM, (c') 4T(out)BM and (d') 4TBM . The 1D plot represents the azimuthally integrated intensity for 2TBM and 4TBM: (e) the respective out-of-plane and (f) in-plane traces for the blend films.

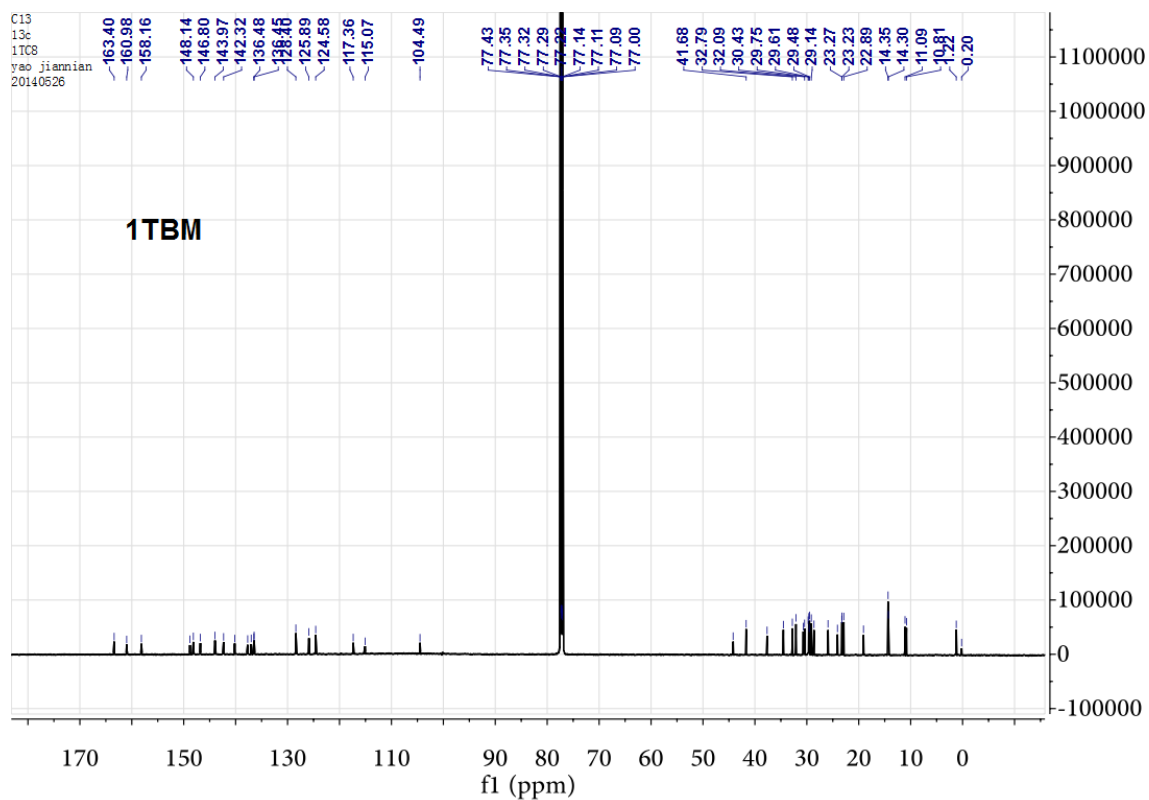
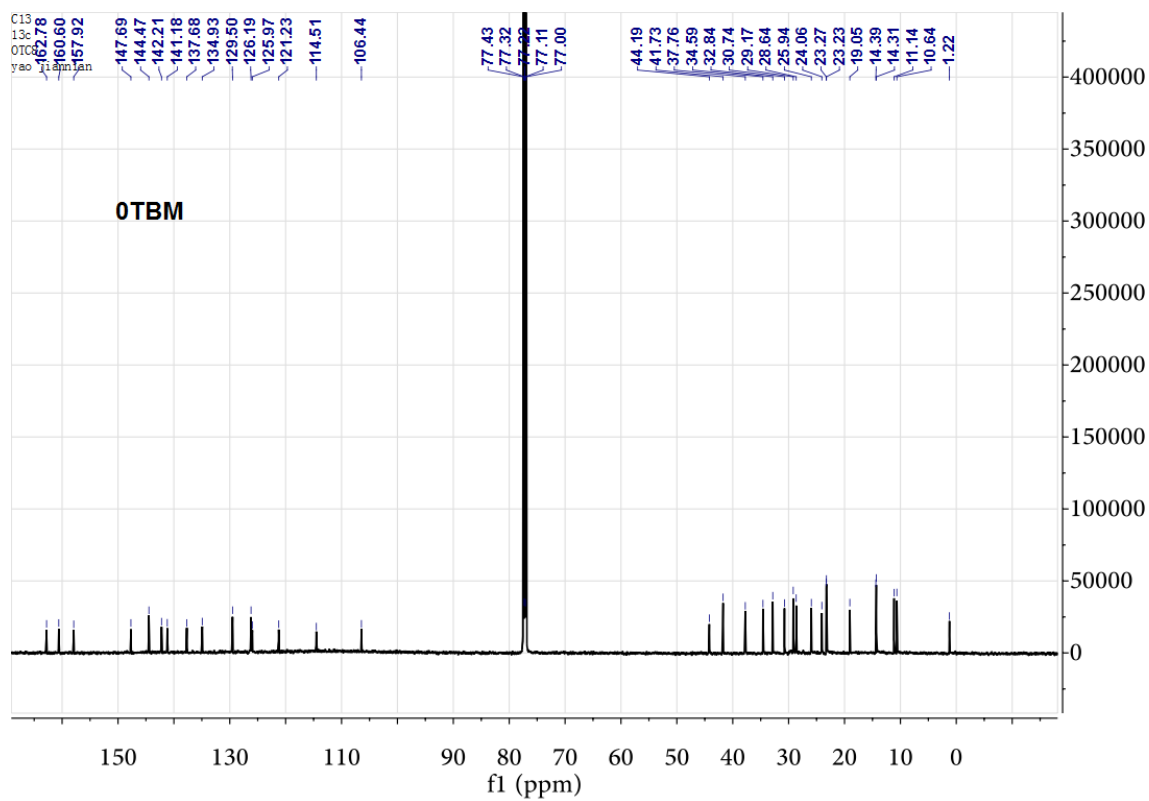
4. NMR Figures

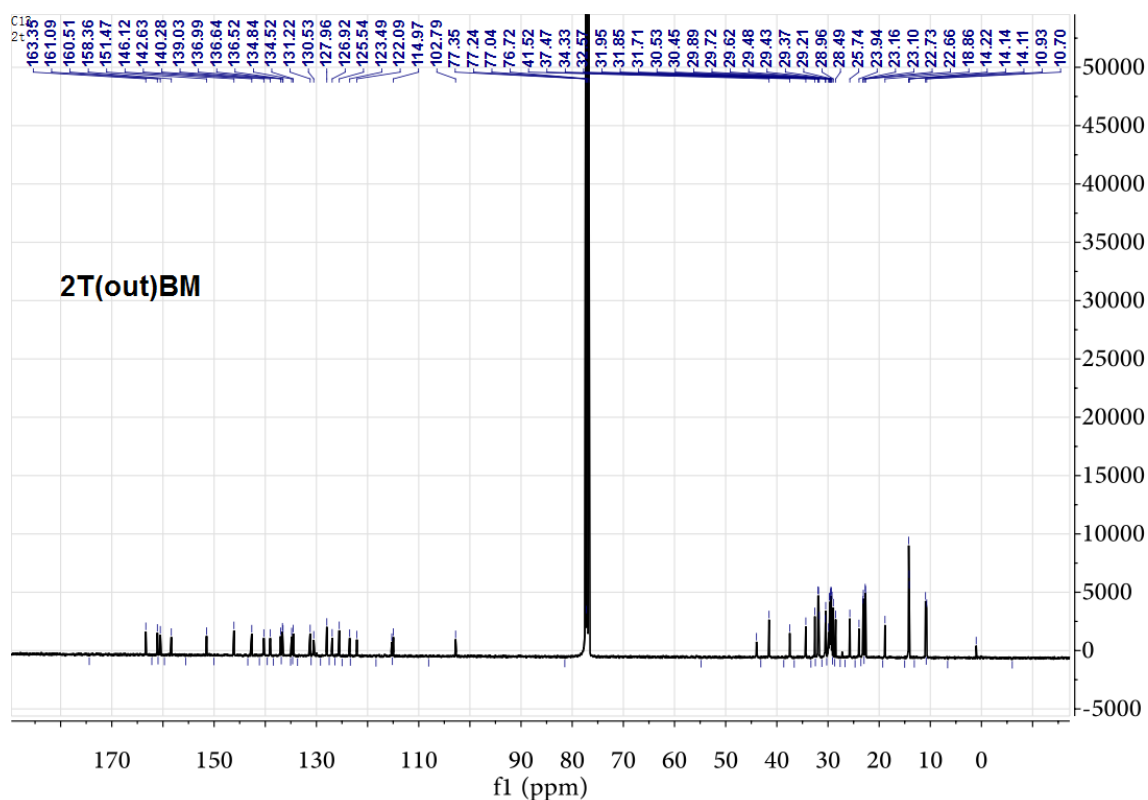
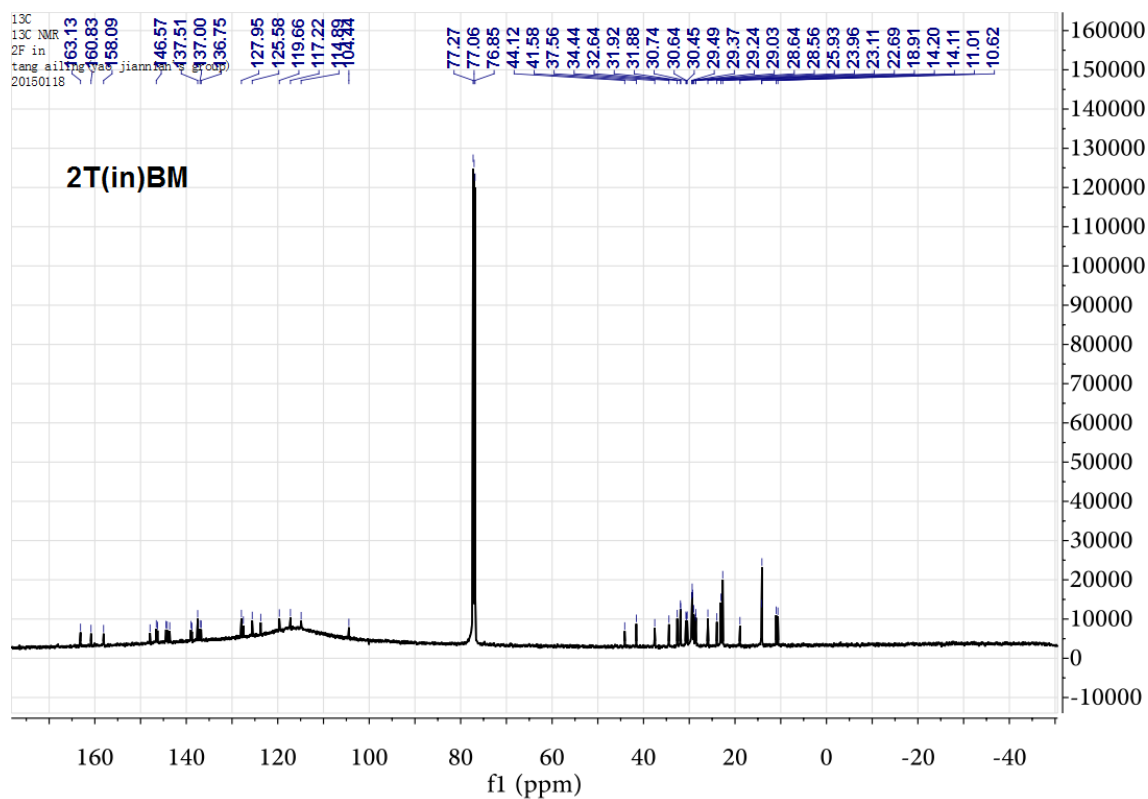


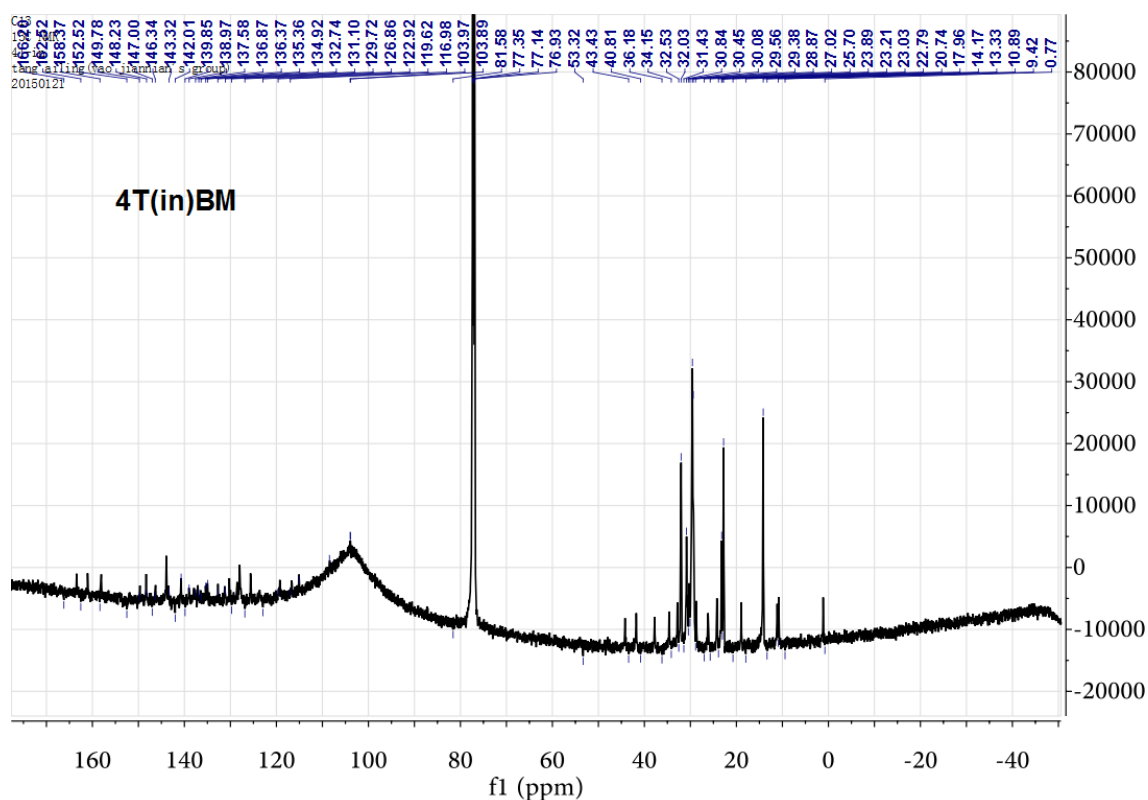
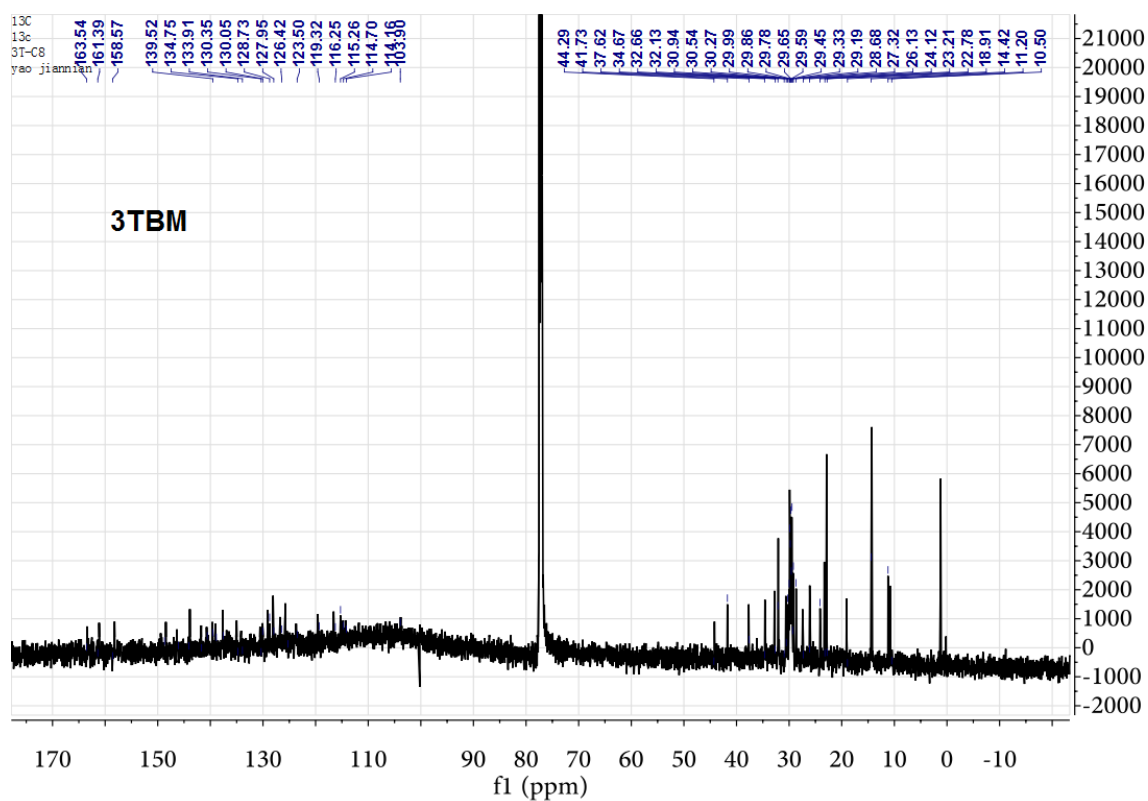


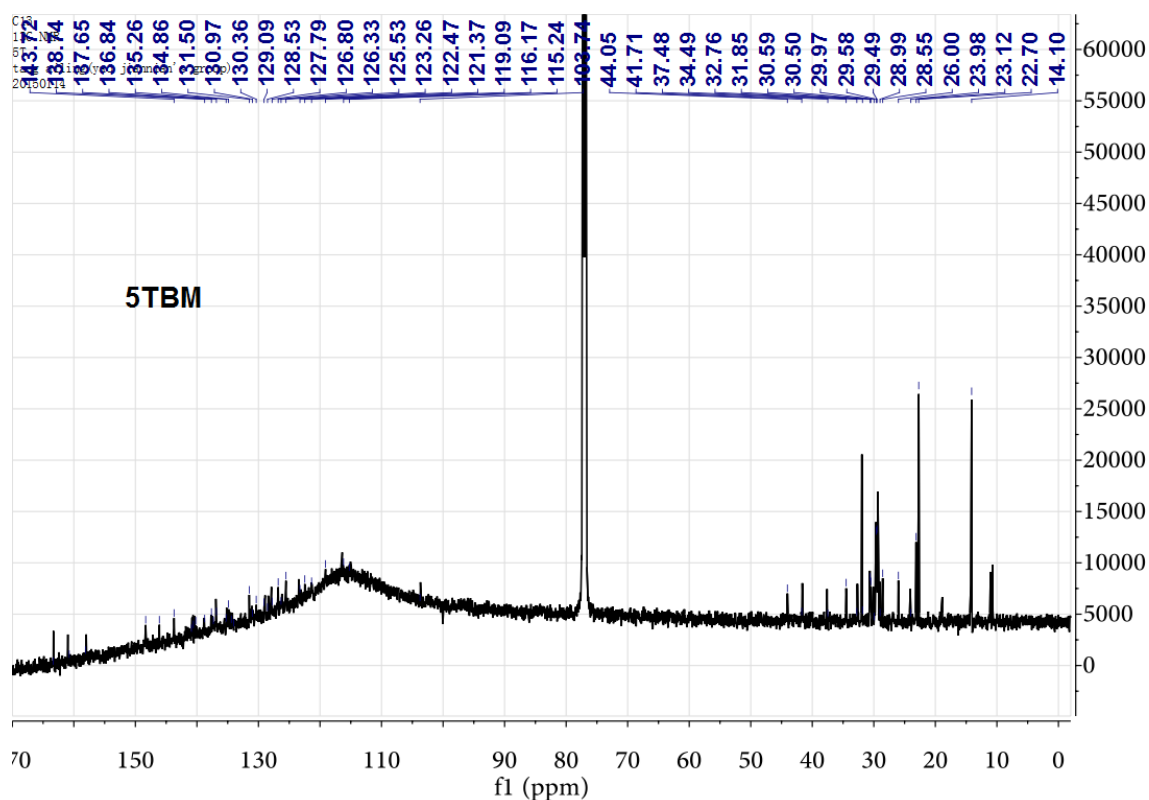
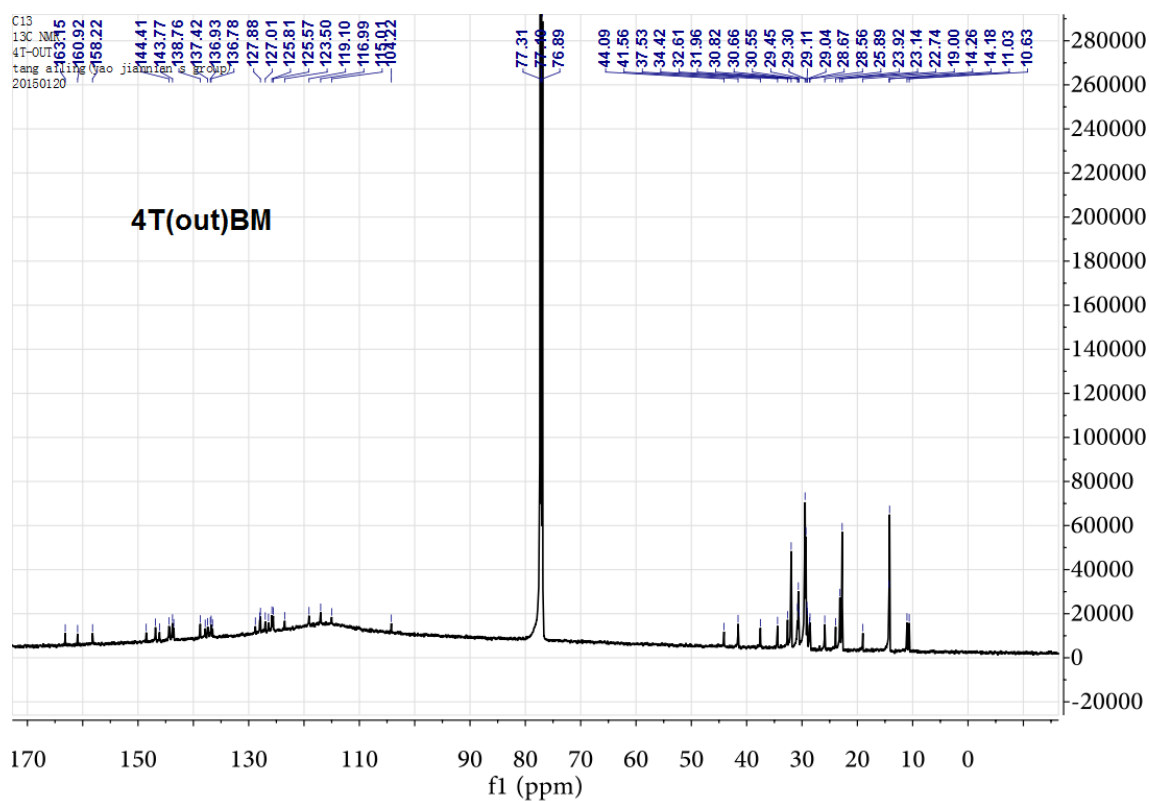












5. References

1. G. G. Malliaras, J. R. Salem, P. J. Brock and C. Scott, *Phys. Rev. B*, 1998, **58**, 13411-13414.
2. T.-Y. Chu and O.-K. Song, *Appl. Phys. Lett.*, 2007, **90**, 203512.