Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

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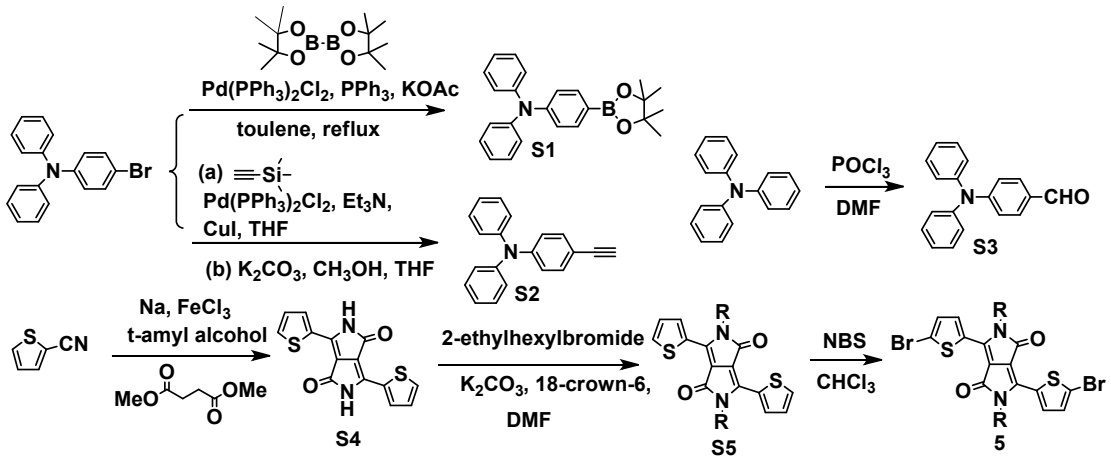
1. Synthetic procedures



N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (S1)[1] A solution of compound N,N-diphenyl-4-bromoaniline (1.62 g, 5.0 mmol), bis(pinacolato)diborane (1.4 g, 5.5 mmol), $Pd(PPh_3)_2Cl_2$ (702 mg, 0.1 mmol), PPh_3 (53 mg, 0.2 mmol) and KOAc (2.45 g, 25 mmol) in dry toluene (50 mL) was refluxed at 110 °C under nitrogen atmosphere for 24 h. After being cooled to room temperature, the mixture was poured into water (200 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 100 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 50:1) to afford compound **S1** as an off-white solid (1.45 g, 78%). M.p.: 94-97 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 6.8 Hz, 2H), 7.25 (t, J = 8.9 Hz, 4H), 7.10 (d, J = 9.5 Hz, 4H), 7.03 (t, J = 8.0 Hz, 4H), 1.33 (s, 12H).

4-Ethynyl-N,N-diphenylaniline (S2)[2]

(a) N,N-Diphenyl-4-[(trimethylsilyl)ethynyl)]aniline To a solution of N,N-diphenyl-4-bromoaniline (2.4 mmol, 775 mg), $Pd(PPh_3)_2Cl_2$ (59 mg, 0.085 mmol), CuI (10 mg, 0.024 mmol) in 8 mL dry THF, Et_3N (20 mL) and trimethylsilyl acetylene (0.73 mL, 3.2 mmol) were added under N_2. The mixture was refluxed at 70 °C for 15 h. The organic solvent was evaporated under reduced pressure the residue was purified by chromatography on silica gel with petroleum ether/dichloromethane (v:v, 8:1) to get compound N,N-diphenyl-4- [(trimethylsilyl)ethynyl]aniline as a colorless liquid (737 mg, 90%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.6 Hz, 2H), 7.25 (t, J = 7.8 Hz, 4H), 7.05 (m, 6H), 6.94 (d, J = 8.6 Hz, 2H), 0.23 (s, 9H).

(b) 4-Ethynyl-N,N-diphenylaniline K_2CO_3 (607 mg, 4.4 mmol) was added to a stirred solution of N,N-diphenyl-4-[(trimethylsilyl)ethynyl]aniline (683 mg, 2.0 mmol) in CH_3OH (30 mL) and the mixture was refluxed for 5 h. After being cooled to room

temperature, the mixture was then dropped into 50 mL of 1M HCl solution. The precipitate was collected, and then dissolved with dichloromethane. The organic solution was dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by chromatography on silica gel with petroleum ether to give compound **S2** as a white solid (511 mg, 95%). M.p.: 101-102 °C (lit. 3, 108-109 °C); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.7 Hz, 2H), 7.29-7.25 (m, 4H), 7.09 (d, J = 7.8 Hz, 4H), 7.07 (d, J = 7.4 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 3.01 (s, 1H).

4-(N,N-Diphenylamino)benzaldehyde (S3) $POCl_3$ (306 mg, 2.0 mmol) was dropwised to 5 mL N,N-dimethylformamide (DMF) at 0 °C and the mixture was stirred at 0 °C for 1 h. Triphenylamine (490 mg, 2.0 mmol) was added and the mixture was stirred at room temperature for 1 h. The reaction mixture was then poured into 50 mL water and neutralized with aqueous NaOH. The aqueous layer was extracted with dichloromethane (2 × 50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v:v, 15:1) as eluent to give the product **S3** as a white solid (461 mg, 83%). M.p.: 128-131°C (lit. 3, 130-131 °C); ^{1}H-NMR (400MHz, $CDCl_3$, ppm): δ 9.81 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 7.3 Hz, 4H), 7.15-7.18 (m, 6H), 7.01 (d, J = 8.8 Hz, 2H).

N-{4-[2-(4-Bromophenyl)]phenyl}{Tang, 2010, 20939570}diphenylamine (1)[4] Compound **S1** (742 mg, 2.0 mmol), 4-bromoiodobenzene (564 mg, 2.0 mmol), 18 mL of 2M K_2CO_3, and $Pd(PPh_3)_4$ (12 mg, 0.1 mmol) were added to a 100 mL three-neck round-bottom flask, then toluene (36 mL) were added under N_2. The reaction mixture was heated at 110 °C for 24 h and monitored via TLC. After being cooled to room temperature, the reaction mixture was poured into 50 mL water and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (v:v, 1:10) as eluent to give the final product as a dark purple solid (332 mg, 65%). M.p.: 122-124 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ7.53 (d, J = 8.6 Hz, 2H), 7.42 (dd, J_1 = 8.7 Hz, J_2 = 1.1 Hz, 4H), 7.30-7.24 (m, 4H), 7.15-7.10 (m, 6H), 7.04 (t, J = 7.3 Hz, 2H).

N-{4-[2-(4-Bromophenyl)vinyl]phenyl}diphenylamine (2) A mixture of N,N-diphenyl-4-iodoaniline (0.37 g, 1.0 mmol), 4-bromostyrene (0.19 mL, 0.27 g, 1.5 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), Na_2CO_3 (0.16 g, 1.5 mmol) and tetrabutyl ammonium bromide (TBAB, 320 mg, 1.0 mmol) in DMF (5 mL) was stirred at 60 °C under nitrogen atmosphere for 36 h. After being cooled to room temperature, the

reaction mixture was poured into water (50 mL). The mixture was extracted with dichloromethane (3 × 20 mL), and the combined organic phases were washed by 20 mL brine and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/dichloromethane (v:v, 5:1) to obtain a yellow powder. Then, the residue was washed with petroleum ether to afford compound **2** (200 mg, 47%). M.p.: 183-185 °C; ^{1}H-NMR (400MHz, $CDCl_3$, ppm): δ 7.45 (d, J = 8.6 Hz, 2H), 7.36 (t, J = 8.6 Hz, 4H), 7.26 (t, J = 7.8 Hz, 4H), 7.11 (d, J = 7.8 Hz, 4H), 7.06-7.02 (m, 5H), 6.91 (d, J = 16.4 Hz, 1H).

N-{4-[2-(4-Bromophenyl)ethynyl]phenyl}-diphenylamine (3) To a solution of **S2** (2.0 mmol, 538 mg), $Pd(PPh_3)_2Cl_2$ (59 mg, 0.085 mmol) and CuI (10 mg, 0.024 mmol) in 8 mL dry THF, Et_3N (20 mL) and 4-bromoiodobenzene (2.0 mmol, 564 mg) were added under N_2. The mixture was refluxed at 70 °C for 15 h. The reaction mixture was poured into 50 mL water and the organic layer was separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by chromatography on silica gel with petroleum ether/dichloromethane (v:v, 10:1) to give compound **3** as a yellow solid (787 mg, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.6 Hz, 2H), 7.42 (dd, J_1 = 8.7 Hz, J_2 = 1.1 Hz, 4H), 7.30-7.24 (m, 4H), 7.15-7.10 (m, 6H), 7.04 (t, J = 7.3 Hz, 2H).

2-(4-bromophenyl)-3-[4-(N,N-diphenylamino)phenyl]-acrylonitrile (4) A solution of NaOH (140 mg, 3.5 mmol) in 5.0 mL ethanol was added dropwise to the mixture of 4-(N,N-diphenylamino)benzaldehyde (810 mg, 3.0 mmol) and 4-bromobenzonitile 690 mg, 3.5 mmol) in ethanol (50 mL) at room temperature. After being stirred for 40 h, the yellow solid was filtered and washed by a great amount of water. The resulting solid was dried to afford compound **4** as a yellow solid (1.2 g, 89%). M.p.: 163-164 °C; ^{1}H-NMR(400MHz, $CDCl_3$, ppm): δ 7.77 (d, J = 8.8 Hz, 2H), 7.49-7.56 (m, 4H), 7.40 (s, 1H), 7.32(t, 7.3 Hz, 4H), 7.11-7.17 (m, 6H), 7.04 (d, J = 8.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 150.23, 146.51, 142.03, 134.08, 132.13, 130.81, 129.64, 127.18, 126.02, 125.84, 124.57, 122.62, 120.69, 118.46, 106.38; MALDI-TOF HRMS: 450.0752[M^+] (calcd for $C_{27}H_{19}N_2Br$: 450.0732).

N,N-diphenyl-4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-4-amine (D1) A solution of compound **1** (798 mg, 2 mmol), bis(pinacolato)diborane (911 mg, 3.6 mmol), KOAc (588 mg, 6.0 mmol), $Pd(PPh_3)_2Cl_2$ (29 mg, 0.04 mmol) and PPh_3 (21 mg, 0.08 mmol) in dry toluene (15 mL) was refluxed at 110 ^{o}C under nitrogen atmosphere for 24 h. After being cooled to room temperature, the mixture was poured into water (100 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated to dryness under reduced

pressure. The crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 50:1) to afford compound **D1** (536 mg, 60%) as a white solid. M.p.: 173-176 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.29-7.24 (m, 4H), 7.13 (d, *J* = 8.5 Hz, 6H), 7.03 (t, *J* = 7.3 Hz, 2H), 1.36 (s, 12H).

N,N-diphenyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)aniline (**D2**) A solution of compound **2** (0.85 g, 2.0 mmol), bis(pinacolato)diborane (560 mg, 2.2 mmol), $Pd(PPh_3)_2Cl_2$ (29 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol) and KOAc (588 mg, 6.0 mmol) in dry toluene (50 mL) was refluxed at 110 °C under nitrogen atmosphere for 24 h. After being cooled to room temperature, the mixture was poured into water (100 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 10:1) to afford compound **D2** as a yellow solid (570 mg, 60%). M.p.: 76-79 °C; ^{1}H-NMR (400 MHz, CDCl3, ppm): δ 7.78 (d, *J* = 8.0Hz, 2H), 7.48(d, *J* = 8.0 Hz, 2H), 7.39(d, *J* = 8.6 Hz, 2H), 7.26(t, *J* = 8.0 Hz, 1H), 7.15-7.10 (m, 5H), 7.06-6.98 (m, 5H), 1.35 (s, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 147.55, 147.53, 140.36, 135.15, 131.32, 129.29, 129.14, 127.48, 126.94, 125.59, 124.57, 123.47, 123.10, 83.74, 24.88; MALDI-TOF HRMS: 473.2504[M^+] (calcd for $C_{33}H_{31}BN_2O_2$: 473.2526).

N,N-diphenyl-4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)aniline (**D3**) A solution of compound **3** (2.115 g, 5.0 mmol), bis(pinacolato)diborane (1.40 g, 5.5 mmol), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.25 mmol), PPh_3 (131 mg, 0.5 mmol) and KOAc (1.47 g, 15mmol), in dry toluene (50 mL) was refluxed at 110 ^{o}C under nitrogen atmosphere for 24 h. After being cooled to room temperature, the mixture was poured into water (200 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 100 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 20:1) to afford compound **D3** (1.719 g, 73%) as an orange solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.30-7.25 (m, 4H), 7.11 (d, *J* = 7.7 Hz, 4H), 7.06 (t, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 1.35 (s, 12H).

3-(4-(diphenylamino)phenyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylonitrile (D4) A solution of compound **4** (2.253 g, 5 mmol), bis(pinacolato)diborane (1.4 g, 5.5 mmol), PPh_3 (131 mg, 0.5 mmol) and KOAc (1.47 g, 15 mmol), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.25 mmol) in dry toluene (50 mL) was refluxed

at 110 °C under nitrogen atmosphere for 24 h. After being cooled to room temperature, the mixture was poured into water (200 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 100 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 5:1) to afford compound **D4** (2.02 g, 81%) as an orange solid. ^{1}H-NMR(400MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.79(d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.32 (t, 4H), 7.10-7.17 (m, 6H), 7.05 (d, *J* = 8.8 Hz, 2H). MALDI-TOF MS: 498.1440 [M^+] (calcd for $C_{33}H_{31}BN_2O_2$: 498.2479).

3,6-Dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (S4) In a dry t-amyl alcohol (48 mL) solution, $FeCl_3$ (0.05 g) and sodium (2.20 g, 96.0 mmol) were added under nitrogen atmosphere. The mixture was heated to 120 °C until the sodium disappeared completely. Then compound 2-thiophenecarbonitrile (5.2 g, 48 mmol) was added. A solution of dimethyl succinate (3.88 g, 19.2 mmol) in dry t-amyl alcohol (20 mL) was added dropwise slowly over 1 h. After stirring for 24 h, acetic acid (20 mL) was added. The mixture was refluxed at 120 °C for 1 h. After being cooled to room temperature, the suspension was filtered and the purple filter cake was washed with hot methanol and water. The crude product was dried in vacuum and could be used directly without further purification (4.6 g, 80%).

2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (S5) In an oven-dried two-necked 100 mL round-bottom flask, 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1.5 g, 3.0 mmol) and anhydrous K_2CO_3 (1.242 g, 9.0 mmol) were dissolved in 60 mL anhydrous DMF, the mixture was heated at 120 °C under N_2 for 1 h. Then 2-Ethylhexylbromide (1.728 g, 9.0 mmol) and 18-crown-6 (396 mg, 1.5 mmol) were added. The reaction mixture was further stirred at 120 °C overnight. The reaction mixture was poured into 200 mL water and the resulting suspension was stirred at room temperature for 1 h. The solid was collected by vacuum filtration, washed with several portions of distilled water and methanol, and dried under vacuum. The crude product was purified by chromatography eluting with petroleum ether/dichloromethane (v:v, 1:2) to yield **S5** as a dark red solid (709 mg, 45%). M.p.: 130-132 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.89 (d, *J* = 3.8 Hz, 2H), 7.62 (d, *J* = 4.9 Hz, 2H), 7.27 (d, *J* = 4.7 Hz, 2H), 4.08-3.97 (m, 4H), 1.92-1.81 (m, 3H), 1.38-1.22 (m, 16H), 0.90-0.83 (m, 12H).

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione) (5) NBS (783 mg, 4.4 mmol) was added to a solution of **S5** (1.05 g, 2.0 mmol) in $CHCl_3$ (60 mL) in a two-neck round-bottom flask covered with aluminum foil. After stirring at room temperature for 48 h, the organic solvent was evaporated under reduced pressure and the crude product was purified by silica

column chromatography eluting with petroleum ether/dichloromethane (v:v, 3:2) to afford compound **5** as a dark purple solid (982 mg, 72%). M.p.: 204-205 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.64 (d, *J* = 4.2 Hz, 2H,), 7.22 (d, *J* = 4.2 Hz, 2H), 3.99-3.87 (m, 4H), 1.82 (d, *J* = 5.9 Hz, 2H), 1.37-1.23 (m, 16 H), 0.86 (t, *J* = 7.5 Hz, 12H).

2. ^{1}H-NMR and ^{13}C-NMR spectra of SMs

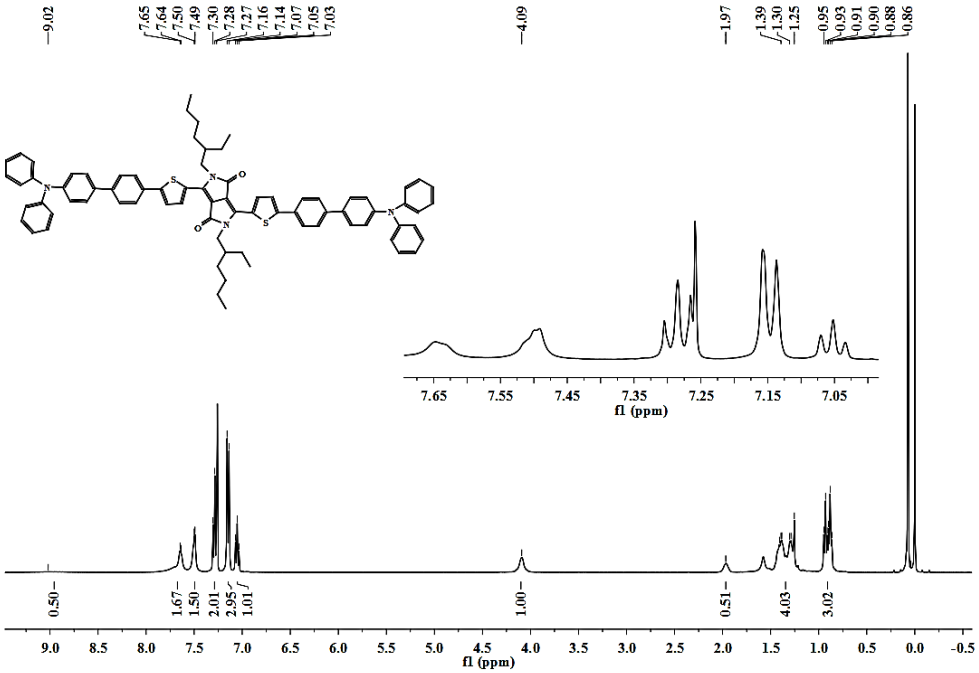


Fig. S1 ^{1}H-NMR spectrum of SM1

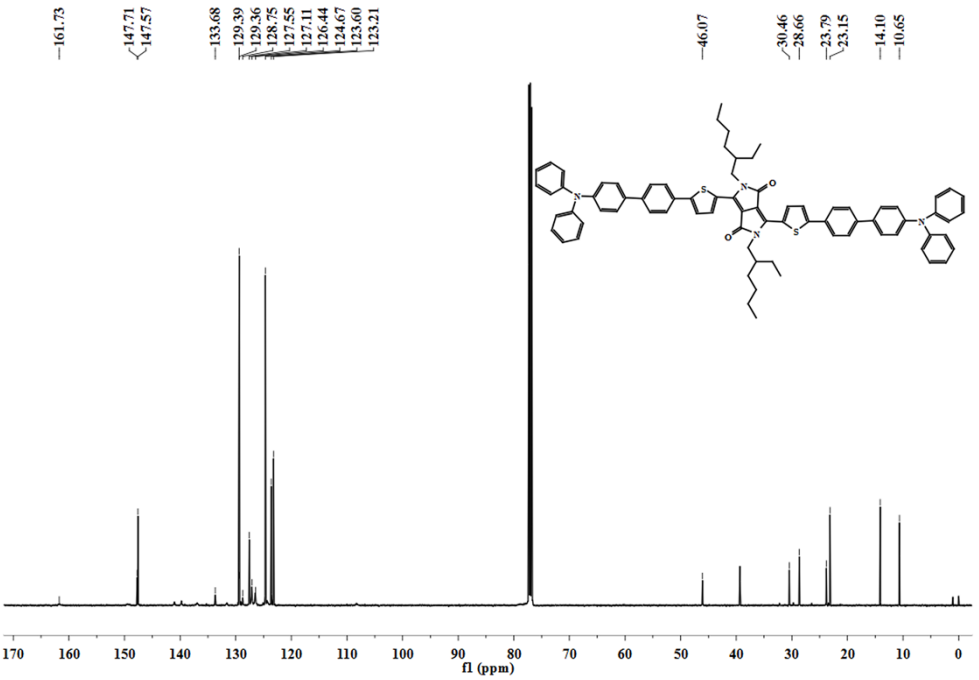


Fig. S2 ^{13}C-NMR spectrum of SM1

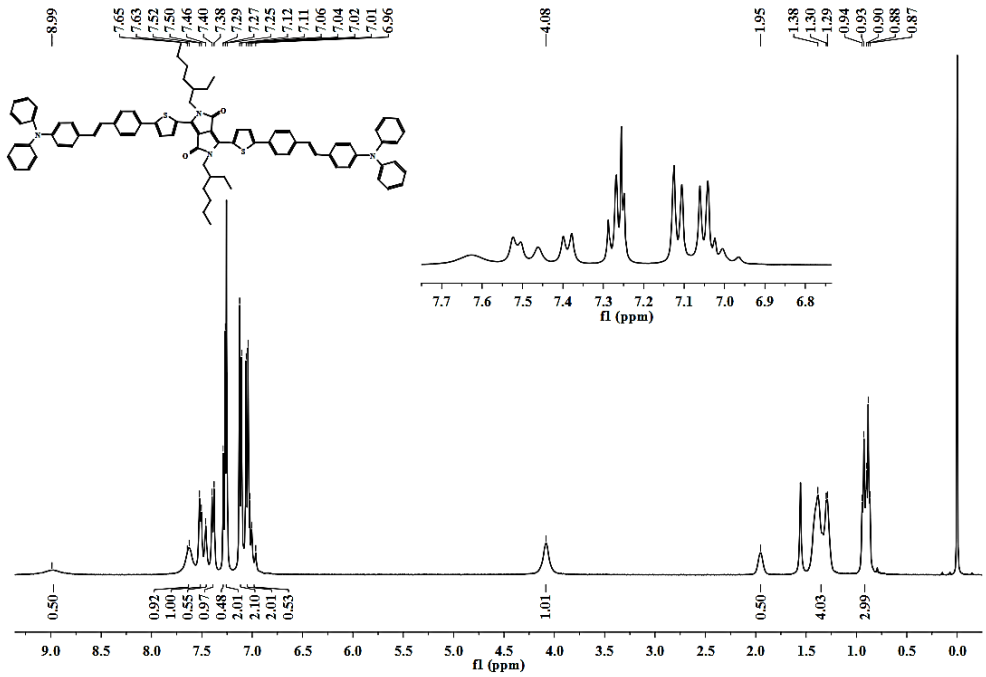


Fig. S3 ^{1}H-NMR spectrum of SM2

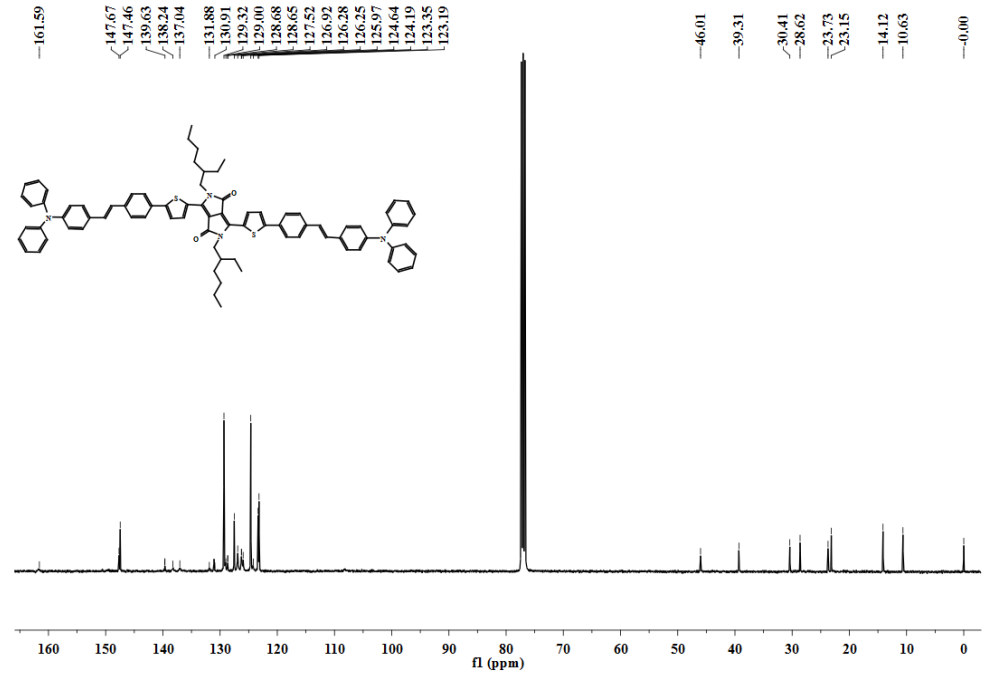


Fig. S4 ^{13}C-NMR spectrum of SM2

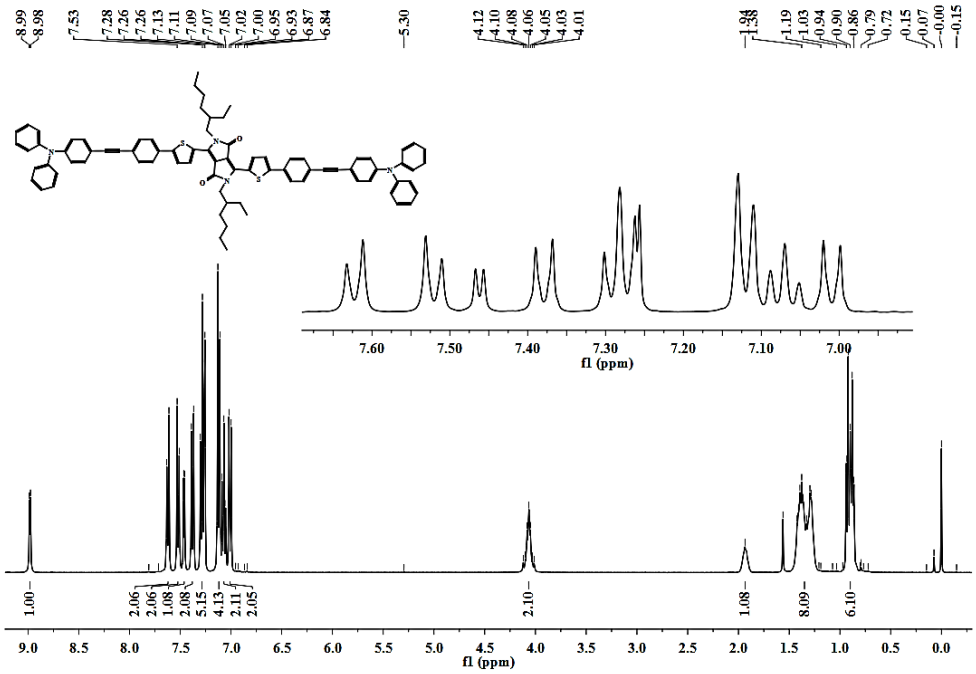


Fig. S5 ^{1}H-NMR spectrum of SM3

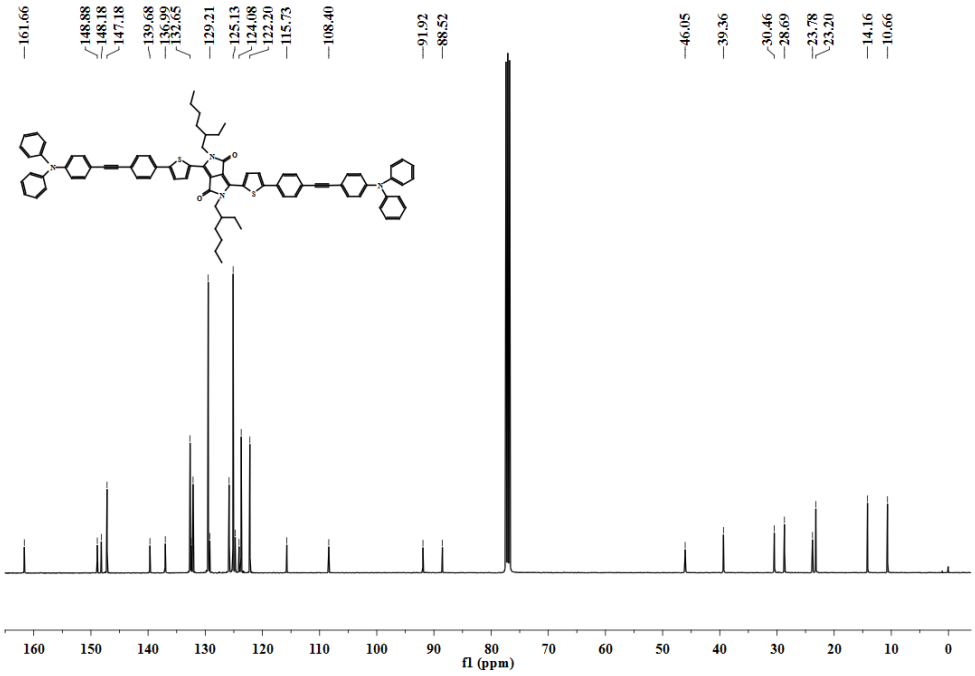


Fig. S6 ^{13}C-NMR spectrum of SM3

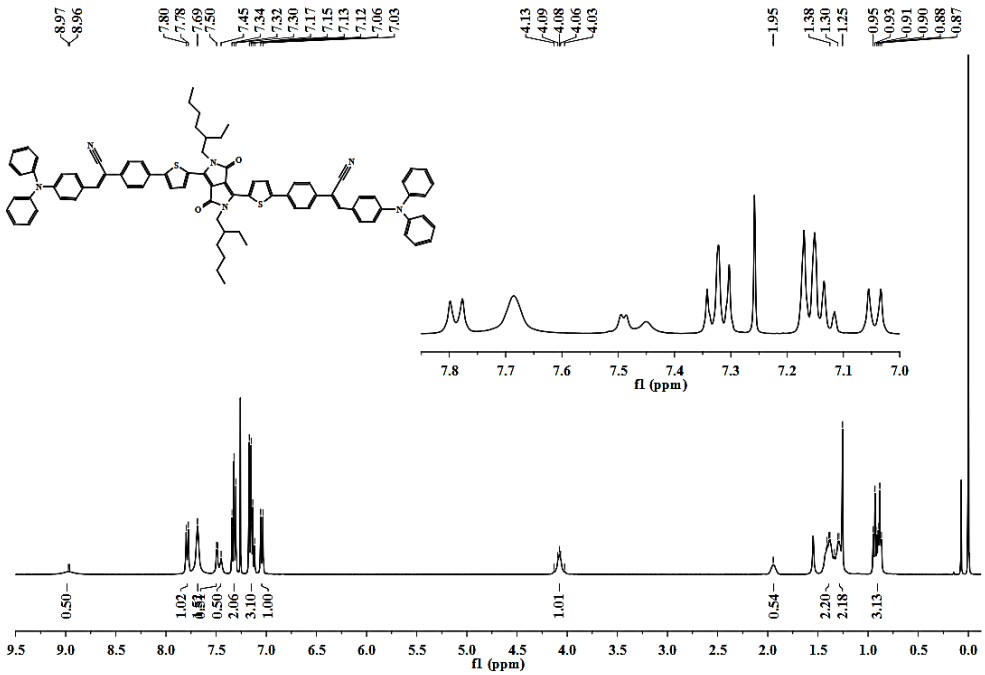


Fig. S7 ^{1}H-NMR spectrum of SM4

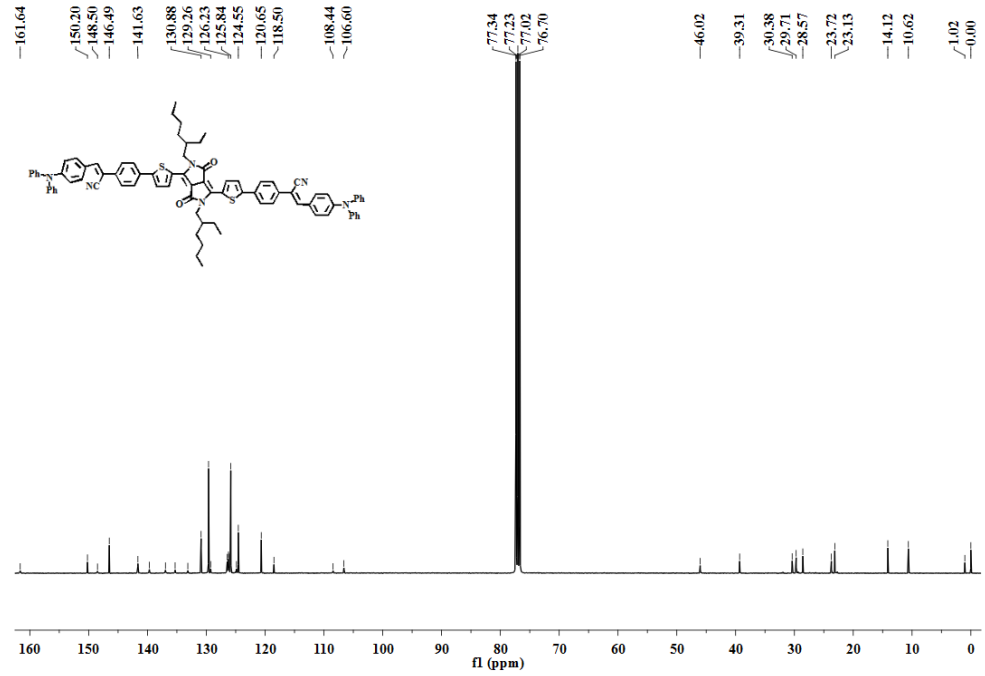


Fig. S8 ^{13}C-NMR spectrum of SM4

3. AFM height and phase images of the active layer based on SMs:$PC_{61}BM$ blended films.

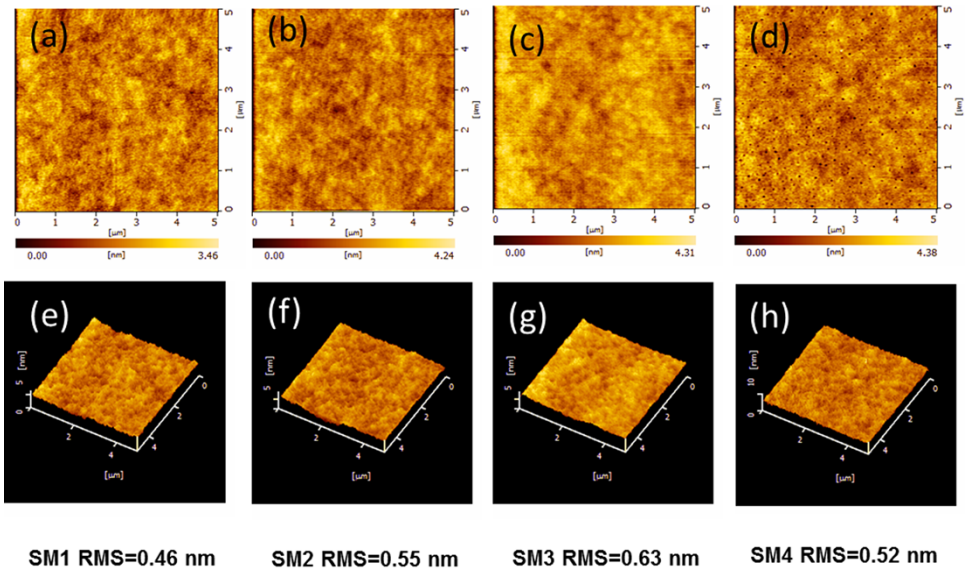


Fig. S9 AFM images of SMs:PCBM (1:2, w/w) blended films: (a) and (e) SM1:$PC_{61}BM$ phase image and height image; (b) and (f) SM2:$PC_{61}BM$ phase image and height image; (c) and (g) SM3:$PC_{61}BM$ phase image and height image; (d) and (h) SM4:$PC_{61}BM$ phase image and height image.

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4. Z. Ci, X. Yu, M. Bao, C. Wang, T. Ma, *Dyes and Pigments*, 2013, **96**, 619.