Tailoring intra-molecular coupling in BDT based copolymers to enhance their performance in fullerene-free Organic solar cells

Newayemedhin A. Tegegne*[1,2], Asfaw Negash*[3], Desalegn Yilma[4], Kidan G. Gebremariam[1], Zewdneh Genene[5], Wendimagegn Mammo[4], Neill J. Goosen[2]

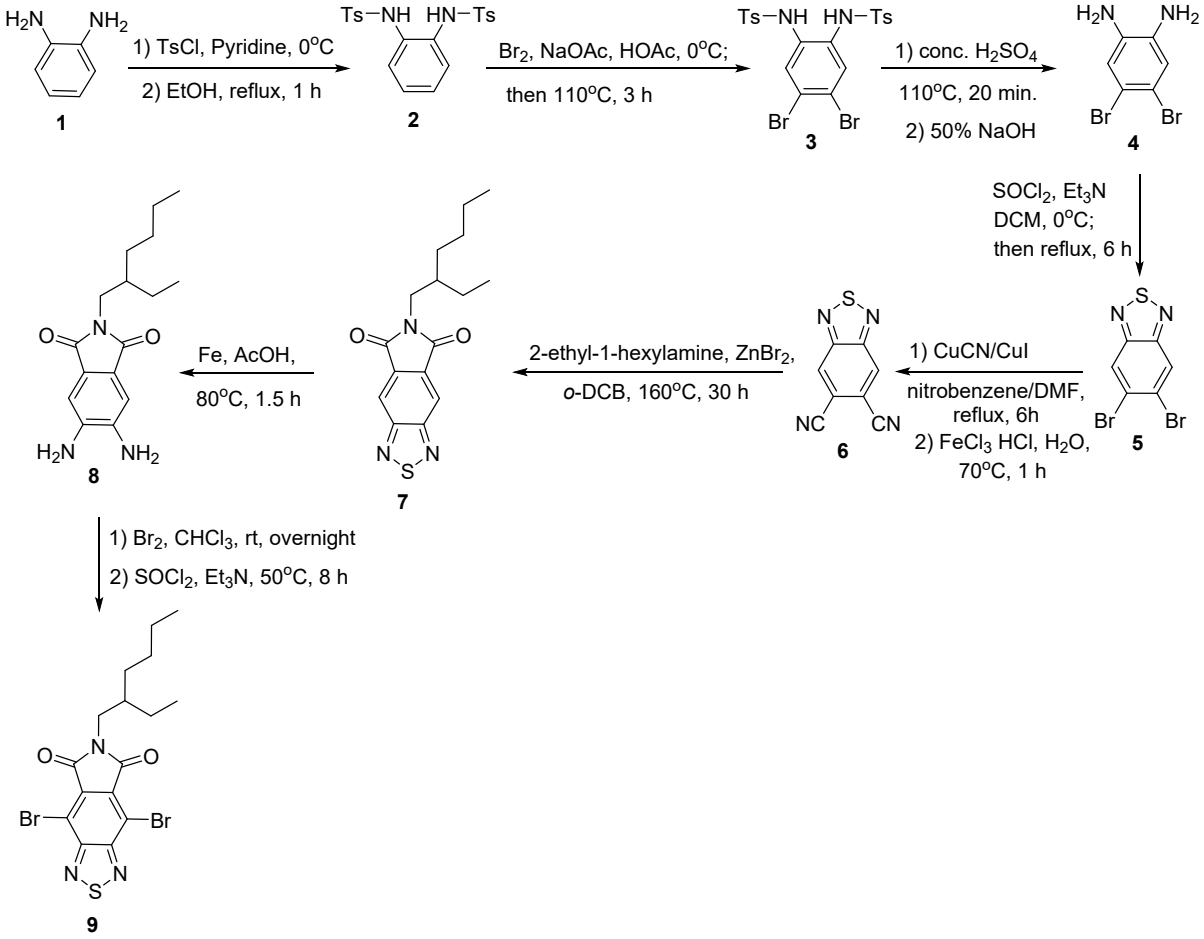
[1] Department of Physics, Addis Ababa University, P.O.Box1176 Addis Ababa, Ethiopia,[2] Department of Chemical Engineering, Stellenbosch University, Stellenbosch 7604, South Africa, [3] Department of Chemistry, Debre Berhan University, P.O.Box 405, Debre Berhan, Ethiopia, [4] Department of Chemistry, Addis Ababa University, P.O.Box 33658, Addis Ababa, Ethiopia, [5] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE412 96, Gothenburg, Sweden

* Corresponding author* newaye.medhin@aau.edu.et and asfaw.negash@dbu.edu.et

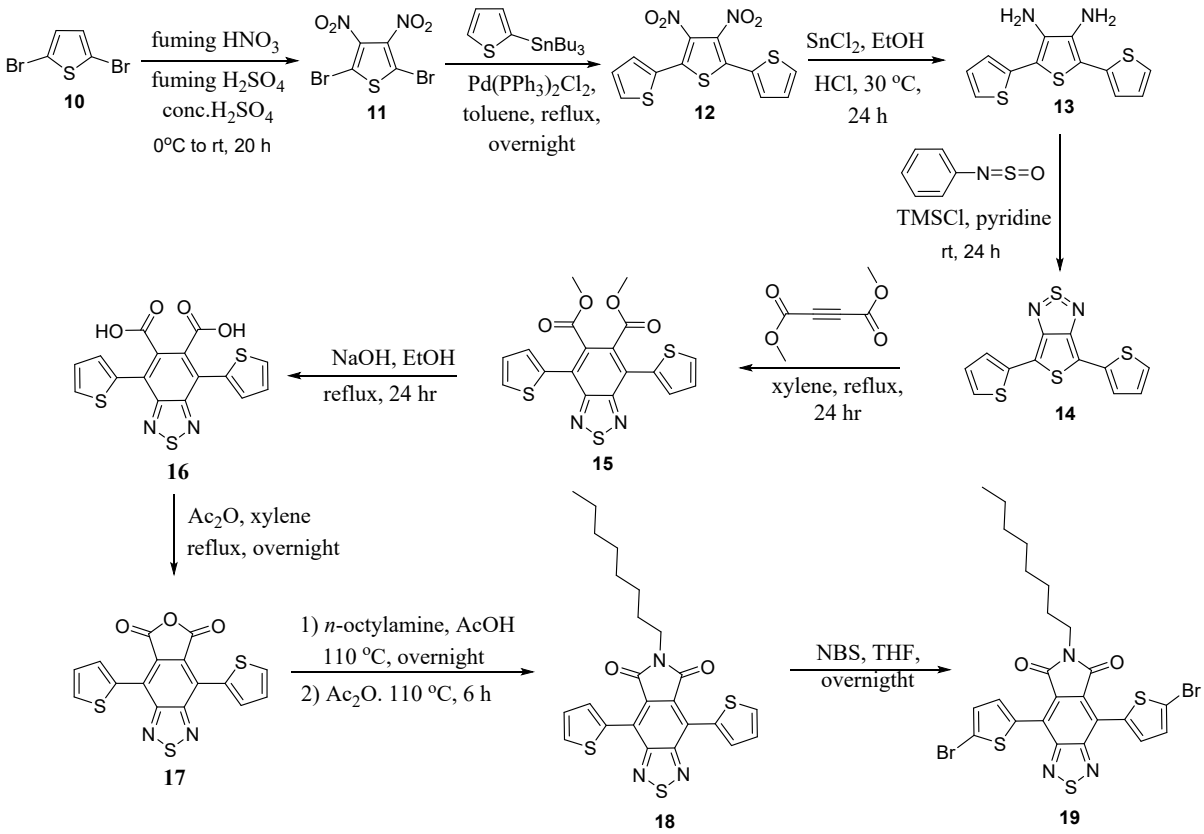
1. Instrumentation

Analytical thin layer chromatographic experiments were performed on Merck 0.25 mm silica gel 60 F_{254} pre-coated plates on aluminum. Column chromatography was conducted on silica gel (Merck) as a stationary phase using different kinds of solvents as eluent. ^{1}H-NMR (400.13 MHz) and ^{13}C-NMR (100.6 MHz) spectra were recorded on a Bruker Avance 400 NMR spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 65 IR spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. Size exclusion chromatography (SEC) was performed on Waters Alliance GPCV2000 with a refractive index detector. Columns: Waters Styvagel HT GE×1, Waters Styvagel HMW GE×2. The eluent was 1,2,4-trichlorobenzene. The working temperature was 135 °C and the resolution time was 2 h.

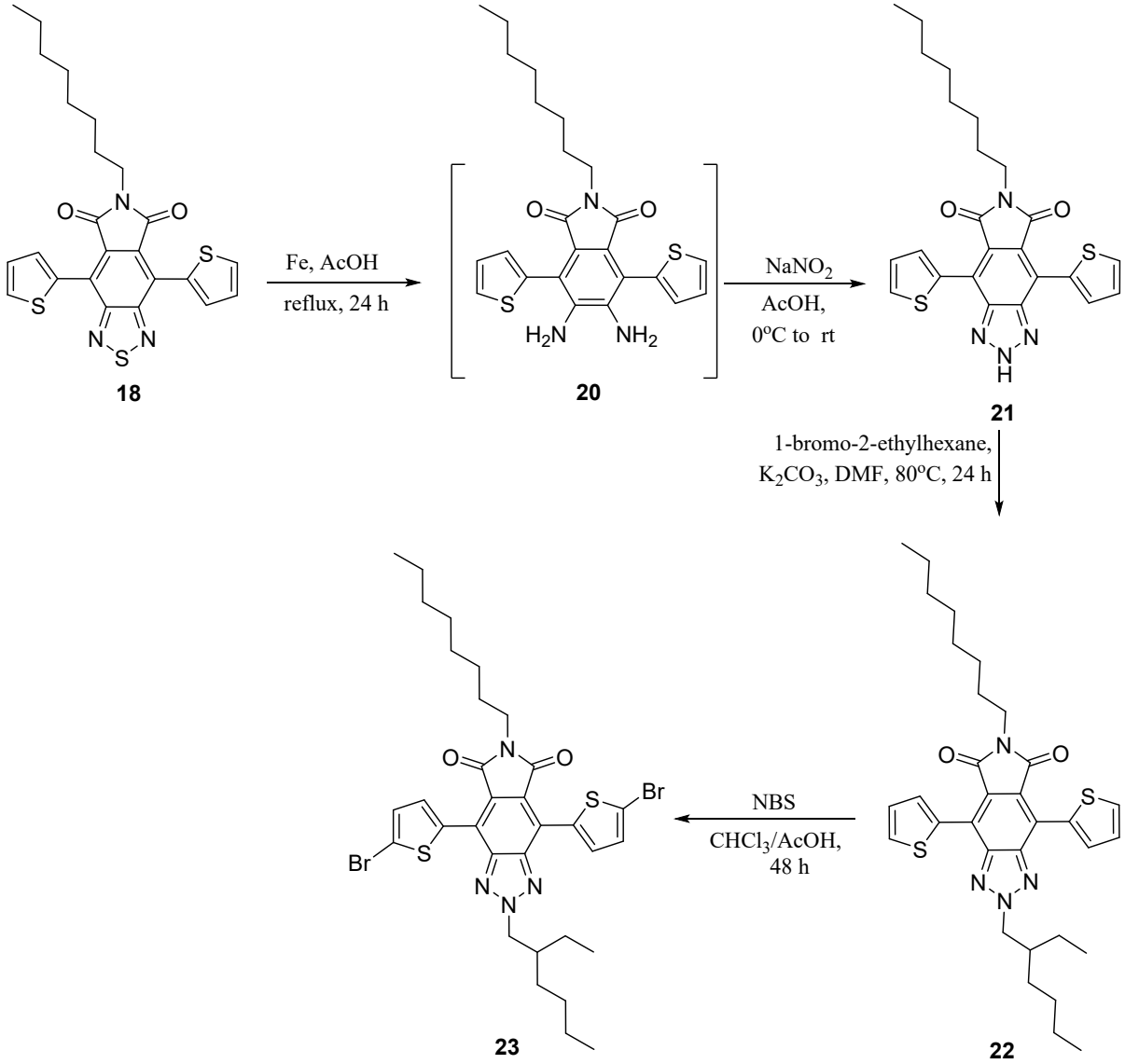
2. Synthesis



Scheme S1. Synthesis of monomer **9**.



Scheme S2. Synthesis of monomer **19**.



Scheme S3. Synthesis of monomer **23**.

3. Reaction Procedures

Synthesis of *N,N′-(*1,2-phenylene)bis(4-methylbenzenesulfonamide) (2)[1]

Pyridine (9 mL) was added into an ice-cold mixture of *o*-phenylenediamine (**1**) (10 g, 92.5 mmol) and *p*-toluenesulfonyl chloride (35.3 g, 185.2 mmol). The resulting mixture was stirred at room temperature for 18 h and 15% aqueous HCl was added. The formed precipitate was dissolved in EtOH (240 mL) and refluxed for 1 h, and then stored in a refrigerator overnight for crystallization. After filtration, **2** (24 g, 72%) was obtained as a

white powder. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.59 (*d*, 4H, *J* = 8.0 Hz), 7.24 (*d*, 4H, *J* = 8.0 Hz), 7.05 (*m*, 2H), 6.97 (*m*, 4H), 2.41 (*s*, 6H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 144.2, 135.4, 130.8, 129.6, 127.6, 127.4, 126.1, 21.6.

Synthesis of *N,N′*-(4,5-dibromo-1,2-phenylene)bis(4-methylbenzenesulfonamide) (3)[1]

Bromine (18.6 g, 116.25 mmol) was added drop-wise to an ice-cold and stirred suspension of **2** (24 g, 57.7 mmol) and anh. NaOAc (9.6 g) in glacial acetic acid (96 mL). The mixture was stirred and heated at 110 °C for 3 h, cooled and poured into ice water (256 mL), and then stirred for an additional 1 h. The precipitate was collected by filtration and washed with EtOH (128 mL) and dried to afford **3** (16.72 g, 50.7%) as white powder. ^{1}H-NMR (400.13 MHz, DMSO-d_6): δ 7.63 (*d*, 4H, *J* = 8.0 Hz), 7.38 (*d*, 4H, *J* = 8.0 Hz), 7.36 (*s*, 2H), 2.38 (*s*, 6H); ^{13}C-NMR (100.6 MHz, DMSO-d_6): δ 144.6, 136.5, 130.7, 130.3, 127.6, 127.4, 120.0, 21.4.

Synthesis of 4,5-dibromobenzene-1,2-diamine (4)[1]

Compound **3** (16.5 g, 28.7 mmol) was mixed with conc. sulfuric acid (34 mL) and heated at 110 °C for about 20 min. After cooling to room temperature, the reaction mixture was poured into ice–water and neutralized with 50% NaOH solution until the color of the solution was off-white. The precipitate was collected by filtration, washed with water and dried to give **4** (7.1 g, 93 %) as white powder. ^{1}H-NMR (400.13 MHz, DMSO-d_6): δ 6.78 (*s*, 2H), 4.88 (*s*, 4H); ^{13}C-NMR (100.6 MHz, DMSO-d_6): δ 136.8, 117.6, 109.2.

Synthesis of 5,6-dibromobenzo[*c*][1,2,5]thiadiazole (5)[1]

To an ice-cold solution of 4,5-dibromobenzene-1,2-diamine (**4**) (7 g, 26.3 mmol) and Et_3N (11.5 g, 109.25 mmol) in dry DCM (80 mL) was added a solution of thionyl chloride (8 g, 67.065 mmol) in DCM (13 mL) slowly. After addition was completed, the reaction mixture was stirred for 6 h under reflux. The mixture was cooled to room temperature and filtered. The solvent was removed from the filtrate and the resulting solid residue was washed with water several times to afford **5** (6.2 g, 80.2%) as light-orange powder. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.35 (*s*, 2H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 153.8, 127.2, 124.9.

Synthesis of benzo[*c*][1,2,5]thiadiazole-5,6-dicarbonitrile (6)[1]

Compound **5** (6 g, 20.4 mmol), CuCN (7.5 g, 83.64 mmol) and CuI (1.4 g, 7.34 mmol) were added into a mixture of nitrobenzene (41 mL) and DMF (125 mL) and the mixture was stirred under reflux for 6 h. It was then cooled to room temperature and was poured into a mixture of hydrated $FeCl_3$ (6.9 g), 37% HCl (1.7 mL) and water (11 mL). The suspension was heated at 70 °C for 1 h, and then the solvent was removed under reduced pressure. The residue was dissolved in DCM and water, and extracted with DCM. The combined organic phase was washed with HCl (6 M, 200 mL), saturated NaCl (200 mL), and saturated $NaHCO_3$ (200 mL) dried over $MgSO_4$, and the solvent was removed by vacuum distillation to obtain **6** (1.9 g, 52%) as light-yellow solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.64 (*s*, 2H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 154.0, 129.8, 113.9.

Synthesis of 6-(2-ethylhexyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (7)[2]

Compound **6** (1.92 g, 10.31 mmol), 2-ethyl-1-hexylamine (1.6 g, 12.37 mmol) and zinc bromide (1.16 g, 5.15 mmol) were mixed in *o*-DCB (20 mL) and heated at 160 °C for 30 h. The progress of the reaction was monitored by TLC (chloroform). The reaction mixture was cooled to room temperature and the solvent was removed by distillation. The residue was purified by silica gel column chromatography using chloroform as eluent to give **7** (2.99 g, 93.4%) as a pale red solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.50 (*s*, 2H), 3.69 (*d*, 2H, *J* = 8 Hz), 1.91 (*septet*, 1H, 8.0 Hz), 1.24-1.42 (*unresolved*, 8H), 0.94 (*t*, 3H, *J* = 8.0 Hz), 0.89 (*d,* 3H, *J* = 8.0 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 166.8, 156.7, 131.6, 118.2, 42.8, 38.2, 30.6, 28.5, 23.9, 23.0, 14.0, 10.4.

Synthesis of 5,6-diamino-2-(2-ethylhexyl)isoindoline-1,3-dione (8)[2]

A mixture of compound **7** (2.99 g, 9.42 mmol), iron powder (5.3 g, 94.2 mmol) in acetic acid (115 mL) was stirred at 80 °C for 1.5 h. The progress of the reaction was monitored by TLC (EtOAc:hexane, 1:10). After cooling to room temperature, the reaction mixture was filtered and the filtrate was extracted with chloroform. Removal of the solvent afforded **8** as a yellow solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.11 (*s*, 2H), 3.90 (*s*, 4H), 3.50 (*d*, 2H, *J* = 8.8 Hz), 1.80 (*m*, 1H), 1.36-1.27 (*unresolved*, 8H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 169.4, 139.4, 124.7, 110.3, 41.6, 38.4, 30.5, 28.6, 23.9, 23.0, 14.1, 10.5.

Synthesis of 4,8-dibromo-6-(2-ethylhexyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (9)[2]

The crude compound **8** (2.99 g, 9.42 mmol) was dissolved in chloroform and bromine (7.54 g, 47.1 mmol) was added dropwise. After the addition was complete, the mixture was stirred at room temperature overnight. The progress of the reaction was monitored by TLC (EtOAc:hexane 2:3). Thionyl chloride (4.51 g, 37.9 mmol) was then added dropwise, followed by addition of Et_3N (4.81 g, 47.56 mmol). The mixture was stirred at 50 °C for 8 h, cooled to room temperature, and the mixture was extracted with chloroform, washed with water, dried over anh. $MgSO_4$ and the solvent was removed. The residue was purified by silica gel column chromatography using $CHCl_3$:EtOAc (80:1) as eluent. The product was recrystallized from THF/ethanol (1:25) to obtain **9** (1.3 g, 30%) as a white solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 3.71 (*d*, 2H, *J* = 7.2 Hz), 1.91 (*m*, 1H), 1.41-1.33 (*unresolved*, 8H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 164.2, 155.3, 129.9, 113.0, 43.2, 38.2, 30.6, 28.5, 24.0, 23.0, 14.1, 10.4.

Synthesis of 2,5-dibromo-3,4-dinitrothiophene (11)[3]

2,5-Dibromothiophene (**10**) (10.73 g, 44.4 mmol) was added slowly into an ice-cold solution of conc. H_2SO_4 (19 mL), fuming H_2SO_4 (29 mL) and fuming HNO_3 (16 mL) in such a way the inside temperature did not exceed 20 ^{o}C. After complete addition, the solution was stirred for about 20 h at room temperature and then slowly poured in to ice (91 g). The precipitated product was filtered off and washed with water several times. Light yellow crystals of **11** (9.14 g, 62.6%) were obtained after recrystallization from isopropanol. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 140.6, 113.6.

Synthesis of 2,5-bis(2-thienyl)-3,4-dinitrothiophene (12)[3]

2,5-Dibromo-3,4-dinitrothiophene (**11**) (8 g, 24.1 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol) and dried toluene (75 mL) were refluxed for 30 min. and to this was added a solution of 2-tributylstannylthiophene (18.8 g, 50.4 mmol) was added slowly and the reaction mixture was refluxed overnight. The progress of the reaction was monitored using TLC (toluene and n-pentane, 1:1). The reaction mixture was concentrated by rotary evaporation and to the

resulting brown precipitate, n-pentane was added and the mixture was filtered. After concentrating the filtrate, the solid product was dried in vacuum oven and **12** (7.3 g, 91.25%) was obtained as yellow fine powder. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.63 (*dd*, 2H, *J* = 5.2, 0.8 Hz), 7.57(*dd*, 2H, *J* = 3.8, 1.2 Hz), 7.20 (*dd*, 2H, *J* = 5.2, 3.8 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 135.9, 134.0, 131.3, 131.2, 128.5, 128.0.

Synthesis of 2,5-bis(2-thienyl)-3,4-diaminothiophene (13)[3]

Under inert atmosphere, 2,5-bis(2-thienyl)-3,4-dinitrothiophene (**12**) (3.5 g, 10.36 mmol) was dissolved in a mixture of EtOH (36 mL) and conc. HCl (73 mL). A solution of anh. $SnCl_2$ (36.23 g, 190 mmol) in EtOH (73 mL) was added and stirred at 30 ^{o}C for 24 h. The progress of the reaction was monitored by TLC (hexane: DCM, 1:1). The solution was poured in to 25% NaOH (250 mL); which formed a yellow gel. Toluene (300 mL) was added followed by filtration. The organic layer was separated and dried over $MgSO_4$. The dried solution was filtered and concentrated to afford **13** (2.77 g 96.2%) as dark brown crystals ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.30 (*dd*, 2H, *J* = 4.8, 1.6 Hz), 7.11 (*m*, 4H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 135.9, 133.6, 127.8, 124.0, 123.9, 110.1.

Synthesis of compound 4,6-di(thiophen-2-yl)-thieno[3,4-*c*][1,2,5]thiadiazole (14)[4]

Under inert atmosphere, *N*-thionylaniline (2.8 g, 9.7 mmol) was added into a stirred solution of 2,5-bis(2-thienyl)-3,4-diaminothiophene (**13**) (2.7 g, 9.7 mmol) and pyridine (40.5 mL). Then TMSCl was added (7.7 g, 70.88 mmol), and stirred for 24 h at room temperature. The progress of the reaction was monitored by TLC (chloroform). Dichloromethane (350 mL) was added and the solution was washed with 1N HCl (250 mL) and with water. The organic layer was separated and dried over $MgSO_4$ followed by filtration and removal of the solvent by rotary evaporation. The excess of *N*-thionylaniline was washed with *n*-hexane and filtered to obtain **14** (2.46 g, 82.8%) as dark blue solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.60 (*dd*, 2H, *J* = 3.8, 1.2 Hz), 7.35 (*dd*, 2H, *J* = 5.0, 1.2 Hz), 7.13 (*dd*, 2H, *J* = 5.0, 4.0 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 156.2, 134.9, 128.2, 125.5, 124.3, 112.4.

Synthesis of dimethyl-4,7-di(2-thienyl)-2,1,3-benzothiadiazole-5,6-dicarboxylate (15)[5]

Into a flask containing *o*-xylene (28 mL) and compound **14** (2.4 g, 7.8 mmol), dimethyl acetylenedicarboxylate (2.2 g, 15.6 mmol) was added and the mixture was refluxed for 24 h under inert atmosphere. The progress of the reaction was monitored by TLC (chloroform). The reaction mixture was concentrated using rotary evaporator and dried under vacuum oven. The crude product was purified by silica gel column chromatography and **15** (3.21 g, 99%) was obtained as a yellow powder. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.62 (*dd*, 2H, *J* = 5.2, 1.2 Hz), 7.45 (*dd*, 2H, *J* = 3.6, 1.2 Hz), 7.22 (*dd*, 2H, *J* = 5.2, 3.6 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 168.0, 153.6, 135.0, 132.0, 129.7, 128.9, 127.3, 126.2.

Synthesis of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole-5,6-dicarboxylic acid (16)[5]

Dimethyl-4,7-di(2-thienyl)-2,1,3-benzothiadiazole-5,6-dicarboxylate (**15**) (3 g, 7.2 mmol) was suspended in EtOH (150 mL). To this aqueous NaOH (20%) was added (100 mL) was added slowly and the reaction mixture was stirred for 24 h under reflux. HCl was added into the reaction mixture until pH = 1 and the mixture was stirred for another 6 h. The yellow solid was collected by filtration, washed with water and EtOH to afford **16** (1.96 g, 70%). ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.10 (*d*, 2H, *J* = 3.6 Hz), 7.82 (*d*, 2H, *J* = 4.8 Hz), 7.33 (*t*, 2H, *J* = 4.4 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 161.1, 156.5, 134.4, 132.3, 131.0, 129.5, 127.4, 123.8.

Synthesis of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole-5,6-dicarboxylic anhydride (17)[5]

Compound **16** (1.9 g, 4.89 mmol) and acetic anhydride (14.5 g, 142 mmol) were added into xylene (42.5 mL), and the mixture was stirred overnight under reflux. After removal of the solvent under reduced pressure, the solid product was dried in vacuum oven. Recrystallization of the resulting solid from EtOH afforded **17** (1.78 g, 98.3%) as a red solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.11 (*dd*, 2H, *J* = 4.0, 1.2 Hz), 7.82 (*dd*, 2H, *J* = 5, 1.2 Hz), 7.33 (*dd*, 2H, *J* = 5.0, 4.0 Hz); ^{13}C-NMR (100.6 MHz, CDCl3): δ 161.1, 156.5, 134.4, 132.3, 131.0, 129.5, 127.3, 123.8.

Synthesis of *N*-octyl-4,7-di(2-thienyl)-2,1,3-benzothiadiazole-5,6-dicarboxylic imide (18)[5]

Compound **17** (1.76 g, 4.75 mmol) and *n*-octylamine (1.47 g, 11.35 mmol) were dissolved in glacial acetic acid and the mixture was stirred overnight at 110 ^{o}C. Acetic anhydride (34 mL) was then added and the mixture was stirred for another 6 h at 110 ^{o}C under nitrogen atmosphere. After removal of the solvent, the crude product was purified by silica gel column chromatography using hexane/$CHCl_3$ 1:2 (v/v) as an eluent. Compound **18** was obtained as an orange powder (2.13 g, 98%). ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.92 (*dd*, 2H, *J* = 3.8, 1.2 Hz), 7.74 (*dd*, 2H, *J* = 5.2, 1.2 Hz), 7.30 (*dd*, 2H *J* = 5.2, 3.8 Hz), 3.74 (*t*, 2H, *J* = 7.6 Hz), 1.71 (*quin*, 2H), 1.20-1.40 (*unresolved*, 10H), 0.88 (*t*, 3H, *J* = 6.8 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 165.8, 156.5, 133.1, 131.5, 130.2, 127.0, 126.9, 38.9, 31.8, 29.1, 28.3, 27.0, 22.6, 14.0.

Synthesis of *N*-octyl-4,7-di(5-bromo-2-thienyl)-2,1,3-benzothiadiazole-5,6-dicarboxyic imide (19)[6]

Under inert atmosphere, compound **18** (2.13 g, 4.65 mmol) was dissolved in THF (200 mL); and *N*-bromosuccinimide (4.14 g, 23 mmol) was added in one portion. The mixture was stirred at room temperature, in the dark, overnight. The progress of the reaction was controlled by TLC using pet. ether/EtOAc 30:2 (v/v) as eluent. The reaction mixture was extracted with chloroform and the organic phase was dried under $MgSO_4$. After filtration, the solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography using dichloromethane as eluent. Compound **19** (2.21 g, 74%) was obtained as red powder after recrystallization from isopropanol. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.81 (*d*, 2H, *J* = 4.0 Hz), 7.24 (*d*, 2H, *J* = 4.0 Hz), 3.75 (*t*, 2H, *J* = 7.2 Hz), 1.71 (*m*, 2H), 1.20-1.40 (*m*, 10H), 0.88 (*t*, 3H, *J* = 6.8 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 165.7, 156.0, 134.0, 133.0, 129.8, 126.4, 125.9, 118.7, 39.0, 31.8, 29.1, 28.2, 27.0, 22.6, 14.0.

Synthesis of 4,8-di(thien-2-yl)-1*H*-6-octyl-5*H*-pyrrolo[3,4-*f*]benzotriazole-5,7-(6*H*)-dione (21)[7]

Compound **18** (1.98 g, 4.11 mmol) and iron powder (7.7 g, 137.5 mmol) were added into glacial acetic acid (68.3 mL) and the mixture was refluxed for 24 h under nitrogen atmosphere. The progress of the reaction was monitored by TLC (chloroform) and when the starting material disappeared completely, the reaction mixture was filtered. It was then cooled in an ice-water bath and to it was added a solution of $NaNO_2$ (1.17 g, 16.96 mmol) in water

(20 mL) drop wise. Then the reaction mixture was stirred overnight at room temperature and extracted with DCM. The combined organic layer was dried over anh. $MgSO_4$, and the solvent was removed by rotary evaporation. The resulting solid was purified by silica gel column chromatography using hexane:EtOAc (3:2) as eluent to afford **21** (1.2 g, 63.2%) as a pale-yellow solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.74 (*d*, 2H, *J* = 4.8 Hz), 7.30 (*m*, 4H), 3.71 (*t*, 2H, *J* = 7.6 Hz), 1.70 (*quin*, 2H), 1.33 – 1.27 (*unresolved*, 10H), 0.88 (*t*, 3H, *J* = 6.8 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 166.3, 141.5, 132.5, 131.2, 129.6, 128.0, 125.1, 122.1, 38.6, 31.7, 29.1, 28.4, 27.0, 22.6, 14.0.

Synthesis of 2-(2-ethylhexyl)-6-octyl-4,8-di(thiophene-2-yl)[1,2,3]triazolo[4,5-*f*]isoindole 5,7(2*H*, 6*H*)-dione (22)

Compound **21** (1.2 g, 2.58 mmol), 1-bromo-2-ethylhexane (1 g, 5.16 mmol), and K_2CO_3 (2 g, 14.47 mmol) were dissolved in DMF (25 mL) and the reaction mixture was stirred at 80 ^{o}C for 24 h. After cooling to room temperature, the mixture was poured in to water and the organic layer was extracted with chloroform, washed with water, dried over anh. $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography using DCM:pet. ether (1:1)) as eluent to give **22** (1.19 g, 80%) as orange oil. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.15 (*dd*, 2H, *J* = 3.6, 1.2 Hz), 7.67 (*dd*, 2H, *J* = 5.2, 1.2 Hz), 7.28 (*dd*, 2H, *J* = 5.2, 3.6 Hz), 4.67 (*d*, 2H, *J* = 6.4 Hz), 3.73 (*t*, 2H, *J* = 7.6 Hz), 2.27 (*m*, 1H), 1.71 (*m*, 2H), 1.40 – 1.27 (*m*, 18H), 1.00 (*t*, 3H, *J* = 7.6 Hz), 0.91 (*m*, 6H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 166.6, 145.5, 133.1, 132.1, 129.7, 126.8 124.9, 123.7, 60.2, 40.4, 38.5, 31.8, 30.6, 29.2, 28.4, 27.1, 24.0, 23.0, 22.7, 14.1, 10.6.

Synthesis of 4,8-bis-(5-bromothiophen-2-yl)-6-octyl-[1,2,3]triazolo[4,5-*f*]isoindole-5-7(2*H*,6*H*)-dione (23)[7]

Compound **22** (1.19 g, 2.06 mmol) was dissolved in 1:1 (v/v) mixture of $CHCl_3$:acetic acid, and *N*-bromosuccinimide (0.97 g, 5.45 mmol) was added in several portions and the mixture was stirred for 24 h at room temperature. The reaction mixture was monitored by TLC (DCM:pet. ether,1:1) and more NBS (0.1 g in total) was added at intervals to ensure the completion of the reaction. After 48 h, all of the starting material was consumed and the reaction mixture was extracted with DCM. The combined organic layer was washed with water and dried over anh. $MgSO_4$. The solvent was removed under reduced pressure and the

crude product was washed with EtOH. The resulting product was further purified by silica gel column chromatography using mixture of DCM and pet. ether (1:1) as eluent to afford **23** (1.24 g, 82.6%) as an orange solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.02 (*d*, 2H, *J* = 4.0 Hz), 7.21 (*d*, 2H, *J* = 4.0 Hz), 4.71 (*d*, 2H, *J* = 6.8 Hz), 3.72 (*t*, 2H, *J* = 7.6 Hz), 2.24 (*quin*, 1H, *J* = 5.6, Hz), 1.70 (*quin*, 2H, *J* = 6.8 Hz), 1.42 – 1.27 (*m*, 18H), 1.00 (*t*, 3H, *J* = 7.6 Hz), 0.91 (*t*, 6H, *J* = 8.0 Hz); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 166.5, 145.2, 133.9, 133.7, 129.8, 123.9 123.5, 118.0, 60.4, 40.5, 38.6, 31.8, 30.5, 29.2, 28.4, 27.0, 24.0, 23.0, 22.6, 14.1, 10.6.

Synthesis of P1

4,8-Dibromo-6-(2-ethylhexyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(2*H*,6*H*)-dione (**9**) (95 mg, 0.2 mmol), (4,8-bis(4,5-dioctylthiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis(trimethylstannane) (**24)** (225.8 mg, 0.2 mmol), $Pd_2(dba)_3$ (7.4 mg, 0.008 mmol), and P(*o*-tol)$_3$ (10 mg, 0.04 mmol) were added into a 25 mL round bottom flask and dissolved in anh. toluene (8 mL) under nitrogen. The mixture was then heated at 100 ^{o}C for 24 h and as the mixture became more viscous, anh. toluene (4 mL) was added and heated for another 10 min followed by addition of 2-bromothiophene (0.15 mL) and the mixture was allowed to react for 1 h. Then, 2-(tributylstannyl)thiophene (0.15 mL) was added and the mixture was heated for an additional 1 h, cooled to room temperature and precipitated from MeOH. The polymer was collected by filtration through a thimble and was subjected to Soxhlet extraction with acetone, diethyl ether, and chloroform. The chloroform extract was concentrated to a small volume and poured into MeOH. The precipitate was collected by membrane filtration (PTFE 0.45 μm) and dried in vacuum oven at 40 ^{o}C to afford **P1** (143.5 mg, 64.2%) as dark green solid.

Synthesis of P2

4,8-Bis(5-bromothiophen-2-yl)-6-octyl-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(2*H*,6*H*)-dione (**19**) (127.8 mg, 0.20 mmol) was mixed with (4,8-bis(4,5-dioctylthiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis(trimethylstannane) (**24**) (225.8 mg, 0.20 mmol), $Pd_2(dba)_3$ (3.7 mg, 0.005 mmol), and P(*o*-tol)$_3$ (4.9 mg, 0.02 mmol) and the mixture was dissolved in anh. toluene (8 mL) and stirred at 100 ^{o}C for 1 h under nitrogen atmosphere. When the reaction mixture became more viscous, anh. toluene (4 mL) was added and heated for another 5 min followed by addition of 2-bromothiophene (0.15 mL) and the mixture was

allowed to react for 1 h. Then, 2-(tributylstannyl)thiophene (0.15 mL) was added and the mixture was heated for an additional 1 h, cooled to room temperature and precipitated from MeOH. The polymer was collected by filtration through a thimble and was subjected to Soxhlet extraction with acetone, diethyl ether, chloroform and *o*-DCB. The *o*-DCB extract was passed through a short silica gel column using *o*-DCB as eluent, concentrated to a small volume and poured into MeOH, The precipitate was collected by membrane filtration (PTFE, 0.45 μm) and dried in vacuum oven at 40 °C to afford **P2** (101 mg, 38.5%).

Synthesis of P3

To 25 mL two-necked round-bottomed flask, 4,8-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-6-octyl-[1,2,3]triazolo[4,5-*f*]isoindole-5,7(2*H*,6*H*)-dione (**23**) (146.9 mg, 0.20 mmol), (4,8-bis(4,5-dioctylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (**24**) (225.8 mg, 0.20 mmol), $Pd_2(dba)_3$ (3.7 mg, 0.005 mmol), and P(*o*-tol)$_3$ (4.9 mg, 0.02 mmol) were added and dissolved in anh. toluene (8 mL) under nitrogen atmosphere. Subsequently, the reaction mixture was heated at 100 °C for 26 h. When the reaction mixture became more viscous, anh. toluene (4 mL) was added and heated for another 5 min followed by addition of 2-bromothiophene (0.15 mL) and the mixture was allowed to react for 1 h. Then 2-(tributylstannyl)thiophene (0.15 mL) was added and the mixture was heated for an additional 1 h. The reaction mixture was then cooled to room temperature and precipitated from MeOH. The polymer was collected by filtration through a thimble and subjected to Soxhlet extraction with acetone, diethyl ether, and chloroform. The chloroform solution was passed through a short silica gel column by using chloroform as eluent. Finally, the chloroform solution was concentrated to a small volume, poured into MeOH and the precipitate was collected by membrane filtration (PTFE, 0.45 μm). **P3** (262 mg, 95.1%) was obtained as dark-red solid after drying in a vacuum oven at 40 °C.

4. NMR spectra of monomers

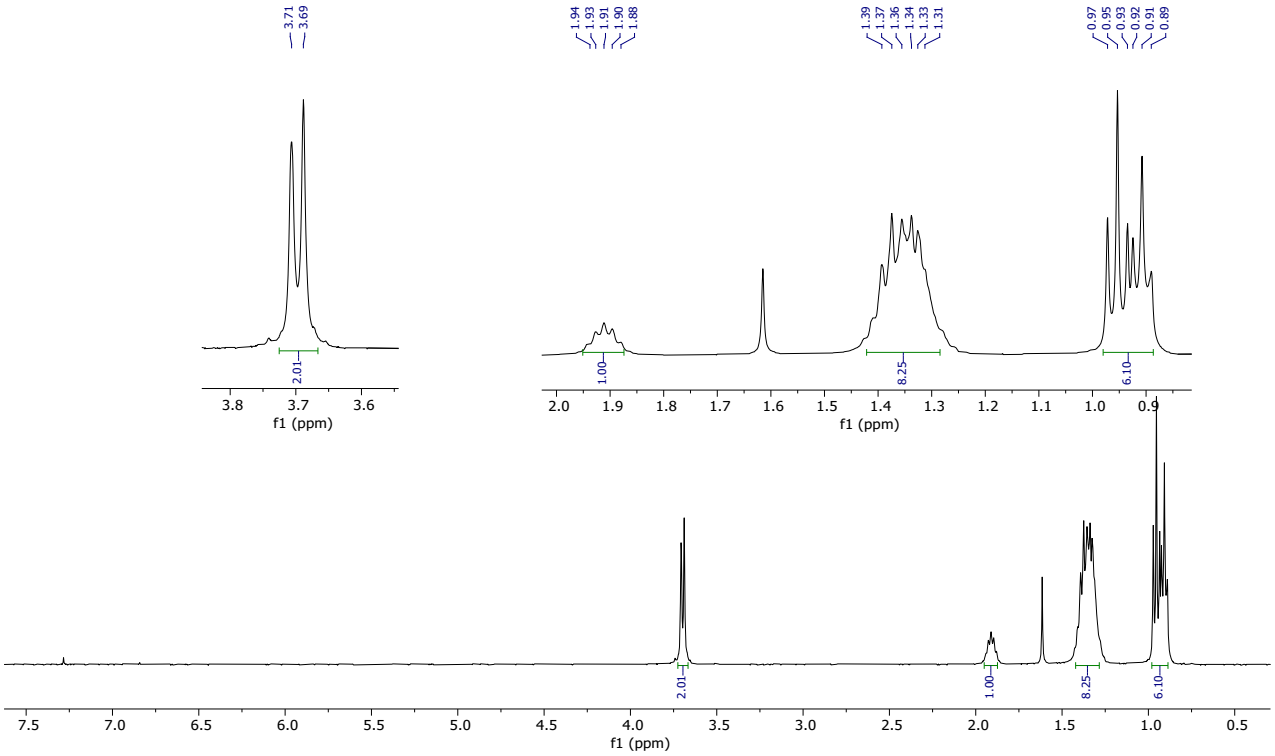


Figure S1. The ^{1}H-NMR spectrum (400.13 MHz, $CDCl_3$) of 4,8-dibromo-6-(2-ethylhexyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (**9**).

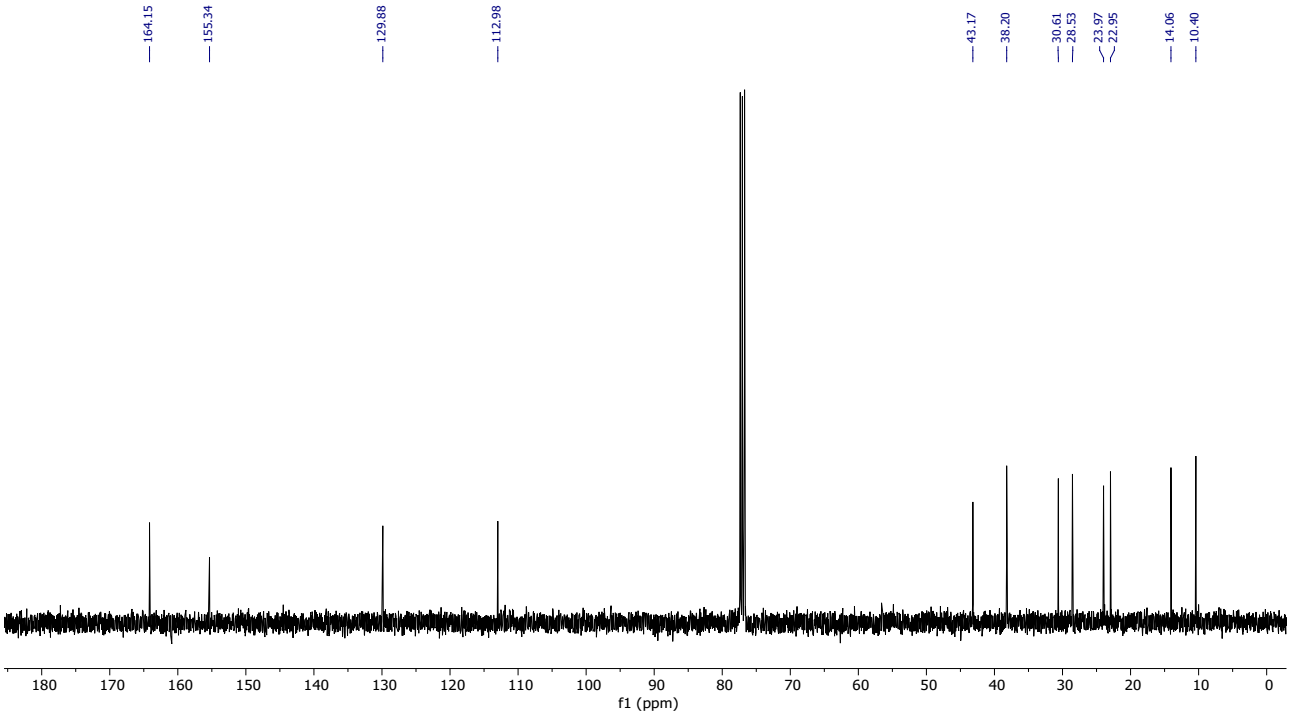


Figure S2. The ^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$) of 4,8-dibromo-6-(2-ethylhexyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (**9**).

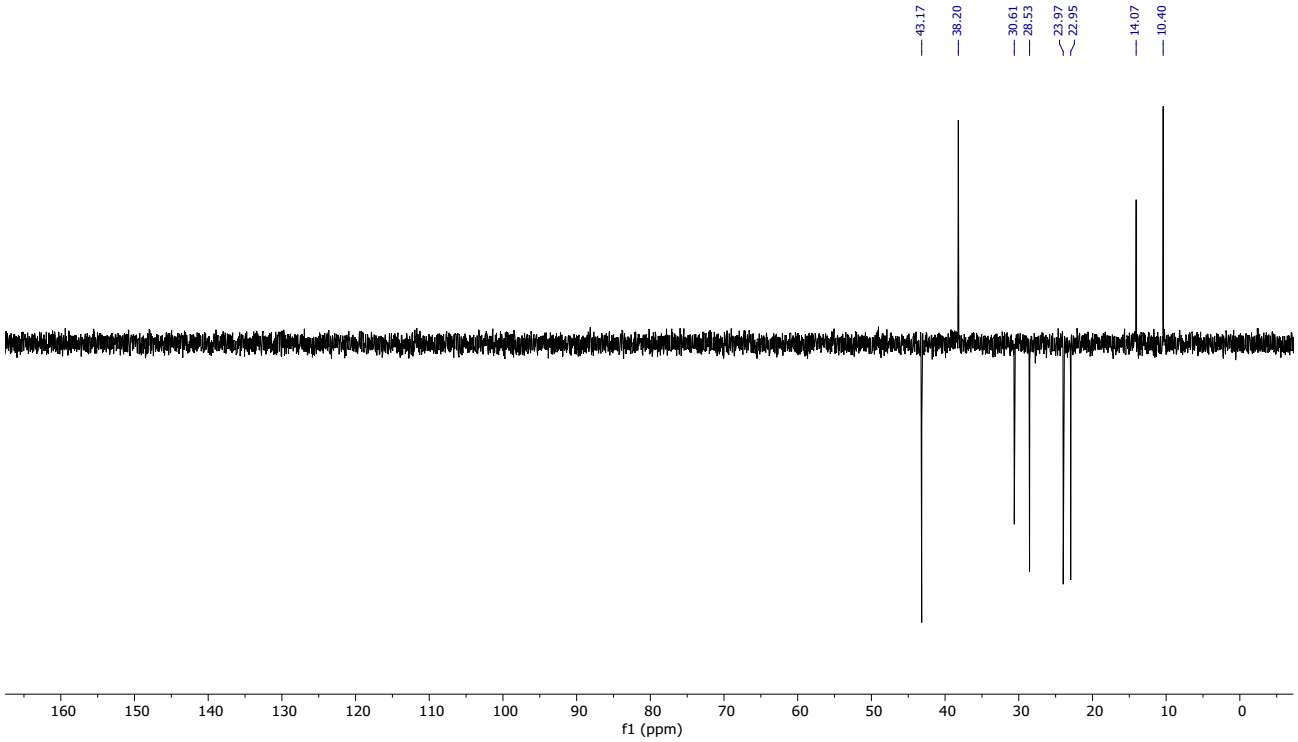


Figure S3. The DEPT-135 spectrum (100.6 MHz, $CDCl_3$) of 4,8-dibromo-6-(2-ethylhexyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (**9**).

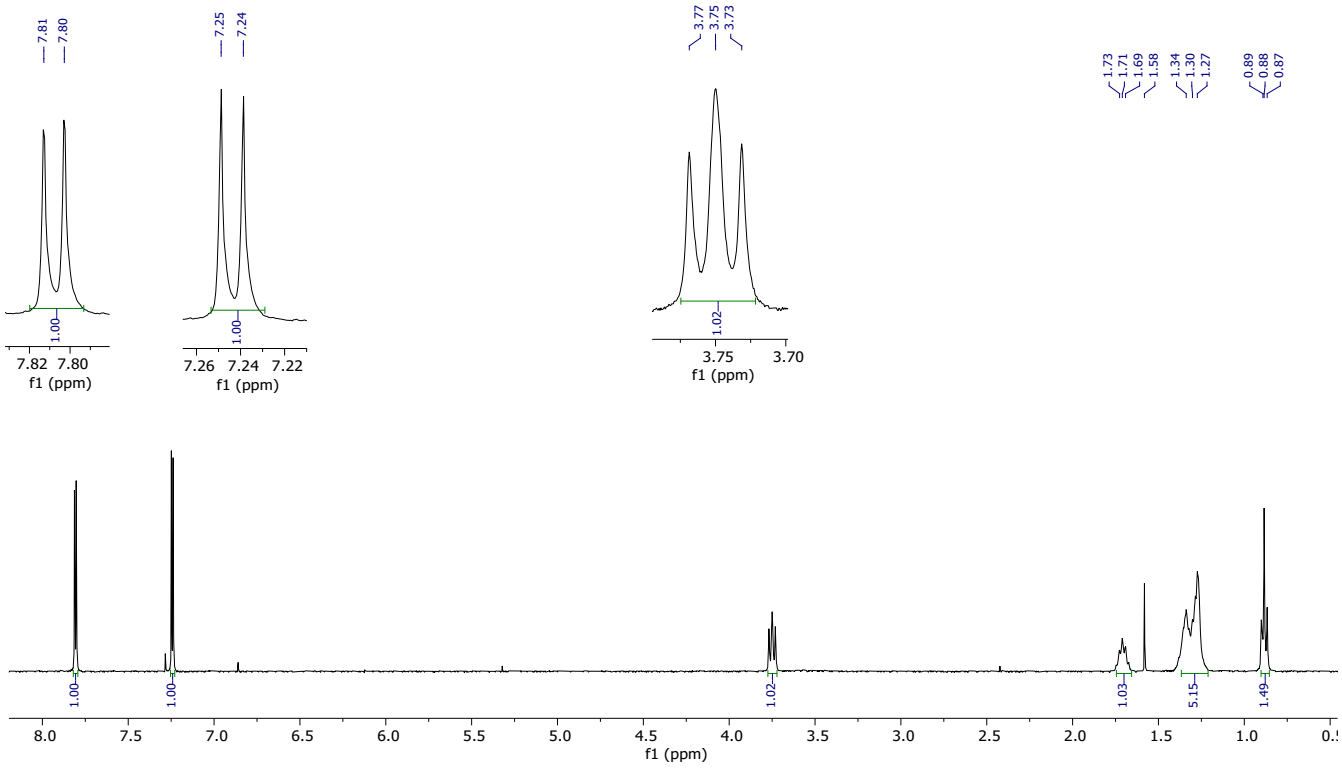


Figure S4. The ^{1}H-NMR spectrum (400.13 MHz, $CDCl_3$) of 4,8-bis(5-bromothiophen-2-yl)-6-octyl-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (**19**).

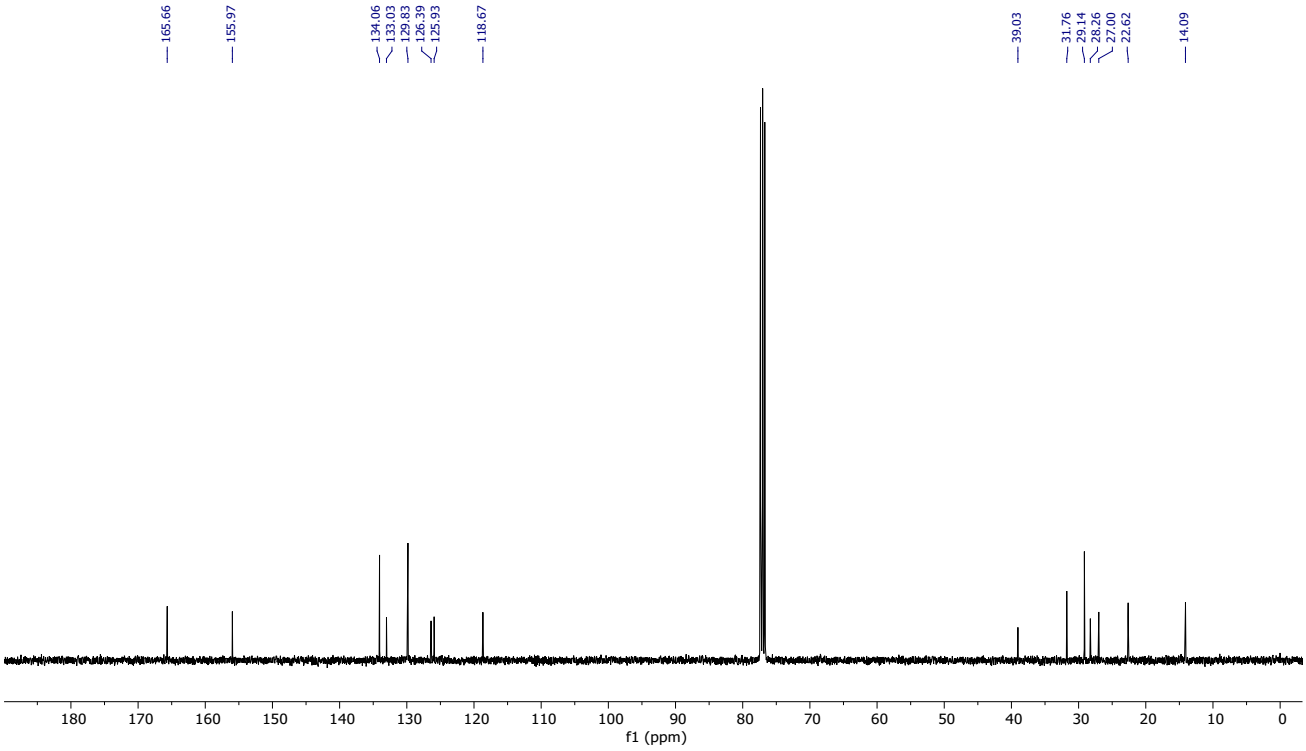


Figure S5. The ^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$) of 4,8-bis(5-bromothiophen-2-yl)-6-octyl-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (**19**).

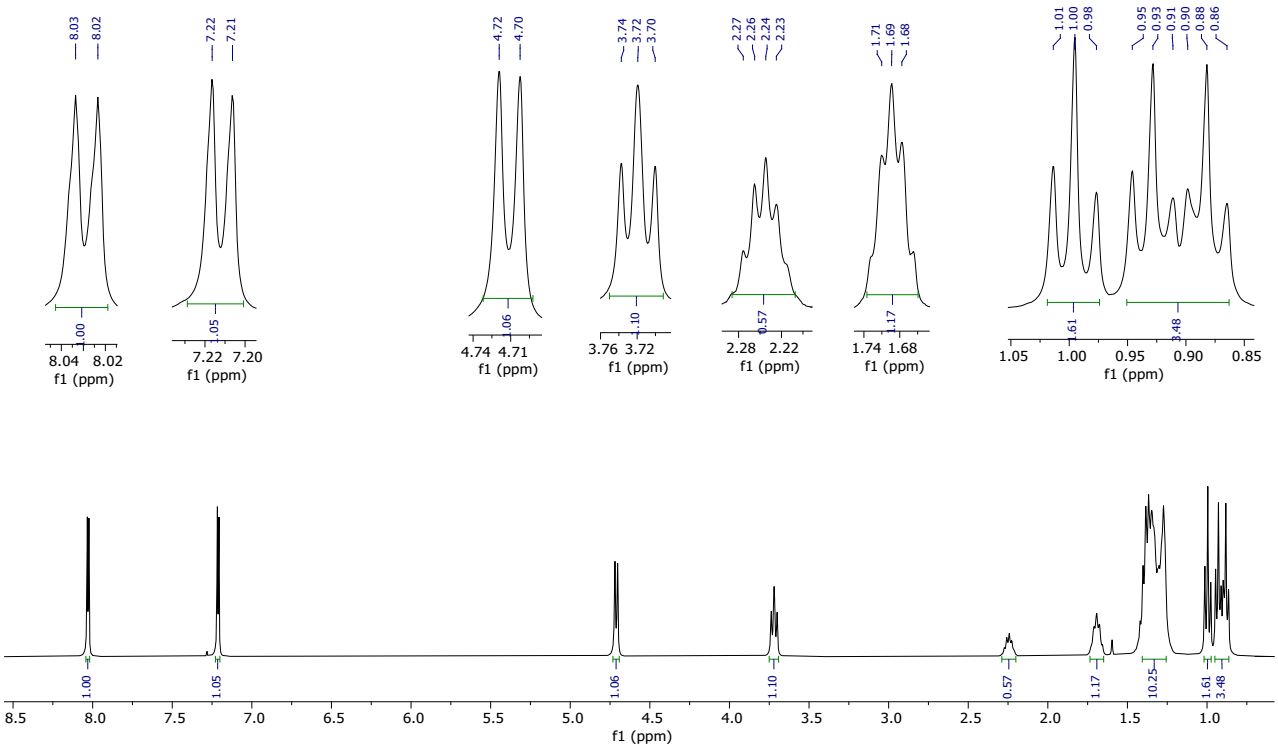


Figure S6. The ^{1}H-NMR spectrum (400.13 MHz, $CDCl_3$) 4,8-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-6-octyl-[1,2,3]triazolo[4,5-*f*]isoindole-5,7(2*H*,6*H*)-dione (**23**).

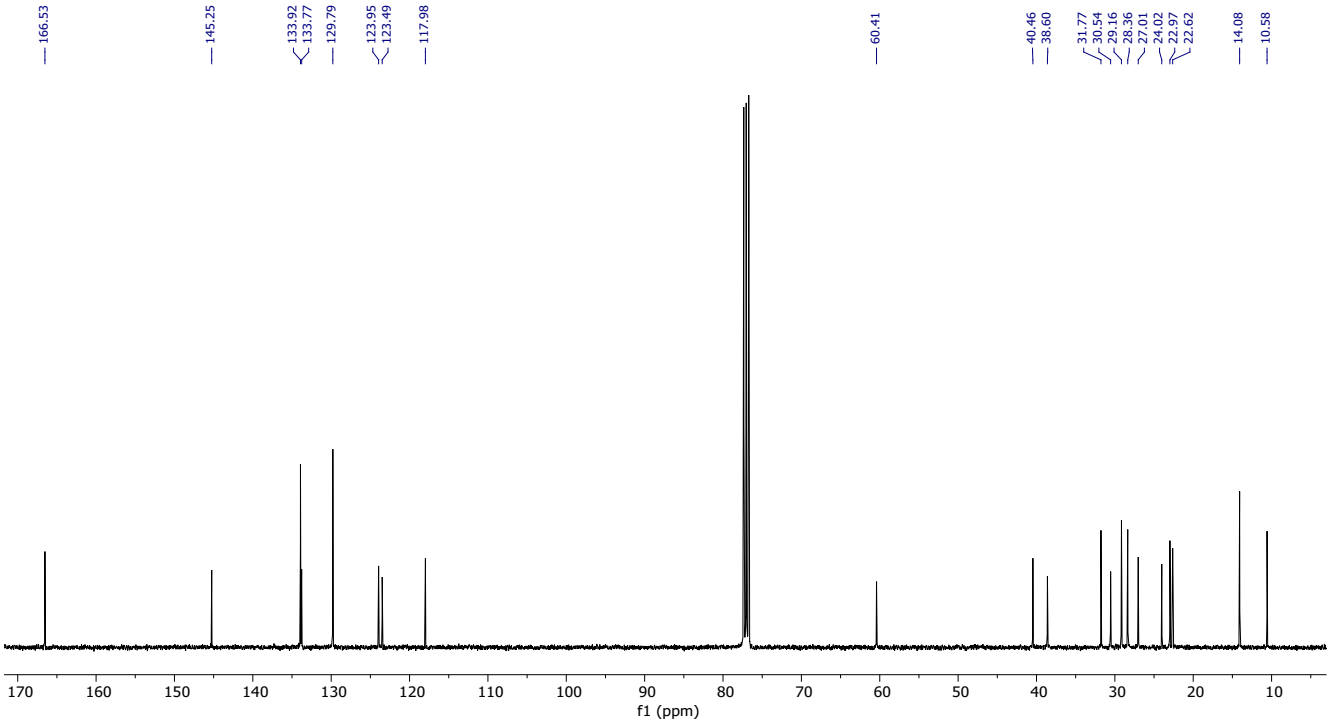


Figure S7. The ^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$) of 4 4,8-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-6-octyl-[1,2,3]triazolo[4,5-*f*]isoindole-5,7(2*H*,6*H*)-dione (**23**).

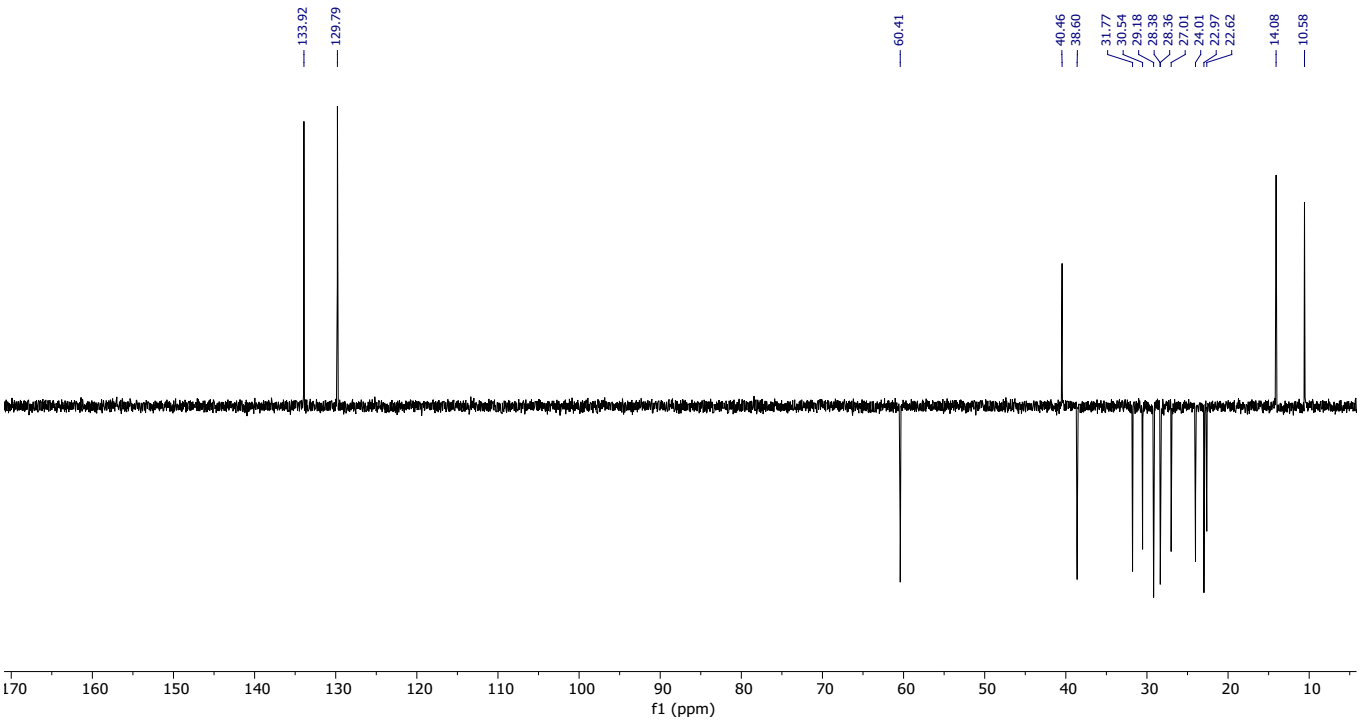


Figure S8. The DEPT-135 spectrum ((100.6 MHz, $CDCl_3$) of 4,8-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-6-octyl-[1,2,3]triazolo[4,5-*f*]isoindole-5,7(2*H*,6*H*)-dione (**23**).

5. Frontier Molecular Orbitals

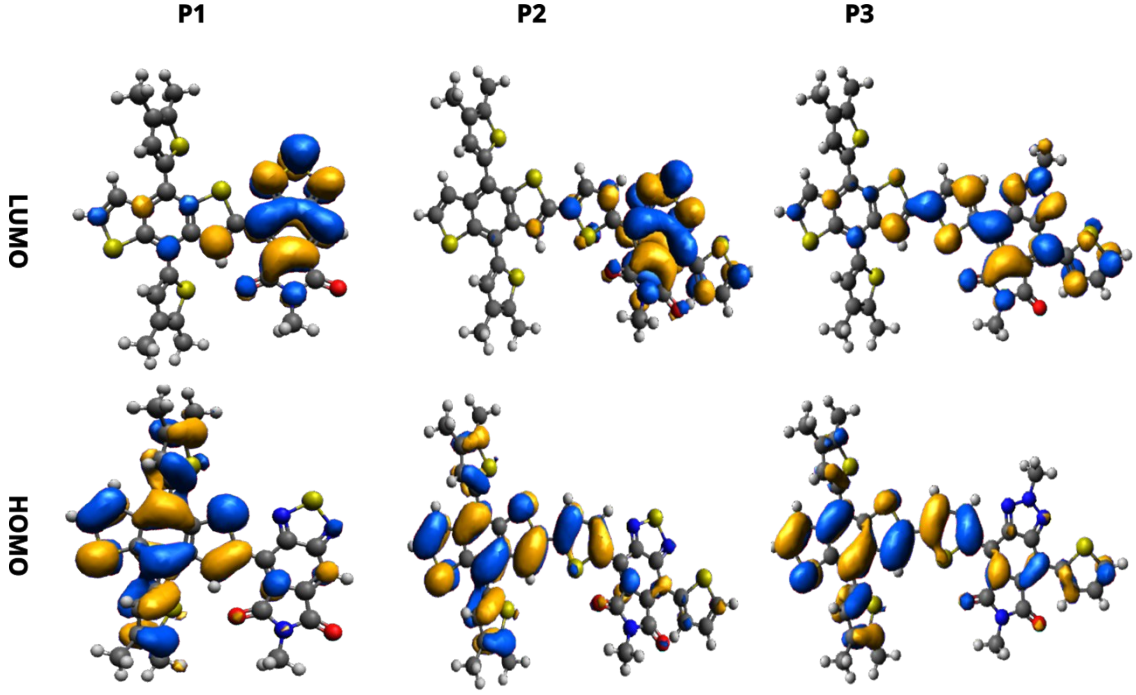


Figure S9: Frontier molecular orbital distributions in **P1, P2** and **P3.**

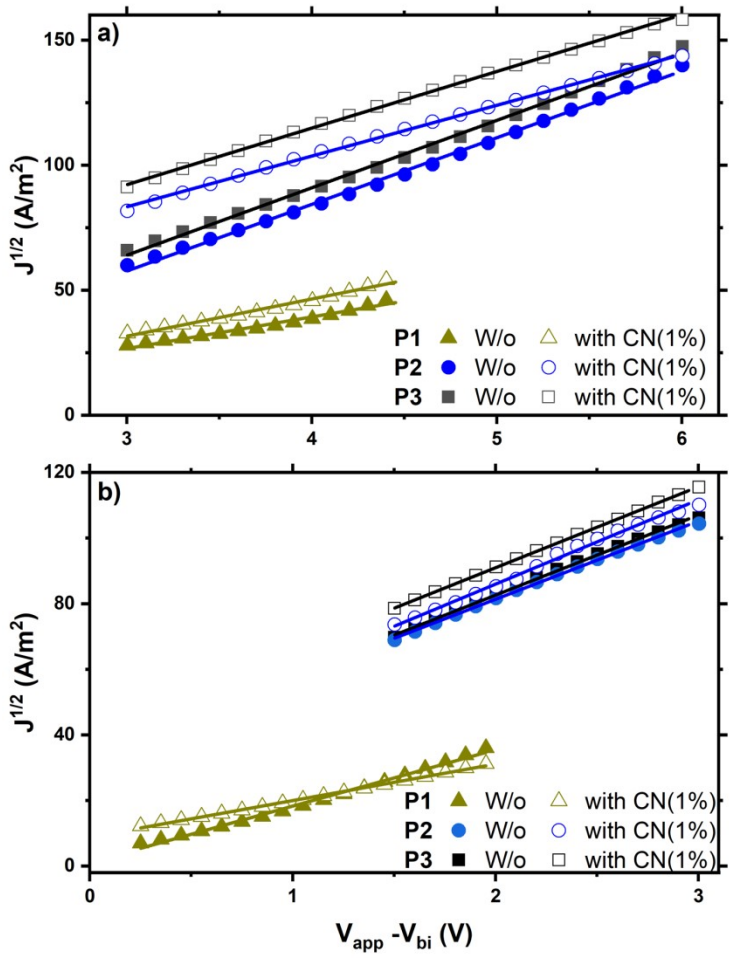


Figure S10 SCLC and Mott-Gurney fit in (a) electron-only (b) hole-only devices

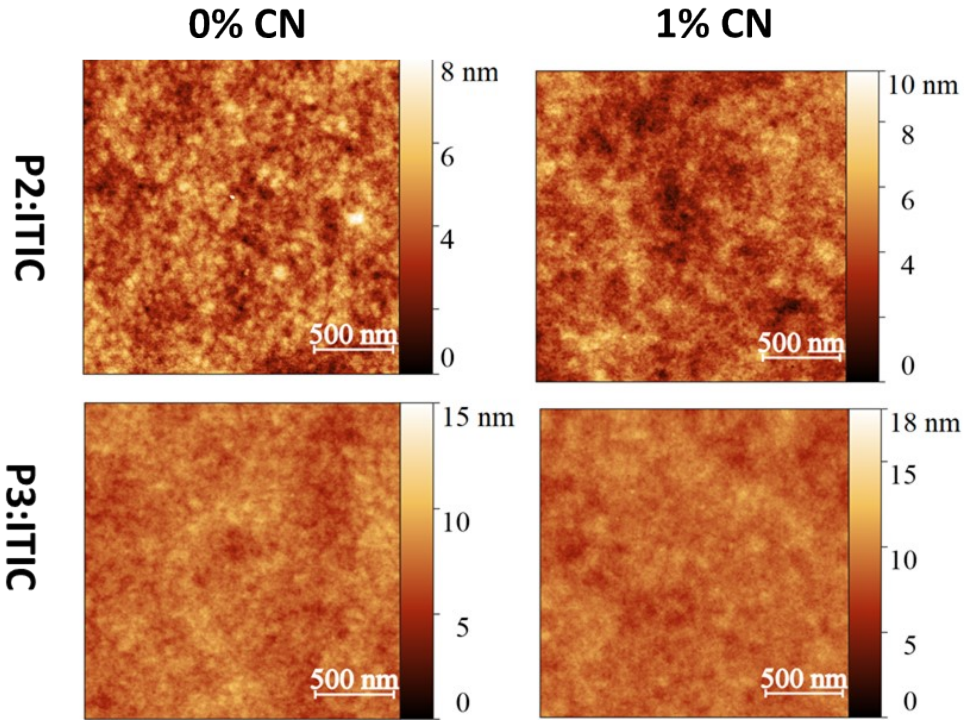


Figure S11: AFM topographic images of P2:ITIC (top) and P3:ITIC based devices with and without CN.

REFERENCES

(1) Shao, J.; Chang, J.; Chi, C. *Org. Biomol. Chem.* 2012, 10, 7045.

(2) Wang, C.; Xu, X.; Zhang, W.; Bergqvist, J.; Xia, Y.; Meng, X.; Bini, K.; Ma, W.; Yartsev, A.; Vandewal, K.; Andersson, M. R.; Inganäs, O.; Fahlman, M.; Wang, E. *Adv. Energy Mater.* 2016, 6, 1600148.

(3) Li, P.; Fenwick, O.; Yilmaz, S.; Breusov, D.; Caruana, D. J.; Allard, S.; Scherf, U.; Cacialli, F. *Chem. Commun.* 2011, 47, 8820.

(4) Steinberger, S.; Mishra, A.; Reinold, E.; Mena-Osteritz, E.; Muller, H.; Uhrich, C.; Pfeiffer, M.; Bauerle, P. *J. Mater. Chem.* 2012, 22, 2701.

(5) Lan, L.; Chen, Z.; Li, Y.; Ying, L.; Huang, F.; Cao, Y. *Polym. Chem.* 2015, 6, 7558.

(6) Wang, L.; Cai, D.; Zheng, Q.; Tang, C.; Chen, S.-C.; Yin, Z. *ACS Macro Lett.* 2013, 2, 605.

(7) Lan, L.; Chen, Z.; Hu, Q.; Ying, L.; Zhu, R.; Liu, F.; Russell, T. P.; Huang, F.; Cao, Y. *Adv. Sci.* 2016, 3, 1600032.