

# Supporting Information

## **Alkoxy Functionalized Benzothiadiazole Based Donor-Acceptor Conjugated Copolymers for Organic Field-Effect Transistors.**

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## **Materials and Methods**

All commercially available solvents, reagents, and chemicals were used as received without further purification unless otherwise stated. Anhydrous solvent tetrahydrofuran was distilled from sodium under argon. 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole, octan-1-ol, sodium tert-butoxide, N-bromosuccinimide were purchased from Sigma Aldrich. Unless otherwise stated, all operations and reactions were carried out under argon using standard Schlenk line techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of  $\text{CDCl}_3$  or TMS as an internal reference and are given in ppm. Number-average ( $M_n$ ) and weight average ( $M_w$ ) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. UV-vis spectra were recorded on a UV- 1601 Shimadzu Uv-vis spectrometer. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh) unless otherwise indicated. Thin Layer Chromatography (TLC) was performed on Merck aluminium-backed plates pre-coated with silica (0.2 mm, 60 F254). Microwave experiments were performed in a Biotage initiator V 2.3. Differential scanning calorimetry (DSC) analysis were recorded on Mettler in nitrogen at 10 °C  $\text{min}^{-1}$  of heating rate from 30 °C to 350 °C in two cycles heating-cooling, and thermogravimetric analysis (TGA) curves were collected on Mettler in nitrogen at 10 °C  $\text{min}^{-1}$  of heating rate from 30 °C to 600 °C. Cyclic voltammetry (CV) measurements of polymers films were performed under argon atmosphere using a CHI760E Voltammetry analyzer with 0.1 M tetra-n-butylammonium hexafluorophosphate in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed, and the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) was used as the internal reference for all measurements. The scanning rate was 100 mV/s. Polymer films were drop-casted from chloroform solutions on a Pt working electrode (2 mm in diameter). XRD analysis of the samples were carried out using a Rigaku Ultima IV multipurpose X-ray diffractometer, equipped with a Cu Ka X-ray tube operated at 40 KV and 30 mA, and a cross-beam optics. The XRD spectra were collected from 3 to 60° of  $2\theta$  angles with a step width of 0.02° and 1°/min. scan speed. A Bruker Dimension Icon Atomic Force Microscopy (AFM) with Nanoscope V controller was used to collect

height and phase images of the samples. The images were collected at  $2 \times 2 \mu\text{m}$  area using tapping method and a Bruker Tespa V2 probe. The scan rate was 0.8 Hz, and the amplitude set point was 11.8 nm.

### **Device Fabrication (BG-BC and TG-BC)**

The **BG-BC** devices were fabricated following the substrate treatment procedures on  $p^{++}$  highly doped silicon substrate with  $\text{SiO}_2$  as the dielectric layer with thickness of 300 nm and Au metal of 30 nm thickness as the S-D electrodes. After the substrates undergone the same processing methods as the top gate devices and were surface-modified with OTS, organic semiconductor materials solution in chloroform at 5 mg/mL were prepared and the formed solution were spin coated on the substrates at 2000 RPM for 60 s. The substrates were then annealed at optimal heat treatment temperature for 15 min.

The **TG-BC** devices were fabricated following the conventional substrate treatment procedures on  $p^{++}$  highly doped silicon substrate with Au as the S-D electrode with thickness of 30nm, which was thoroughly cleaned by placing the substrates in piranha solution. The channel length and channel width were  $5 \mu\text{m}$  and 1.4 mm, respectively. The piranha solution was removed and the substrates were rinsed thrice with deionized (DI) water. The solution was sonicated with DI water, toluene, and isopropyl alcohol (IPA) for 5 min each in that order. UV-ozone (UV/O3) treatment was done for 15 min, and then baked at  $90 \text{ }^\circ\text{C}$  for 0.5 h at 0.1 Pa in a vacuum oven. OTS treatment was performed by placing the cleaned substrates in OTS vapor for 3 h at  $120 \text{ }^\circ\text{C}$  in the vacuum environment. copolymer solution in chloroform at 5 mg/ mL was prepared and heated using the hot platform at  $60 \text{ }^\circ\text{C}$  for 10 min, and the formed solution was spin coated on the substrates at 2000 RPM for 60 s. The substrates were then annealed at  $120 \text{ }^\circ\text{C}$  for 15 min. PMMA at the concentration of 60mg/mL was spin coated on the semiconductor layer at 2000 RPM for 60 s as insulating layer, then annealed at  $80 \text{ }^\circ\text{C}$  for 1 h in air. Measured by Dektak thickness profilometer, the thin film thickness of PMMA was  $1 \mu\text{m}$  . Finally, top gate aluminum metal of 80 nm thickness was deposited using the thermal vacuum deposition chamber.

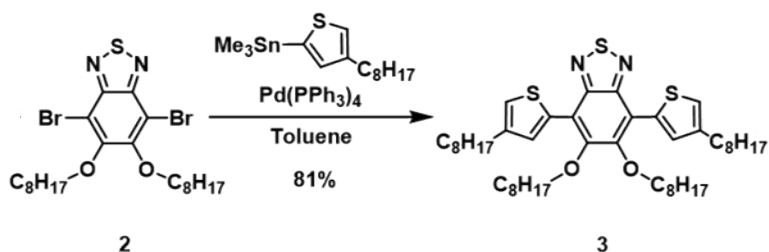
Devices were characterized using Keithley 4200-SCS semiconductor parameter analyzer in the nitrogen environment. The threshold voltage ( $V_{th}$ ) and field-effect mobility ( $\mu$ ) in the saturation region were determined from the following equation:

$$I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$$

where  $W$  and  $L$  are the channel width and length, respectively.  $C_i$  is the capacitance of the polymer insulator. As an example, devices based on **CP3**, effective field-effect mobilities were calculated from the above equation.

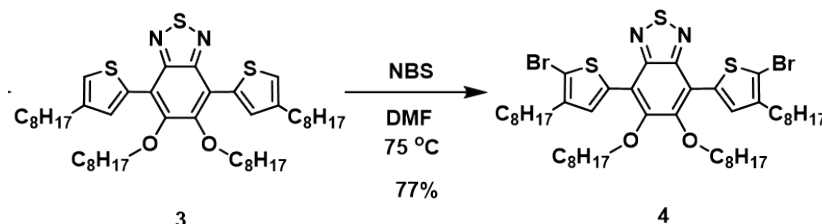
## Experimental Procedures

### 4,7-bis(4-octylthiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (3):

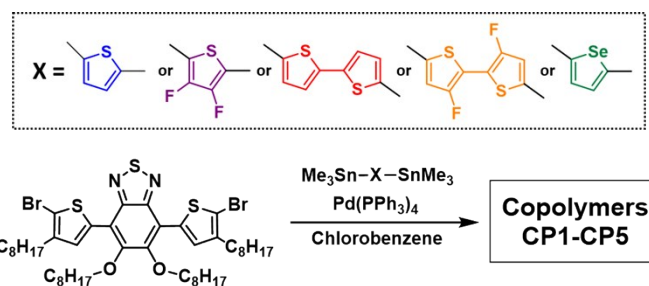


In a microwave vial compound **2** (2.0 g, 4.6 mmol)<sup>1, 2</sup> and trimethyl(4-octylthiophen-2-yl)stannane (3.5 g, 9.6 mmol)<sup>3</sup> were dissolved in anhydrous toluene (1 mL). Tetrakis(triphenylphosphine)palladium(0) (1 mol%, 48 mg) was added, and the resultant mixture was degassed for 30 min with argon and securely sealed. The vial was placed into a microwave reactor and heated at 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min, and followed by 180 °C for 30 min. The crude mixture was filtrated over basic silica using hexane as an eluent and the solvent was removed under reduced pressure. The crude product was precipitated in MeOH to afford compound **4** as a yellow solid (2.5 g, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 2H), 7.50 (s, 2H), 3.95 (t, *J* = 7.2 Hz, 4H), 2.65 (t, *J* = 8.0 Hz, 4H), 1.94 (m, 4H), 1.68 (m, 4H), 1.28-1.5 (m, 40H), 0.88 (t, *J* = 6.7 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.5, 150.5, 141.8, 133.7, 131.6, 125.9, 116.9, 74.5, 31.9, 31.8, 30.3, 29.9, 29.7, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. FTMS (ESI, *m/z* of [MH<sup>+</sup>]) found: 782.2705, calculated for C<sub>46</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub><sup>+</sup>: 782.2714.

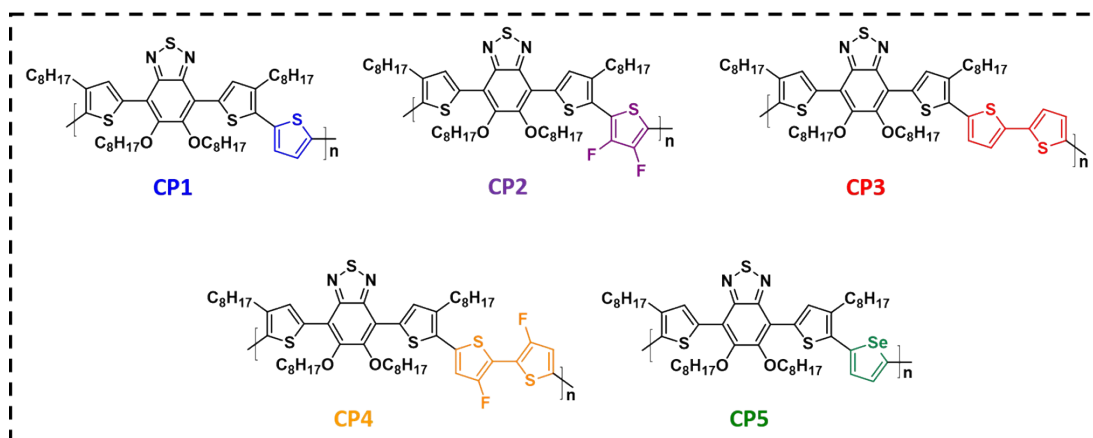
**4,7-bis(5-bromo-4-octylthiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (4):**



To a solution of **3** (1.0 g, 1.45 mmol) in DMF (1 mL), NBS (0.79 g, 4.36 mmol) was added. The mixture was stirred at 75 °C for 4 h. The mixture was then cooled to room temperature and water (100 mL) was added. The aqueous layer was extracted with diethyl ether (3 x 100 mL) and the organic layer was then washed with 5% NH<sub>4</sub>Cl (3 x 100 mL), brine, water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The crude mixture was precipitated in MeOH to afford compound **4** as yellow solid (0.92 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (s, 2H), 4.11 (t, *J* = 7.2 Hz, 4H), 2.66 (t, *J* = 8.0 Hz, 4H), 1.94 (m, 4H), 1.68 (m, 4H), 1.28-1.5 (m, 40H), 0.88 (t, *J* = 6.7 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.5, 150.5, 141.8, 133.7, 131.6, 116.9, 112.6, 74.5, 31.9, 31.8, 30.3, 29.9, 29.7, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. FTMS (ESI, *m/z* of [MH<sup>+</sup>]) found: 940.3008, calculated for C<sub>46</sub>H<sub>70</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub><sup>+</sup>: 940.3017.



**General procedure for the Synthesis of copolymers CP1-CP5**



In a microwave vial equimolar amounts of monomer (0.20 mmol) and bis(trimethylstannyl) [thiophene (**CP1**) or 3,4-difluorothiophene (**CP2**) or bithiophene (**CP3**) or 3,3'-difluoro-2,2'-bithiophene (**CP4**) or selenophene (**CP5**)] were dissolved in anhydrous chlorobenzene (0.5 mL) followed by addition of tetrakis(triphenylphosphine)palladium(0) (2 mol%, 5.02 mg), the resultant mixture was degassed for 30 min with argon and securely sealed. The glass vial was placed into a microwave reactor and heated at 140 °C for 2 min, 160 °C for 2 min, and followed by 180 °C for 30 min. After being cooled to room temperature, the reaction mixture was precipitated into a mixture of methanol (200 mL) and concentrated HCl (2 mL) and stirred for 1 h at RT. The precipitate was filtered and extracted (Soxhlet) with methanol, acetone, n-hexane, chloroform. The remaining polymer was dissolved in chlorobenzene and precipitated into methanol, filtered and dried under vacuum to achieve the desired polymers as a dark purple solid. The <sup>1</sup>H NMR spectrum for all polymers exhibited considerable broadening of the aromatic and methylene peaks and only alkyl sidechain protons were observable. We attribute this to the aggregation effects.

**CP1:** Yield 95 mg, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.48 (2H), 7.71 (1H), 7.53 (1H), 4.21 (4H), 2.92 (4H), 2.02 (4H), 1.82 (4H), 1.20-1.60 (40H), 0.89 (12H); GPC:  $M_n = 30,400$  g/mol,  $D = 2.1$ ; UV-Vis:  $\lambda_{max} = 565$  nm (dilute chlorobenzene solution).

**CP2:** Yield 92 mg,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (2H), 4.18 (4H), 2.87 (4H), 2.02 (4H), 1.79 (4H), 1.20-1.60 (40H), 0.88 (12H); GPC:  $M_n = 25,600$  g/mol,  $D = 2.1$ ; UV-Vis:  $\lambda_{max} = 579$  nm (dilute chlorobenzene solution).

**CP3:** Dark Purple, Yield 95 mg,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (2H), 7.72 (1H), 7.51 (1H), 7.42 (2H), 4.22 (4H), 2.92 (4H), 2.02 (4H), 1.82 (4H), 1.20-1.60 (40H), 0.89 (12H); GPC:  $M_n = 30,600$ g/mol,  $D = 1.9$  UV-Vis:  $\lambda_{max} = 551$  nm (dilute chlorobenzene solution).

**CP4:** Dark Purple, Yield 92 mg,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (2H), 7.21 (1H), 7.17 (1H), 4.20 (4H), 2.91 (4H), 2.00 (4H), 1.78 (4H), 1.20-1.60 (40H), 0.90 (12H); GPC:  $M_n = 27,400$  g/mol,  $D = 2.1$ ; UV-Vis:  $\lambda_{max} = 571$  nm (dilute chlorobenzene solution).

**CP5:** Dark Purple, Yield 95 mg,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (2H), 7.72 (1H), 7.53 (1H), 4.21 (4H), 2.95 (4H), 2.02 (4H), 1.81 (4H), 1.20-1.60 (40H), 0.89 (12H); GPC:  $M_n = 29,300$  g/mol,  $D = 2.0$ ; UV-Vis:  $\lambda_{max} = 551$  nm (dilute chlorobenzene solution).

## NMR characterization

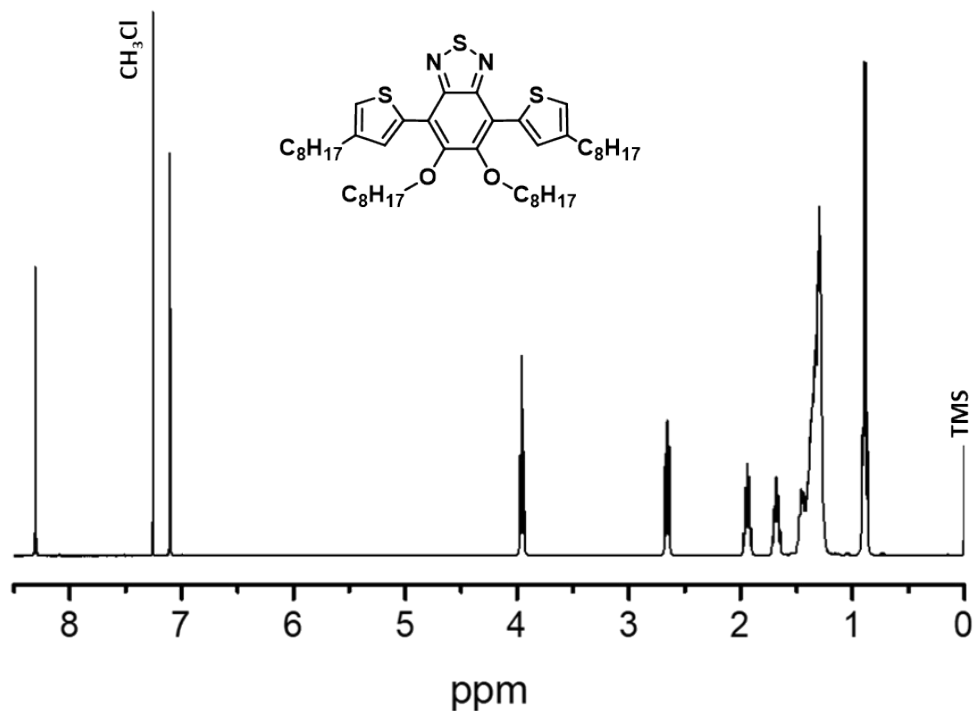




Figure S1.  $^1\text{H}$  NMR spectrum of 3.

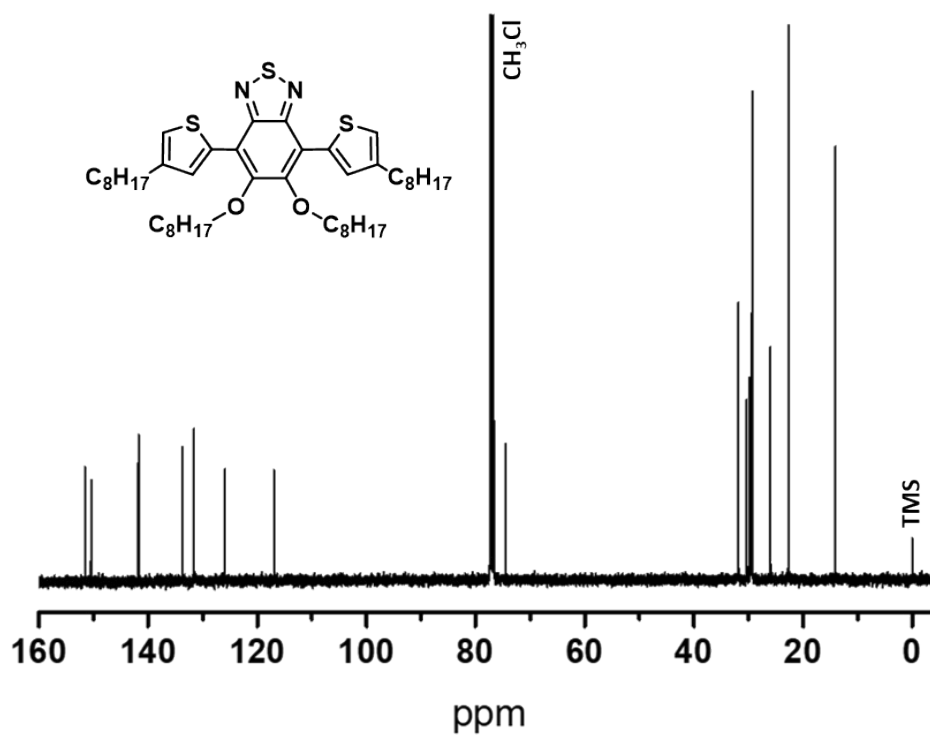


Figure S2.  $^{13}\text{C}$  NMR spectrum of 3.

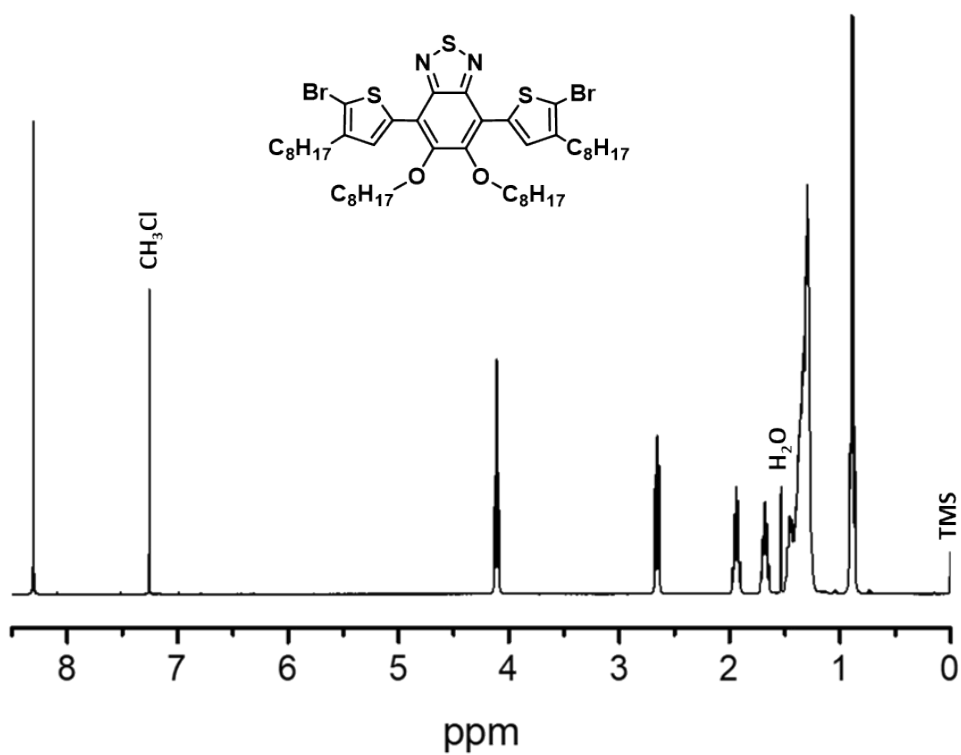


Figure S3.  $^1\text{H}$  NMR spectrum of 4.

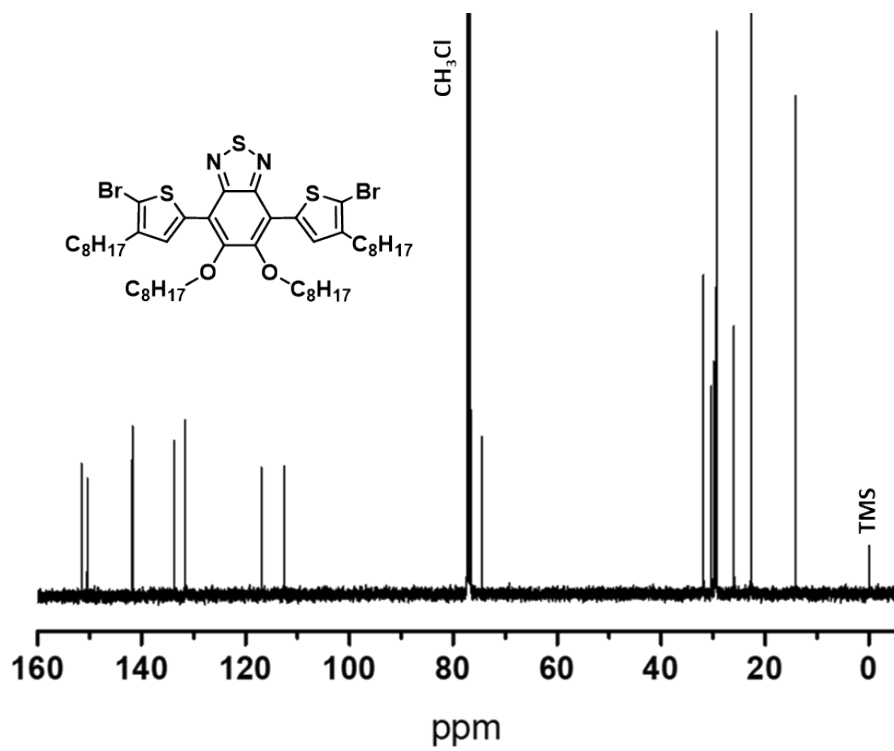


Figure S4.  $^{13}\text{C}$  NMR spectrum of 4.

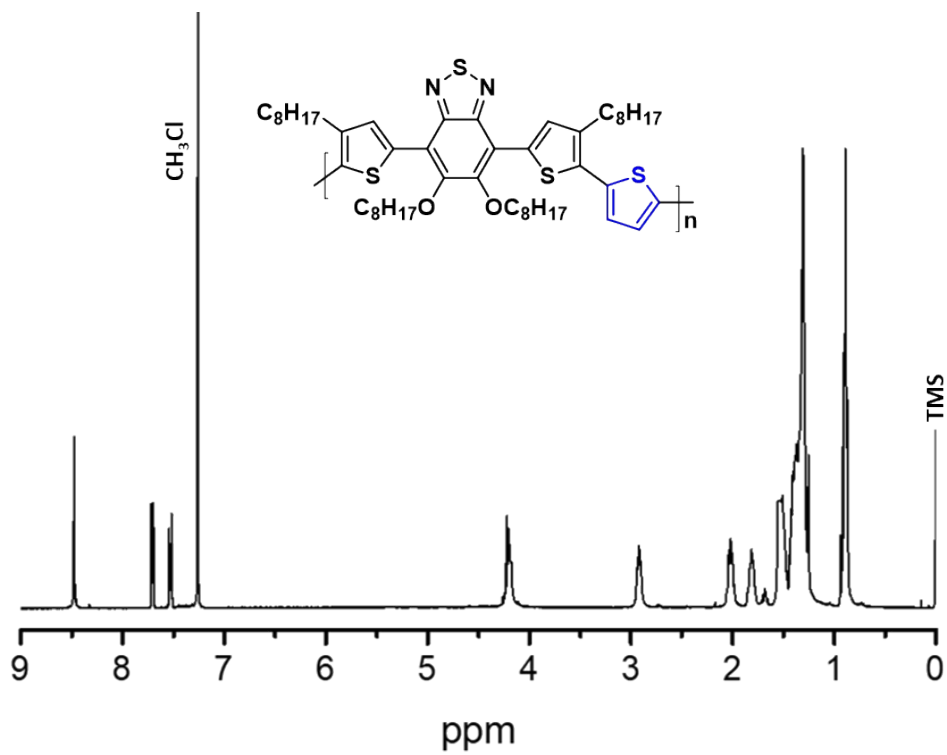


Figure S5.  $^1\text{H}$  NMR spectrum of CP1.

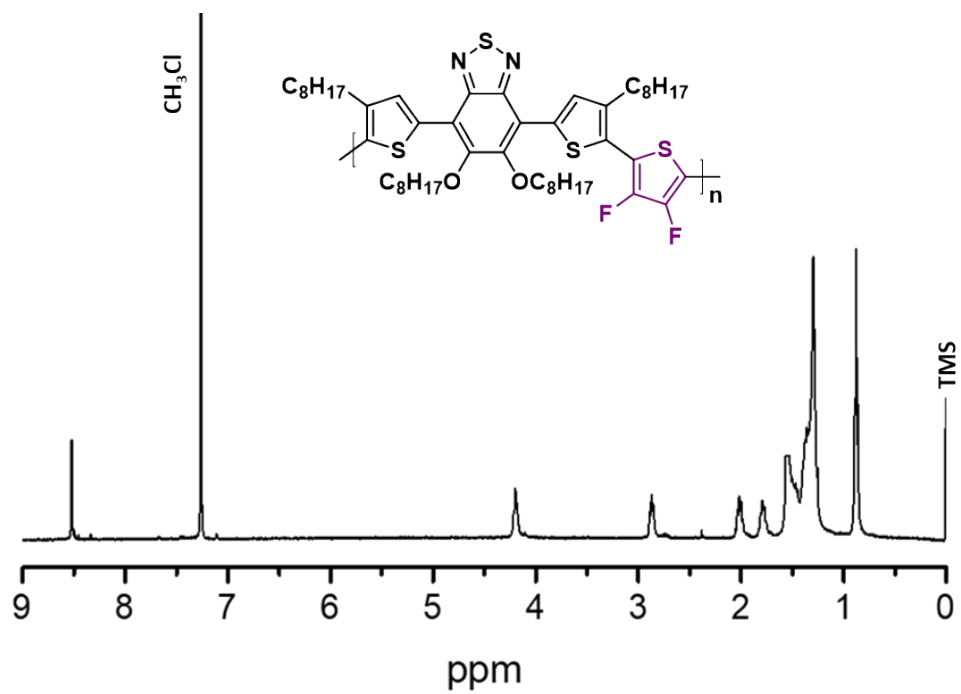


Figure S6.  $^1\text{H}$  NMR spectrum of CP2.

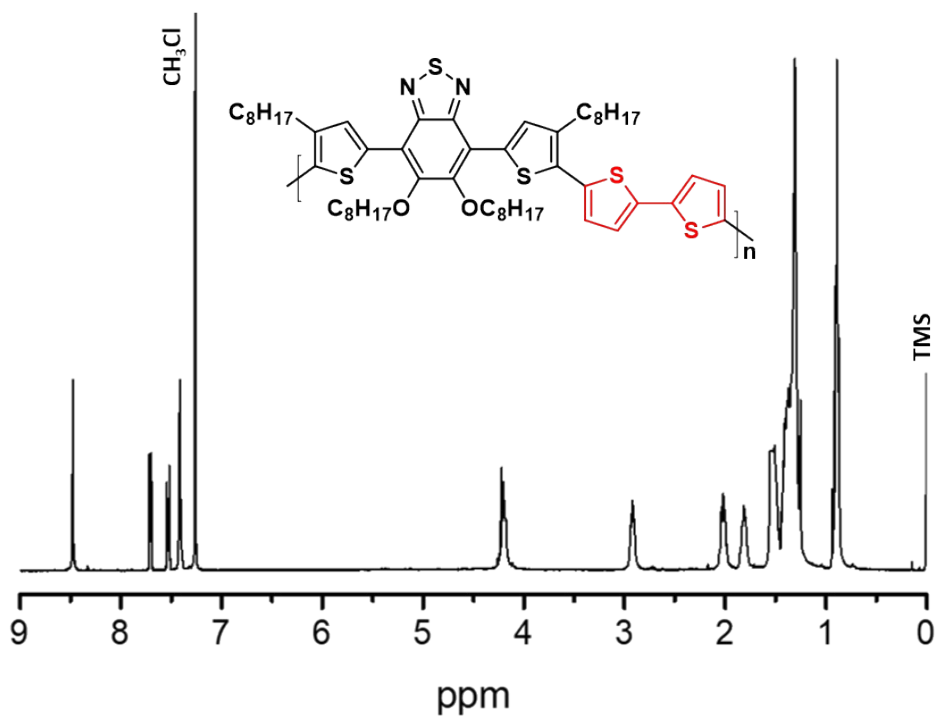


Figure S7.  $^1\text{H}$  NMR spectrum of CP3.

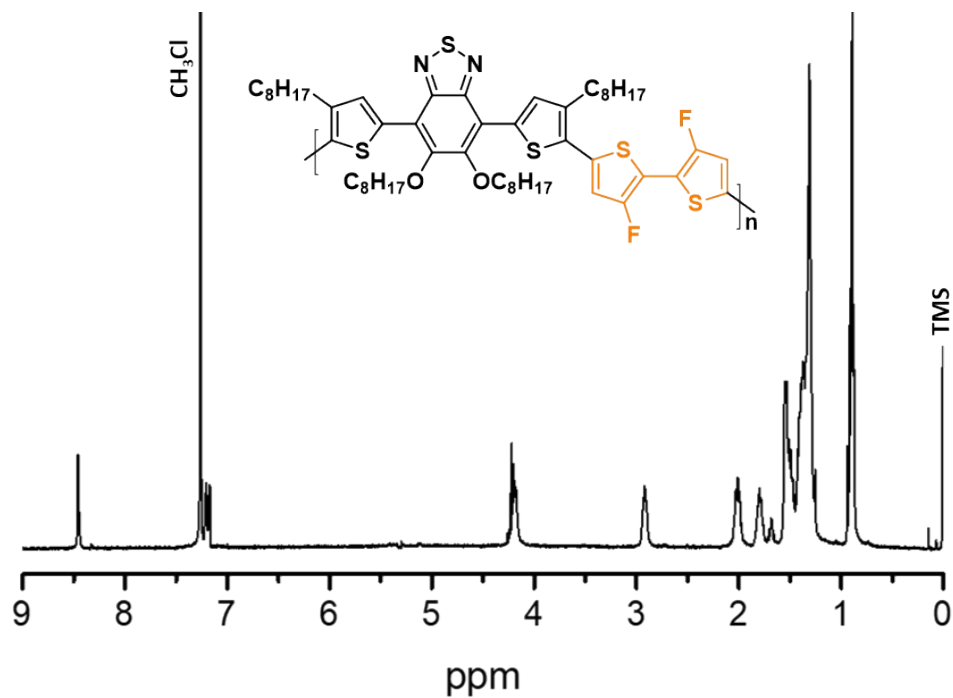


Figure S8.  $^1\text{H}$  NMR spectrum of CP4.

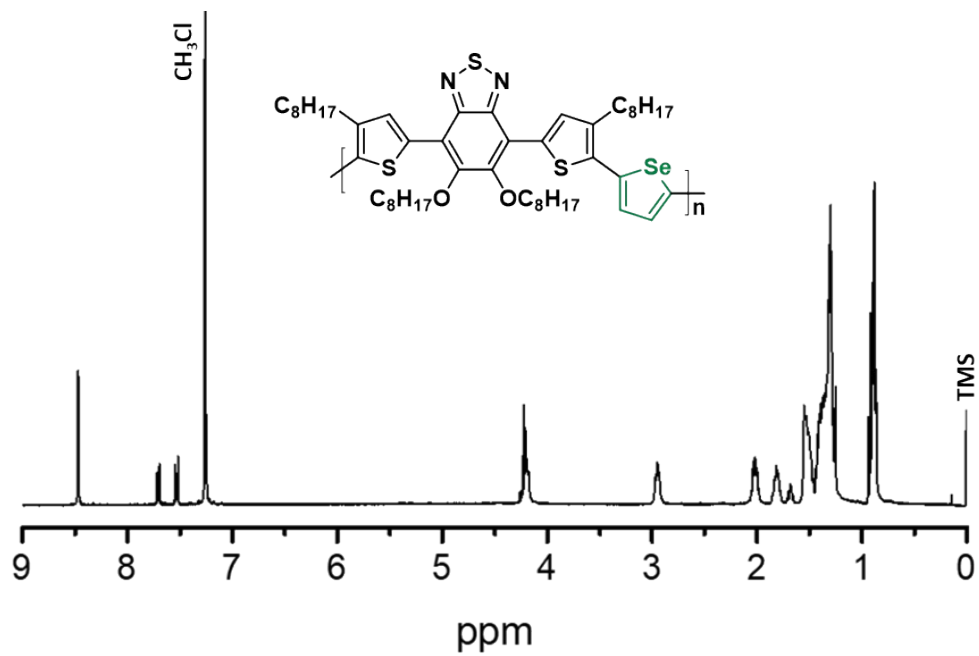
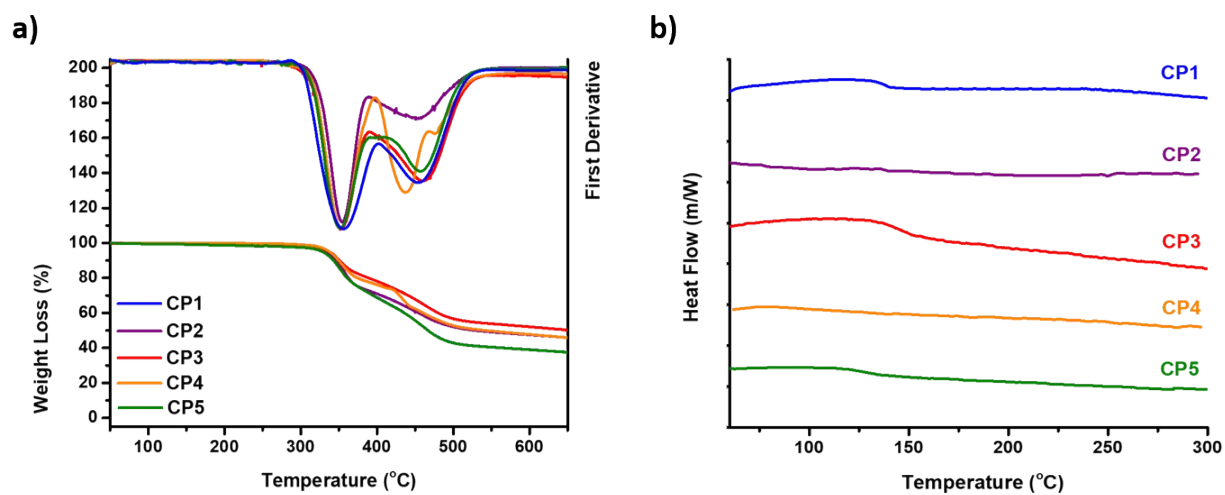


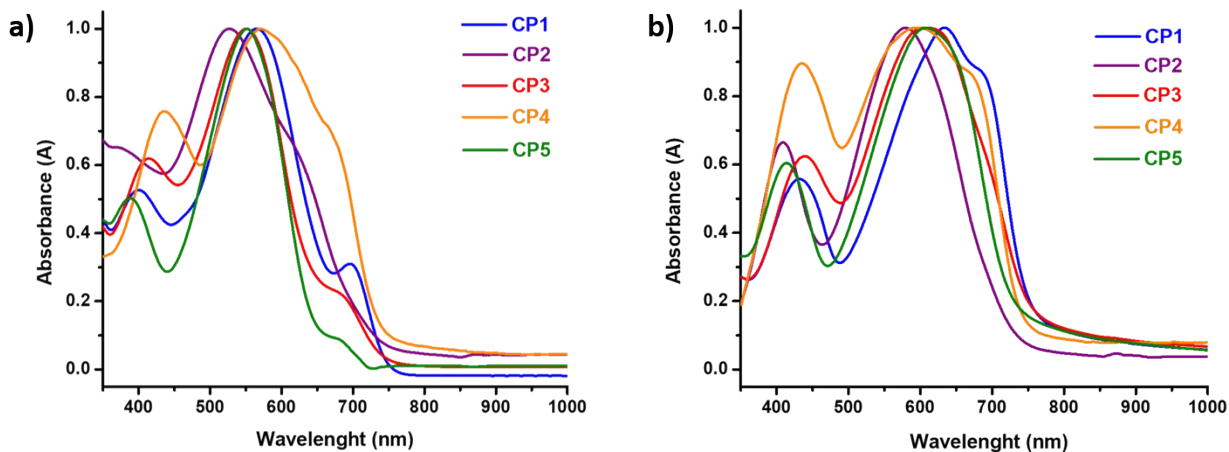
Figure S9.  $^1\text{H}$  NMR spectrum of CP5.

### Polymer Thermal Properties



**Figure S10.** (a) TGA thermograms of copolymers **CP1-5** under nitrogen flow at 10 °C min<sup>-1</sup> of heating rate from 30 °C to 600 °C. (b) DSC thermograms of second heating scan for copolymers **CP1-5**, 30 °C to 350 °C, in heating-cooling-heating scans with a ramp rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> as the purge gas.

## Polymer Optical Properties



**Figure S11.** UV-vis absorption of copolymers **CP1-5** in diluted chlorobenzene solution (a) and thin films from (b).

## DFT Calculations

Theoretical calculations for **CP1-CP5** polymers, using as models the monomer, dimer, trimer and tetramer structures were carried out in the frame of density functional theory (DFT), using the B3LYP functional<sup>4-6</sup> and the 6-31G\*\* basis set<sup>7, 8</sup> as implemented in the Gaussian 16 program.<sup>9</sup> The octyl and octyloxy chains on the thiophene and benzothiadiazole units of **CP1-CP5** were replaced with methyl and methyloxy groups to simplify the calculations. Geometry optimizations were performed without any symmetry constrains. On the basis of the resulting ground-state geometries, harmonic vibrational frequencies were calculated at the same theoretical level corroborating that the optimized geometries are minima (zero imaginary frequencies). The

reorganization energies were calculated directly from the relevant points on the potential energy surfaces by using previously reported standard procedures.

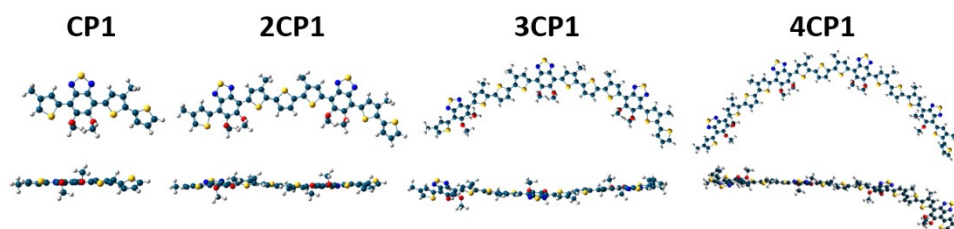


Figure S12. B3LYP/6-31G\*\* optimized geometries of CP1 monomer-tetramer structures.

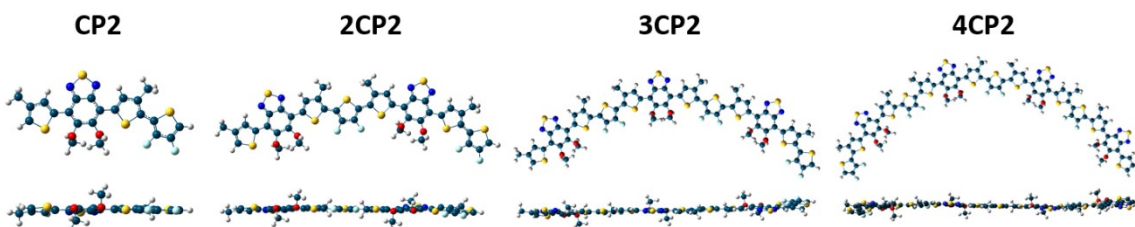


Figure S13. B3LYP/6-31G\*\* optimized geometries of CP2 monomer-tetramer structures.

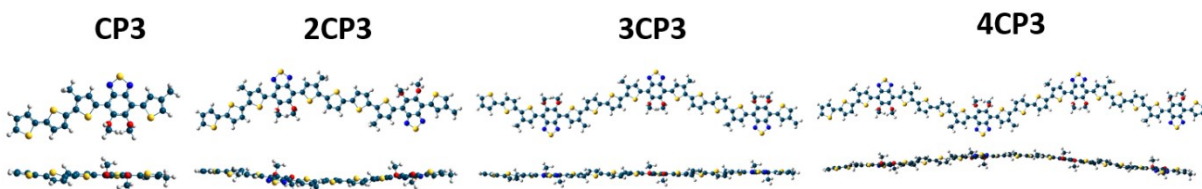


Figure S14. B3LYP/6-31G\*\* optimized geometries of CP3 monomer-tetramer structures.

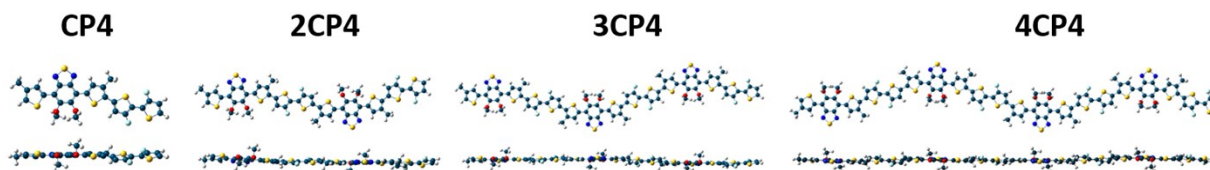


Figure S15. B3LYP/6-31G\*\* optimized geometries of CP4 monomer-tetramer structures.

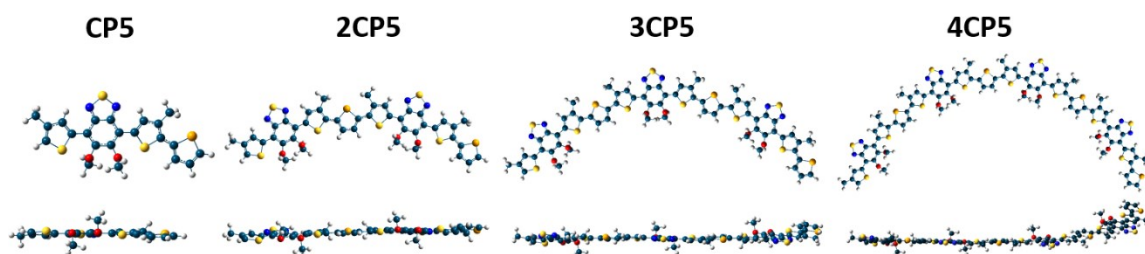


Figure S16. B3LYP/6-31G\*\* optimized geometries of CP5 monomer-tetramer structures.

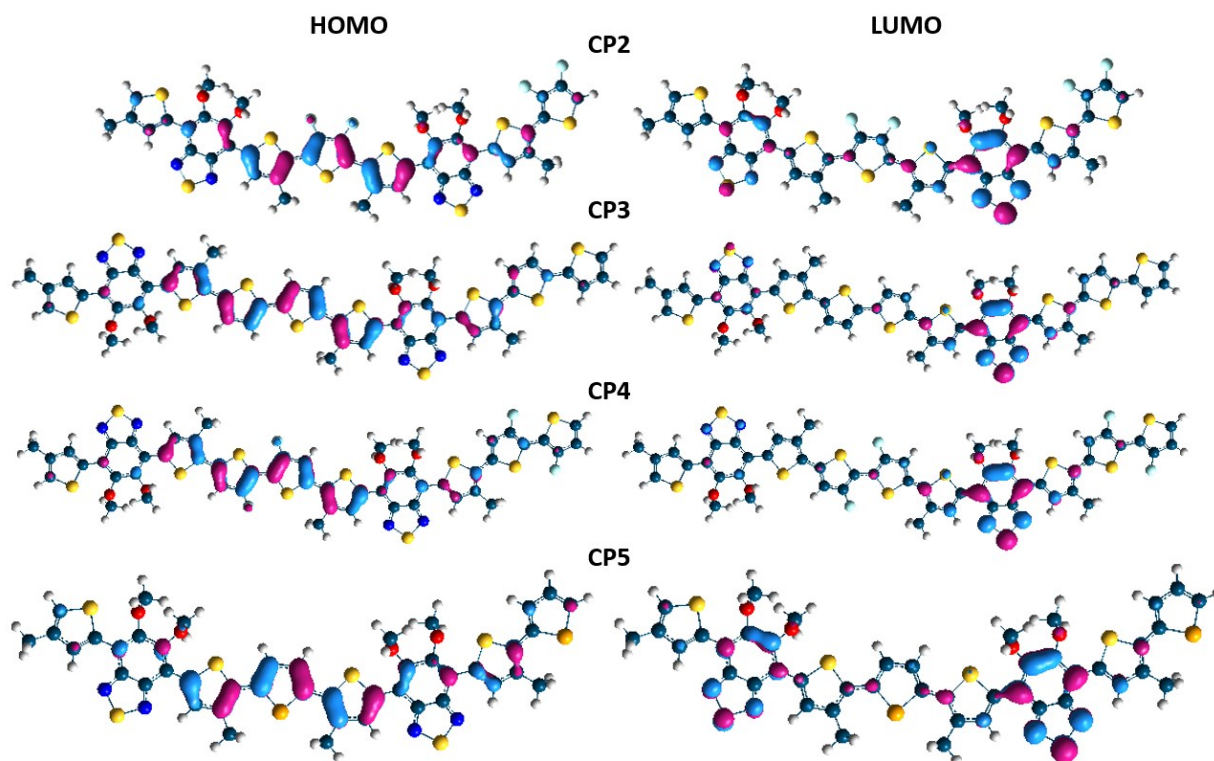
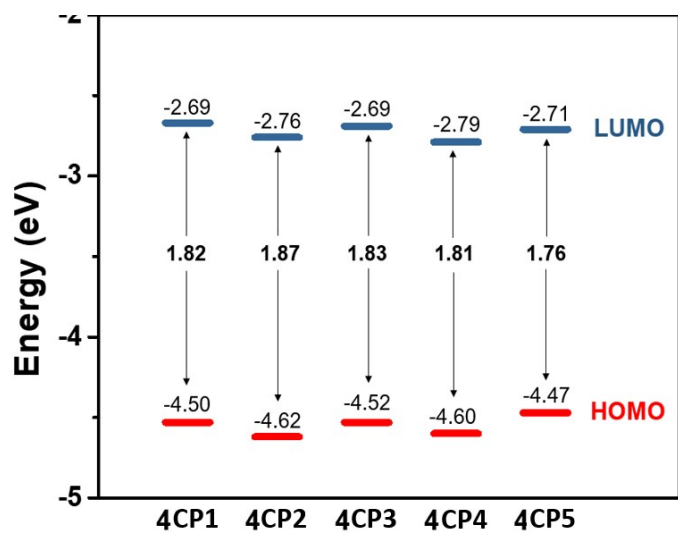


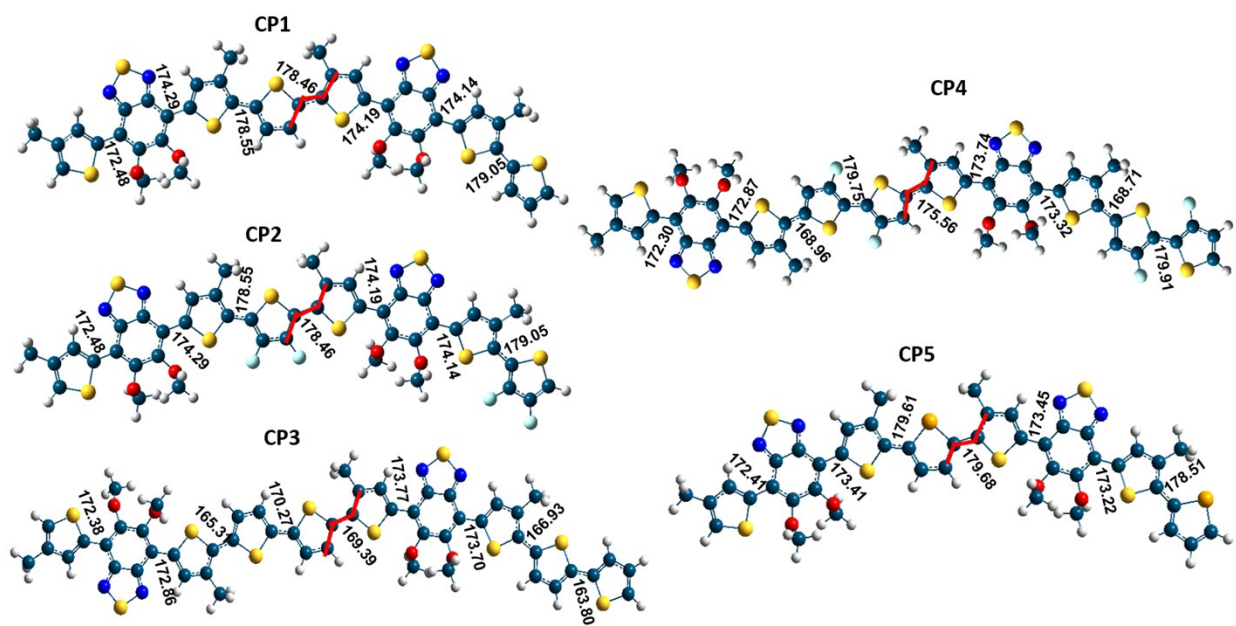
Figure S17.  
molecular orbital  
CP5 dimeric



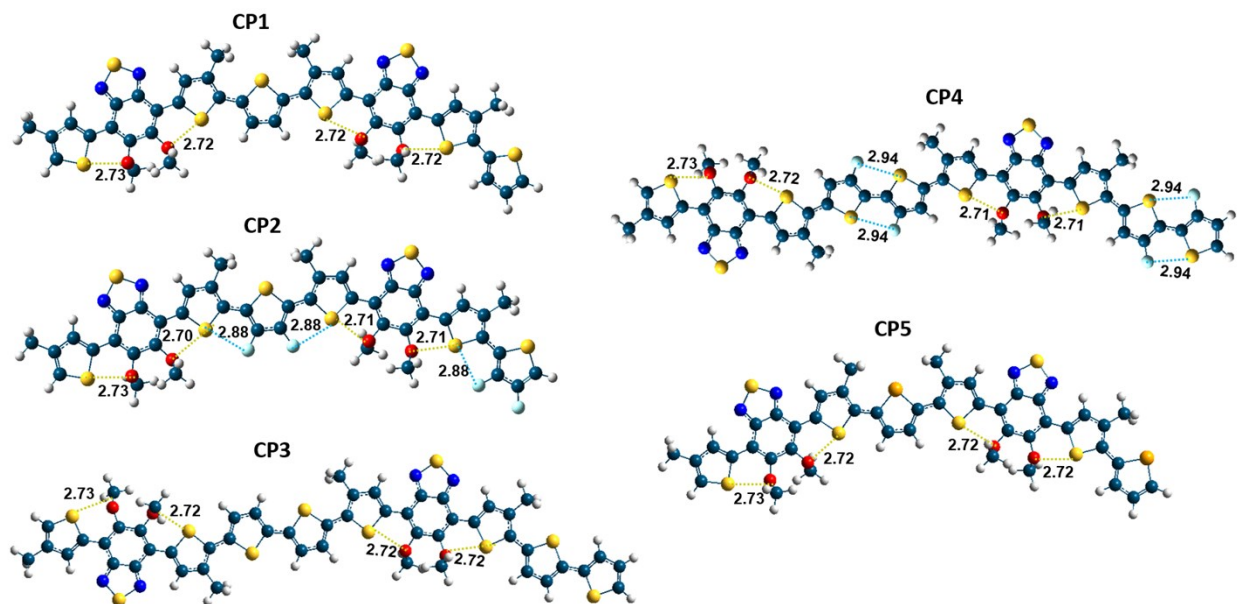
B3LYP/6-31G\*\*  
topologies of CP2-  
structures.



**Figure S18.** B3LYP/6-31G\*\* frontier molecular orbital topologies predicted for **CP1-CP5** tetramers and the energy gap values.



**Figure S19.** Dihedral angles of the B3LYP/6-31G\*\* optimized geometries of **CP1-CP5** trimer structures.



**Figure S20.** Intramolecular interaction in the B3LYP/6-31G\*\* optimized geometries of **CP1-CP5** trimer structures.

**Table S1.** Calculated (B3LYP/6-31G\*\*) internal reorganization energies, for both electron and hole transports, for **CP1-CP4** monomers.

	$\lambda_e$ (meV)	$\lambda_h$ (meV)
<b>CP1</b>	265	339
<b>CP2</b>	255	307
<b>CP3</b>	252	315
<b>CP4</b>	247	300
<b>CP5</b>	243	300

## References

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