

Supporting Information

Investigating the Optical Properties of Thiophene Additions to s-Indacene Donors with Diketopyrrolopyrrole, Isoindigo, and Thienothiophene Acceptors

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Figure S1: Structure of the starting compounds used for polymer 1-6 synthesis.

Figure S2-S7: NMR spectra of polymers P1-P6.

Figure S8. Electronic geometries for donor-acceptor monomers.

Figure S9: Electronic structure for the ground state (left) and excited state (right) that contribute to the low energy S_0 to S_1 transition for P1 (a.) and P4 (b.). The red arrows represent the qualitative magnitudes of the electron density change.

Figure S10: Electronic structure for the ground state (left) and excited state (right) that contribute to the high energy transition for P1 (a.) and P4 (b.). The red arrows represent the qualitative magnitudes of the electron density change.

Figure S11: Electronic structure for the ground state (left) and excited state (right) that contribute to the low energy S_0 to S_1 transition for P2 (a.) and P5 (b.). The red arrows represent the qualitative magnitudes of the electron density change.

Figure S12: Electronic structure for the ground state (left) and excited state (right) that contribute to the high energy S_0 to S_{22} transition for P2 (a.) and P5 (b.). The red arrows represent the qualitative magnitudes of the electron density change.

Figure S13: Electronic structure for the ground state (left) and excited state (right) that contribute to the low energy S_0 to S_1 transition for P3 (a.) and P6 (b.). The red arrows represent the qualitative magnitudes of the electron density change.

Figure S14: Electronic structure for the ground state (left) and excited state (right) that contribute to the high energy S_0 to S_9 transition for P3 (a.) and P6 (b.). The red arrows represent the qualitative magnitudes of the electron density change.

Figure S15: Cyclic voltammograms of P1 to P6.

The synthetic Procedure of D-A polymers

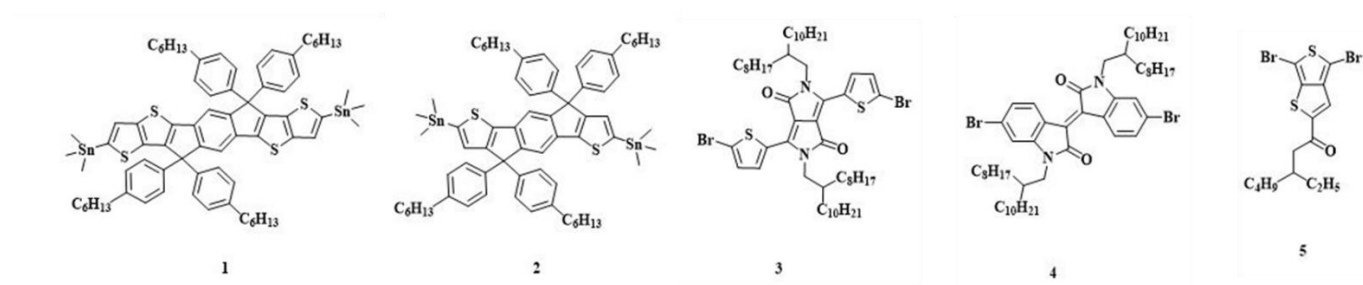


Figure S1.

Compound 1 and 2 was synthesized according to the previous report.^{1,2}

Synthesis of P1. Compound 1 (130 mg, 0.10 mmol) and compound 3 (71 mg, 0.10 mmol) were taken in a Schlenk tube under nitrogen atmosphere with 10 mL of anhydrous toluene. Tris(dibenzylideneacetone)dipalladium (0) ($\text{Pd}_2(\text{dba})_3$) (0.88 mg) and tri(o-tolyl)phosphine ($\text{P}(\text{o-tol})_3$) (2.4 mg) were added in one portion. The tube was charged with nitrogen through a freeze–pump–thaw cycle for three times. The mixture was stirred for 24 h at 90 °C under nitrogen.

After cooling to room temperature, the highly viscous black gel-like solution was poured into methanol and the resulting precipitate was filtered. The polymer was purified by Soxhlet extraction using methanol, acetone, hexane and chloroform sequentially. The residue was collected and dried under vacuum to afford polymer (172 mg, 95%). ^1H NMR (400 MHz, CDCl_3 , δ): 8.91 (s, 2H), 7.51 (s, 4H), 7.19 (d, 8H), 7.11 (d, 8H), 4.04 (m, 4H), 2.57 (s, 8H), 1.96 (m, 2H), 1.59 (s, 8H), 1.31-1.20 (m, 92H), 0.86-0.83 (m, 24H) GPC: M_n = 25.9 kDa, M_w = 48.2 kDa, PDI = 1.86. Anal. Calcd for $\text{C}_{122}\text{H}_{160}\text{N}_2\text{O}_2\text{S}_6$: C, 77.98; H, 8.58; N, 1.49, S, 10.24. Found: C, 78.25; H, 8.56; N, 1.56; S, 10.25.

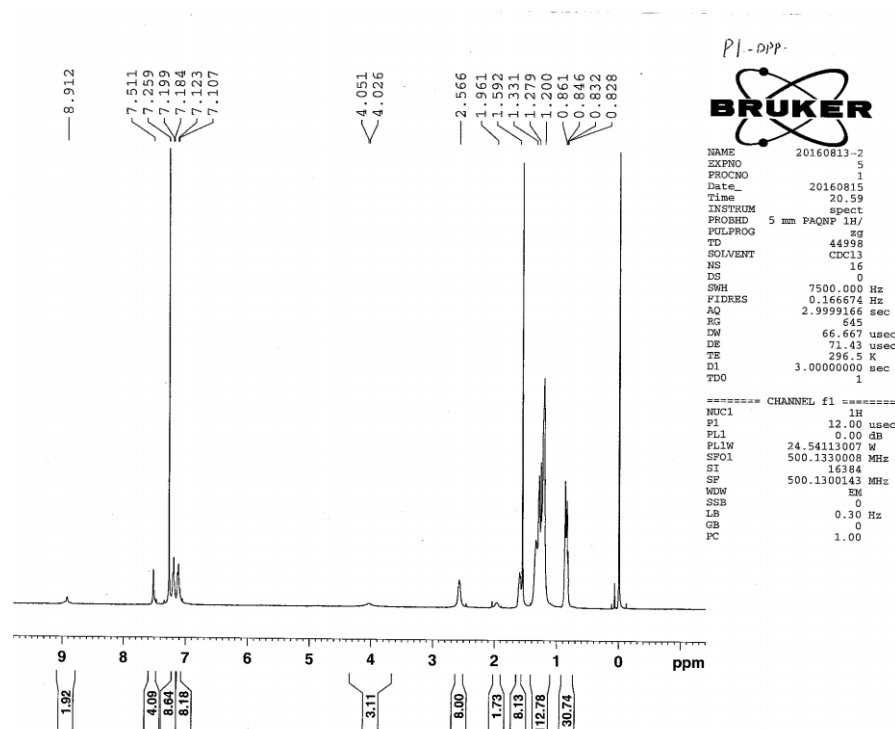


Figure S2.

Synthesis of P2. This was prepared following the general procedure given for the preparation of **P1**. From **1** (130 mg, 0.10 mmol) and **4** (93 mg, 0.10 mmol), there was obtained **P2** (164 mg, 92.7 % yield). ¹H NMR (400 MHz, CDCl₃, δ): 9.13 (s, 2H), 7.62 (s, 2H), 7.52 (d, 2H), 7.22 (d, 8H), 7.11 (d, 8H), 6.94 (s, 2H), 3.70 (d, 2H), 2.57 (s, 8H), 1.94 (s, 2H), 1.59 (s, 8H), 1.34-1.22 (m, 94H), 0.86-0.84 (m, 24H) GPC: M_n = 42.5 kDa, M_w = 88.4 kDa, PDI = 2.08. Anal. Calcd for C₁₂₄H₁₆₂N₂O₂S₂: C, 80.90; H, 8.87; N, 1.52, S, 6.97. Found: C, 80.73; H, 8.82; N, 1.54; S, 7.09.

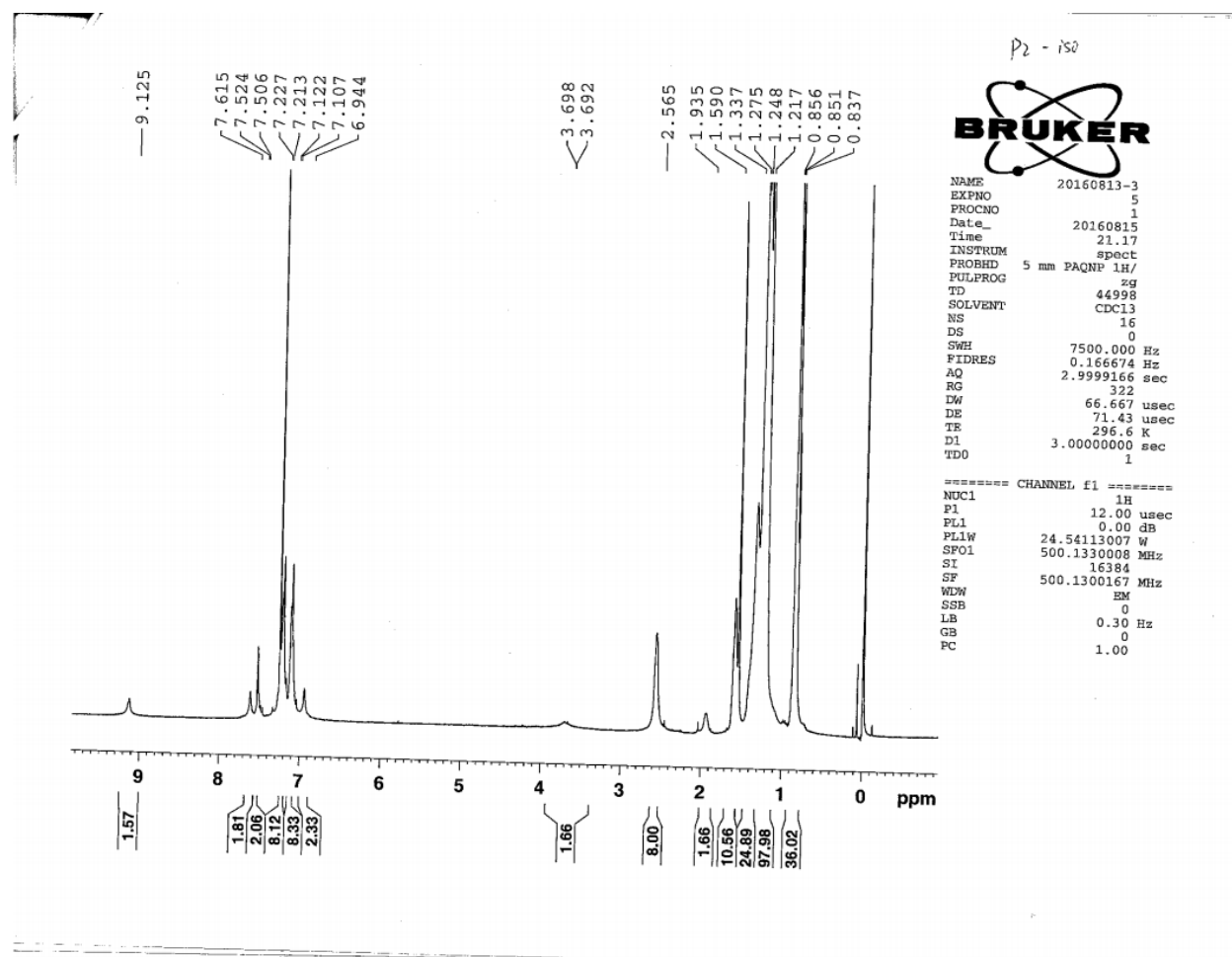


Figure S3.

Synthesis of P3. This was prepared following the general procedure given for the preparation of **P1**. From **1** (133 mg, 0.10 mmol) and **5** (41.1 mg, 0.10 mmol), there was obtained **P3** (118 mg, 92.9 % yield). ^1H NMR (400 MHz, CDCl_3 , δ): 7.57 -7.52 (m, 3H), 7.23 (m, 8H), 7.16 (m, 8H), 3.25 (s, 2H), 2.60 (s, 8H), 1.91 (s, 1H), 1.88 (s, 10H), 1.36-1.11 (m, 30H), 1.00 (s, 4 H), 0.89 (m, 18H). GPC: M_n = 22.6 kDa, M_w = 59.1 kDa, PDI = 2.61. Anal. Calcd for $\text{C}_{83}\text{H}_{92}\text{OS}_6$: C, 76.80; H, 7.14; S, 14.82. Found: C, 74.85; H, 6.95; S, 14.20.

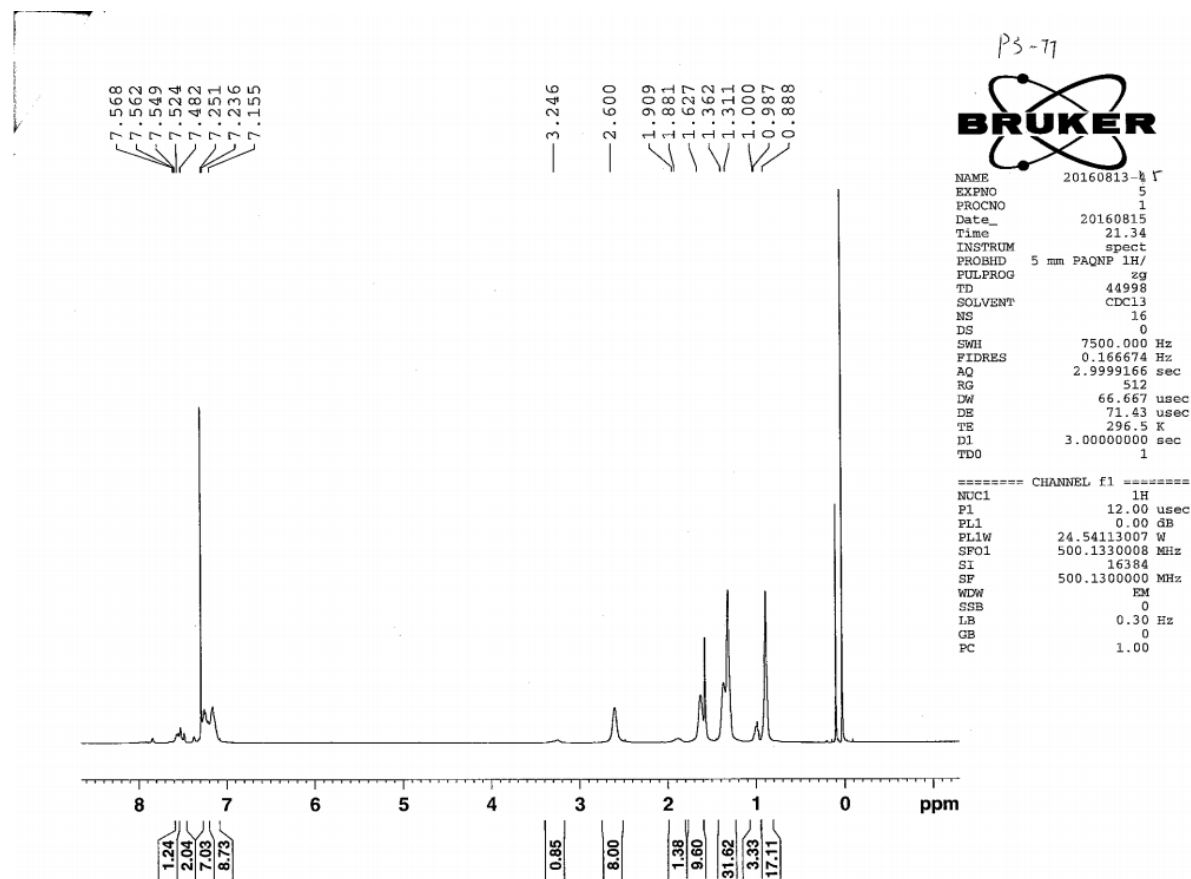


Figure S4.

Synthesis of P4. This was prepared following the general procedure given for the preparation of **P1**. From **3** (200 mg, 0.16 mmol) and **3** (162 mg, 0.16 mmol), there was obtained **P4** (262 mg, 90.8 % yield). ^1H NMR (400 MHz, CDCl_3 , δ): 8.86 (s, 2H), 7.41 (s, 2H), 7.17 (m, 10H), 7.09 (m, 8H), 3.01 (s, 4H), 2.57 (s, 8H), 1.94 (s, 2H), 1.59 (m, 8H), 1.23-1.81 (m, 92H), 0.87-0.81 (m, 24H). GPC: M_n = 34.1 kDa, M_w = 62.8 kDa, PDI = 1.84. Anal. Calcd for $\text{C}_{118}\text{H}_{160}\text{N}_2\text{O}_2\text{S}_4$: C, 80.22; H, 8.13; N, 1.59; S, 7.26. Found: C, 80.25; H, 8.13; N, 1.66; S, 7.27.

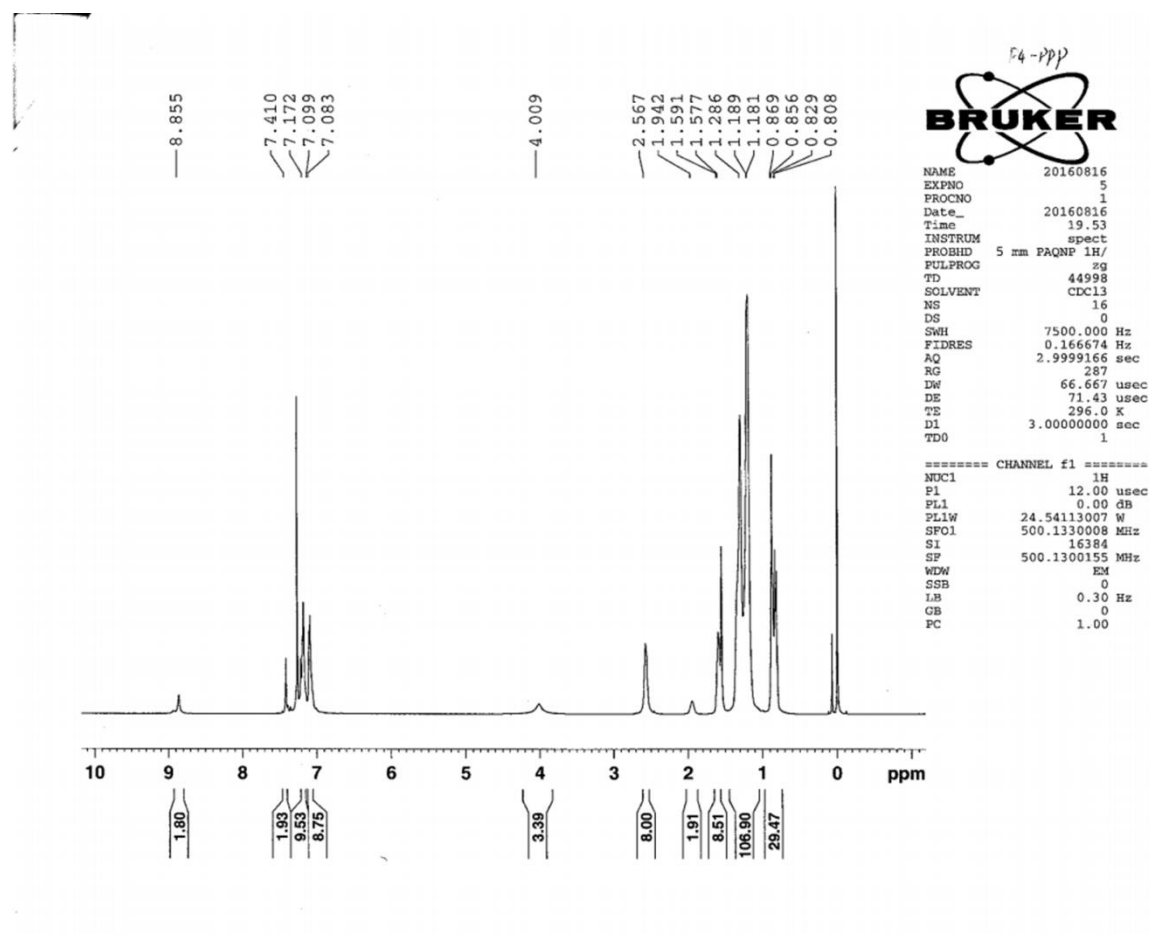


Figure S5.

Synthesis of P5. This was prepared following the general procedure given for the preparation of **P1**. From **2** (200 mg, 0.16 mmol) and **4** (68 mg, 0.16 mmol), there was obtained **P5** (261 mg, 94.3

% yield). ^1H NMR (400 MHz, CDCl_3 , δ): 9.12 (s, 2H), 7.45 (s, 2H), 7.33 (s, 2H), 7.22 (d, 8H), 7.09 (m, 8H), 6.93 (s, 2H), 3.69 (s, 2H), 2.57 (s, 8H), 1.92 (s, 2H), 1.59 (m, 8H), 1.34-1.20 (m, 94H), 0.87-0.82 (m, 24H). GPC: M_n = 22.6 kDa, M_w = 46.8 kDa, PDI = 1.90. Anal. Calcd for $\text{C}_{120}\text{H}_{162}\text{N}_2\text{O}_2\text{S}_2$: C, 83.37; H, 9.45; N, 1.62; S, 3.71. Found: C, 83.27; H, 9.34; N, 1.61; S, 3.79.

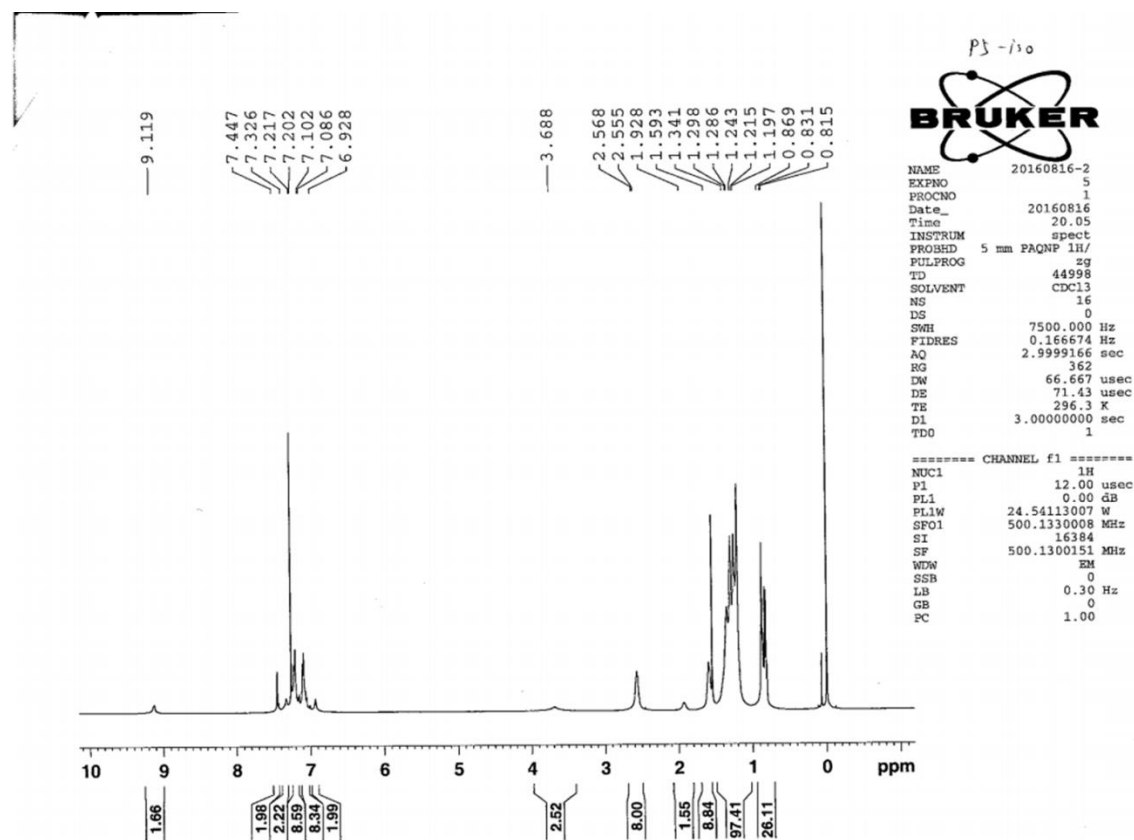


Figure S6.

Synthesis of P6. This was prepared following the general procedure given for the preparation of **P1**. From **2** (200 mg, 0.16 mmol) and **5** (157 mg, 0.16 mmol), there was obtained **P6** (173 mg, 91.2 % yield). ^1H NMR (400 MHz, CDCl_3 , δ): 8.02 (m, 1H), 7.49 (m, 2H), 7.20 (m, 8H), 7.11 (m, 8H), 3.26 (s, 2H), 2.60 (s, 8H), 1.81 (s, 1H), 1.62 (m, 10H), 1.32 (m, 30H), 1.0-0.9 (m, 22H). GPC:

Mn = 28.3 kDa, Mw = 55.5 kDa, PDI = 1.96. Anal. Calcd for C₇₉H₉₂N₂OS₄: C, 80.01; H, 7.82; S, 10.82. Found: C, 80.01; H, 7.64; S, 10.60.

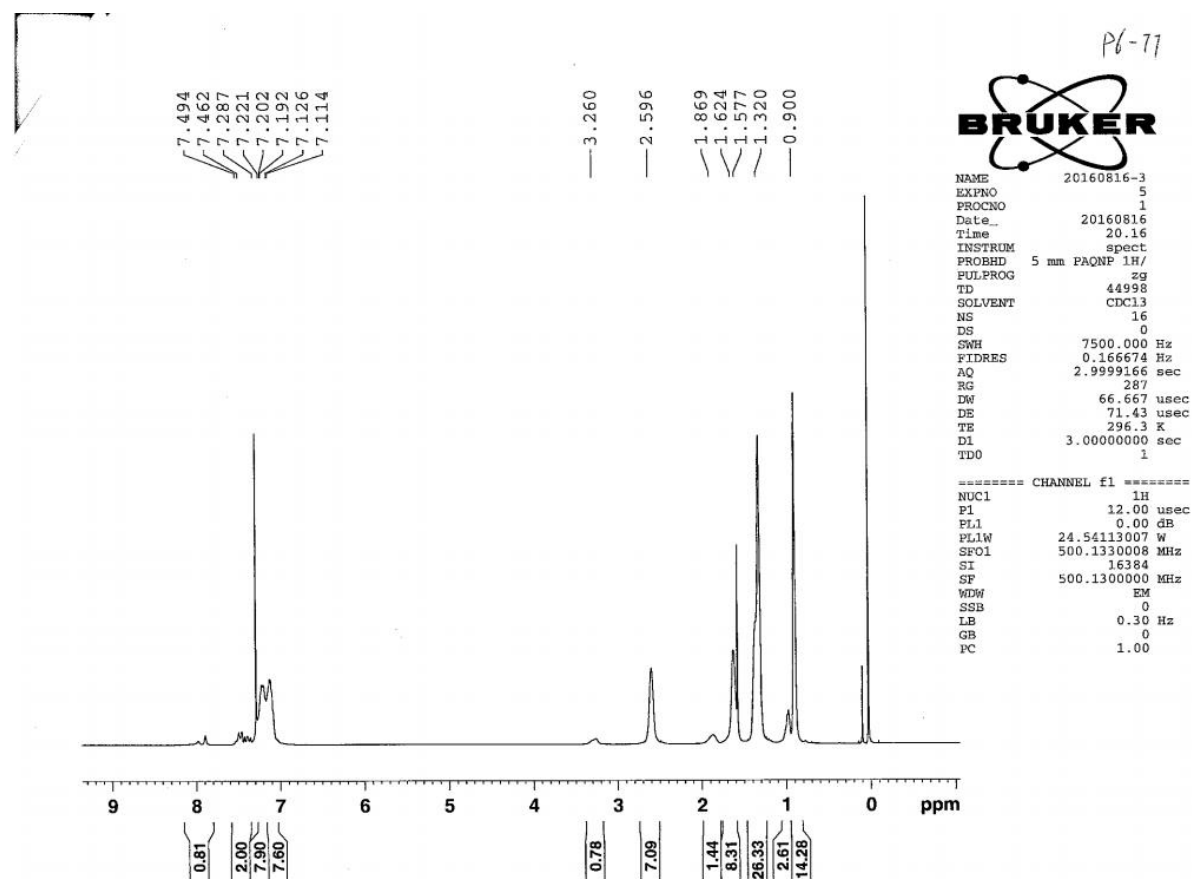


Figure S7.

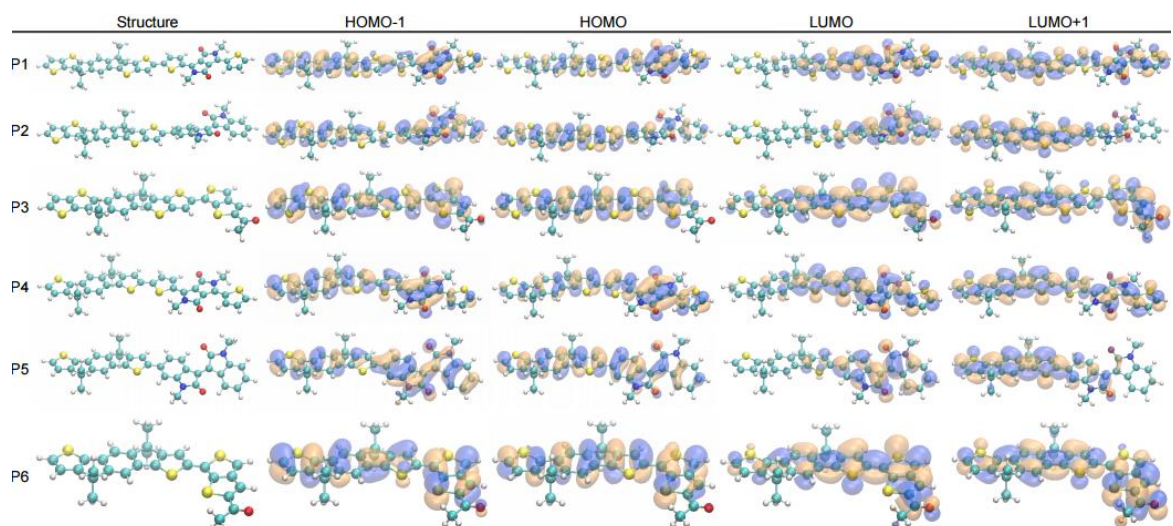


Figure S8.

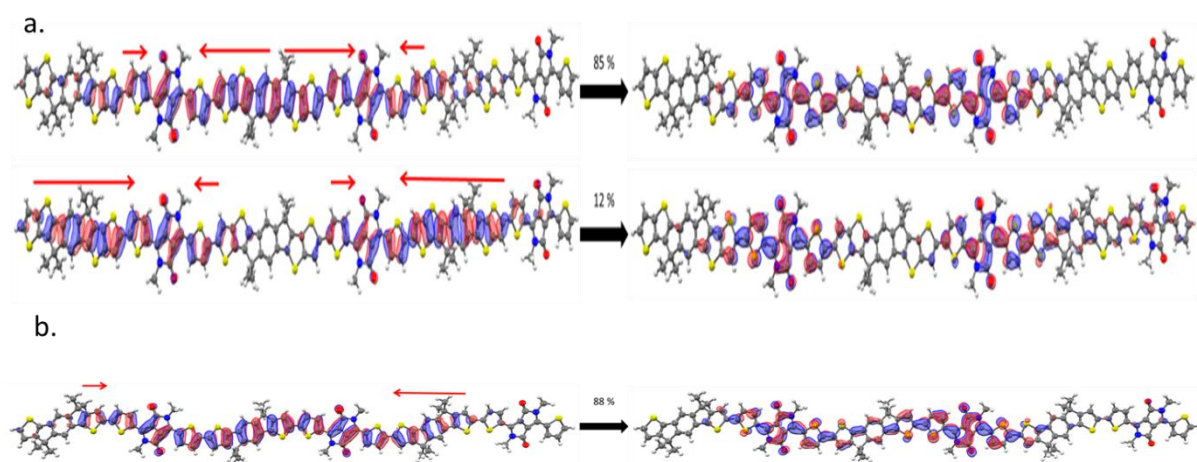


Figure S9.

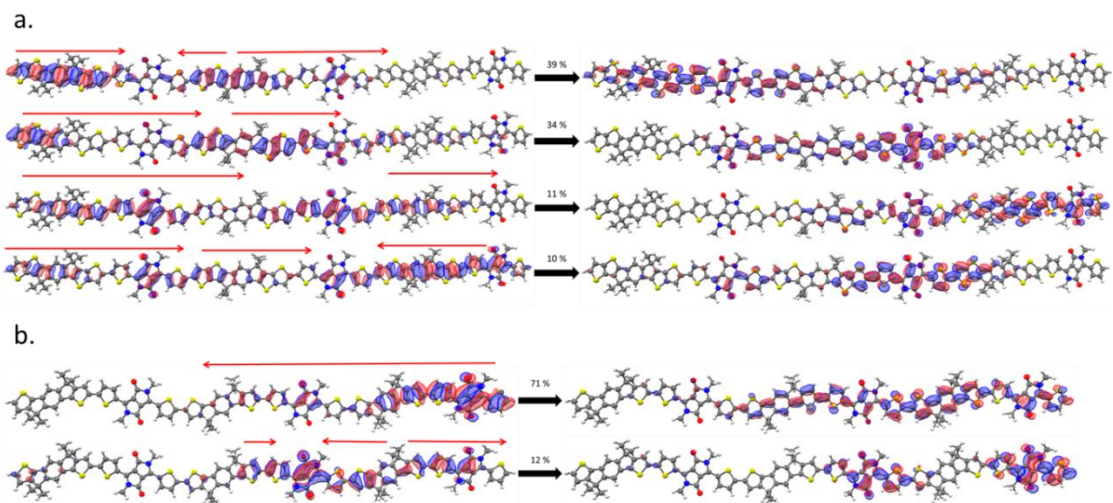


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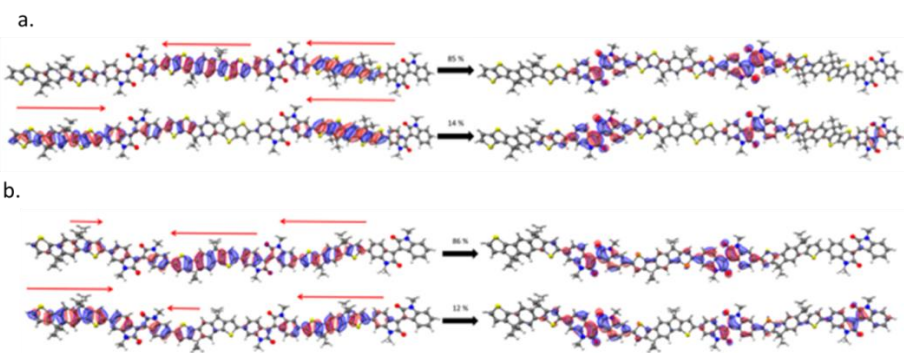


Figure S11.

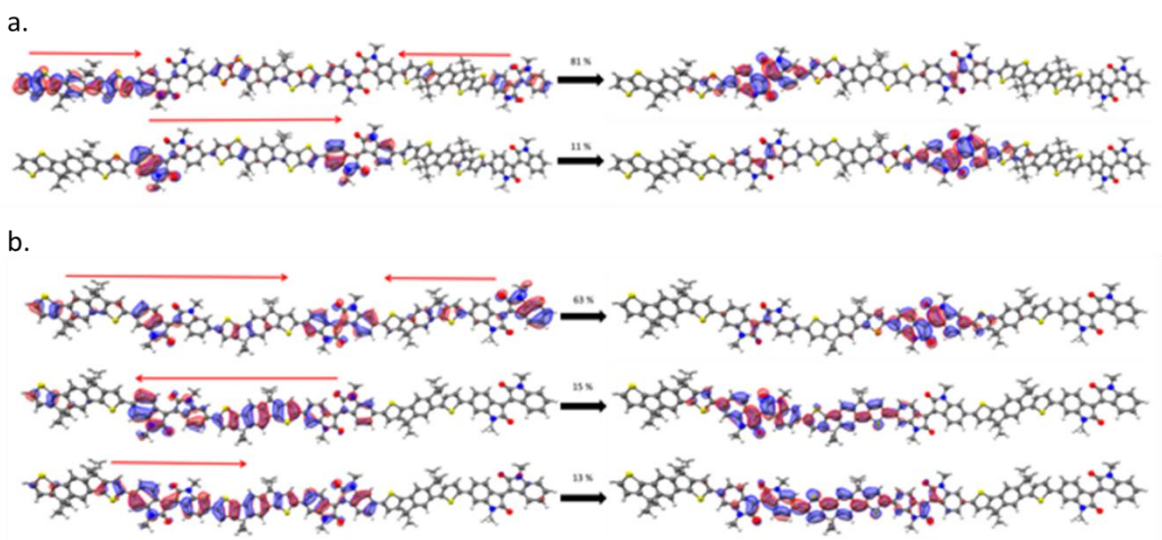


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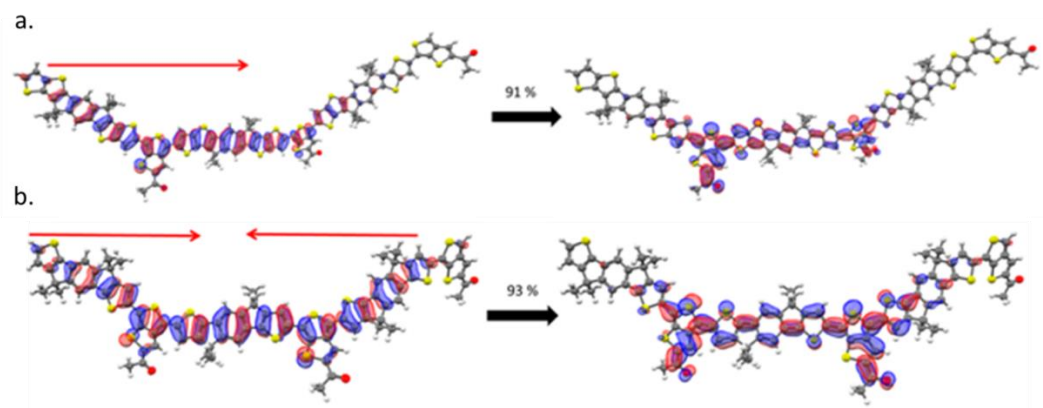


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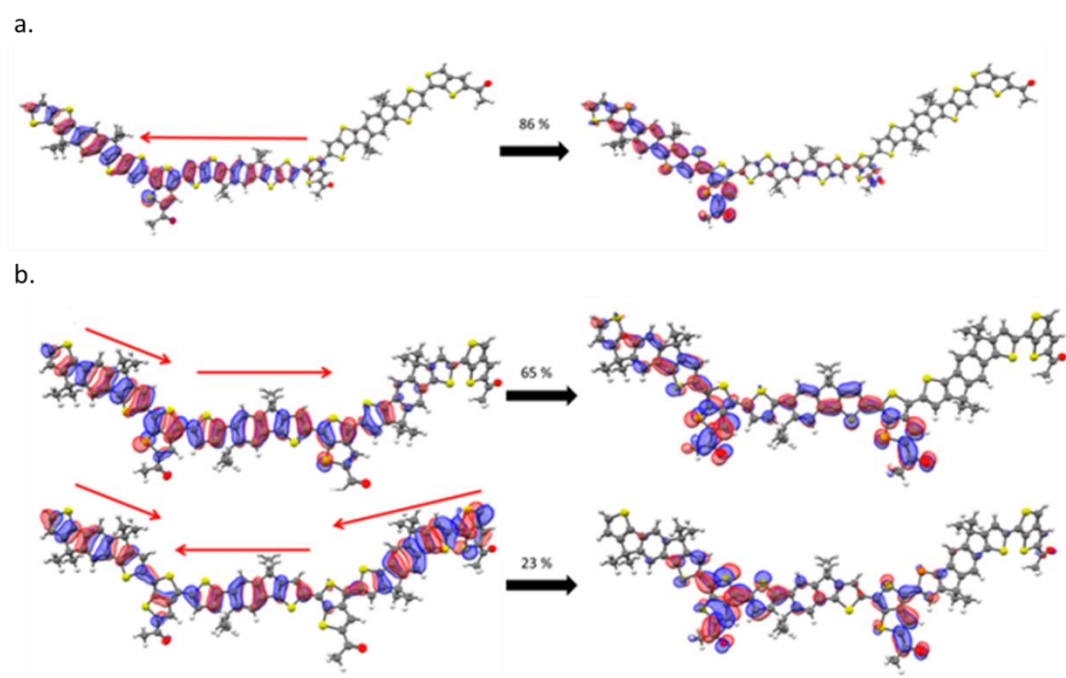


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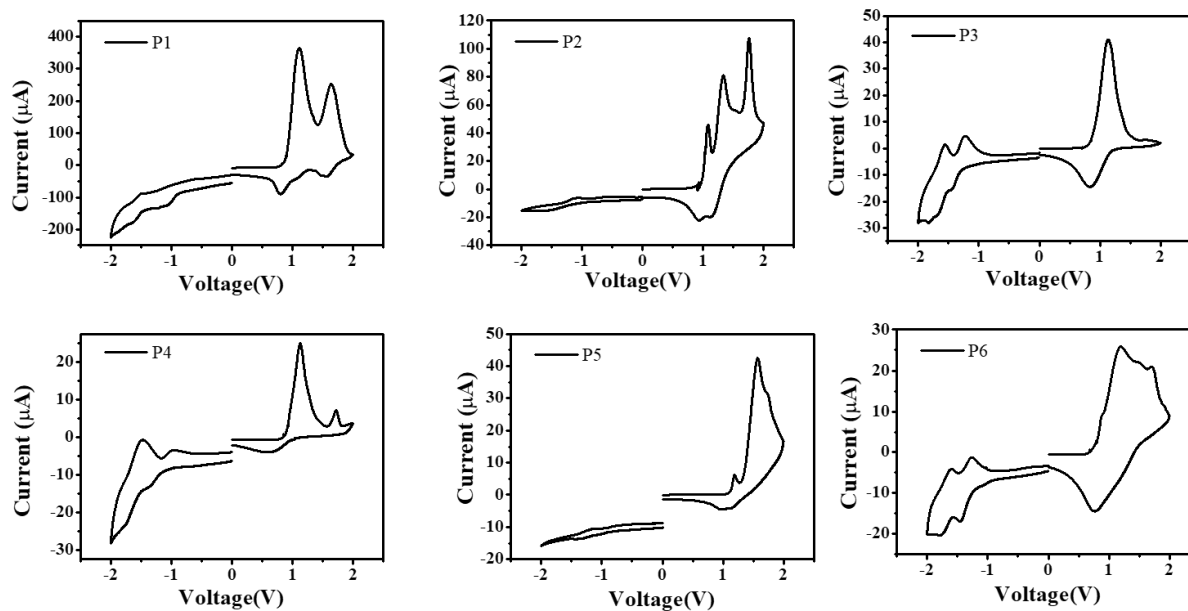


Figure S15.

REFERENCES

1. Sun Y., Chien S.-C., Yip H.-L., Zhang Y., Chen K.-K., Zeigler D. F., Chen F.-C., Lin, B., Jen A. K.-Y. High-Mobility Low-Bandgap Conjugated Copolymers Based on Indacenodithiophene and Thiadiazolo[3,4-*c*]Pyridine Units for Thin Film Transistor And Photovoltaic Applications. *J. Mater. Chem.*, **2011**, *21*, 13247-13255.
2. Xu Y.-X., Chien S.-C., Yip H.-L., Ding F. Z., Li Y. X., Li C.-Z., Li X., Chen W.-C. Improved Charge Transport and Absorption Coefficient in Indacenodithieno[3,2-*b*]thiophene-based Ladder-Type Polymer Leading to Highly Efficient Polymer Solar Cells. *Adv. Mater.*, **2012**, *24*, 6356-6361.