

Supporting Information

Effect of Thiadiazole Out-Backbone Displacement in Indacenodithiophene Semiconductor Polymers

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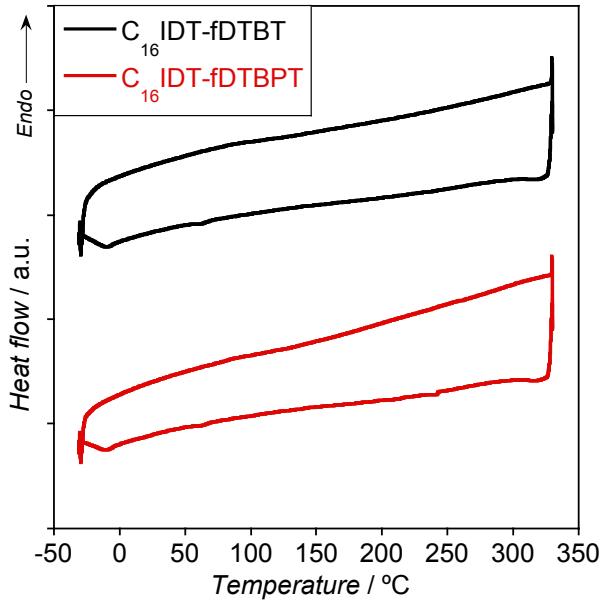


Figure S1. DSC traces of $C_{16}\text{IDT-fDTBT}$ (black line) and $C_{16}\text{IDT-fDTBPT}$ (red line).

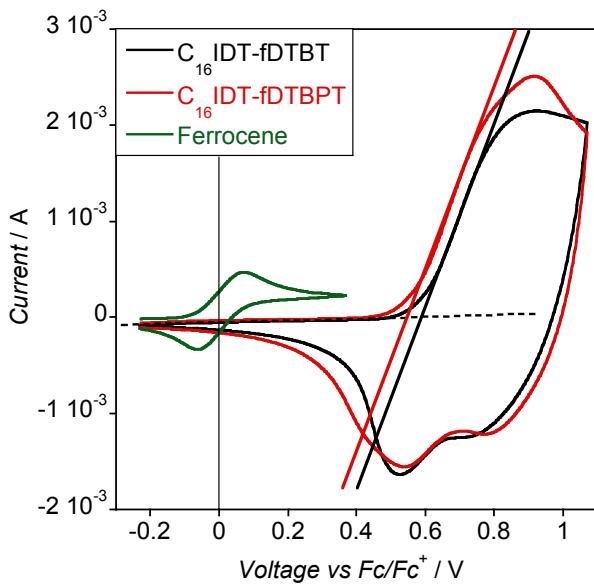


Figure S2. Cyclic voltammetry traces of drop casted $C_{16}\text{IDT-fDTBT}$ (black line) and $C_{16}\text{IDT-fDTBPT}$ (red line) into ITO substrate and measured in 0.1 M [TBA][PF₆] acetonitrile solution. Oxidation potentials were determined by the electrochemical onset and reference to ferrocene $E_{1/2}$ (green line).

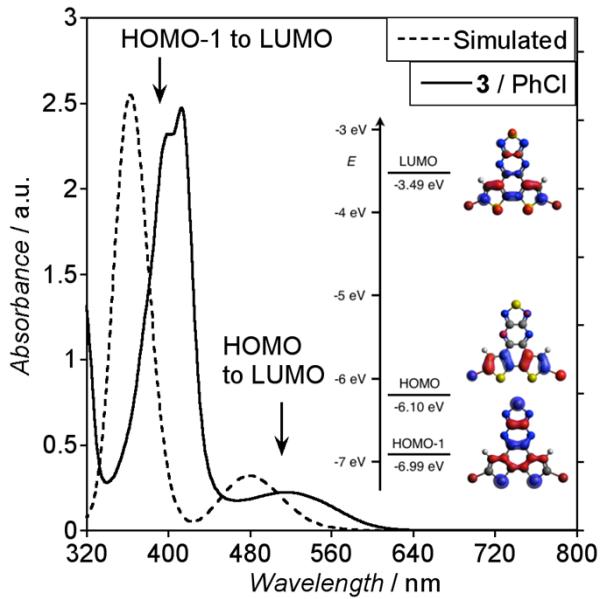


Figure S3. Absorption spectrum of **3** in chlorobenzene (*solid line*) and simulated by TD-DFT means (*dashed line*). *Inset:* Molecular orbital distribution and energies of **3**.

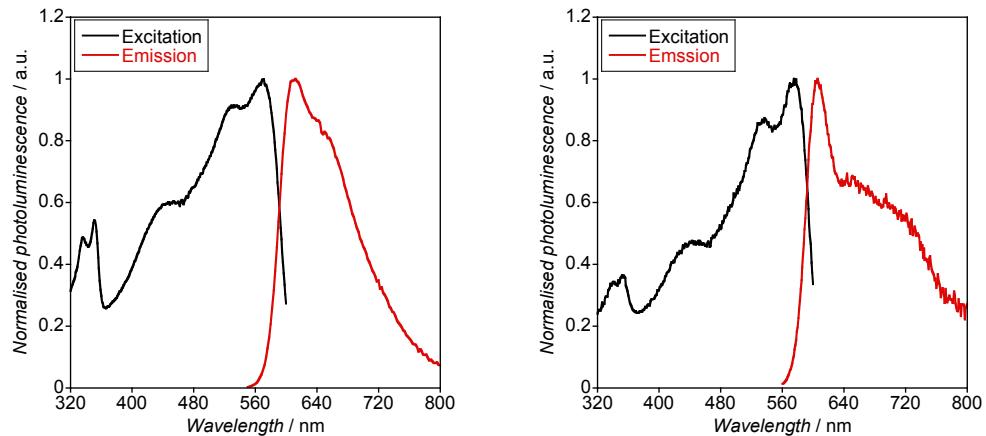


Figure S4. Photoluminescence emission (*red line*) and excitation (*black line*) spectra of $C_{16}\text{IDT-fDTBPT}$ in chloroform solution (*left*) and spin-coated film (*right*).

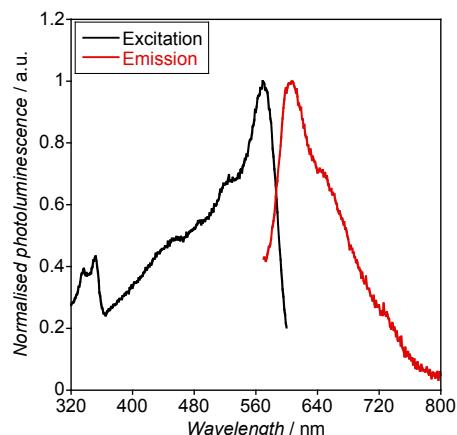


Figure S5. Photoluminescence emission (*red line*) and excitation (*black line*) spectra of $C_{16}\text{IDT-fDTBPT}$ in chloroform solution. Note that no photoluminescence was observed for spin-coated film.

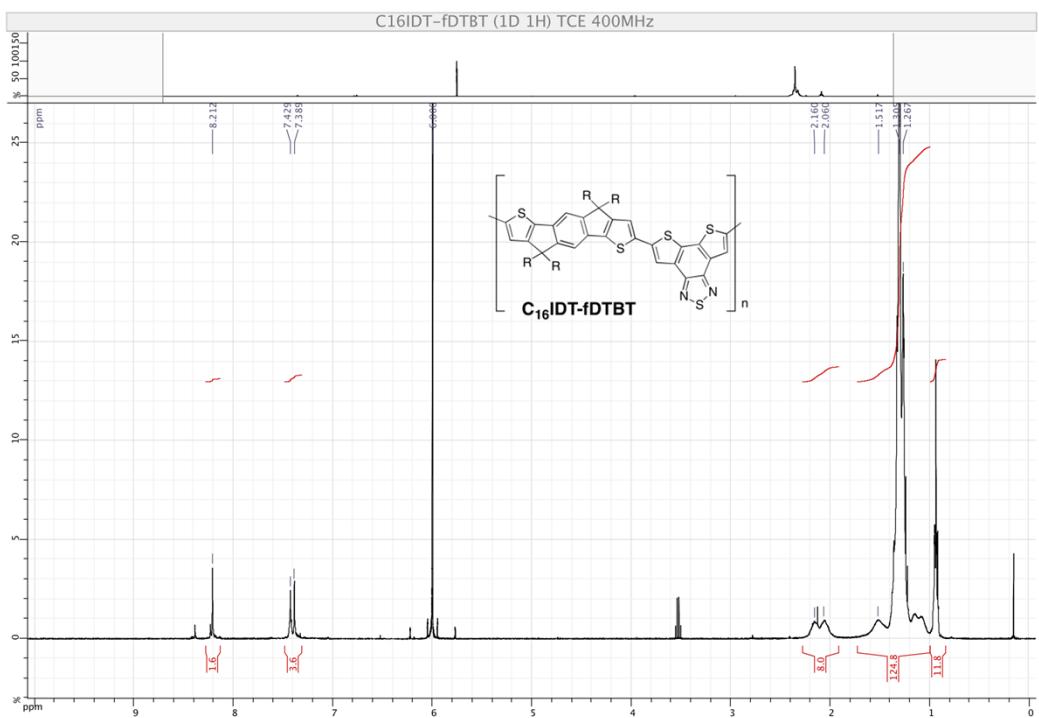


Figure S6. ¹H-NMR of C₁₆IDT-fDTBT polymer acquired in TCE-*d*₂ at 120 °C.

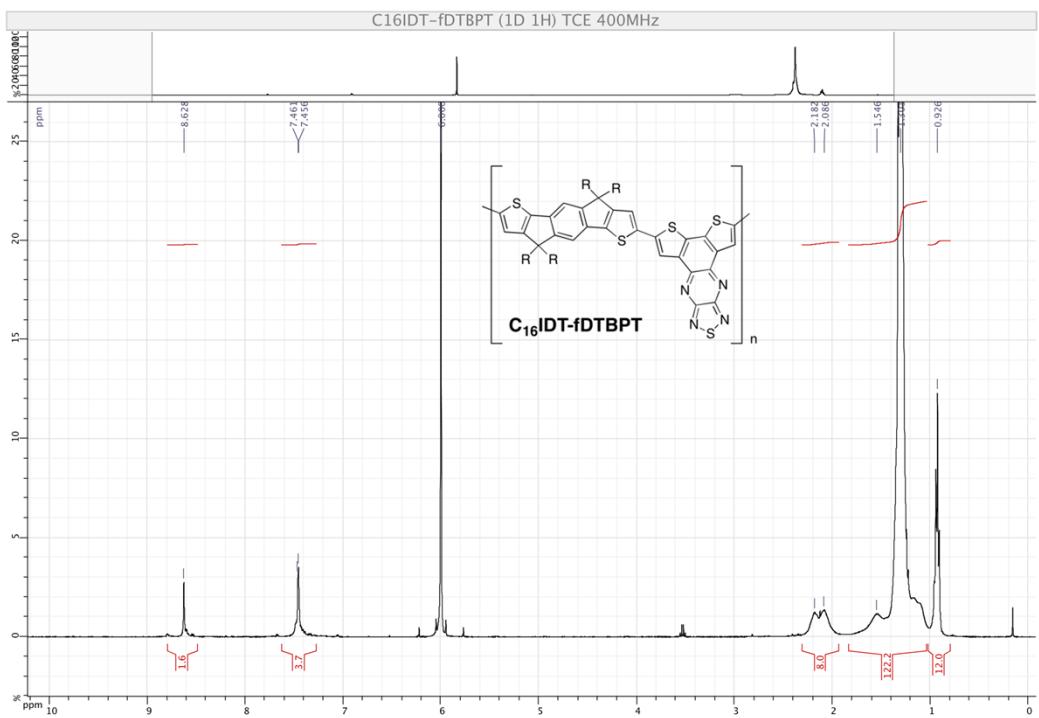


Figure S7. ¹H-NMR of C₁₆IDT-fDTBPT polymer acquired in TCE-*d*₂ at 120 °C.

Supporting Information Tables

Table S1. Selected TD-DFT calculated energies and compositions (only oscillator strength higher than 0.2 are shown) at B3LYP/6-31G(d) from the first ten singlet electronic transitions.

Polymer	Composition ^a		ΔE (nm) ^b	f^c	Character
C₁₆IDT-fDTBT	HOMO → LUMO	86 %	661.07	3.915	$\pi\text{-}\pi^*$
	HOMO → LUMO+3	54%			
	HOMO → LUMO+4	29%	488.76	1.0844	$\pi\text{-}\pi^*$
C₁₆IDT-fDTBPT	HOMO → LUMO	46 %			
	HOMO → LUMO'	19 %	1028.39	0.4584	ICT ^d
	HOMO → LUMO''	19 %			
	HOMO-3 → LUMO''	69%			
	HOMO → LUMO+1	19%	588.54	0.9399	$\pi\text{-}\pi^*$
	HOMO-3 → LUMO''	20%			
	HOMO → LUMO+1	66%	586.98	3.5027	$\pi\text{-}\pi^*$
	HOMO-1 → LUMO+2	90%	475.19	0.8468	$\pi\text{-}\pi^*$

^aCompositions of electronic transitions (only higher than 8% are shown) are expressed in terms of contributing excitations between ground state Kohn–Sham molecular orbitals. ^bTransition energy from the ground state to the excited state. ^cOscillator strength. ^dIntramolecular charge transfer band.

Complete reference 9

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision B.01*; Gaussian Inc. Wallingford CT. 2009.