Supporting Information for

Modulation of Electronic and Self-Assembly Properties of a Donor-Acceptor-Donor Based Molecular Material *via* Atomistic Approach

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Synthesis:

4,7-dibromo-2,1,3-benzothiadiazole, 4,7-dibromo-2,1,3-benzoselenadiazole and 4-hexyl-2-tributylstannylthiophene were synthesized following the reported synthetic procedure from literature.[1] Then by coupling 4-hexyl-2-tributylstannylthiophene with 4,7-dibromo-2,1,3-benzothiadiazole and 4,7-dibromo-2,1,3-benzoselenadiazole 4,7-bis(3'-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (T4BT) and 4,7-bis(3'-hexylthiophen-2-yl)-2,1,3-benzoselenadiazole (T4BSe) were synthesized, respectively.

4,7-Bis(3'-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (T4BT): To a 100 mL two-neck round-bottomed flask 4-hexyl-2-tributylstannylthiophene (4.85 g, 10.3 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (1.0 g, 3.9 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg), toluene (60 mL) were taken in inert atmosphere. The solution mixture was heated to 110 °C overnight. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was then loaded on a silica gel column and eluted with hexane affording the desired product as the orange colored solid. Yield: 73%

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, 2H), 7.83 (s, 2H), 7.04 (d, 2H), 2.72-2.68 (t, *J* = 7.6 Hz, 4H), 1.71-1.69 (m, 4H), 1.40-1.33 (m, 12H), 0.92-0.89 (t, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.04, 144.79, 139.45, 129.43, 126.41, 125.93, 121.96, 32.18, 31.12, 30.94, 29.53, 23.11, 14.59 ppm. (ESI-MS) calculated for $C_{26}H_{32}N_2S_3$ $(M)^+$: m/z: 469.21

4,7-Bis(3'-hexylthiophen-2-yl)-2,1,3-benzoselenadiazole (T4BSe): Following same reaction condition as it was followed to synthesize T4BT, 4,7-Bis(3'-hexylthiophen-2-yl)-2,1,3-benzoselenadiazole (T4BSe) was synthesized using 4-hexyl-2-tributylstannylthiophene and 4,7-dibromo-2,1,3-benzoselenadiazole. (Yield: 69%)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (s, 2H), 7.73 (s, 2H), 7.04 (s, 2H), 2.70-2.66 (t, *J* = 7.6 Hz, 4H), 1.71-1.68 (m, 4H), 1.41-1.32 (m, 12H), 0.92-0.89 (t, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.68, 144.48, 139.76, 129.35, 127.91, 126.25, 122.31, 32.17, 31.10, 30.94, 29.53, 23.10, 14.59 ppm. (ESI-MS) calculated for $C_{26}H_{32}N_2S_2Se$ $(M)^+$: m/z: 517.34

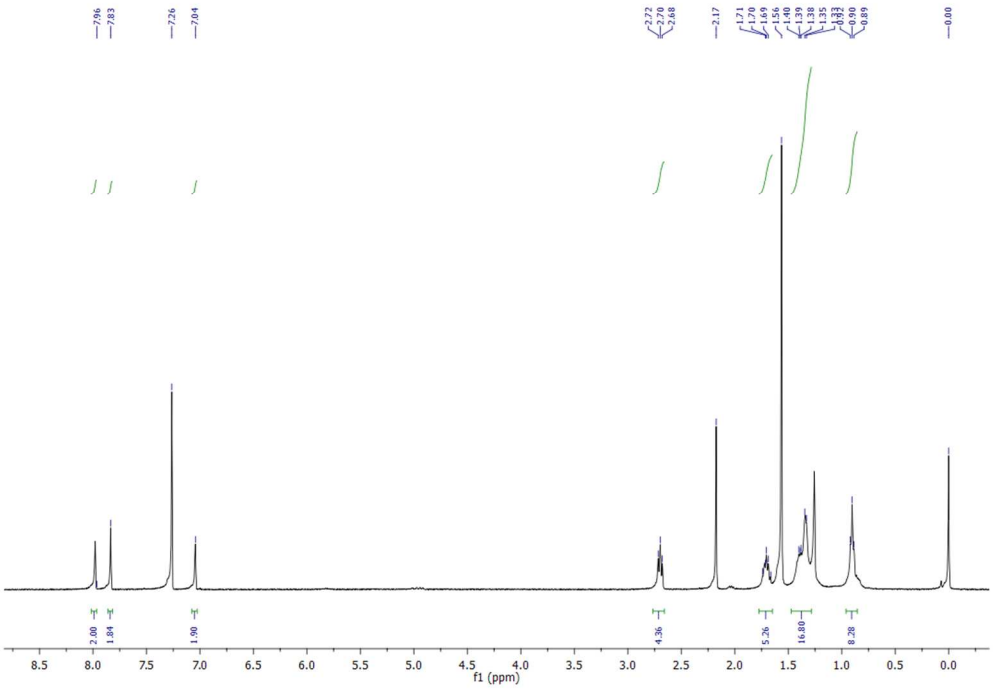

Figure S1. ^{1}H NMR spectrum of T4BT

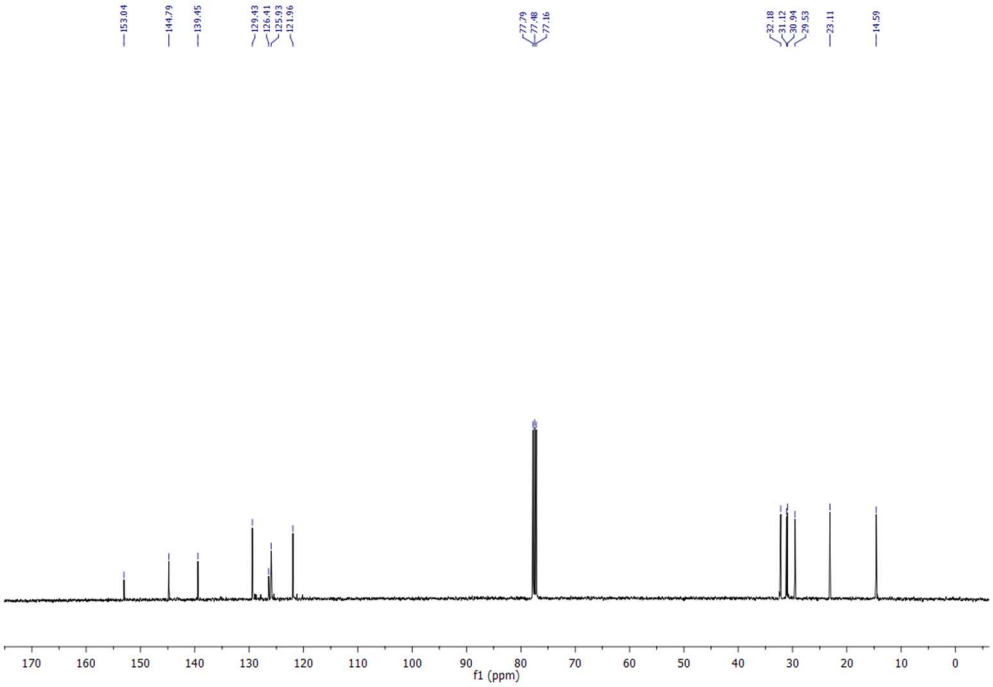

Figure S2. ^{13}C NMR spectrum of T4BT

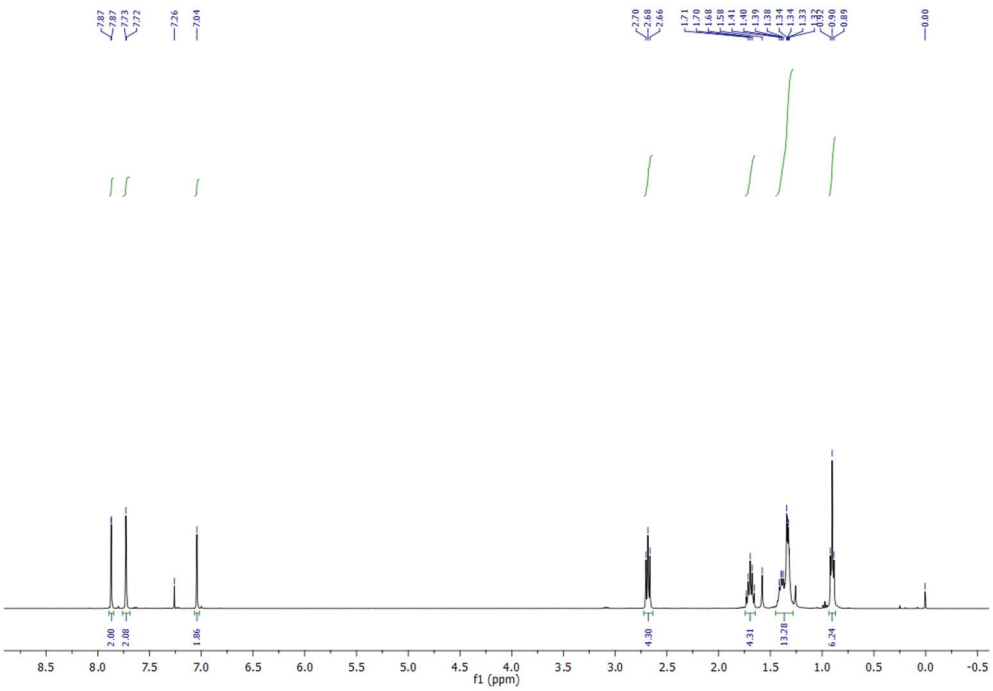

Figure S3: ^{1}H NMR spectrum of T4BSe

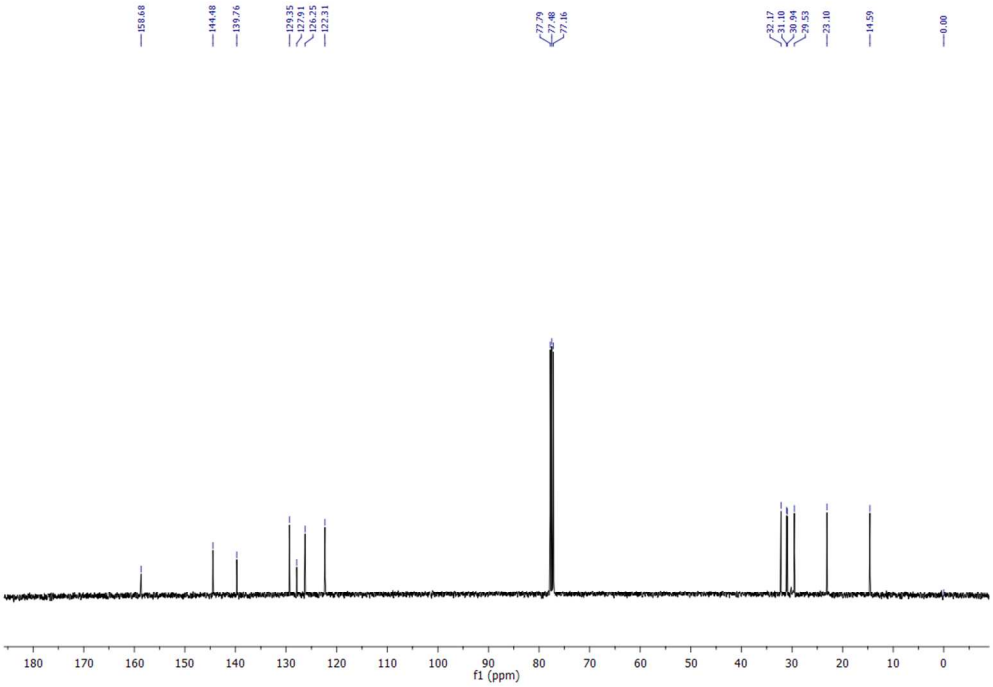

Figure S4: ^{13}C NMR spectrum of T4BSe

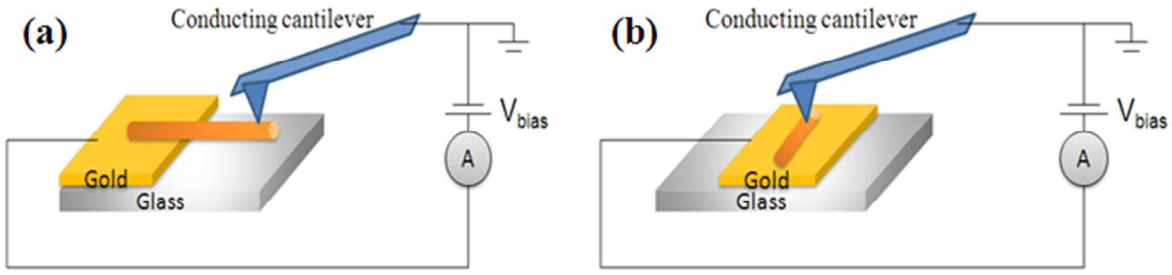

Figure S5. General device configuration for CP-AFM measurements in vertical (a) and in horizontal (b) geometries

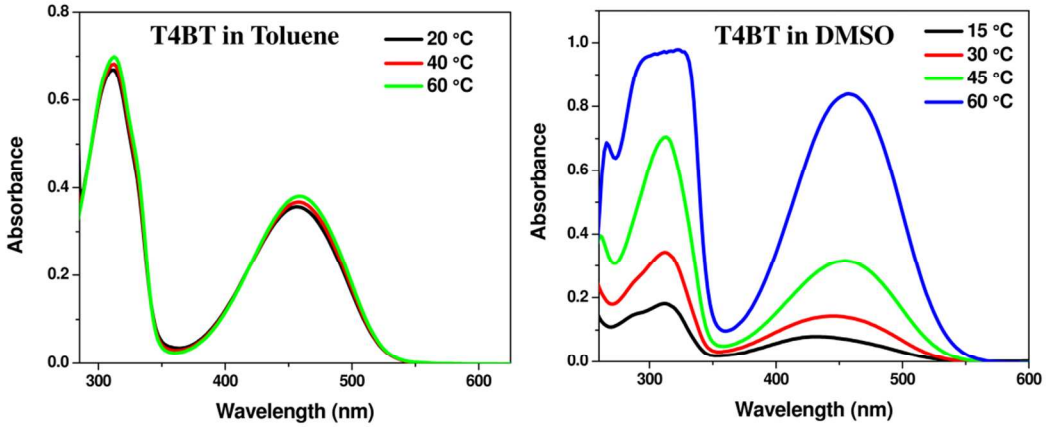

Figure S6: Temperature dependent absorption spectra of T4BT in toluene and DMSO

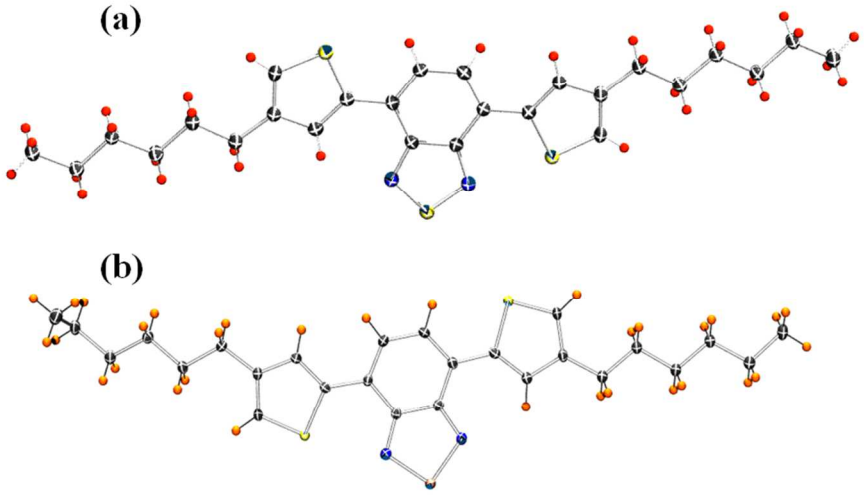

Figure S7. ORTEP representation of T4BT (a) and T4BSe (b)

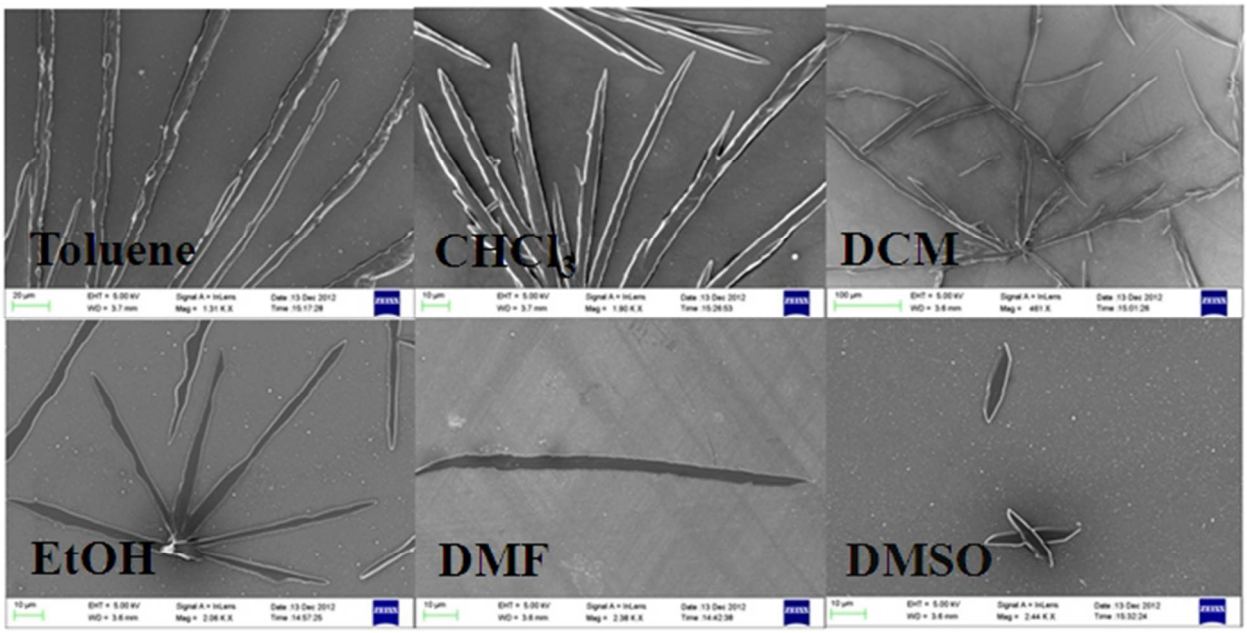

Figure S8. FESEM images of T4BSe microstructures drop-casted from solvent of different polarities

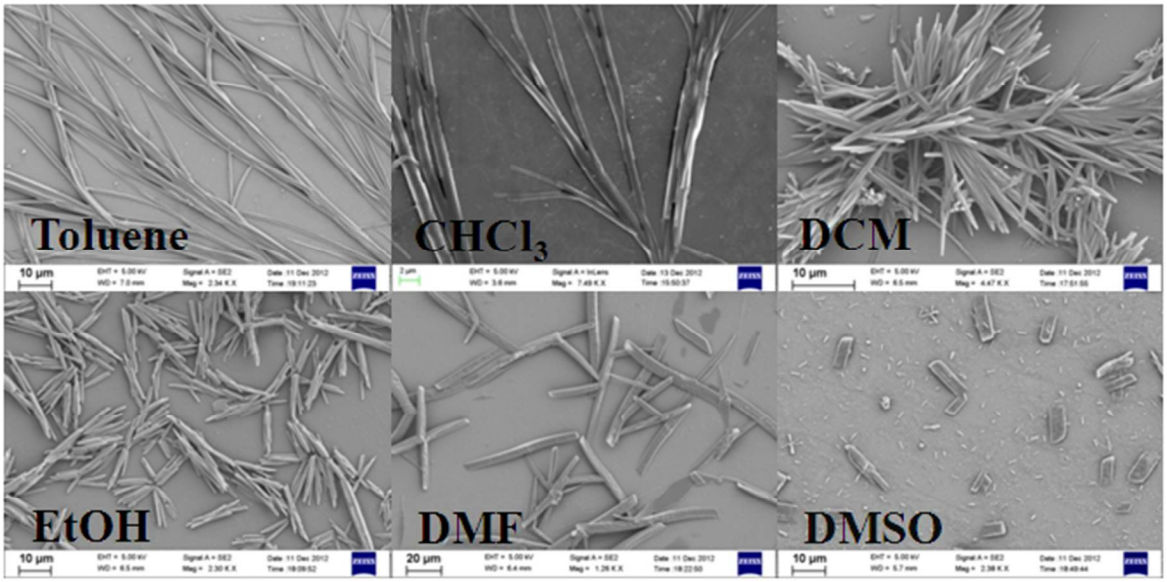

Figure S9. FESEM images of T4BT microstructures in solvent of different polarities

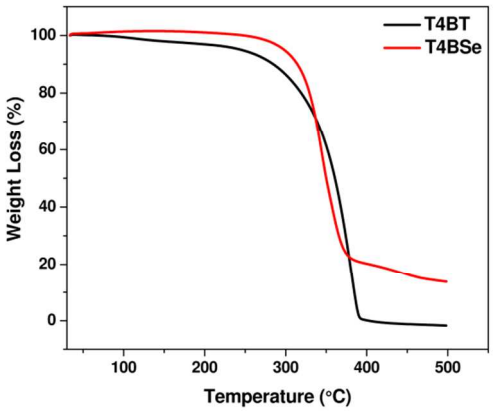

Figure S10. TGA plot of T4BT and T4BSe recorded at 10 °C/min heating rate in nitrogen atmosphere

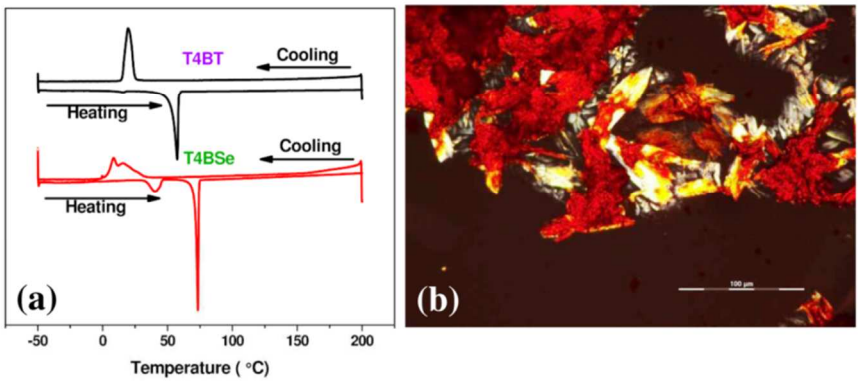

Figure S11. DSC thermograms of both the semiconductors (a) and polarizing microscopic image (b) of T4BSe at 50 °C

T1. Excited state fluorescence lifetime and corresponding amplitude of T4BT and T4BSe in solvent of different polarities

	T4BT				T4BSe			
Solvent	**Amp. (%)**	**τ_1 (ns)**	**Amp. (%)**	**τ_2 (ns)**	**Amp. (%)**	**τ_1 (ns)**	**Amp. (%)**	**τ_2 (ns)**
Toluene	**100**	**10.88**	**-**	**-**	**100**	**6.64**	**-**	**-**
EtOH	**100**	**4.27**	**-**	**-**	**90.22**	**1.07**	**9.78**	**2.25**
DMSO	**62.61**	**9.73**	**37.39**	**5.43**	**100**	**4.8**	**-**	**-**

References.

(1) Yang, R. Q.; Tian, R. Y.; Yan, J. G.; Zhang, Y.; Yang, J.; Hou, Q.; Yang, W.; Zhang, C.; Cao, Y. Deep-Red Electroluminescent Polymers: Synthesis and Characterization of New Low-Band-Gap Conjugated Copolymers for Light-Emitting Diodes and Photovoltaic Devices *Macromolecules* **2005**, *38*, 244-253.