Supporting Information

Impact of Rotamer Diversity on the Self-Assembly of Nearly Isostructural Molecular Semiconductors

Caitlin McDowell,^a Kamatham Narayanaswamy,^b Bommaramoni Yadagiri,^b Thumuganti Gayathri,^b Martin Seifrid,^a Ram Datt,^c Sean M. Ryno,^d Michael C. Heifner, Vinay Gupta,^c Chad M. Risko,^d Surya Prakash Singh^b*, and Guillermo C. Bazan^a*

^a Department of Chemistry and Biochemistry, Center for Polymers and Organic Solids, University of California, Santa Barbara, USA

^b Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, India

^c Organic and Hybrid Solar Cells, Physics of Energy Harvesting Division, CSIR-National Physical Laboratory, New Delhi-110012, India

^d Department of Chemistry & Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40506-0055, USA

* Corresponding authors: G.C. Bazan bazan@chem.ucsb.edu, S.P. Singh spsingh@iict.res.in, C.M. Risko chad.risko@uky.edu.

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1. Supplemental Tables and Figures



Figure S1. Cyclic voltammograms of a) **PT-TT** in dichloromethane and b) **FBT-TT** in chloroform solution, using ferrocene as an internal reference. The ferrocene traces are shown in grey.

Film Treatment	Figure	Feature	q-value (Å⁻¹)	d-spacing (nm)	CCL (nm)
PT-biTh	3 a	Alkyl	0.32	1.94	35
As-cast		π-π	1.77	0.35	9.9
PT-biTh:PC ₇₀ BM	62	Alkyl	0.31	2.06	8.8
As-cast	0a	π-π	1.77	0.35	9.8
PT-biTh :PC ₇₀ BM	66	Alkyl	0.30	2.06	12
0.25% DIO	00	π-π	1.76	0.36	4.1
PT-TT	26	Alkyl	0.38	1.67	32
As-cast	30	π-π	1.76	0.36	9.7
PT-TT:PC ₇₀ BM	6c	Alkyl	0.36	1.73	13
As-cast		π-π	1.75	0.36	11
PT-TT:PC ₇₀ BM	6d	Alkyl	0.37	1.70	24
0.25% DIO		π-π	1.74	0.36	10
FBT-biTh	45	Alkyl	0.28	2.24	17
As-cast	4d	π-π	1.70	0.37	7.9
FBT-biTh:PC ₇₀ BM	70	Alkyl	0.25	2.47	4.4
As-cast	7 d	π-π	1.68	0.37	10
FBT-biTh:PC ₇₀ BM	76	Alkyl	0.27	2.37	11
0.4% DIO	70	π-π	1.69	0.37	10
FBT-TT	46	Alkyl	0.41	1.52	22
As-cast	40	π-π	1.75	0.36	9.6
FBT-TT:PC ₇₀ BM	7c	Alkyl	0.43	1.45	3.8
As-cast		π-π	1.74	0.36	2.2
FBT-TT:PC ₇₀ BM		Alkyl	0.41	1.52	22
0.4% DIO	7d	π-π	1.74	0.36	12

Table S1. Crystallite parameters obtained from 2D GIWAXS images shown in various Figures. Peak q-values were calculated by fitting Gaussian curves to linecuts along the q_z (for alkyl features) and q_{xy} axes (for π - π features). The π - π features for FBT-TT were determined for along a linecut angled 7° above the q_{xy} axis to better capture the peak. The d-spacings are equal to $2\pi/q$ -value and CCLs were calculated using the Scherrer equation, equal to $2\pi/FWHM$ of the Gaussian fit.



Figure S2. Thermal transition temperatures (T) and enthalpies (Δ H) of melting (m) and crystallization (c) for the four molecules, determined by differential scanning calorimetry (DSC).



Figure S3. Temperature-dependent X-ray diffraction of a) **FBT-biTh** and b) **FBT-TT** films, confirming the melting temperatures observed by DSC in Figure S6.



Figure S4. Represenative absorbance for blend films of a) **PT-TT**:PC₇₀BM and b) **FBT-TT**:PC₇₀BM, as cast (circles) and processed with DIO (triangles). Representative IPCE spectra for c) **PT-TT**:PC₇₀BM (blue) (compared to **PT-biTh**:PC₇₀BM¹ in grey), and d) **FBT-TT**:PC₇₀BM (green, compared to **FBT-biTh**:PC₇₀BM² in grey).



Figure S5. Histogram of PCE values for optimized a) **PT-TT**:PC₇₀BM solar cells (D:A 7:3 and 0.25% DIO), and b) **FBT-TT**:PC₇₀BM solar cells (D:A 6:4 and 0.4% DIO), obtained for 40 devices.



Figure S6. a) Representative current-voltage characteristics and b) incident photocurrent efficiency (IPCE) spectra for **PT-TT**:PC₇₀BM (7:3) solar cells at various % DIO (v/v).

Devices	DIO (v/v %)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
	0	0.75	8.9	37.0	2.5
PT-biTh:	0.25	0.73	12.7	60.0	5.6
$PC_{70}BM^1$	0.6	0.70	9.1	53.5	3.4
	1	0.60	1.3	33.3	0.3
	0.0	0.74 ± 0.02	11.4 ± 0.2	47.4 ± 0.3	4.0 ± 0.2^{a}
PT-TT:	0.25	0.74 ± 0.01	13.4 ± 0.1	64.0 ± 0.1	6.4 ± 0.1 ^b
PC ₇₀ BM	0.6	0.73 ± 0.01	10.0 ± 0.2	55.0 ± 0.1	4.0 ± 0.1^{a}
	1	0.63 ± 0.02	6.2 ± 0.5	41.8 ± 0.4	1.6 ± 0.2^{a}

Table S2. Average current-voltage characteristics of **PT-biTh**:PC₇₀BM, and **PT-TT**:PC₇₀BM (D:A ratio 7:3) solar cells at various % DIO (v/v), based on 20 (^a) or 40 (^b) devices. The devices were annealed at 80°C for 15 minutes after spin-casting. **PT-biTh**:PC₇₀BM device data is reported from the literature.¹



Figure S7. Representative current-voltage characteristics for **FBT-TT**:PC₇₀BM (7:3) solar cells at various % DIO (v/v).

Devices	DIO (v/v %)	V _{oc} (V)	J _{sc} (mA cm⁻²)	FF (%)	PCE (%)
	0	0.78	6.6	36.0	1.8
	0.4	0.81	12.8	68.0	7.0
	1	0.55	2.4	31.0	0.4
	0	0.84 ± 0.02	12.1 ± 0.2	60.0 ± 0.3	6.1 ± 0.2^{a}
FRT-TT.	0.25	0.83 ± 0.01	14.1 ± 0.1	71.2 ± 0.1	8.3 ± 0.1^{a}
PC ₇₀ BM	0.4	0.84 ± 0.01	14.3 ± 0.1	73.4 ± 0.1	8.8 ± 0.1^{b}
	0.6	0.78 ± 0.01	13.4 ± 0.2	73.1 ± 0.1	6.5 ± 0.1^{a}
	1	0.74 ± 0.02	10.8 ± 0.5	41.8 ± 0.4	3.7 ± 0.2^{a}

Table S3. Average current-voltage characteristics of **FBT-biTh**:PC₇₀BM, and **FBT-TT**:PC₇₀BM (D:A ratio 6:4) solar cells at various % DIO (v/v), based on 12 (^a) or 45 (^b) devices. All devices were annealed at 80°C for 15 minutes after spin-casting. Device data for **FBT-biTh**:PC₇₀BM (as d-DTS(PTTh₂)₂:PC₇₀BM) is reported from the literature.³

Devices	D:A Ratio	V _{oc} (V)	J _{sc} (mA cm⁻²)	FF (%)	PCE (%)
	20:80	0.90 ± 0.02	9.8 ± 0.2	49 ± 0.5	4.3 ± 0.2^{a}
	30:70	0.88 ± 0.01	11.3 ± 0.1	57.0 ± 0.3	5.7 ± 0.1^{a}
FBT-TT:	40:60	0.87 ± 0.01	13.5 ± 0.1	61.2 ± 0.3	7.2 ± 0.1^{a}
PC ₇₀ BM	50:50	0.85 ± 0.01	13.8 ± 0.2	70.4 ± 0.3	8.2 ± 0.1^{a}
	60:40	0.84 ± 0.01	14.3 ± 0.1	73.4 ± 0.1	8.8 ± 0.1 ^b
	70:30	0.84 ± 0.01	13.1 ± 0.2	66.1 ± 0.1	7.2 ± 0.1^{a}
	80:20	0.83 ± 0.02	12.5 ± 0.2	46.2 ± 0.3	4.7 ± 0.1^{a}

Table S4. Average current-voltage characteristics of **FBT-TT**:PC₇₀BM solar cells at various D:A ratios and 0.4% v/v DIO additive, based on 12 (^a) or 45 (^b) devices. All devices were annealed at 80°C for 15 minutes after spin-casting.



Figure S8. Rotational barriers in vacuum and in chlorobenzene solvent PCM, as a function of dihedral angle between FBT and TT (blue, purple) or biTh (yellow, orange). The most stable conformations occur at 15-20°, predicting an approximately planar structure for both FBT-TT and FBT-biTh linkages. The 0° planar configuration for each fragment is shown on the left.

a)		0 U	1 U	2 U	3 U	4 U	
		DDSDD	DUSDD	DUSUD	UUSUD	UUSUU	
			UDSDD	UDSDU	UUSDU		
				UUSDD		Unique: 10	
				DUSDU		Total: 16	
b)	0 U	1 U	2 U	3 U	4 U	5 U	6 U
-	DDDSDDD	DDUSDDD	UDDSDDU	UUUSDDD	DUUSUUD	UUUSUUD	UUUSUUU
		DUDSDDD	DDUSUDD	UUDSUDD	UUDSDUU	UUUSUDU	
		UDDSDDD	DUDSDUD	UDUSUDD	UDUSUDU	UUUSDUU	
			UUDSDDD	DUUSUDD	UUUSUDD		
			UDUSDDD	DUUSDUD	UUUSDUD		
			UUDSDDD	UDUSDUD	UUUSDDU		
			DUUSDDD	UUDSDUD	DUUSDUU		
			DDUSDDU	UUDSDDU	UDUSDUU		
			DDUSDUD	UDUSDDU	UUDSDUU	Unique: 36	
				DUUSDDU		Total: 64	

Table S5. List of all possible rotamers for a) **PT-TT** and **FBT-TT**, and b) **PT-biTh** and **FBT-biTh**, based onthe nomenclature established in Figure S9. Rotamers are arranged in columns based on the number of Uunits in the structure, with symmetric structures in black and asymmetric structures (with degeneracy =2) in red.



Figure S9. Representative examples of the sixteen possible near planar conformations for **PT-TT**, due to the four points of rotation in the DADAD structure shown in Figure 8. We arbitrarily designate the substructures as upward (U) or downward (D) – this is analogous to bit representation (0 and 1).⁴ Note that the orientation of the central dithienosilole unit (S) does not change. The top four symmetrical structures (in black) represent a single rotomer. However, the lower six structures (in red) represent two degenerate structures due to asymmetry *e.g.* UUSUD has an energetically equivalent rotational isomer, DUSUU (not pictured). Thus, there are ten unique near planar structures, out of a total of sixteen possible.



Figure S10. Rotation of the outer thiophene units in the biTh moiety causes **PT-biTh** to possess additional conformations for each backbone structure for **PT-TT**. For example, the backbone of the first rotomer in Figure S9 has four biTh analogs – two symmetric (left and right) and a pair of degenerate asymmetric rotamers (center).



Figure S11. Dipole moments associated with **FBT-Th/TT** and **PT-Th/TT**, ordered from highest predicted crystallinity (top, **FBT-TT**) to lowest predicted crystallinity (bottom, **PT-biTh**). The most populated states are on the left, while the second most populated states are on the right. The (symmetric) lowest energy structures are colored black and (asymmetric) second-lowest energy structures are red. Total molecular dipole moments are colored blue and positioned next to the short-axis molecular dipole moment and orientation. The in-plane dipole moment vector of each fragment is superimposed on top of the fragment with the associated dipole moment magnitude.

2. Characterization and Measurement Methodologies

2.1. General Characterization

2.1.1 Chemical Structure Confirmation: ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on an ADVANCE 500 MHz Spectrometers at 25°C unless otherwise noted. Those spectra were referenced to SiMe₄ using the residual solvent peak impurity of the given solvent CDCl₃: ¹H: δ = 7.26 ppm, ¹³C: δ = 77.23 ppm. Chemical shift was reported in ppm and coupling constants in Hz as absolute values. Full-scan, low-resolution FD mass spectroscopy was carried out at the Department of Chemistry mass spectroscopy facility, University of California, Santa Barbara.

2.1.2 Thermal Properties: Differential scanning calorimetry (DSC) was determined by a TA Instruments DSC (Model Q-20) with about 2 mg samples at a rate of 10 °C/min in the temperature range of 0 to 300 °C.

2.1.3 Optical Absorbance: UV-Vis absorption spectra of synthesized compounds were recorded on a Shimadzu UV-1800 PC dual beam spectrometer and a Perkin Elmer Lambda 750 UV/Vis spectrometer at room temperature. All solution UV-Vis absorption was measured in dilute chlorobenzene (at concentrations of less than 1x10⁻³ M). Molar absorptivity was determined by the average of five measurements at concentrations between 5x10⁻⁵ M and 1x10⁻³ M. Films were prepared by spincasting from chlorobenzene solution (20 mg ml⁻¹) onto glass substrates at 1500 rpm.

2.1.4. Electrochemical Properties: Cyclic voltammetry was performed on a CH instrument with a three-electrode system consisting of Ag/AgCl reference electrode, a working electrode, and a platinum wire counter-electrode. The redox potential of **PT-TT** was measured in dichloromethane containing 0.1 M Bu₄NClO₄ at a scan rate of 100 mV s⁻¹. The redox potential of FBT-TT was measured in chloroform containing 0.1 M TBAPF₆ at a scan rate of 100 mV s⁻¹.

2.1.5. Temperature Dependent XRD: X-ray diffraction spectra were obtained using a Bruker D8 Advance X-ray diffractometer using a copper K α 1 source with an incident wavelength of 1.5406 Å. Films were dropcast from 20 mg ml⁻¹ solutions in chlorobenzene onto clean glass microscope cover slips. The films were scanned over a range from 5 or 6 to 21° 20, with a 0.0288° step size and 1.0 s integration per step. Samples were probed at 10°C intervals from 30°C to 220°C until no scattering peaks were observed, with 2 min equilibration time between scans.

2.2. Computational Methods

2.2.1 Rotational barriers: Density functional theory (DFT) at the ω B97X-D/6-31G(d,p) level of theory was used to generate the rotational barriers in Figure S8. Rotational barriers were assessed by fixing the dihedral of interest, at 20° intervals. The conductor-like polarizable continuum model

was used to simulate the effects of the chlorobenzene solvent. All DFT calculations were carried out with the Gaussian09 (Rev. E.01) software suite.⁵

2.2.2 Energetic Distribution of Rotomers: The optimized geometries for all possible rotamers were determined at the ω B97X-D/6-31G(d,p) level of theory. The results of these calculations are summarized in Figure 9 for all four molecules. The energies of the optimized rotamers were then used to predict those states that are most likely to be populated at room temperature (300 K) via the Boltzmann distribution. The fraction of molecules **p**_i in a state, **i**, is given by:

$$\mathbf{p}_{i} = \mathbf{N}_{i} / \mathbf{N} = \mathbf{g}_{i} \mathbf{e}^{-\varepsilon_{i} / \mathbf{k}_{b} T} / \sum_{j=0}^{N} \mathbf{g}_{j} \mathbf{e}^{-\varepsilon_{j} / \mathbf{k}_{b} T}$$
(1)

where N is the total number rotamers, N_i is the number of molecules in state i, $g_{i\{j\}}$ is the degeneracy of the state i $\{j\}$, \mathbf{k}_b is the Boltzmann constant, and T is the temperature. The relative population of a particular state (shown by blue bars) is expressed as:

$$p_i/p_0 = \frac{g_i}{g_0} e^{-(\varepsilon_i - \varepsilon_0)/kT}$$
 (2)

where p_0 represents the state with the highest population, taking into account the degeneracy. Energies (shown in orange) are normalized relative to the lowest energy state. The short-axis dipole moment vector for each conformer is shown in gray.

2.3. Fabrication of Organic Solar Cells

Pre-patterned ITO substrates on glass were progressively cleaned by ultrasonication in aqueous detergent, deionized water, acetone, and isopropyl alcohol. The substrates were then exposed to UV-ozone treatment for 15 minutes.

Solutions and devices were prepared according to procedures reported earlier for d-DTS(PTTh₂)₂¹ or p-DTS(FBTTh₂)₂.³ **PT-TT** and PC₇₀BM were dissolved in chlorobenzene (CB) at various donor:acceptor (D:A) ratios with an overall concentration of 40 mg ml⁻¹. Blend solutions of FBT-TT:PC₇₀BM were prepared at 35 mg ml⁻¹ total solids in CB, for the various D:A ratios. Blend solutions of both molecules were also prepared with 1,8-diodooctane (DIO) in chlorobenzene, at 0.25, 0.4, 0.6 and 1.0% volume per volume percent. Solutions were stirred at 60°C overnight and blend solutions of FBT-TT:PC₇₀BM heated to 90°C for 15 min directly prior to spin casting.

For **PT-TT**:PC₇₀BM devices, MoOx (10 nm) was thermal evaporated on to the substrates in a glovebox at a chamber pressure of $\sim 10^{-7}$ torr. Active layers were then spin-coated using the prepared solutions at 60°C and 1500 r.p.m. in a N₂ glove box, yielding films of 150 ± 10 nm thickness as determined by a surface profiler. Films containing DIO were baked to 80°C for 10 min to evaporate residual solvent. Finally, an Al (100 nm) cathode was thermally evaporated. The final

device architecture was glass/ITO/MoOx/Donor:PC₇₀BM/AI. As-cast films used an active layer of a 7:3 D:A ratio cast from 20 mg mL⁻¹ chlorobenzene. The optimum DIO concentration was 0.25% v/v.

For FBT-TT:PC₇₀BM devices, PEDOT:PSS (Clevios PH) was deposited as a hole-transport material, spin-coated at 5000 rpm for 40 s to obtain a film thickness of approx. 30 nm. This layer was annealed at 140°C for 15 minutes before proceeding. Active layers were obtained by spin-casting the prepared solutions onto the substrates at 90°C and 2000 rpm for 45 s. Films containing DIO were baked to 80°C for 10 min to evaporate residual solvent. BHJ film thicknesses were 110 \pm 10 nm, as determined by a surface profiler. Then, the Ca layer was thermally evaporated with thickness of 20 nm, and the Al cathode was continuously deposited to approx. 80 nm, vacuum pressures less than $4x10^{-6}$ torr. The final device architecture was glass/PEDOT:PSS/Donor:PC₇₀BM/Ca/Al. As-cast films used an active layer of a 6:4 D:A ratio cast from 35 mg mL⁻¹ chlorobenzene. The optimum DIO concentration was 0.4% v/v.

Both types of fabricated solar cells were encapsulated using epoxy and a cover glass and cured for 15 min under ultraviolet irradiation before characterization.

2.4. Device Characterization

The J-V characteristics of the solar cells were measured using a Keithley 2420 source meter unit. The light source was calibrated by using silicon reference cell (NREL) with an AM 1.5 G solar simulator with an intensity of 100 mW/cm². During the testing, an aperture with an area of 10 mm² was used to accurately measure the performance of solar cells. The IPCE was measured using a CEP-25ML Spectral Response Measurement System after monochromatic power calibration using reference silicon diode.

2.5. GIWAXS Characterization

Films were spincast directly onto silicon substrates with approx. 200 nm native oxide layer, which were prepared as the ITO-glass described above. Casting solutions were various concentrations and temperatures in chlorobenzene: 20 mg ml⁻¹ at room temperature for neat films of all four molecules, 40 mg ml⁻¹ at 60°C for **PT-biTh**:PC₇₀BM and **PT-TT**:PC₇₀BM films or 35 mg ml⁻¹ at 90°C for **FBT-biTh**:PC₇₀BM and **FBT-TT**:PC₇₀BM films. Grazing-incidence wide-angle X-ray scattering measurements were performed at the Advanced Light Source at Lawrence Berkeley National Lab on the 7.3.3 beamline⁶. Samples were scanned for 2 to 10 s at an incidence angle of 0.14° and a photon energy of 10 keV ($\lambda = 1.24$ Å), while under a helium environment to minimize beam damage and reduce air scattering. The width of the incident x-ray beam is about 1 mm and silver behenate was used to calibrate the lengths in the reciprocal space. A 2D detector (PILATUS 2M from Dectris) with a

sample-to-detector distance of 305.4 mm was used to collect the images. The Nika software package⁷ and WAXS Toolkit⁸ for Igor (by Wavemetrics) was used to process the images.

2.6. Single Crystal Structure of FBT-TT

Suitable single **FBT-TT** crystals were grown in chloroform via vapor diffusion of acetonitrile. Single crystal x-ray crystallography was completed at the Advanced Light Source at Lawrence Berkeley National Lab on the 11.3.1 beamline.

Identification code	SPS1_a			
Empirical formula	C60 H68 F2 N4 S8 Si			
Formula weight	1167.75 g/mol			
Temperature	100(2) K			
Wavelength	0.7749 Å			
Crystal system	Triclinic			
Space group	P -1			
Unit cell dimensions	a = 8.3190(7) Å	$\alpha = 92.141(4)^{\circ}$		
	b = 17.7676(16) Å	β = 99.217(4)°		
	c = 20.0174(18) Å	γ = 93.398(4)°		
Volume	2912.1 Å ³			
Z	2			
Density (calculated)	1.332 Mg/m ³			
Absorption coefficient	0.472 mm ⁻¹			
F(000)	1232			
Crystal size	0.200 x 0.030 x 0.010 mm ³			
Theta range for data collection	1.644 to 19.724°			
Index ranges	-7 ≤ h ≤ 7, -15 ≤ k ≤ 15, -17 ≤ l ≤	£ 17		
Reflections collected	13903			
Independent reflections	4021 [R(int) = 0.0776]			
Completeness to theta = 19.724°	99.6%			
Absorption correction	Semi-empirical from equivalents			
Max. and min. transmission	0.995 and 0.753	0.995 and 0.753		
Refinement method	Full-matrix least-squares on F ²			
Data / restraints / parameters	4021 / 203 / 394			
Goodness-of-fit on F2	dness-of-fit on F2 2.393			
Final R indices [I>2sigma(I)]	R1 = 0.1447, wR2 = 0.3744			
R indices (all data)	R1 = 0.1939, wR2 = 0.3969			
Extinction coefficient	n/a			
Largest diff. peak and hole	0.775 and -0.631 e.Å ⁻³			

3. Materials

Toluene was dried over CaH₂, distilled under nitrogen and stored with sodium wire before use. Syringes that were used to transfer reagents or solvents were purged with nitrogen prior to use. Anhydrous chlorobenzene, chloroform and dichloroform were purchased from Sigma Aldrich and used as received. 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (**2a**) was purchased from 1-Material Organic Nano Electronic Corporation. (5-hexylthieno[3,2-b]thiophen-2-yl)trimethyl stannane (**1**), 4,7-

dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (**2b**) and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4H-silolo[3,2-b:4,5-b']dithiophene (**4**) were prepared according to the literature procedures, with negligible modification.⁹⁻¹¹

4. Synthesis



Scheme 1. Chemical structures and synthetic route for PT-TT.

4.1. Synthesis of 7-bromo-4-(5-hexyl thieno[3,2-b]thiophen-2-yl)-[1,2,5]thiadiazolo[3,4c]pyridine (3a):

A solution of compound **1** (393 mg, 1.01 mmol) and compound **2a** (300 mg, 1.01 mmol) in dry toluene (15 mL) was purges with nitrogen gas for 15 minutes followed by the addition of tri(o-tolyl)phosphine (15.2 mg, 0.05 mmol) and tris(dibenzylideneacetone)dipalladium(0)-chloroform (25.8 mg, 0.025 mmol). The mixture was reacted at 85°C for 3 days. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, and then dried over Na₂SO₄. After removal of solvent, the crude product was purified by column chromatography on silica gel with hexane and chloroform as eluent to afford compound **3a** as yellowish solid (202mg, 46%). ¹H NMR (400 MHz, CDCl₃): δ ppm 8.85 (s, 1H), 8.62 (s, 1H), 7.02 (s, 1H), 2.92 (t, *J* = 7.5 Hz 2H), 1.79-1.72 (m, 2H), 1.42-1.33 (m, 6H), 0.92 - 0.90 (t, 3H). ¹³C NMR (101 MHz, CDCl₃): δ ppm 156.29, 153.20, 147.85, 145.84, 143.25, 140.79, 139.06, 125.74, 116.96, 107.74, 31.58, 31.51, 31.36, 28.83, 22.60, 14.12. MALDI-TOF MS: calcd. for C₁₇H₁₆BrN₃S₃, [M]⁺ m/z 436.96; found: 436.97.

4.2. Synthesis of PT-TT:

In a 15 mL glass tube, solution of compound 4 (60 mg, 0.080 mmol) and compound 3a (77.7 mg, 0.177 mmol) in dry toluene (6 mL) was purged with nitrogen gas for 15 minutes, followed by the addition of tri(o-tolyl)phosphine (3 mg, 0.010 mmol) and tris(dibenzylideneacetone)dipalladium(0)chloroform (5mg, 0.005 mmol) then sealed with a Teflon® cap. The mixture was reacted at 85°C for 4 days. After removal of solvent, the reaction mixture was extracted with dichloromethane poured into water. The organic layer was washed with sodium chloride solution, and then dried over Na₂SO₄. The crude product was then washed with methanol (100 mL, three times) followed by hexane (100 mL, three times) and finally purified by column chromatography on silica gel (230 - 400 mesh) with hexane and dichloromethane as eluent to afford compound PT-TT as dark blue solid (72mg, 79.5 %). ¹H NMR (500 MHz, CDCl₃): δ ppm 8.78 (s, 2H), 8.72 (s, 2H), 8.18 (t, J = 4.7 Hz, 2H), 7.02 (s, 2H), 2.92 (t, J = 7.6 Hz, 4H), 1.80 - 1.75 (m, 4H), 1.60 - 1.57 (m, 2H), 1.45 - 1.42 (m, 4H), 1.35 -1.33 (m, 14H), 1.25 - 1.24 (m, 10H), 1.13 - 1.11(m, 4H), 0.91(t, J = 7.1 Hz, 6H), 0.86- 0.84 (m, 12H). ¹³C NMR (126 MHz, CDCl₃): δ ppm 154.32, 152.37, 150.43, 147.75, 145.48, 145.13, 142.63, 141.82, 139.83, 139.08, 138.65, 130.98, 124.60, 120.35, 116.93, 36.12, 35.89, 31.62, 31.49, 31.38, 29.11, 29.02, 28.89, 23.14, 22.63, 17.82, 14.32, 14.13, 10.95. MALDI-TOF MS: calcd. for C₅₈H₆₈N₆S₈Si, [M]⁺ m/z 1132.30; found: 1132.29.



Figure S12. ¹H NMR spectra of 3a.



Figure S13. ¹³C NMR spectra of 3a.



Figure S14. FD-MASS spectra of 3a.

Figure S15. ¹H NMR spectra of PT-TT.

Figure S16. ¹³C NMR spectra of PT-TT.

Figure S17. FD-mass spectra of PT-TT.

Scheme 2. Chemical structures and synthetic route for FBT-TT.

4.3. Synthesis of (2-hexylthieno[3,2-b]thiophen-5-yl)trimethylstannane 4-bromo-5-fluoro-7-(2-hexylthieno[3,2-b]thiophen-5 yl)benzo[c][1,2,5]thiadiazole (3b):

In a N₂ filled glove box, a 20 mL glass tube was charged with **2b** (327.5 mg, 1.05), (2-hexylthieno[3,2-b]thiophen-5-yl)trimethylstannane **1** (406.5 mg, 1.05 mmol), Pd(PPh₃)₄ (62 mg, .04 mmol), and toluene (15 mL), and sealed with a Teflon[®] cap. The reaction mixture was heated to 80°C for 48 hr. Upon cooling, the material was then loaded onto silica and purified by flash

chromatography using hexanes/chloroform gradient. After fraction collection and solvent removal, an orange solid (compound **3b**) was obtained. Recovered yield: 283 mg, 59%. ¹H NMR (600 MHz, Methylene Chloride- d_2 , 298 K) δ = 8.41 (s, 1H, TT), 7.68 (d, ³ J_{FH} = 10.2 Hz, 1H, FBT), 7.02 (s, 1H, TT), 2.92 (t, ³ J_{HH} = 7.6 Hz, 2H, ^aCH₂), 1.75 (p, ³ J_{HH} = 7.6 Hz, 2H, ^bCH₂), 1.42 (m, 2H, ^cCH₂), 1.33 (m, 4H, ^dCH₂, ^eCH₂), 0.90 (t, ³ J_{HH} = 7.0 Hz, 3H). ¹³C NMR (151 MHz, Methylene Chloride- d_2 , 298 K) δ = 161.1 (d, ¹ J_{FC} = 250 Hz, CF), 154.7 (d, ³ J_{CF} = 7.4 Hz, C=N), 152.1 (^{TT}C-^aCH₂), 149.3 (C=N), 140.9 (^{TT}C), 138.9 (^{TT}C), 137.5 (d, ⁴ J_{FC} = 2.8 Hz, ^{TT}C-FBT), 128.5 (d, ³ J_{FC} = 10.3 Hz, ^{FBT}C-TT), 122.7 (^{TT}CH), 116.9 (^{TT}CH), 115.8 (d, ² J_{FC} = 31.0 Hz, ^{FBT}CH), 96.0 (d, ² J_{FC} = 24.8 Hz, C-Br), 32.0 (^dCH₂), 31.9 (^bCH₂), 31.7 (^aCH₂), 29.2 (^cCH₂), 23.0 (^eCH₂), 14.3 (CH₃).

4.4. Synthesis of FBT-TT:

In a N₂ filled glove box, a 20 mL glass tube was charged with compounds **3b** (300 mg, 0.658 mmol) and **4** (245 mg, 0.329 mmol), Pd(PPh₃)₄ (30 mg) and toluene (15 mL) and sealed with a Teflon[®] cap. The reaction mixture was heated to 100°C for 1 min, 125°C for 1min, 140°C for 10 min, 150°C for 10 min, and 160°C for 10 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a hexanes/chloroform gradient in *duplicate*. After fraction collection and solvent removal, a metallic solid was obtained. The solid was slurried in a 3:1 mixture of methanol and hexanes, sonicated for 1 hr and stirred overnight. The suspension was filtered, washed with acetone and dried under vacuum. The product **FBT-TT** was recovered as a metallic purple solid. Recovered yield: 283 mg, 75% yield. ¹**H NMR** (600 MHz, CDCl₃, 298 K): δ 8.39 (s, 2H, TT), 8.34 (s, 2H, SDT), 7.7 (d, ³*J*_{FH} = 12.9 Hz, 2H, FBT), 6.98 (s, 2H, TT), 2.91 (t, 4H, TT-C*H*₂), 1.75 (t, 4H, TT-C*H*₂*CH*₂), 1.42 (m, 4H), 1.34 (m, 16H), 1.23 (m, 10H), 1.13-1.109 (m, 4H), 0.91 (m, 6H), 0.84(m, 12H). ¹³**C NMR** (151 MHz, Chloroform-*d*, 298 K): δ 158.7, 157.4, 153.5, 151.9, 151.0, 144.3, 140.1, 138.7, 138.2, 134.5, 133.5, 125.7, 121.6, 116.6, 116.4 3, 111.7, 36.2, 36.0, 31.7, 31.6, 31.5, 29.9, 29.2, 28.9, 23.2, 22.8, 18.0, 14.33, 14.25, 11.0.

Figure S18. ¹H NMR spectra of PT-TT.

Figure S19. ¹³C NMR spectra of PT-TT.

Figure S20. MALDI spectra of PT-TT.

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