Electronic Supplementary Information For

A New Ladder-Type Benzodi(cyclopentadithiophene)-Based Donor-Acceptor Polymer and a Modified Hole-Collecting PEDOT:PSS Layer to Achieve Tandem Solar Cells with Open-Circuit Voltage of 1.62 V

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Experimental Section

General Measurement and Characterization: All chemicals were obtained from commercial sources and used as received unless otherwise specified. NMR measurements are reported for Varian Unity-300 spectrometers (^{1}H, 300 MHz). Chemical shifts (δ values) are reported in ppm with respect to Me_4Si (δ = 0 ppm) for ^{1}H NMR. Multiplicities of peaks are denoted by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Thermogravimetric analysis (TGA) was recorded on a PerkinElmer Pyris analyzer under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Absorption spectra were collected on a HP8453 UV-Vis spectrophotometer. The molecular weight of polymers was determined by gel permeation chromatography on a Viscotek VE2001GPC instrument, polystyrene was used as the internal standard, and THF is the eluent. Electrochemical cyclic voltammetry (CV) was conducted on an Autolab ADC 164 analyzer. A carbon glass coated with a thin polymer film was used as the working electrode and Ag/Ag^+ electrode as the reference electrode, while 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile was the electrolyte. CV curves were calibrated using ferrocence as the standard, whose oxidation potential is set at –4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO = $-(E_{ox}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV. The LUMO levels were obtained from the equation LUMO = $-(E_{red}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV

Synthesis of PBDCPDT-FBT

To a 50 mL round-bottom flask were introduced Sn-**BDCPDT** (163 mg, 0.107 mmol), 5,6-difluoro-4,7-diiodo-benzothiadizole (45.4 mg, 0.107 mmol), $Pd_2(dba)_3$ (3.9 mg, 0.0043 mmol), tri(*o*-tolyl)phosphine (10.4 mg, 0.034 mmol), and dry chlorobenzene (6 mL). The mixture was degassed by bubbling nitrogen for 10 min at room temperature. The reaction was then carried out in a microwave reactor and reacted for 50 min under 270 Watt. In order to end-cap the resulting polymer, tributyl(thiophen-2-yl)stannane (20.2 mg, 0.054 mmol) was added to the mixture and the microwave reaction was continued for 10 min under 270 Watt. Subsequent to tributyl(thiophen-2-yl)stannane, another end-capping reagent, 2-bromothiophene (9.4 mg, 0.058 mmol) was added and the reaction was continued for another 10 min under otherwise identical conditions. The mixture was then added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone and hexane sequentially for three days. The crude polymer was dissolved in hot THF and the residual Pd catalyst and Sn metal in THF solution were removed by Pd-thiol gel and Pd-TAAcOH (Silicycle Inc.). After filtration and removal of the solvent, the polymer was re-dissolved in THF and re-precipitated by methanol. The resultant polymer was collected by filtration and dried under vacuum for 1 day to give a dark-green fiber-like solid (120 mg, 82%, Mn = 49900, PDI = 1.48): ^{1}H NMR ($CDCl_3$, 300 MHz) 0.86 (br, 12 H), 1.26-1.41 (br, 40 H), 1.73 (br, 8 H), 3.89 (br, 8 H), 6.81 (br, 8 H), 7.26 (br, 8 H), 7.93 (s, 2 H), 8.30 (s, 2 H).

Preparation of the m-PEDOT:PSS solution. 10 mL of PEDOT:PSS (Clevios PVP AI-4083), 10 mL of isopropanol, and Zonyl FSN (0.0265 mL) were mixed together and stirred for 3 days.

Inverted Device Fabrication. Indium tin oxide (ITO)-coated glass substrate was ultrasonically washed by detergent, de-ionic water, acetone and isopropanol sequentially for 15 min/each and then cleaned by UV-ozone for another 15 min. A methanol (1 mL) solution of Zinc acetylacetonate hydrate (20 mg) was filtered, heated at 80 ^{o}C under nitrogen atmosphere, and spin-coated on the cleaned

ITO-coated glass at 1000 rpm for 60 s to produce a 20 nm thick interlayer, followed by baking it at 150 ˚C under air atmosphere for 5 min. An ODCB (1 mL) solution of P3HT (17 mg) and $IC_{60}BA$ (17 mg) and an ODCB (1 mL) solution of **PBDCPDT-FBT** (18 mg) and $PC_{71}BM$ (18 mg) were heated at 70 °C for 12 h and filtered. The filtrates were then spin-coated on top of the ZnO layer respectively at various spin-coating conditions (P3HT/$IC_{60}BA$: 500 rpm, 40 s, 220 nm thickness for device A; **PBDCPDT-FBT**/$PC_{71}BM$: 600 rpm, 4 min, 90 nm thickness for device B). The P3HT/$IC_{60}BA$ film was covered in a Petri dish to allow the solvent to slowly evaporate (solvent annealing) until the film is dried and then baked at 150 ^{o}C for 15 min. The **PBDCPDT-FBT**/$PC_{71}BM$ film was directly thermally annealed at 140 ^{o}C for 10 min. For device A, the m-PEDOT:PSS solution was then spin-coated on top of the active layer (P3HT/$IC_{60}BA$) at 600 rpm for 8 s followed by 1300 rpm for 4 min. It was heated to 80 ^{o}C for 5 min in a glove box. The top electrode was then prepared by evaporation of Ag (150 nm) at reduced pressure below 10^{-6} torr to furnish the BHJ solar-cell devices. For device B, the hole transporting layer and top electrode were then prepared by sequential thermal evaporation of MoO_3 (7 nm) and Ag (150 nm) at reduced pressure below 10^{-6} torr to furnish the BHJ solar-cell devices. All devices contain an active area of 0.04 cm^2 and the photovoltaic parameters were measured at room temperature under air atmosphere with a Xenon lamp coupled to an AM1.5G solar filter (YAMASHITA DENSO YSS-50A solar simulator). *J-V* characteristics were recorded in a Keitheley 2400 Source Measurement Unit.

Tandem Inverted Device Fabrication. Indium tin oxide (ITO)-coated glass substrate was ultrasonically washed by detergent, de-ionic water, acetone and isopropanol sequentially for 15 min/each and then cleaned by UV-ozone for another 15 min. A methanol (1 mL) solution of Zinc acetylacetonate hydrate (20 mg) was filtered, heated at 80 ^{o}C under nitrogen atmosphere, and spin-coated on the cleaned ITO-coated glass at 1000 rpm for 60 s to produce a 20 nm thick interlayer, followed by baking it at 130 ˚C under air atmosphere for 5 min. An ODCB (1 mL) solution of P3HT (17 mg) and $IC_{60}BA$ (17 mg) and an ODCB (1 mL) solution of **PBDCPDT-FBT** (18 mg) and $PC_{71}BM$

(18 mg) were heated at 70 °C for 12 h and filtered. The P3HT/$IC_{60}BA$ filtrate was then spin-coated on top of the ZnO layer at 600 rpm for 40 s to form a film of 190 nm thickness. It was covered in a Petri dish to allow the solvent to slowly evaporate (solvent annealing) until the film is dried and then baked at 150 ^{o}C for 5 min. The m-PEDOT:PSS solution was then spin-coated on top of the P3HT/$IC_{60}BA$ layer at 600 rpm for 8 s followed by 1300 rpm for 4 min to furnish a 100 nm thick film. It was then heated to 80 ^{o}C for 5 min in a glove box. Afterwards, a filtered and pre-heated (80 ^{o}C, under nitrogen atmosphere) methanol (1 mL) solution of Zinc acetylacetonate hydrate (20 mg) was spin-coated on the m-PEDOT:PSS layer at 1000 rpm for 60 s to produce a 20 nm thick interlayer, followed by baking it at 130 ˚C in a glove box for 5 min. The interconnection layer was thus made up of ZnO and m-PEDOT:PSS. The **PBDCPDT-FBT**/$PC_{71}BM$ filtrate was then spin-coated on top of the interconnection layer at 600 rpm for 4 min to form a film of 90 nm thickness which was thermally annealed at 140 ^{o}C for 10 min. Lastly, the hole transporting layer and top electrode were then prepared by sequential thermal evaporation of MoO_3 (7 nm) and Ag (150 nm) at reduced pressure below 10^{-6} torr to furnish the BHJ solar-cell devices. All devices contain an active area of 0.04 cm^2 and the photovoltaic parameters were measured at room temperature under air atmosphere with a Xenon lamp coupled to an AM1.5G solar filter (YAMASHITA DENSO YSS-50A solar simulator). *J-V* characteristics were recorded in a Keitheley 2400 Source Measurement Unit.

Hole-only devices.

In order to investigate the respective hole mobility of the different copolymer films, unipolar devices have been prepared following the same procedure except that the active layer is made of pure **PBDCPDT-FBT** and the Ca/Al cathode is replaced by evaporated gold (40 nm). The hole mobilities were calculated according to space charge limited current theory (SCLC). The J-V curves were fitted according to the following equation:

$$J = \frac{9}{8}\varepsilon\mu\frac{V^2}{L^3}$$

Where ε is the dielectric permittivity of the **PBDCPDT-FBT**, μ is the hole mobility and L is the film thickness (distance between the two electrodes).

Synthetic Scheme of Monomer

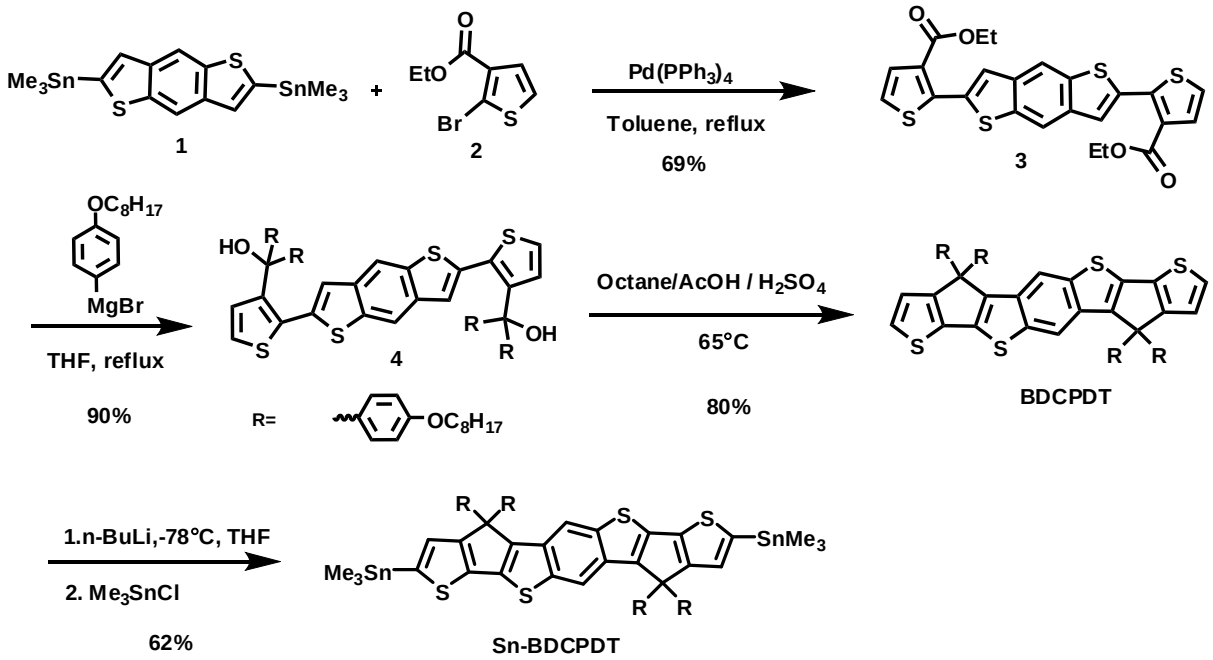


Fig. S1 Synthetic scheme of distannylated **BDCPDT** monomer.

Transmission Spectrum of Interconnecting Layer and Absorption Spectra of the Tested Device

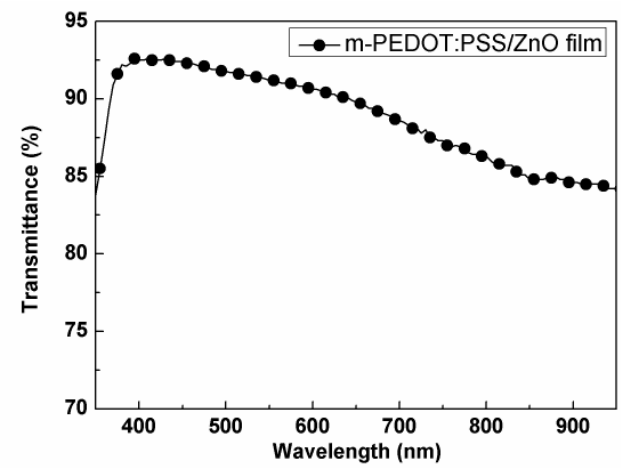
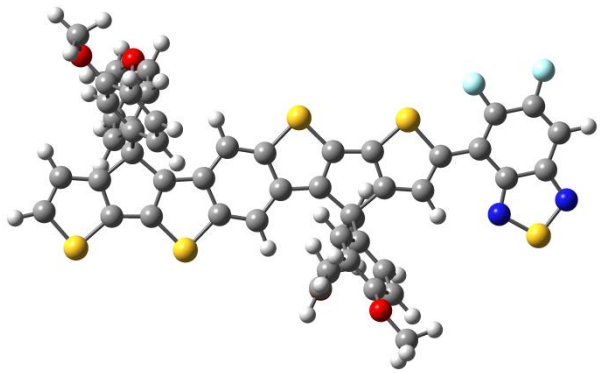


Fig. S2 Transmission spectrum of the m-PEDOT:PSS (100 nm)/ZnO (20 nm) film

Computational Details

Quantum−chemical calculations were performed with the Gaussian09 suite[1] employing the B3LYP density functional in combination with the 6−311G(d,p) basis set. Geometry optimizations were performed with solvation in toluene by applying the polarized continuum model (PCM) and with tight SCF and convergence criteria and an ultrafine integration grid by applying the GEDIIS optimization algorithm. The minimum nature of each stationary point was confirmed by a frequency analysis. Time−dependent density functional (TDDFT) calculations were performed including the keyword IOP(9/40=2) in order to output information on smaller contributions to each electronic transition. Electron density difference maps for electronic transitions were generated from TDDFT output by GaussSum 2.2 and visualized by GaussView 5.0. The electronic transitions can therefore be visualized through EDDMs. Red indicates a decrease in charge density, while green indicates an increase. Considering an insignificant effect on electronic properties, all the side-chain substituents were replaced with methyl groups for simplicity.

Cartesian coordinates (Å) and energy (Hartree) of the Gaussian B3LYP/6−311G(d,p) optimized structure of PBDCPDT–FBT



Top view

E= –4679.91297758 (N_{img} = 0)

C	3.044130904115	−0.452804491569	−0.171564662759
C	2.268168470918	−1.653001019769	−0.074880355456
C	0.884771210221	−1.655192723788	−0.056986767307
C	0.212024497850	−0.424668042344	−0.131875598995
C	0.987264716226	0.775132207507	−0.232232520714
C	2.371250871305	0.776413511808	−0.255861992625
H	0.329270365823	−2.580368872330	0.014974336367
H	2.926173906011	1.701182166286	−0.335419562866
C	−1.188469390702	−0.132472835814	−0.142269654433
C	−2.494271120376	−0.941010236185	−0.022253728100
C	−3.514179446777	0.209527500797	−0.077684664857
C	−2.873144170998	1.426515051313	−0.211480544286
C	−1.453967888214	1.212358106924	−0.239038171493
S	−0.035667665620	2.221038398771	−0.325920027044
C	−2.752483453796	−1.873381360205	−1.220904808831
C	−3.836617108512	−2.755291326264	−1.201906627706
C	−1.981051582640	−1.821047970371	−2.388474104165
C	−4.146359281475	−3.564305147701	−2.293443188716
H	−4.455828560772	−2.828142488961	−0.315426083370
C	−2.275872883964	−2.620275935672	−3.485056230277

H	−1.137710927043	−1.145186310459	−2.449383136650
C	−3.361292177615	−3.500558027637	−3.448816361527
H	−4.994205435051	−4.232847223749	−2.229885237003
H	−1.672490189620	−2.577356677404	−4.383863009382
C	−2.510233427255	−1.673884501701	1.337944182920
C	−2.845361688163	−0.994558871746	2.510314939413
C	−2.110435376681	−3.012215113765	1.457892926489
C	−2.794934971284	−1.612515170221	3.759427119723
H	−3.154942753539	0.042465048444	2.460228851888
C	−2.055809125826	−3.643029749596	2.692539800291
H	−1.850846519908	−3.579946376305	0.572919656314
C	−2.398223635506	−2.948471761078	3.857658113840
H	−3.067910109795	−1.044352224071	4.638345005119
H	−1.750458538027	−4.679164577743	2.776917971296
C	−4.911803707191	0.325609457488	−0.046408653005
C	−5.353266480437	1.639310988631	−0.153366923667
S	−3.966389655578	2.749541987910	−0.306001862182
C	−6.725803838779	2.114920777490	−0.148563516007
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C	−9.227748679490	1.739192949359	0.004741744692
C	−9.497795977852	3.124129688378	−0.149525201149
H	−10.505382889649	3.513877695877	−0.152921915241
F	−6.127168639931	4.386760559987	−0.442879221588
F	−8.558539346199	5.256363152105	−0.443037014995
N	−7.814457730672	−0.093085439427	0.165983010028
N	−10.153093245475	0.792029682651	0.159708755350
S	−9.357673749343	−0.633927464141	0.298564023540
C	4.444833200590	−0.748018666440	−0.181064399340
C	4.709393726055	−2.091259678408	−0.091094274594

C	6.133598824366	−2.304844193873	−0.077728790123
C	6.775213148404	−1.086982030525	−0.143432025694
S	3.292252732041	−3.098809867628	0.009546507035
C	5.755295001024	0.061991117796	−0.215637468371
C	5.983560420180	0.813849349182	−1.542096629805
C	7.059326937024	1.694702057597	−1.652702755973
C	5.184377448366	0.581548031448	−2.668604284500
C	7.343227012133	2.341575950904	−2.859413743665
H	7.696932435599	1.910477309561	−0.804413408937
C	5.468416708118	1.227223302439	−3.867642934523
H	4.348453888585	−0.102286147729	−2.612317576918
C	6.540868263394	2.109910540092	−3.980650015135
H	4.842523888772	1.043586638200	−4.733894579054
H	6.737180063137	2.600680638274	−4.923988351405
C	5.814998721658	0.977762863611	1.026584302950
C	6.210242740800	0.473388558687	2.266358018956
C	5.395507782860	2.314736195693	0.976002497498
C	6.198361568377	1.259271015562	3.418627114827
H	6.536943869974	−0.556371397076	2.346943232130
C	5.378797104939	3.110919678406	2.111936695182
H	5.092484720616	2.751324019623	0.032411428527
C	5.780724235017	2.590307751855	3.346796902921
H	6.517376010063	0.823046593725	4.355540560031
H	5.059166197283	4.145041204099	2.064163539048
C	8.188192523107	−1.206953538984	−0.140591922614
C	8.588476563679	−2.515013513179	−0.067906855752
S	7.242611936237	−3.628253690299	−0.008369796343
H	9.593111472910	−2.908270769855	−0.047822712575
H	8.884838528565	−0.381488656875	−0.188994561054
H	−5.602505732712	−0.495680678996	0.052629690681
O	−3.568427606432	−4.244977985305	−4.571464821162

O	−2.318123132485	−3.653740483455	5.021120520460
O	8.421135270022	3.177656300757	−2.837264600012
O	5.734208269740	3.450558965195	4.403071130034
C	−4.664690672113	−5.153420773762	−4.590922505287
H	−4.564109448417	−5.919200750884	−3.814476765890
H	−5.619472761681	−4.631587631178	−4.467062532186
H	−4.638751717346	−5.628481828640	−5.569889782140
C	8.767065726093	3.870591137740	−4.031970964791
H	7.958900965316	4.533309210501	−4.359049804770
H	9.643534827295	4.467089662183	−3.785342761937
H	9.018036341125	3.175442559954	−4.840067233888
C	−2.640904883162	−2.990506414195	6.239165653659
H	−2.502299209945	−3.730317464920	7.025462798797
H	−1.975072399358	−2.140242630886	6.420245436527
H	−3.680774341274	−2.646955445937	6.244751250156
C	6.123491084523	2.970246867742	5.685608012981
H	6.003711676360	3.811215908315	6.366239265079
H	5.484288490960	2.144165375796	6.014555995782
H	7.169667475068	2.646305688818	5.691361354228

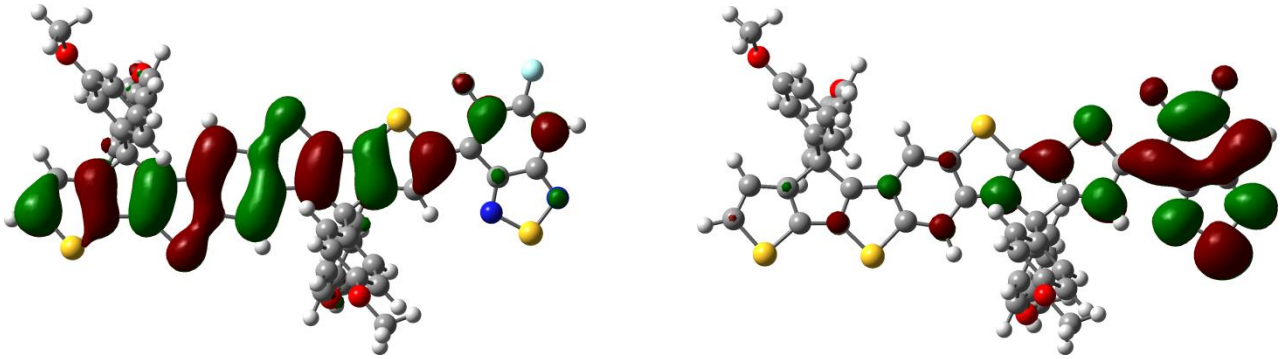
Table S1. Calculated[a] HOMO/LUMO energy, excitation energy, oscillator strength, and configuration (with large CI coefficients) of the excited state of **PBDCPDT-FBT**

HOMO (eV)	LUMO (eV)	Excitation energy		Oscillator strength	Symmetry	Configuration[c]
		$\lambda_{max,exp\ (nm)}$[b]	$\lambda_{calc\ (nm)}$			
−5.06	−2.86	658	651	0.6404	Singlet-A	**H→L**
		433	456	0.848	Singlet-A"	**H→L+1**
						H−2→L

[a] TD-B3LYP/6-311G(d,p), PCM=Toluene

[b] Experimental values were measured for non-simplified **PBDCPDT-FBT** in toluene solution

[c] Configurations with largest coefficients in the CI expansion of each state are highlighted in boldface



HOMO **LUMO**

Fig. S3 Plots (isovalue = 0.02 au) of frontier orbitals of **PBDCPDT-FBT** calculated at the level of B3LYP/6-311G (d,P) in chloroform.

TGA and ^{1}H NMR Spectra of PBDCPDT-FBT

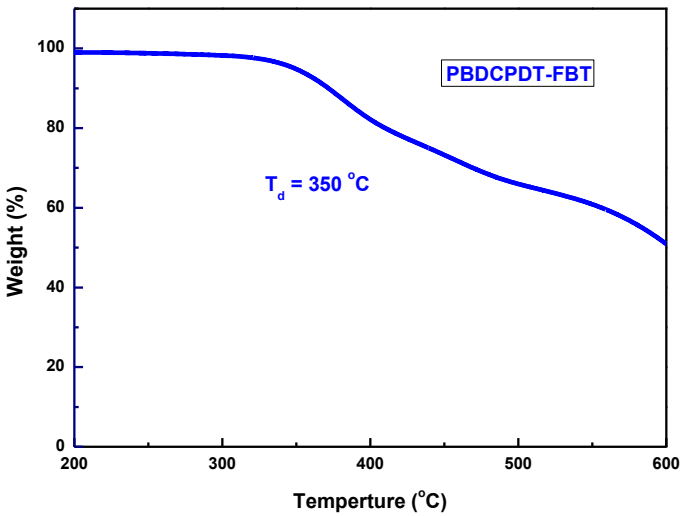


Fig. S4 Thermogravimetric analysis of **PBDCPDT-FBT**

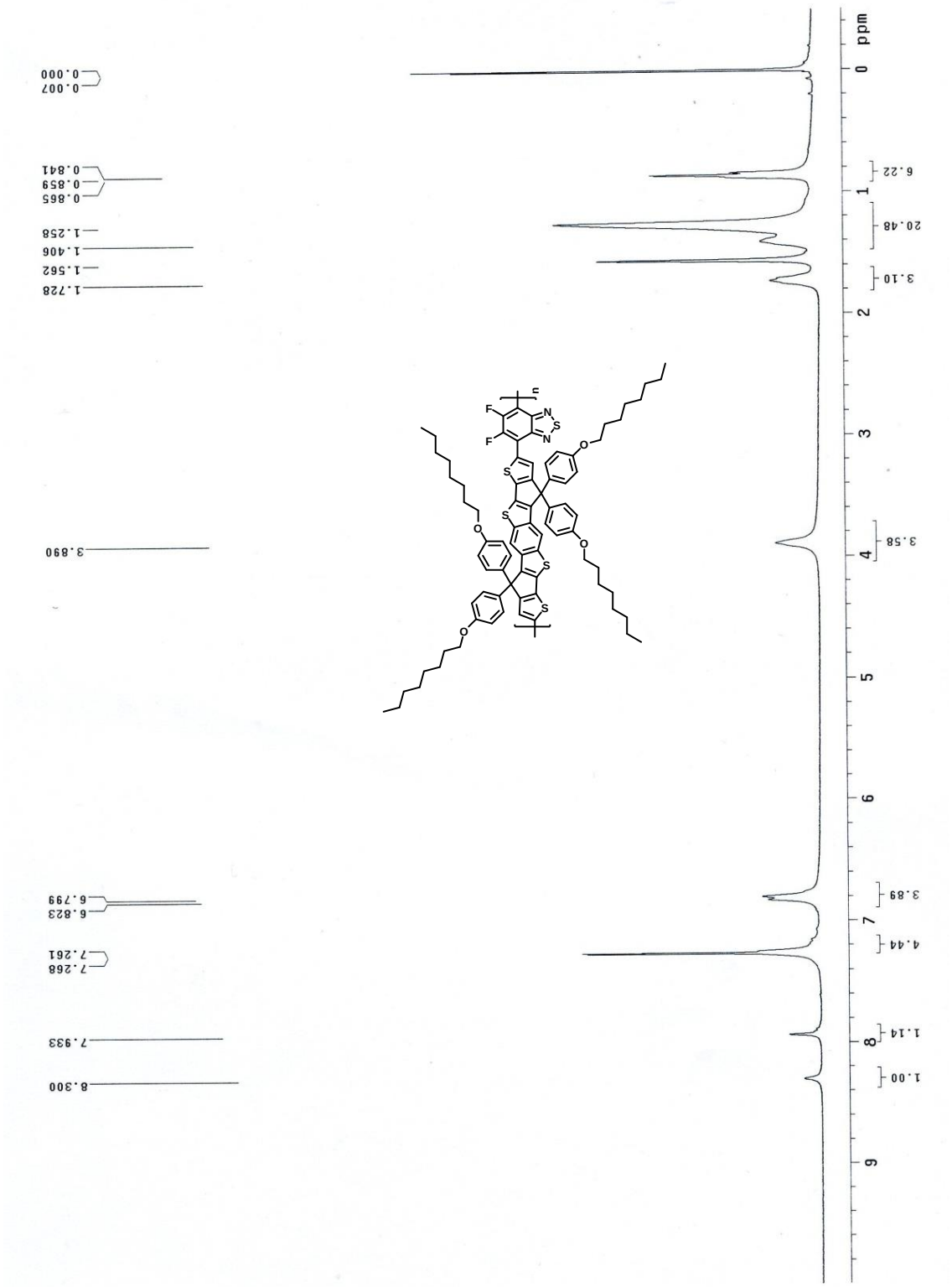


Fig. S5 ^{1}H NMR spectrum of **PBDCPDT-FBT** in $CDCl_3$

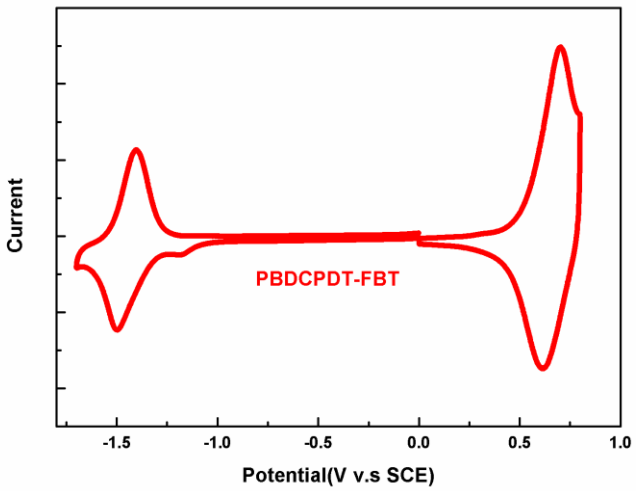


Fig. S6 Cyclic voltammogram of PBDCPDT-FBT in the thin film at a scan rate of 100 mV/s.

Reference

(1) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(2) N. M. O'Boyle, A. L. Tenderholt, K. M. Langner. *J. Comp. Chem.*, **2008**, *29*, 839–845.