

Supporting Information

A Conjugated Polymer Containing a B←N Unit for Unipolar n-Type Organic Field-Effect Transistors

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Experimental details

General. ^1H NMR spectra were measured with a Bruker AV-400 (400 MHz for ^1H NMR) spectrometer in CDCl_3 or C_6D_6 at 25 °C or deuterated 1,1,2,2-tetrachloroethane ($\text{C}_2\text{D}_2\text{Cl}_4$) as solvent at 100 °C. Elemental analysis was performed on a VarioEL elemental analyzer. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a PL-GPC 220-type at 150 °C. 1,2,4-Trichlorobenzene (TCB) was used as the eluent and monodisperse polystyrene was used as the standard. UV/vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer. Thermal analysis was performed on a Perkin-Elmer 7 instrument under nitrogen flow at a heating rate of 20 °C min^{-1} . Atomic force microscopy (AFM) was performed with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source.^[1] Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°–0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. Cyclic voltammetry (CV) was performed on an CHI660a electrochemical workstation using Bu_4NClO_4 (0.1 M) in acetonitrile as electrolyte solution and ferrocene as an internal reference at a scan rate of 50 mV s^{-1} . The CV cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The polymer was casted on the working electrode for measurements. The redox potentials were calibrated with ferrocene as the standard. The HOMO and LUMO energy levels of the materials were estimated by the equations: $E_{\text{HOMO}}/E_{\text{LUMO}} = -(4.80 + E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}})$.

OFET device fabrications and measurements

OFET devices. Top-gate/bottom-contact (TGBC) organic field-effect transistors (OFETs) were fabricated on silicon wafer covered with 300 nm SiO₂. The substrates were first cleaned with double-distilled water, acetone and isopropanol in an ultrasonic bath and then dried under a nitrogen flow. The substrates were heated at 120 °C for 1 hour and finally treated through UV-zone instrument for 15 min. First, Au source/drain electrodes (~25 nm) were deposited on cleaned bare Si/SiO₂ wafer with W/L = 70 (W = 5.6 mm, L = 80 μm). **PBN-13** was first dissolved in hot CB solutions (85 °C, 2 mg/mL) by stirring for 2 hours, and then aging for more than 8 hours. The polymer films were spin-coated on the substrates, followed by thermal annealing at 200 °C for 10 min. Then the solution of 80 mg/mL poly(methylmethacrylate) (PMMA) (product no. 182230 from Aldrich, M_w = 120 kDa) in butyl acetate (~500 nm) as dielectric was deposited by spin coating at 2000 rpm for 2 min and then annealed at 100 °C for 1 h. Finally, Au (~60 nm) was vacuum-deposited as gate electrode. Field-effect mobility was extracted in the saturation regime by using the equation: $I_D^{\text{sat}} = (\mu C_i W/2L)(V_G - V_T)^2$, where I_D is the drain-source current, μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer (dielectric constant of PMMA, 500 nm, 3.6), V_G and V_T are the gate voltage and threshold voltage, respectively.

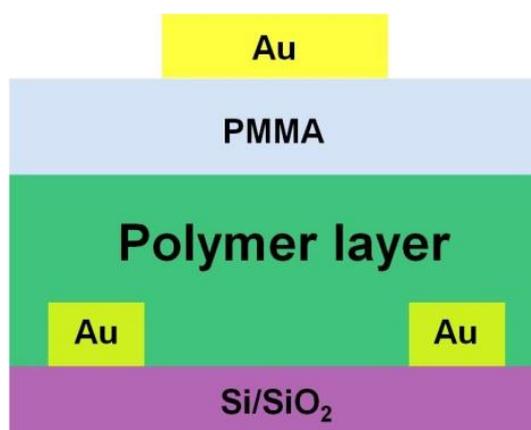
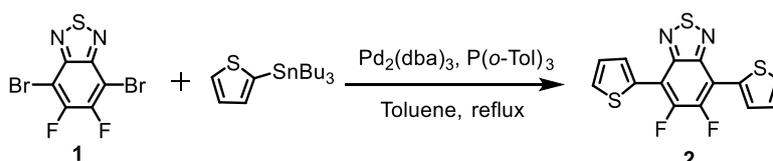


Figure S1. OFET device structure with TGBC geometry.

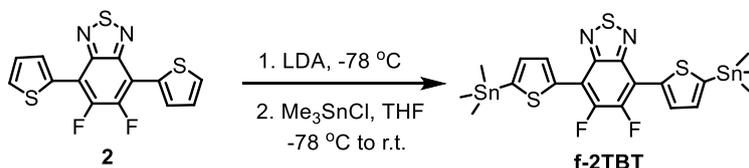
Syntheses and characterizations

All reactions were performed under argon atmosphere according to previous reports. Starting materials, 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole was purchased from Suzhou Rosen Chemical Co., Ltd. and were used without further purification. Toluene, THF and CH₂Cl₂ were dried using sodium or calcium hydride before use. Monomer BNPB was synthesized according to our reported synthesis.^[2] **2** and **f-2TBT** were synthesized according to the previous report.^[3]



5,6-difluoro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **2**:

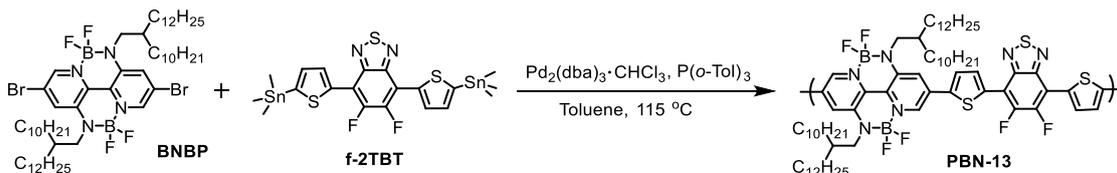
4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole **1** (330.0 mg, 1.0 mmol), tributyl(thiophen-2-yl)stannane (932.9 mg, 2.5 mmol), Pd₂(dba)₃ (36.6 mg, 0.04 mmol), P(*o*-Tol)₃ (24.3 mg, 0.08 mmol) were placed in a three-necked flask under argon. Then dried toluene (12 mL) was added. The mixture was stirred at 120 °C overnight. After cooling down, the mixture was concentrated under reduced pressure to give brown-yellow crude product. The crude product was precipitated in methanol and purified by flash column chromatography on silica gel with chloroform. The product **2** was obtained as orange needle-like crystals by recrystallization in ethanol/chloroform mixture. Yield: 252.0 mg, 75%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.30 (d, *J* = 3.6 Hz, 2H), 7.63 (d, *J* = 5.2 Hz, 2H), 7.28 (d, *J* = 4.4 Hz, 2H). This ¹H NMR spectrum is consistent with that in the previous report.^[3]



5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **f-2TBT**:

Starting materials **2** (200.0 mg, 0.6 mmol) was dissolved in freshly distilled THF (40 mL) under argon. LDA (0.75 mL, 1.5 mmol) was added dropwise at -78 °C, and the solution was kept for 2 h under this temperature. Me₃SnCl (322.8 mg, 1.6 mmol) was then added to the mixture quickly, and the reaction was allowed to warm to room temperature slowly. The

mixture was stirred for 5 h. After adding KF aqueous solution, the mixture was extracted using ether and H₂O. The organic phase was dried using Na₂SO₄, and the crude solid was purified by recrystallization from ethanol and dichloromethane. **f-2TBT** was obtained as an orange solid in 76%. ¹H NMR (400 MHz, C₆D₆): δ (ppm) 8.56 (d, *J* = 3.2 Hz, 2H), 7.31 (d, *J* = 3.2 Hz, 2H), 0.28 (s, 18H). This ¹H NMR spectrum is consistent with that in the previous report.^[3]



Polymer PBN-13: Starting materials of **BNBP** (111.3 mg, 0.1 mmol), **f-2TBT** (66.2 mg, 0.1 mmol), Pd₂(dba)₃CHCl₃ (2.1 mg, 0.002 mmol) and P(*o*-Tolyl)₃ (4.9 mg, 0.016 mmol) were placed in a two-necked flask under argon, and then dried toluene (20 mL) was added. After the mixture being stirred at 120 °C for 6 h, end-capping reaction was carried out by adding bromobenzene (1 mL). After cooling, the gel-like product was completely dissolved in hot CB assisted with strong stirring, and then filtered immediately. The filtrate was concentrated under reduced pressure and dispersed in methanol and then the precipitate was collected. The obtained dark solid was purified by Soxhlet extraction using acetone, hexane and CHCl₃. The residue was dissolved in hot CB solution (ca. 20 mL), and then dispersed in methanol, which were collected and dried in vacuum overnight. Yield: 101.0 mg (79%). ¹H NMR (400 MHz, C₂D₂Cl₄, 100 °C): δ (ppm) 8.23 (broad), 8.07 (broad), 7.56 (broad), 7.26 (broad), 3.60 (s, 4H), 1.86 (s, 2H), 1.32–1.18 (m, 80H), 0.77 (s, 12H). GPC (TCB, polystyrene standard, 150 °C): *M_n* = 72538, PDI = 2.09. Anal. Calcd for C₇₂H₁₀₆B₂F₆N₆S₃ (%): C, 67.06; H, 8.44; B, 1.68; F, 8.84; N, 6.52; S, 7.46. Found: C, 67.26; H, 8.32; N, 6.65.

Thermal properties

The thermal property of **PBN-13** was determined by thermogravimetric analysis (TGA) under N₂ condition. TGA analysis shows the decomposition temperature (T_d) at 5% weight loss of 410 °C for **PBN-13**.

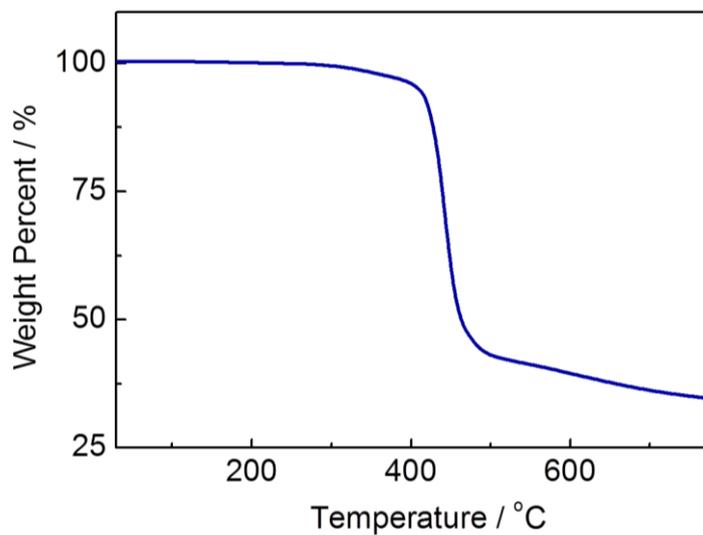


Figure S2. TGA curve of **PBN-13**.

Photophysical properties

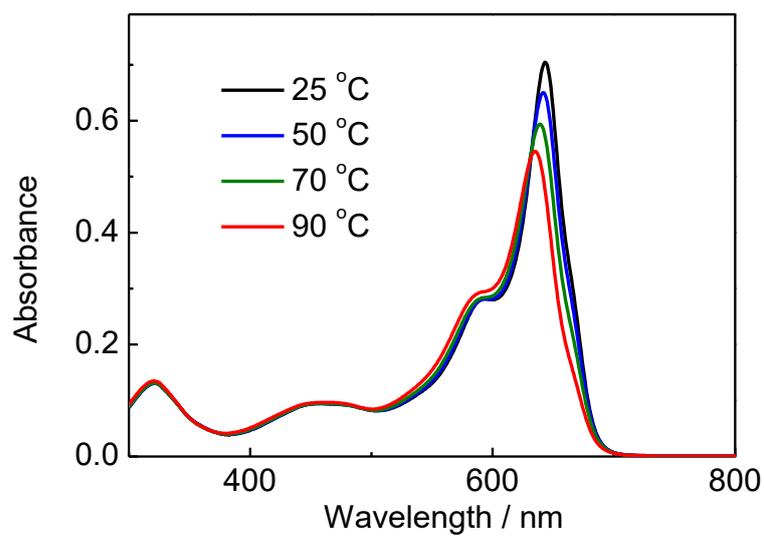


Figure S3. Temperature-dependent absorption spectra of **PBN-13** in CB solution.

Molecular stacking

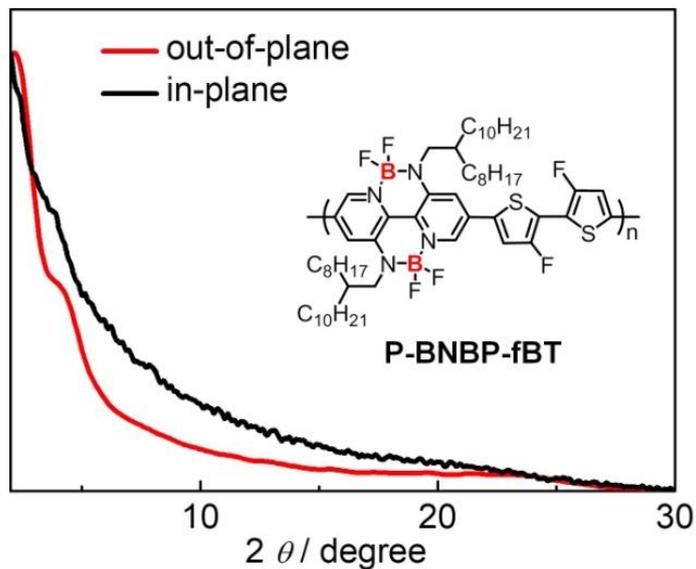


Figure S4. XRD patterns of P-BNBP-fBT ($\mu_e = 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in out-of-plane and in-plane directions.^[4] P-BNBP-fBT film exhibits only a weak (100) diffraction peak at $2\theta = 4.4^\circ$ along the out-of-plane direction in the XRD pattern. No (010) peak is observed in P-BNBP-fBT film along the in-plane direction. It is suggested that P-BNBP-fBT has very weak crystallinity in thin film. This figure is reproduced by permission of The Royal Society of Chemistry.

Electrochemical properties

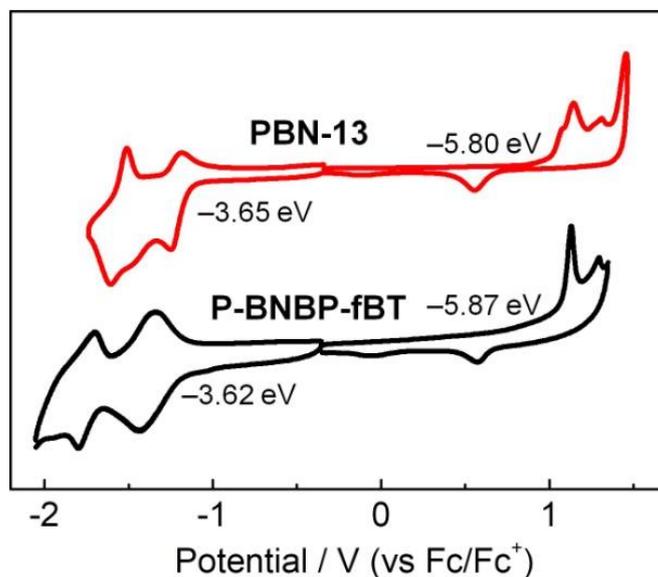


Figure S5. CV curves of **PBN-13** and P-BNBP-fBT.

Table S1. The optoelectronic properties and electron transporting characteristics of the reported BNBP-based semiconductors and **PBN-13** reported in this work.

Polymer	$E_{\text{HOMO/LUMO}}$ (eV)	unipolar	p-channel			n-channel		
			$\mu_{\text{h,max}}$ ($\text{cm}^2 \text{v}^{-1} \text{s}^{-1}$)	$V_{\text{T}}^{[\text{a}]}$ (V)	$I_{\text{on/off}}^{[\text{b}]}$	$\mu_{\text{e,max}}$ ($\text{cm}^2 \text{v}^{-1} \text{s}^{-1}$)	V_{T} (V)	$I_{\text{on/off}}$
P-BNBP-TV ^{T[4]}	-5.69/-3.47	No	0.015	-60 to -70	10^5 - 10^6	0.32	55 to 65	10^5 - 10^7
P-BNBP-B ^{T[4]}	-5.76/-3.52	No	0.0014	-55 to -60	10^0 - 10^1	0.05	60 to 70	10^5 - 10^7
P-BNBP-f ^{BT[4]}	-5.87/-3.62	Yes	/	/	/	0.02	45 to 50	10^4 - 10^5
PBN-13	-5.80/-3.65	Yes	/	/	/	0.19	22 to 28	10^4 - 10^5

^[a]Threshold voltage. ^[b]On/off current ratio.

OFET device characteristics

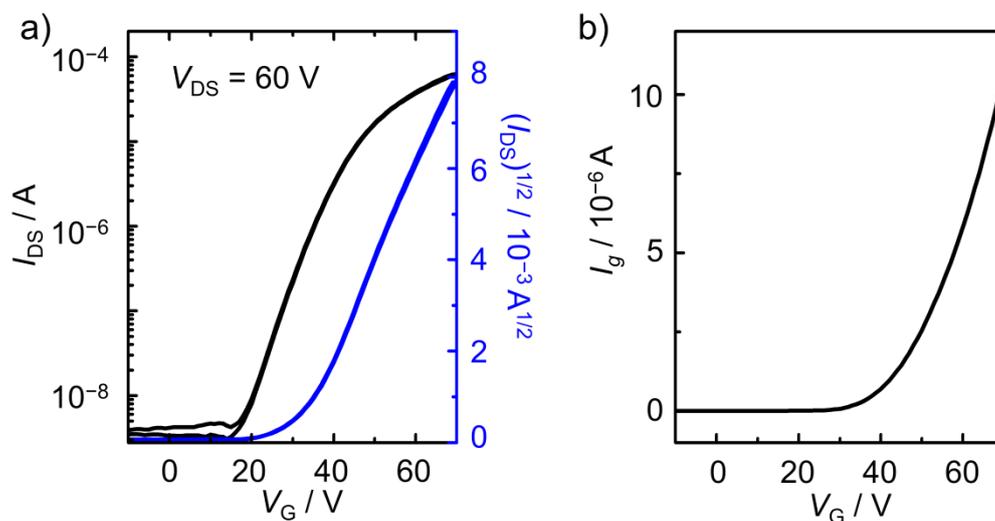


Figure S6. a) The hysteresis for I_{DS} and b) the gate-drain leakage current versus the gate voltage of the OFET device of **PBN-13**.

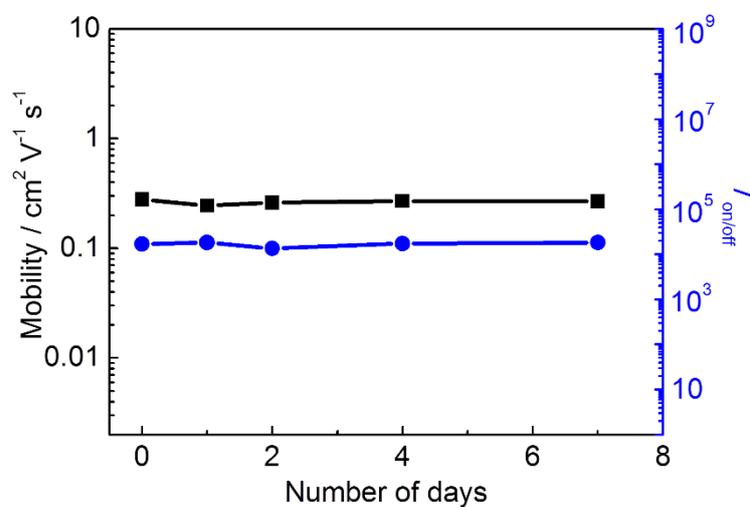


Figure S7. The typical curves of performance versus storage time of the OFET device of **PBN-13**. Less than 5% degradation in electron mobility was observed after storing the device in air for one week, indicating the high stability of the device.

¹H NMR spectra

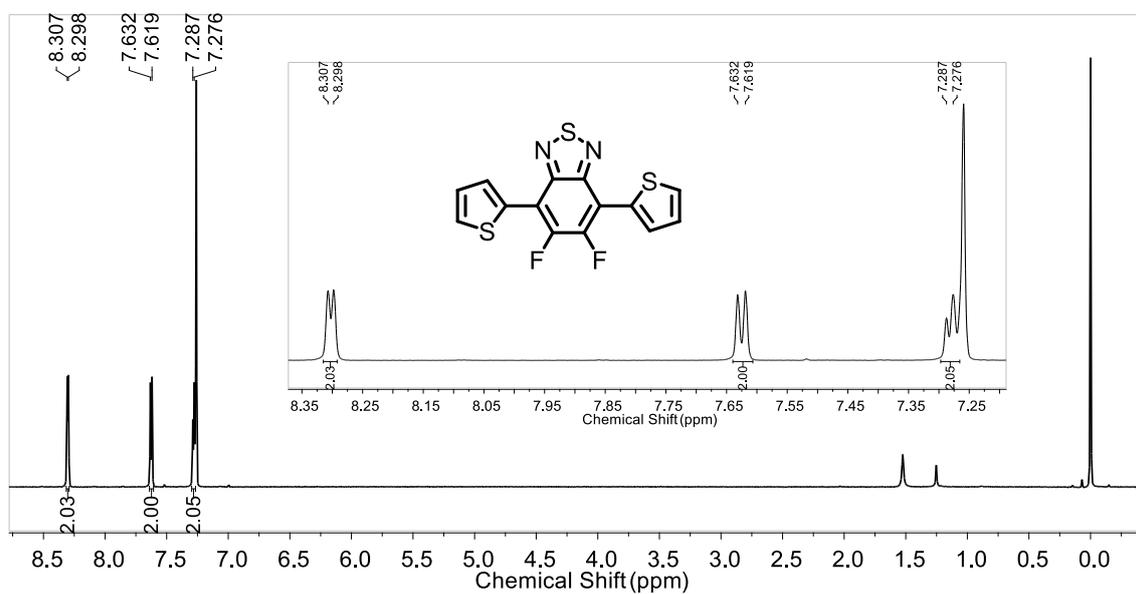


Figure S8. ¹H NMR spectrum of **2**.

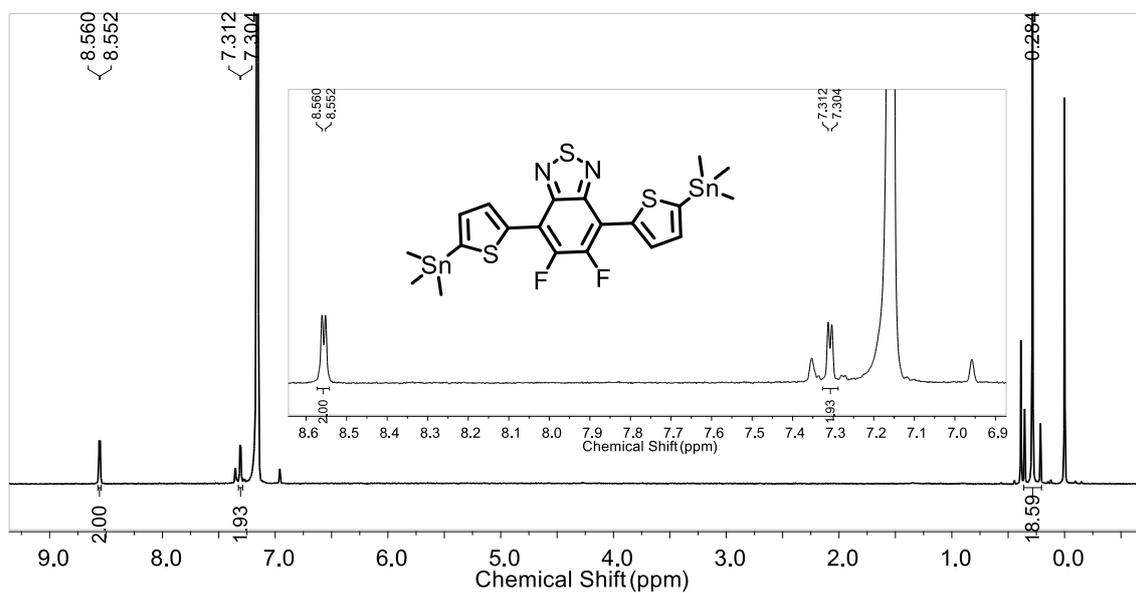


Figure S9. ¹H NMR spectrum of **f-2TBT**.

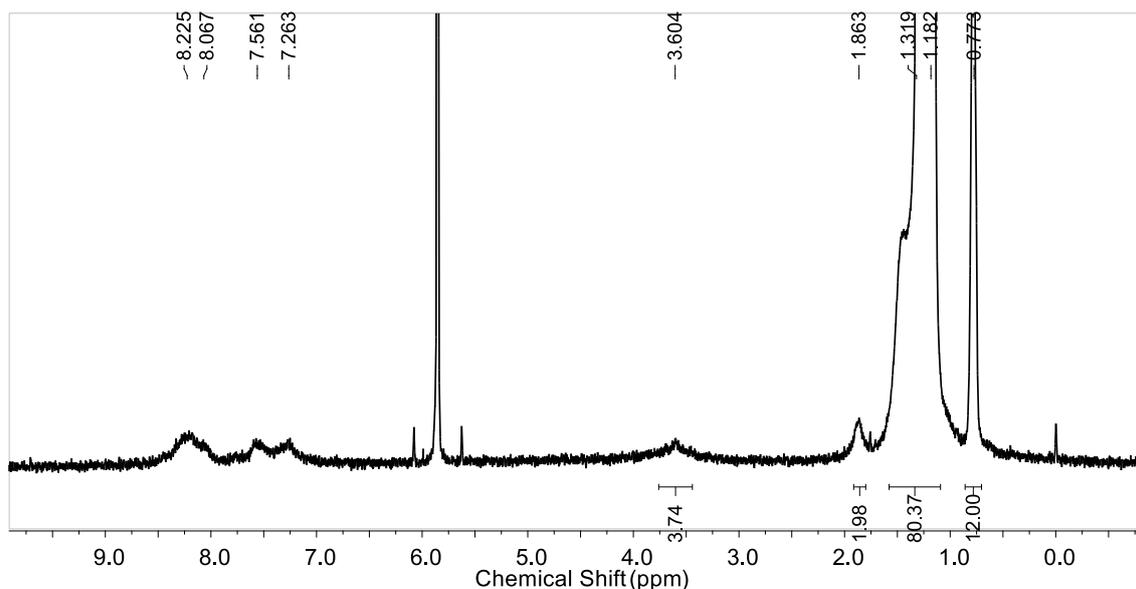


Figure S10. ^1H NMR spectrum of **PBN-13**.

References

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- (3) Hu, H.; Jiang, K.; Yang, G.; Liu, J.; Li, Z.; Lin, H.; Liu, Y.; Zhao, J.; Zhang, J.; Huang, F.; Qu, Y.; Ma, W.; Yan, H. Terthiophene-Based D–A Polymer with an Asymmetric Arrangement of Alkyl Chains That Enables Efficient Polymer Solar Cells. *J. Am. Chem. Soc.* **2015**, *137*, 14149–14157.
- (4) Long, X.; Gao, Y.; Tian, H.; Dou, C.; Yan, D.; Geng, Y.; Liu, J.; Wang, L. Electron-Transporting Polymers Based on a Double B \leftarrow N Bridged Bipyridine (BNBP) Unit. *Chem. Commun.* **2017**, *53*, 1649–1652.