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Bifunctional donor polymers bearing amino pendant groups for efficient cathode interlayer-free polymer solar cells

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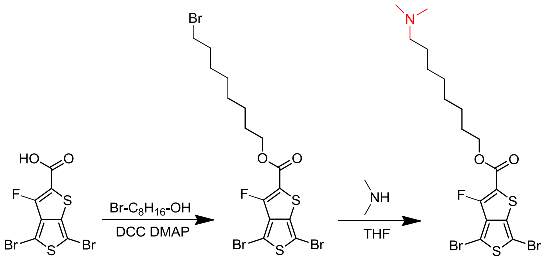
Materials and methods.

The acceptor (6,6)-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) was purchased from Solarmer Materials Inc. Intermediate materials were purchased from Adamas, Aldrich, and Alfa and used without any further purification. ^1H and ^{13}C NMR spectra were measured on a Bruker 400 MHz AVANCE III with tetramethylsilane as an internal reference. Molecular weights of the polymers were determined by GPC with polystyrene as standard and tetrahydrofuran as eluent. UV-Vis absorption spectra were recorded on a Cary 5000 UV-VIS-NIR spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI600D electrochemical workstation at a scan rate of 50 mV s^{-1} with an Ag/AgCl as the reference electrode. Ultraviolet photoelectron spectroscopy (UPS) characterizations were carried out with monochromatized HeI radiation at 21.22 eV in ultra-high vacuum. The polymer thin films were spin coated onto ITO glass. The highest occupied molecular orbital (HOMO) values were here defined as the vertical ionization potential derived from UPS. The tapping-mode AFM images were obtained by using a scanning probe microscope on a Bruker Metrology Nanoscope II-D. Photoluminescent (PL) spectra were recorded on a FLS920 spectrophotometer. The charge carrier mobilities were deduced from the space-charge-limited current (SCLC) measurements. The influences of amino groups on the surface potential thus work function (WF) of the active layer film were studied by scanning Kelvin probe microscopy (SKPM). Each value was calculated relative to the highly oriented pyrolytic graphite (HOPG), which was given a reference value of 4.60 eV.

Synthetic details.

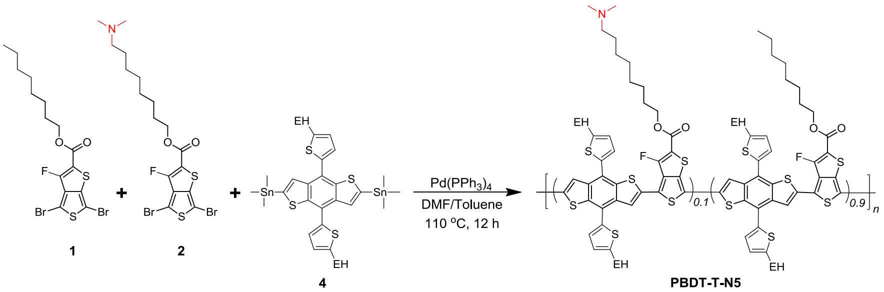
The monomers **1** and **3** in the paper (Scheme 1) were synthesized according to the literature procedures.[1,2] The monomer **2** and the polymer PBDT-T-N5 were synthesized as below.



TT-COOH **TT-Br** **2**

Synthesis of compound TT-Br: In a 100 mL 3-neck flask, compound TT-COOH (1 g, 2.78 mmol), N,N'-dicyclohexylcarbodiimide (DCC, 0.74 g, 3.17 mmol), and 4-dimethylaminopyridine (DMAP, 0.14 g, 0.95 mmol) were dissolved in CH_2Cl_2 (30 mL) under nitrogen atmosphere. Then 8-bromo-1-octanol (2.4 mL, 14 mmol) was added. The mixture was kept at room temperature and stirred for 20 h. After that, 100 mL H_2O was added and the solution was extracted with CH_2Cl_2 for three times. The organic layer was separated and dried over anhydrous $MgSO_4$. After removing the solvent, the crude product was purified by silica gel column chromatography with CH_2Cl_2:hexane (1:1) as eluent. The compound TT-Br was obtained as an orange solid. (0.58 g, 53%) ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.32 (s, 2H), 3.41 (s, 2H), 1.87 (m, 2H), 1.75 (m, 2H), 1.50~1.25 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.83, 150.17, 147.37, 118.57, 102.22, 99.34, 65.97, 34.15, 28.97, 28.60, 28.46, 28.06, 25.75.

Synthesis of monomer ***2***: To a solution of the compound TT-Br (0.3 g, 0.55 mmol) in THF (10 mL) was added dimethylamine (2.7 mL, 5.4 mmol, 2M in THF) in one portion at room temperature and the reaction was heated to 70 °C and stirred for 24 h. CH_2Cl_2 (50 mL), 1M NaOH, and water (20 mL) were added and stirred for 10 min. Then the mixture was extracted with CH_2Cl_2. The organic layer was separated and dried over anhydrous $MgSO_4$. After removing the solvent, the crude product was purified by silica gel column chromatography with CH_2Cl_2:hexane (1:1) as eluent. The monomer **2** was obtained as an orange liquid (0.26 g, 80%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.25 (s, 2H), 3.41 (s, 2H), 2.96 (s, 6H), 1.87 (m, 2H), 1.75 (m, 2H), 1.50~1.25 (m, 8H).



Synthesis of PBDT-T-N5: The polymer PBDT-T-N5 was synthesized according to the same procedure as that of the PBDT-Nx in the paper. The monomers **1** (0.0546 g, 0.116 mmol), 2 ((0.007 g, 0.0129 mmol), and 4 (0.116 g, 0.129 mmol) were used. Yield: 0.0683 g, 75%. Mn=43.1 kg mol^{-1}; Mw=76.1 kg mol^{-1}.

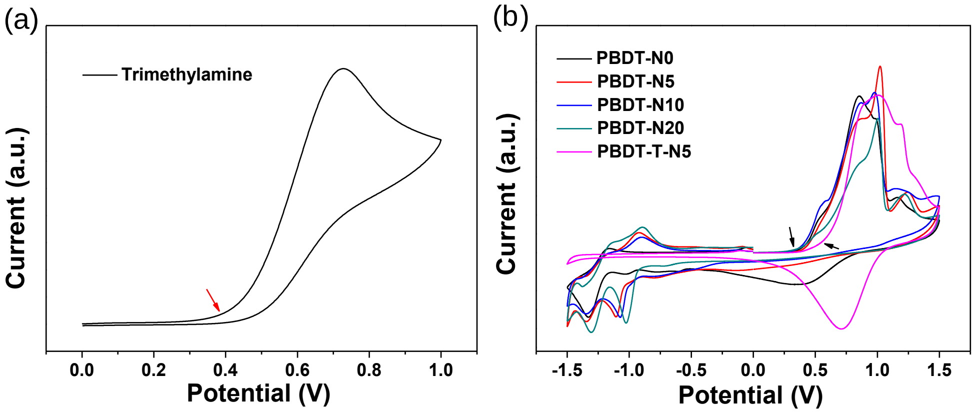


Fig. S1 Cyclic voltammetry (CV) curves of trimethylamine (a) and polymers (b). The HOMO and LUMO energy levels were estimated based on the onset potentials and the empirical formulas E_{HOMO}=-(E_{ox}+4.8-E_{Fc}) eV and E_{LUMO}=-(E_{red}+4.8-E_{Fc}) eV, where the E_{Fc}=0.05 eV.

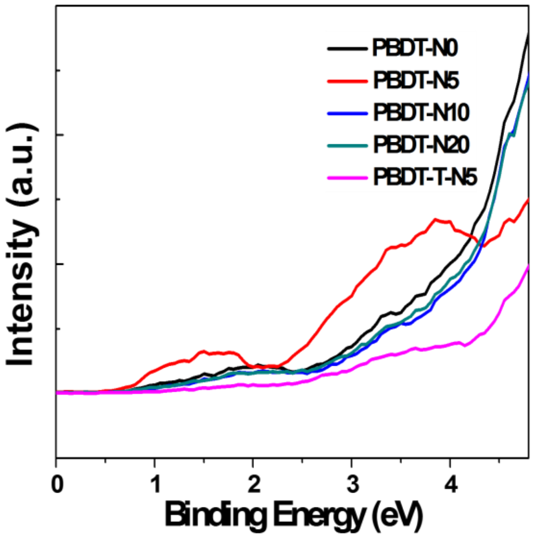


Fig. S2 UPS Fermi edge spectra of PBDT-Nx and PBDT-T-N5 polymers. The Fermi edge was used to calculate the HOMO level.

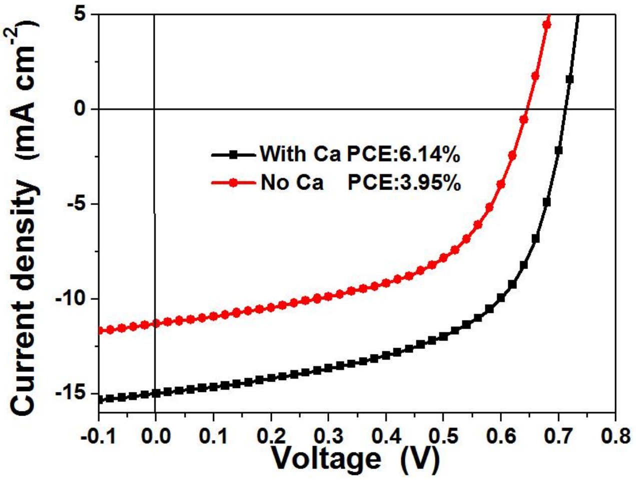


Fig. S3 J-V cures of PBDT-N0-based devices with and without Ca as the CIL.

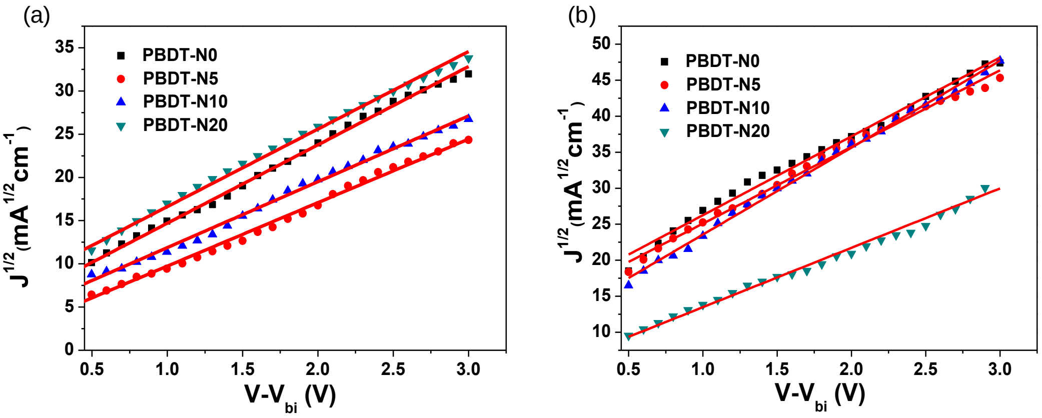


Fig. S4 $J^{1/2}$-V fitting results of the hole-only (a) and electron-only (b) devices based on PBDT-Nx:PC$_{71}$BM measured by the SCLC method. The device structures for the measurement of hole and electron mobilities were ITO/PEDOT:PSS/PBDT-Nx:PC$_{71}$BM/MoO$_3$/Au and ITO/Al/PBDT-Nx:PC$_{71}$BM/Al, respectively.

Table S1. Hole and electron mobilities of the PBDT-Nx:PC$_{71}$BM blend films.

Samples	Hole mobility (cm^2 V^{-1} s^{-1})	Electron mobility (cm^2 V^{-1} s^{-1})
PBDT-N0:PC$_{71}$BM	3.1×10^{-5}	5.0×10^{-5}
PBDT-N5:PC$_{71}$BM	3.6×10^{-5}	5.8×10^{-5}
PBDT-N10:PC$_{71}$BM	3.7×10^{-5}	6.6×10^{-5}
PBDT-N20:PC$_{71}$BM	2.9×10^{-5}	3.0×10^{-5}

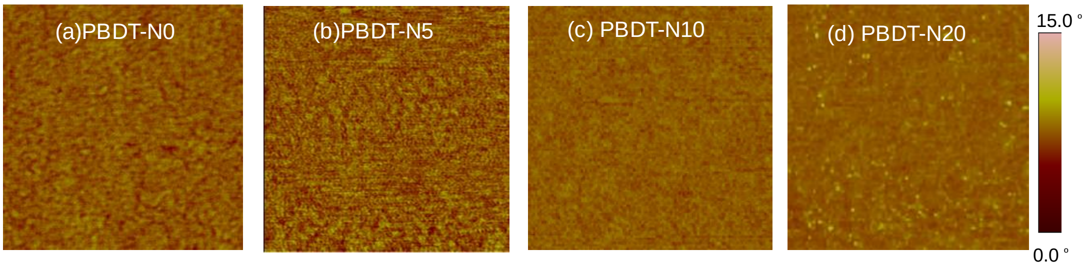


Fig. S5 AFM phase images (1 μm×1 μm) of the PBDT-Nx:PC$_{71}$BM films.

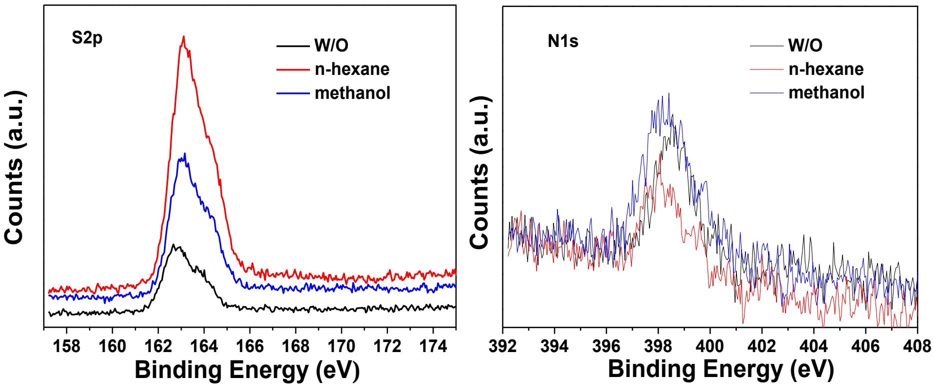


Fig. S6 XPS results based on PBDT-N5:PC$_{71}$BM blend films with different solvent treatments.

Table S2. XPS results based on PBDT-N5:PC$_{71}$BM blend films after different solvent treatments.

Atomic ratio	N	S	N/S
None	0.018	0.039	0.46
N-hexane	0.018	0.071	0.26
Methanol	0.026	0.043	0.60

Table S3. EDX results based on PBDT-N5:PC$_{71}$BM blend films after different solvent treatments.

Atomic ratio	N	S
None	0.009	0.0071
N-hexane	0	0.0066
Methanol	0.0121	0.0056

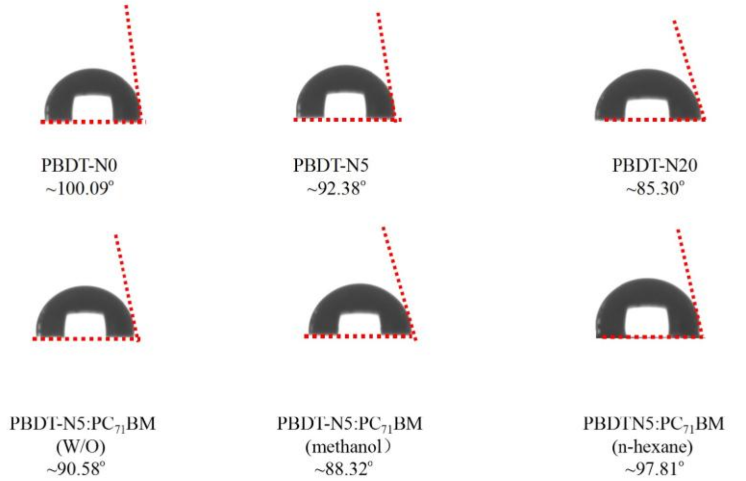


Fig. S7 Water contact angle measurements of PBDT-Nx polymers and their blend films with PC$_{71}$BM after different solvent treatments.

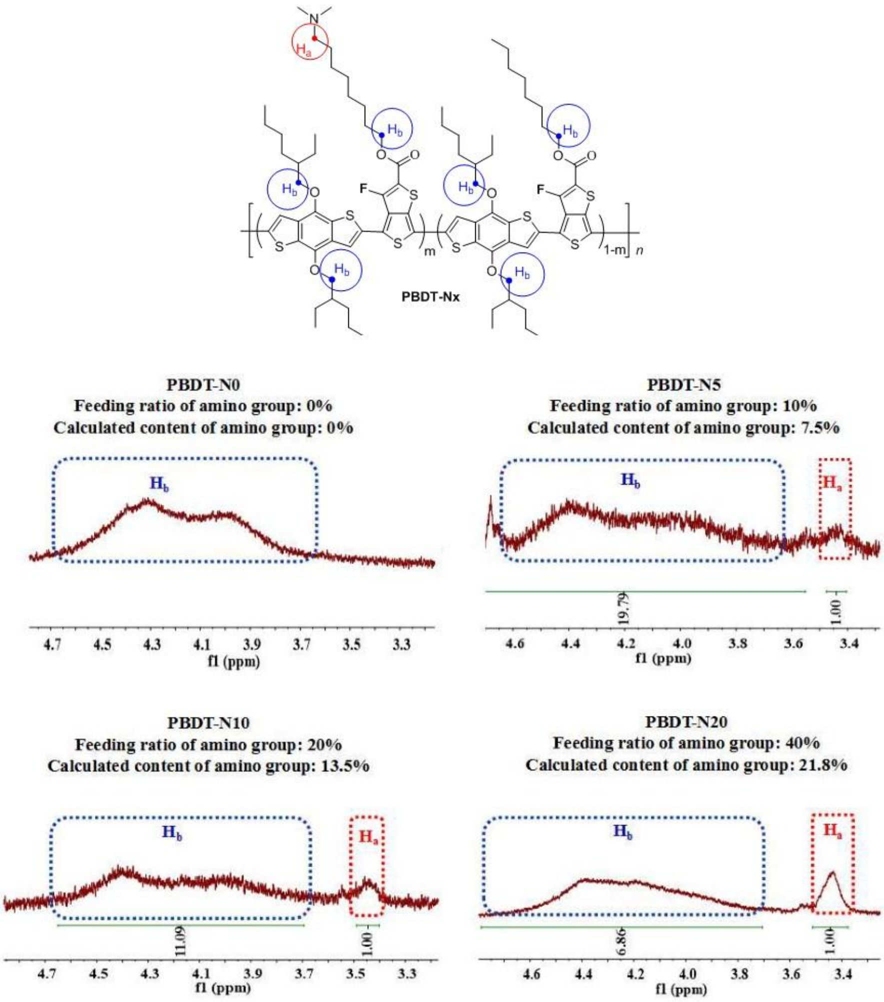


Fig. S8 ^{1}H NMR spectra of PBDT-Nx for calculating the actual content of amino group in polymer. Calculated content of amino group=3×(Integral area of H$_a$)/2×(Integral area of H$_b$+H$_a$).

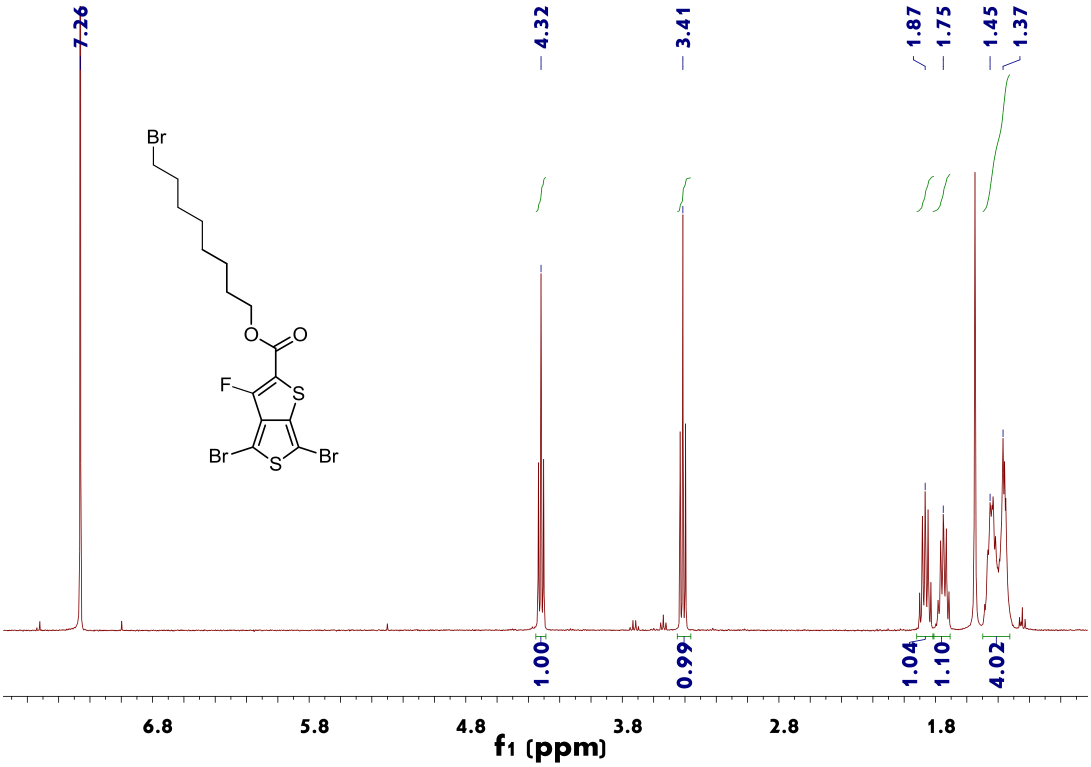


Fig. S9 ^{1}H NMR spectrum of compound TT-Br.

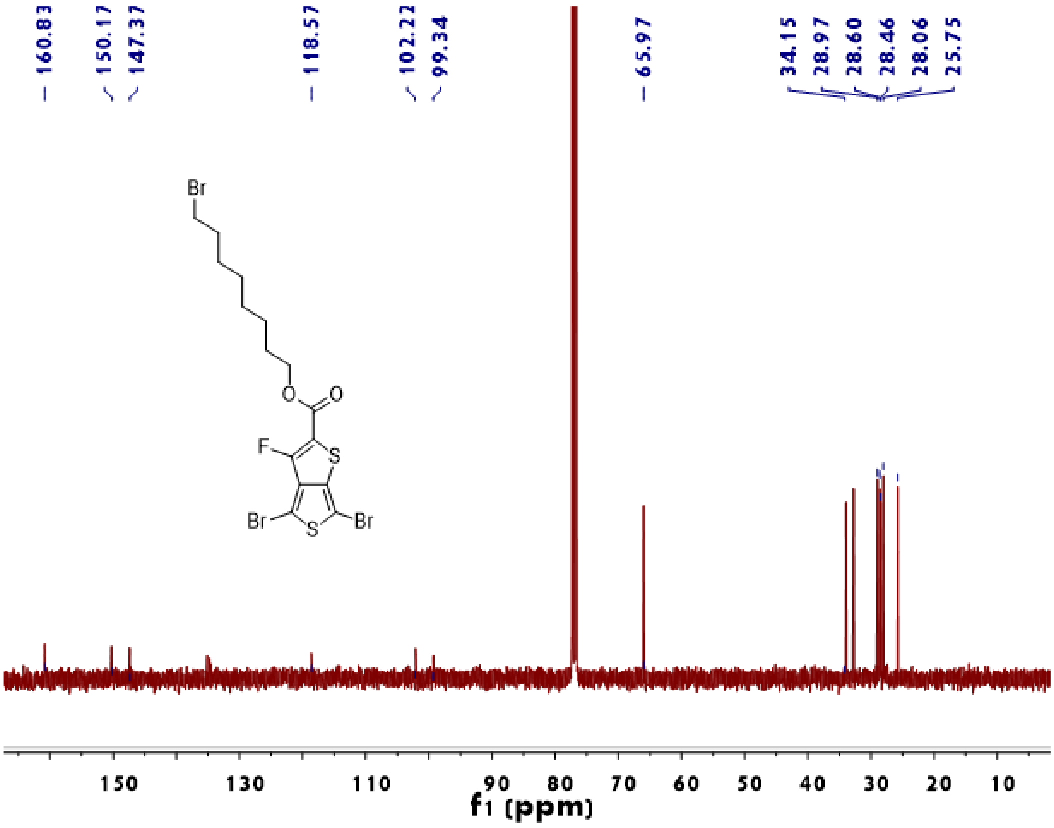


Fig. S10 ^{13}C NMR spectrum of compound TT-Br.

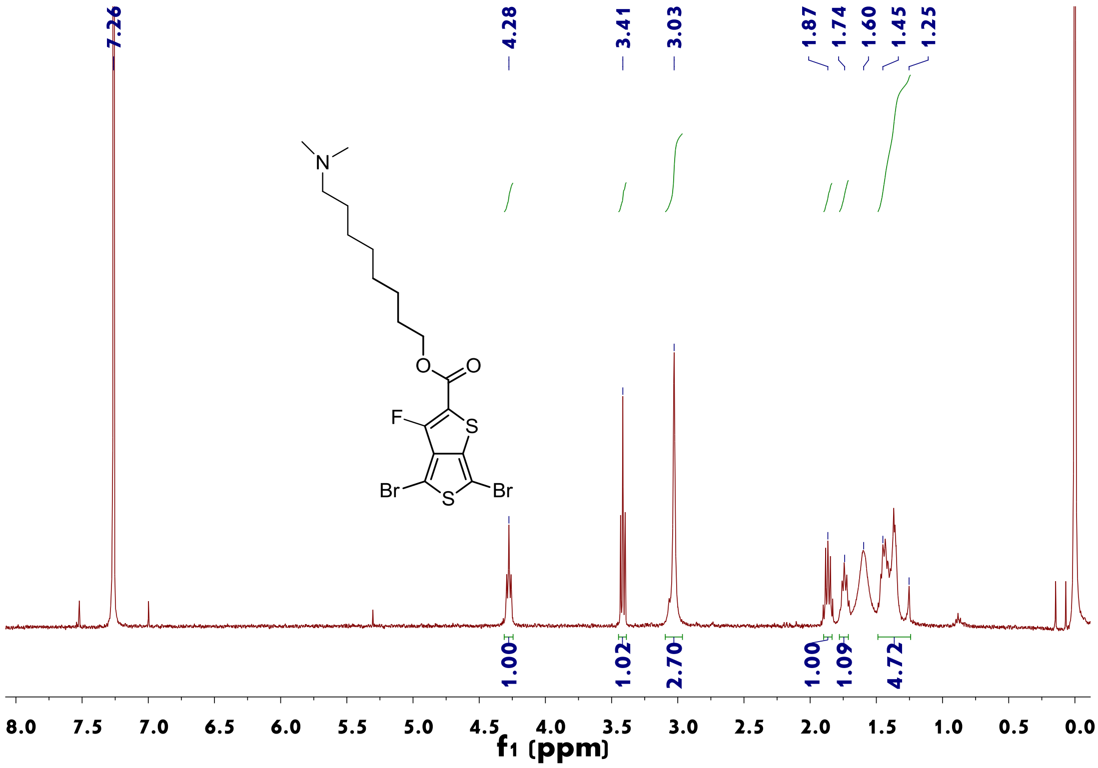


Fig. S11 ^{1}H NMR spectrum of monomer **2**.

References:

1. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, Adv. Mater. 2010, 22 , E135.

2. C. Cui, W.-Y. Wong, Y. Li, Energy Environ. Sci. 2014, 7, 2276.