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Electronic Supplementary Information for

PTB7-based narrow band-gap conjugated polyelectrolyte as efficient cathode interlayer in PTB7-based polymer solar cells

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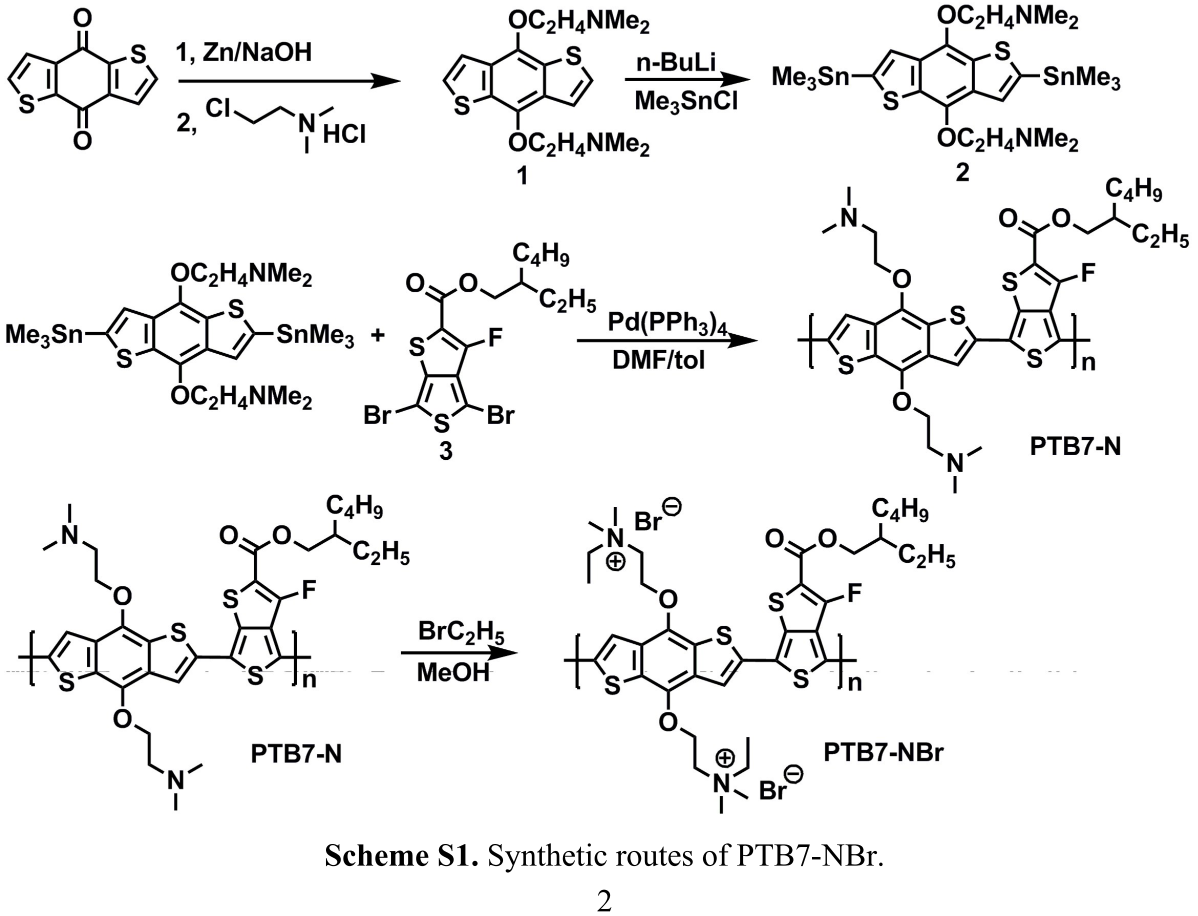
Experimental part

Materials: Donors PTB7 and PTB7-Th were purchased from 1-Material Chemscitech Incorporated. (6,6)-Phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) and benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione were purchased from American Dye Source Incorporated and Derthon Optoelectronic Materials Science Technology Co LTD (Shenzhen, China) respectively. Other intermediate materials were purchased from Energy Chemical without further purification.

Device fabrication and characterization: Patterned ITO/glass substrates were cleaned stepwise by sonication in detergent, deionized water, acetone and isopropyl alcohol for 20 min each and dried in a nitrogen stream, followed by a UV ozone treatment. Then poly (3,4-ethylenedioxythiophene):(polystyrene sulfonic acid) (PEDOT:PSS) (Baytron P VP A1 4083) was spin-coated and subsequently baked at 140 °C for 15 min. Quickly the substrates were transferred to a nitrogen-filled glovebox and a photoactive layer of PTB7 or PTB7-Th/$PC_{71}BM$ (10:15, w/w) was spin-coated from chlorobenzene solution with 3% (v) 1,8-diiodooctane. Various thickness of PTB7-NBr layer was deposited on the photoactive layer by spin-coating of various concentration of PTB7-NBr methanol or CF_3CH_2OH solution at 5000 rpm for 1 min. Finally, a 100 nm Al layer was evaporated through a shadow mask to define the active area as 0.06 cm^2. The electron-only devices were fabricated with a similar procedure with ITO/ZnO/photoactive layer/cathode interlayer/Al architecture. The cathode Al thickness was monitored upon deposition by using a crystal thickness monitor (Sycon). The current-voltage (*J-V*) characteristics were recorded using a Keithley 2400 source meter under an AM1.5G solar simulator. The light intensity was calibrated by a standard silicon solar cell from National Renewable Energy Laboratory (NREL).

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 400 MHz AVANCE Ⅲ with tetramethylsilane as an internal reference. UV-vis absorption spectra were recorded on a mapada UV-3300 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 electrode reference electrode and an argon saturated anhydrous acetonitrile solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte. PTB7-NBr films for UV-vis absorption and CV were coated from its methanol solution. The tapping-mode AFM images were obtained by using a scanning probe microscope (Dimension3100V). Ultraviolet photoelectron spectroscopy (UPS) were carried out in a Multifunctional X-ray Photoelectron Spectroscope (Kratos AXIS ULTRA DLD) using a He I (21.22 eV) discharge lamp.

Synthesis



Scheme S1. Synthetic routes of PTB7-NBr.

4,8-Bis(4-(2-(dimethylamino)ethoxy))benzo[1,2-b:4,5-b']dithiophene (1): Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (1.00 g, 4.5 mmol) was suspended in a mixture of ethanol (4 mL) and NaOH aqueous solution (15 mL, 20%) in a round flask. Zinc dust (0.65 g, 10.0 mmol) was added slowly and the mixture was refluxed for 1 h. Dilute hydrochloric acid was added to neutralize the mixture and the resulting precipitate was filtered, washed with water for 3 times and dried under vacuum. Then the crude intermediate phenol derivative was dissolved in tetrahydrofuran (THF, 20 mL), followed by successive addition of NaOH (3.60 g, 9.0 mmol) and 2-chloro-*N,N*-dimethylethyl-1-amine hydrochloride (2.59 g, 18.0 mmol). The mixture was then refluxed for 2 day in a nitrogen atmosphere. After cooling down to room temperature, the mixture was neutralized with hydrochloric acid and extracted with dichloromethane. The organic phase was dried with Na_2SO_4, filtrated, and evaporated by rotatory evaporator. Colum chromatography on silica gel using dichloromethane:methanol:triethylamine mixture as eluents yielded the compound 1 (1.34 g, 76%) as a light yellow solid. ^{1}H NMR (400 MHz, MeOH-d_4, δ, ppm): 7.55 (s, 4H), 4.37 (t, 4H, J = 5.6 Hz), 2.87 (t, 4H, J = 8.4 Hz), 2.41 (s, 12H). ^{13}C NMR (100 MHz, MeOH-d_4, δ, ppm): 144.20, 131.56, 130.14, 126.46, 119.75, 70.84, 58.75, 44.56.

2,6-Bis(trimethyltin)-4,8-di(4-(2-(dimethylamino)ethoxy))benzo[1,2-b:4,5-b']dithiophene (2): To a round flack compound 1 (393 mg, 0.1 mmol) was added and the flask was subjected to three successive cycles of vacuum followed by refilling with nitrogen. Anhydrous THF (10 mL) was added and the flask was cooled down to -78 °C by a low-temperature stirring reaction bath. *n*-Butyllithium solution (0.9 mL, 2.5 M) was added dropwise via a syringe with stirring. After reaction for 1 h, trimethyltin chloride solution (2.5 mL, 1.0 M) was added and was stirred at room temperature overnight. The reaction mixture was then quenched with water and extracted with dichloromethane three times. The organic phase was combined, washed with brine, dried over Na_2SO_4, and filtered. The solvent was evaporated by rotatory evaporator, yielding the crude product 2 (642 mg, 89%). The crude product was used directly in the next step without further purification. ^{1}H NMR (400 MHz, MeOH-d_4, δ, ppm): 7.54 (s, 2H), 4.73 (t, 4H, J = 4.0 Hz), 3.44 (br, 4H, J = 8.4 Hz), 2.97 (s, 12H), 0.48 (s, 18H).

Poly[(4-(2-(dimethylamino)ethoxy))benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-ethylhexyl-3-fuorothithieno[3,4-b]thiophene-2-carboxylate-4,6-diyl] (PTB7-N): To a schlenk tube compound 2 (625 mg, 0.87 mmol), octyl 4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (410 mg, 0.87 mmol), and tetrakis(triphenylphosphine)palladium (30 mg, 3% eq) were added. The tube was subjected to three successive cycles of vacuum followed by refilling with nitrogen and then toluene (8.0 mL) and *N,N*-dimethylformamide (2.0 mL) were added. The mixture was then heated to 110 °C for 48 h with stirring under nitrogen atmosphere. After cooling down to room temperature, the mixture was poured into methanol and the precipitate was filtered. The residue was then wash successively with petroleum ether, acetone, and chloroform. The chloroform solution was concentrated and precipitated by petroleum ether. The precipitate was filtered and dried in vacuum for 8 h to afford polymer PTB7-N (550 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.59 (br, 2H), 4.44 (br, 6H), 3.00-2.00 (br, 16H), 1.57-0.75 (br, 15H). GPC: Mw (19.3x10^3 g/mol), PDI (1.32).

PTB7-NBr: To a round flask PTB7-N (57 mg, 0.081 mmol), bromoethane (0.7 mL, 8.1 mmol), and THF (10 mL) were added. The solution was stirred at 80 °C for 8 h and then methanol (10 mL) was added. After maintaining at 80 °C for 3 day, the reaction mixture were poured into acetone. The precipitate was filtered, washed successively with flash acetone and THF, and dried to afford PTB7-NBr (60 mg, 87%). 1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.25-7.50 (br, 2H), 5.00-4.00 (br, 6H), 4.00-3.00 (br, 20 H), 2.00-0.75 (br, 21H).

Table S1 Device parameters of PTB7-Th devices with methanol or CF_3CH_2OH treatment.

Solvent	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	PCE [%]
MeOH	0.64^a (0.65^b)	16.66 (16.17)	59.13 (58.72)	6.35 (6.15)
CF_3CH_2OH	0.79 (0.79)	16.00 (15.23)	61.27 (62.48)	7.79 (7.49)

^{a}The optimal value; ^{b}average value calculated from six devices.

Table S2 Device parameters of PTB7-Th devices with active area of 1 x 1 cm^2.

Interlayer	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	PCE [%]
PTB7-NBr	0.81^a (0.81^b)	14.35 (14.26)	55.69 (55.68)	6.49 (6.44)
CF_3CH_2OH	0.75 (0.74)	14.11 (14.10)	48.54 (48.42)	5.14 (5.08)
None	0.64 (0.64)	14.31 (14.05)	42.79 (42.69)	3.94 (3.82)

^{a}The optimal value; ^{b}average value calculated from four devices.

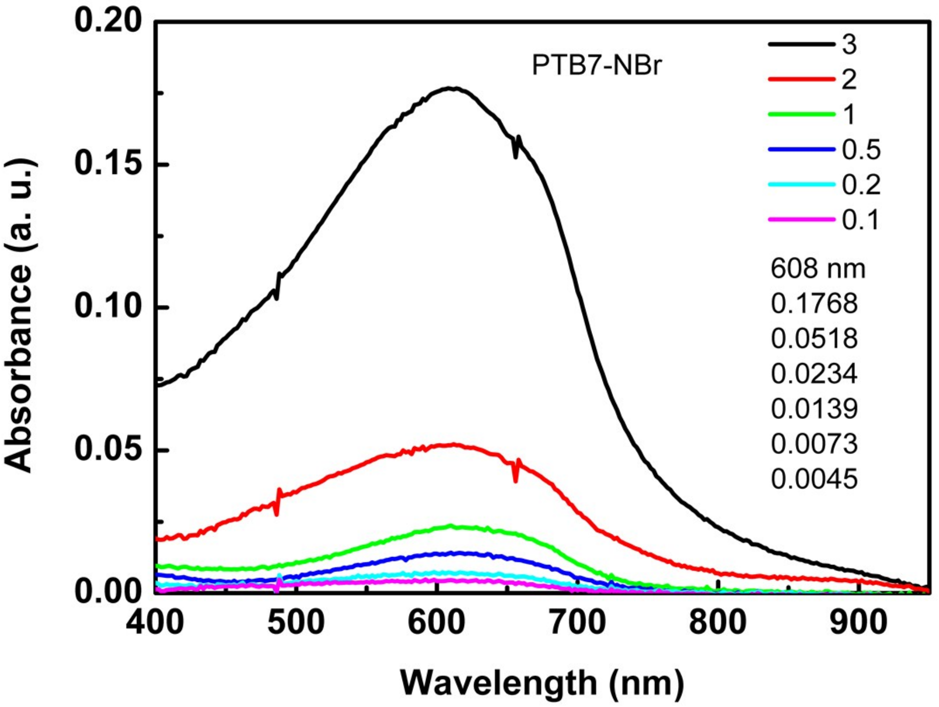


Fig. S1 UV-vis absorption spectra of PTB7-NBr films spin-coated from different concentration of its solution at 5000 rpm for 60 s. The thickness of PTB7-NBr of 3 mg/mL was determined to be about 35 nm by a profilometer, and the thickness of other concentration PTB7-NBr was estimated by an absorbance-thickness curve assuming a linear dependence of the absorbance at 608 nm on thickness.

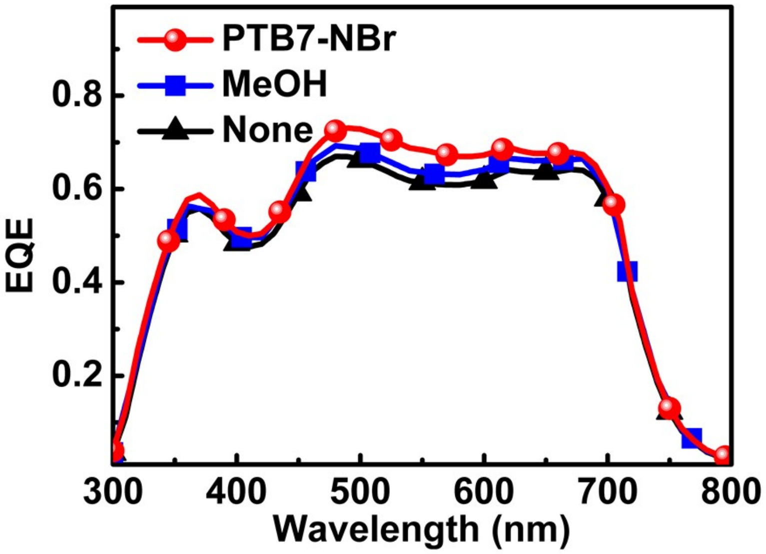


Fig. S2 the corresponding EQE spectra of PTB7 devices with PTB7-NBr CIL and solvent treatment.

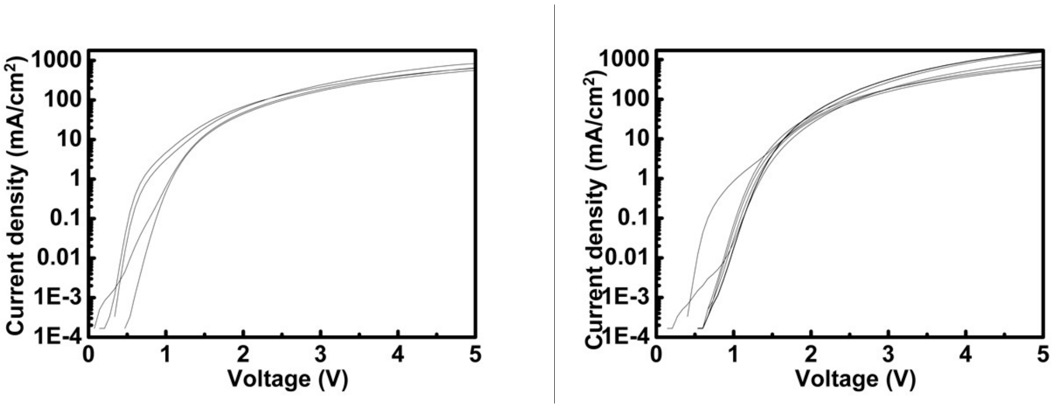


Fig. S3 *J-V* curves of the electron-only devices of ITO/ZnO/PTB7-Th:PC$_{71}$BM/CF$_3$CH$_2$OH (left) or PTB7-NBr (right)/Al.

The apparent electron mobilities were determined by fitting the *J-V* curves with a field-dependent mobility equation, given as:

$$J = \left(\frac{9}{8}\right)\varepsilon_0\varepsilon_r\mu\left(\frac{V^2}{L^3}\right)$$

Where J is the current density, μ is the electron mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the materials (typically assumed to be 3 for organic semiconducting materials), L the film thickness, and V the effective voltage.

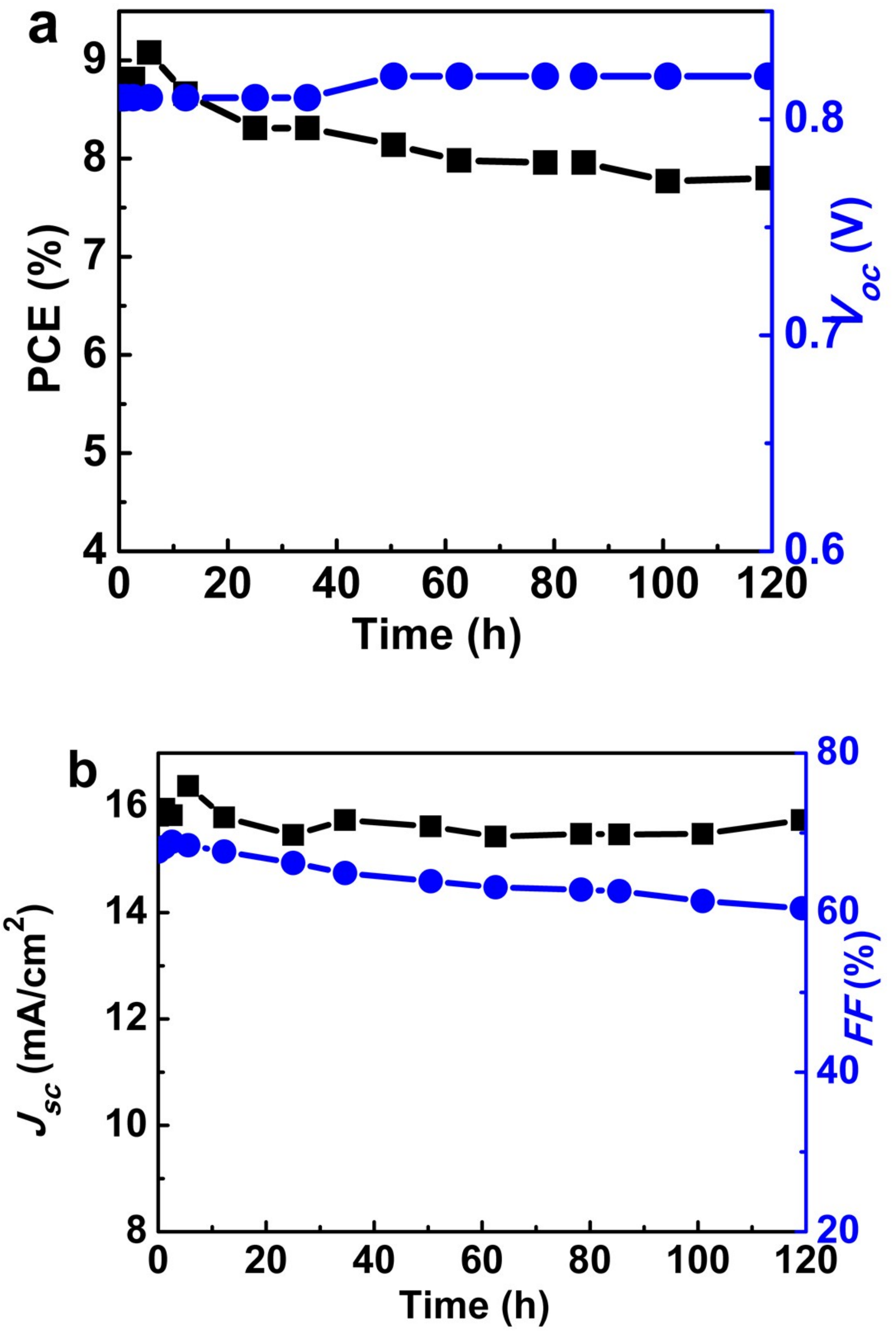


Fig. S4 Degradation profile of the PTB7-Th device with PTB7-NBr as a function of storage time in glove box.

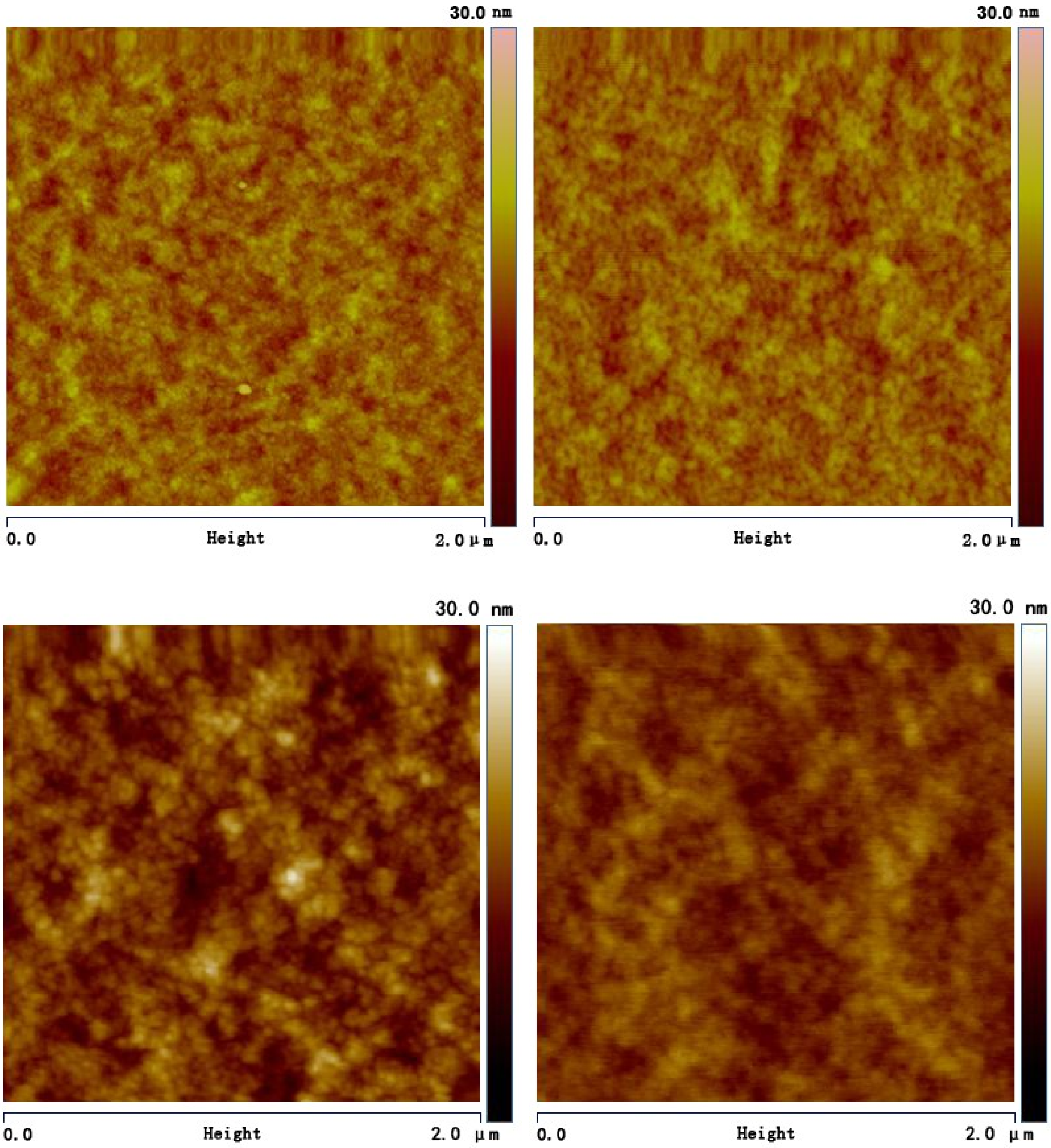


Fig. S5 Tapping-mode AFM height images of the PTB7: $PC_{71}BM$ film (up) PTB7-Th:$PC_{71}BM$ film (down) after spin-coating solvent (left, RMS = 1.60 and 2.18 nm respectively) or PTB7-NBr film (right, RMS = 1.54 and 1.76 nm respectively).

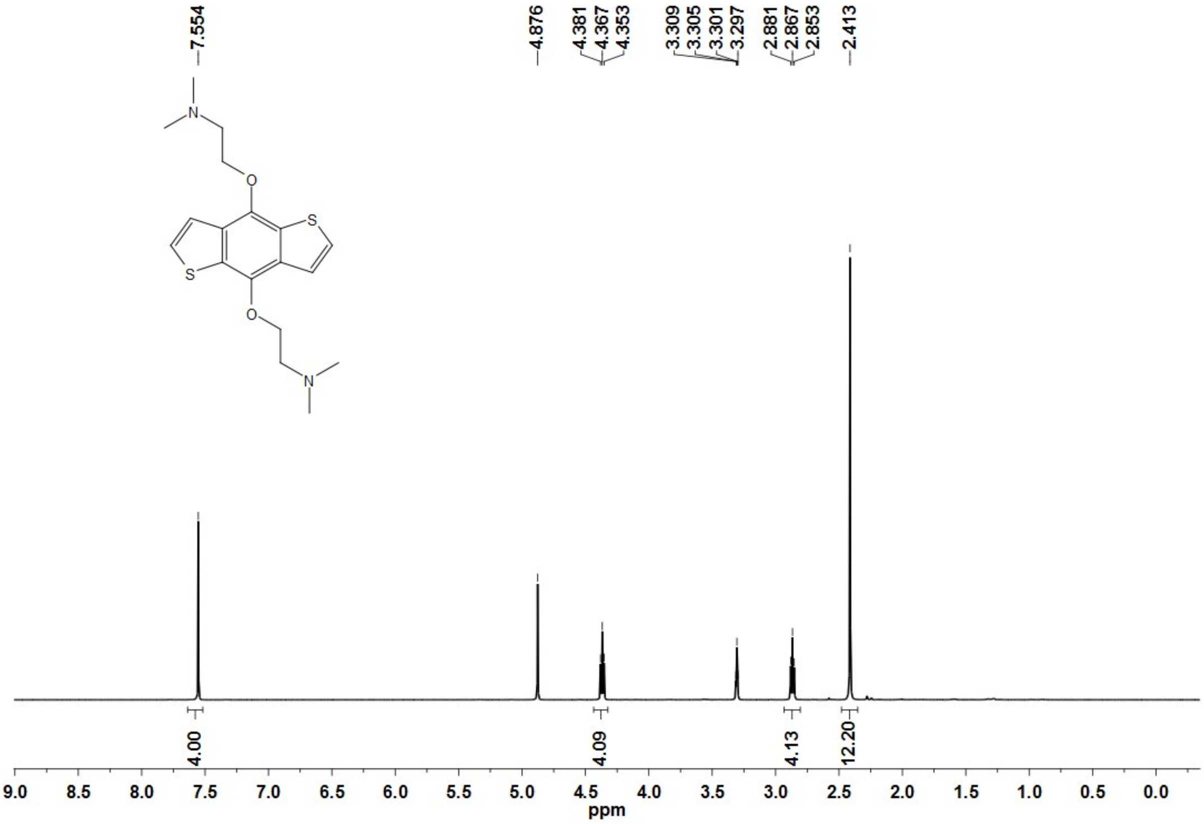


Fig. S6 ^{1}H NMR spectra of compound 1.

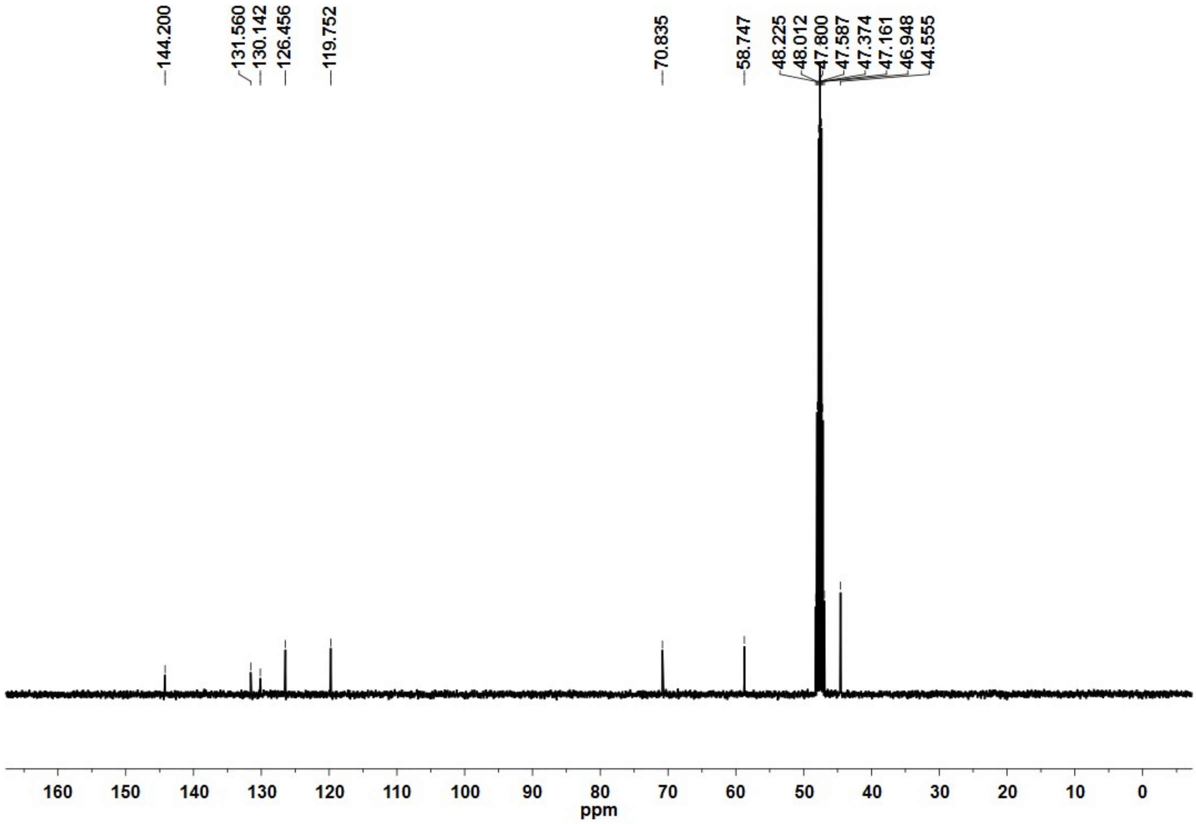


Fig. S7 ^{13}C NMR spectra of compound 1.

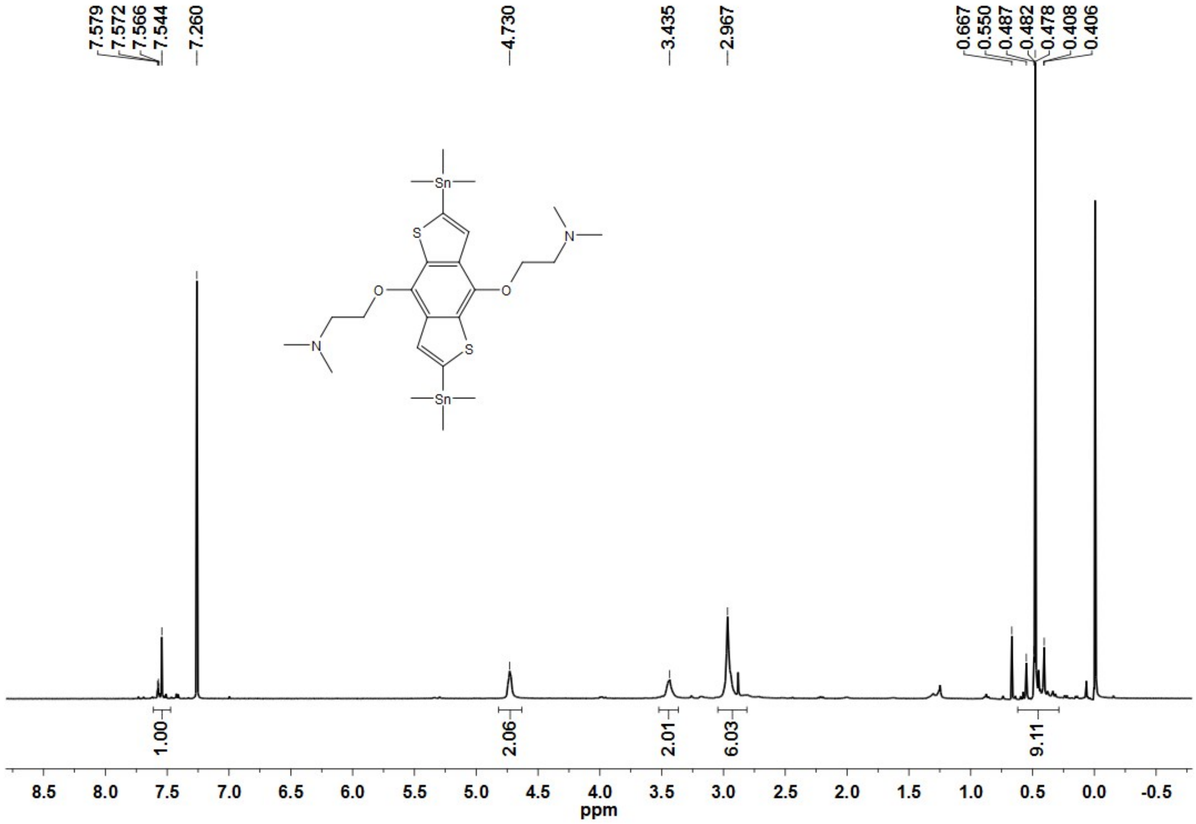


Fig. S8 ^{1}H NMR spectra of monomer 2.

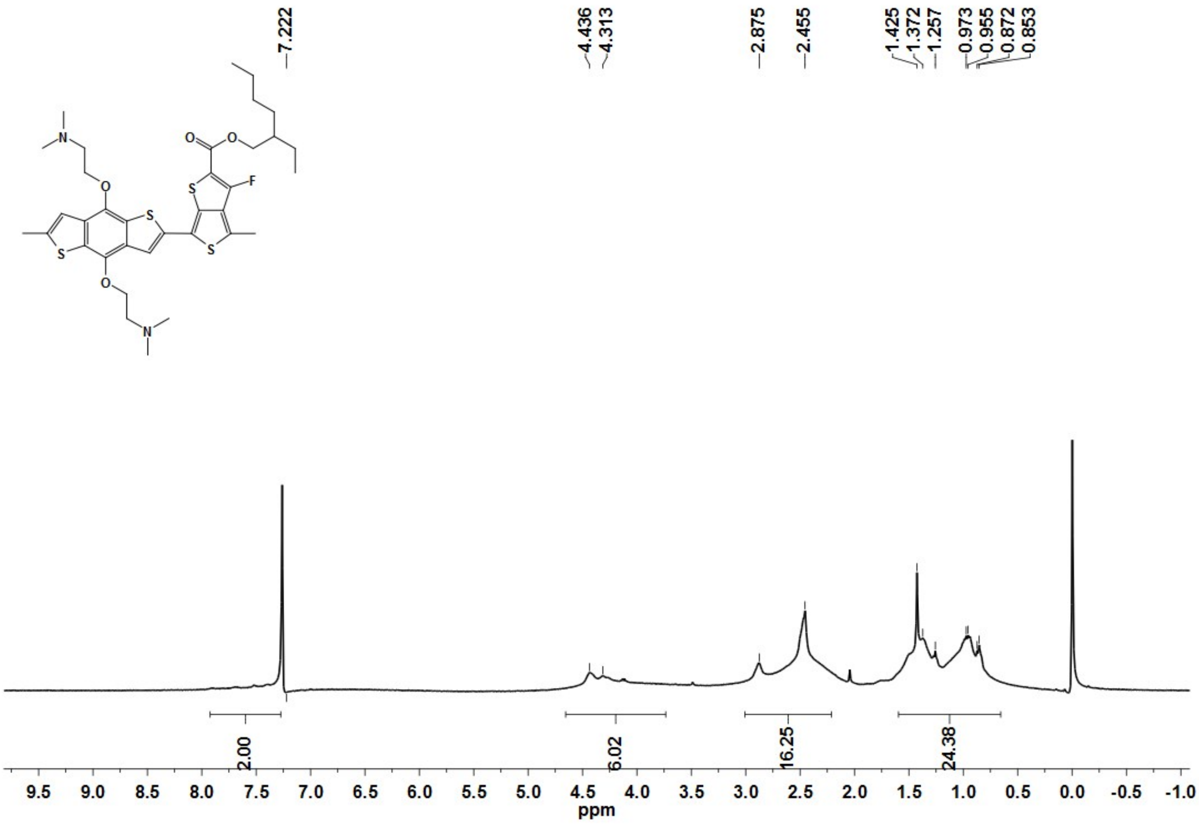


Fig. S9 ^{1}H NMR spectra of compound PTB7-N.

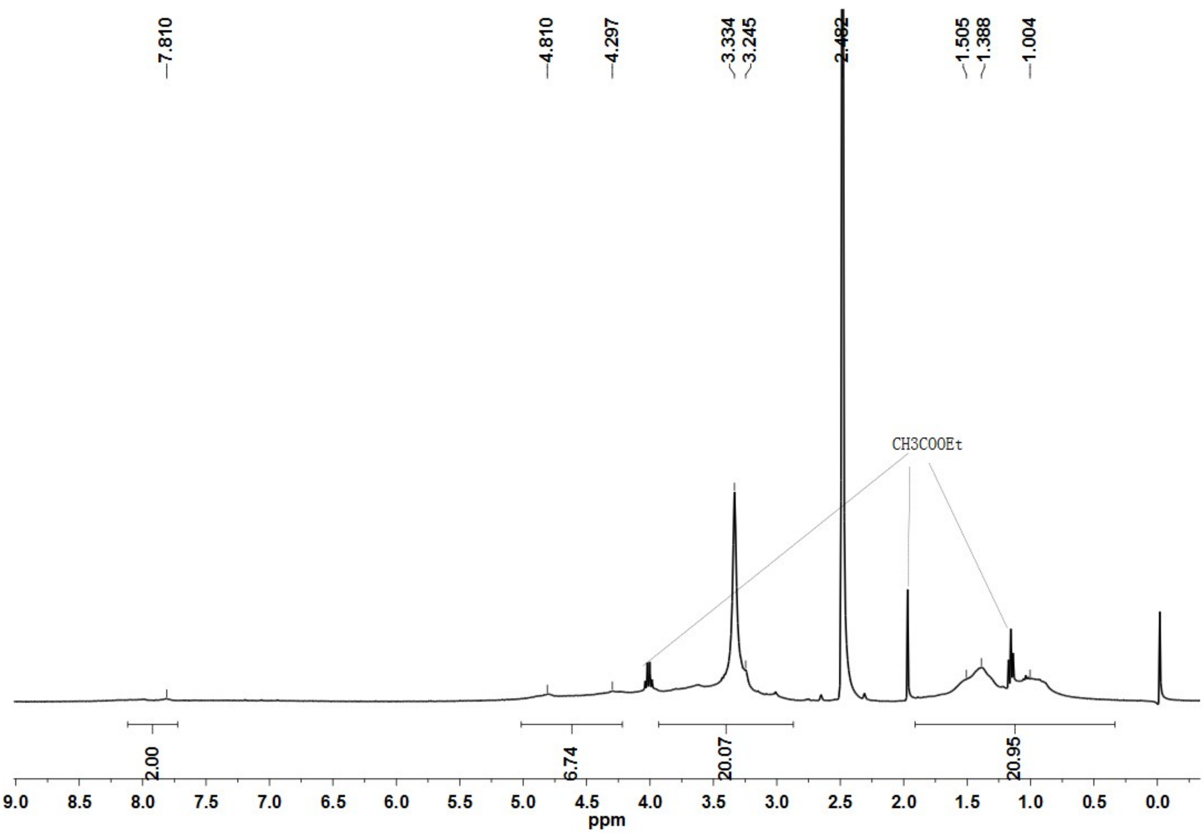


Fig. S10 ^{1}H NMR spectra of compound PTB7-NBr.