

Electronic Supplementary Information

for

Enabling Close Backbone Stacking in Near-Amorphous n-Type Polymer Semiconductors via Side-Chain Engineering

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1. Experimental details

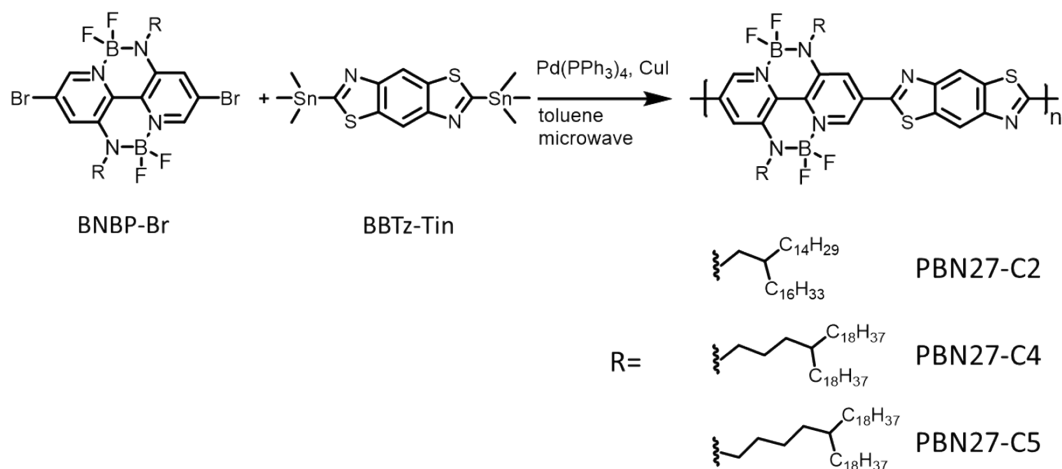
General. ^1H and ^{13}C NMR spectra were measured with a Bruker AV-400 (500 MHz for ^1H and 126 MHz for ^{13}C) spectrometer in CDCl_3 at 25 °C or deuterated *o*-dichlorobenzene (*o*-DCB) at 110 °C. Chemical shifts are reported in δ ppm relative to the residual solvent peak at 7.26 ppm (CDCl_3) for ^1H NMR and 77.16 ppm (CDCl_3) for ^{13}C NMR. Elemental analysis was performed on a VarioEL elemental analyzer. Microwave assisted polymerizations were conducted in a CEM Discover microwave reactor. 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. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer 7 instrument at a heating rate of 10 °C min^{-1} under nitrogen flow. Differential scanning calorimetry (DSC) was performed with a TA DSC Q2000 instrument under nitrogen at the heating and cooling rates of 10 °C min^{-1} for two heating/cooling cycles. UV/Vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer. Cyclic voltammetry (CV) was performed on an CHI660a electrochemical workstation using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) 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 polymers were 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: $E_{\text{HOMO}}/E_{\text{LUMO}} = - (4.80 + E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}})$ eV. Atomic force microscopy (AFM) was performed with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. Two-dimensional grazing-incidence wide angle X-ray scattering (2D-GIWAXS) was measured at the 1W1A Diffuse X-ray Scattering Station, Beijing Synchrotron Radiation Facility (BSRF-1W1A). The monochromatic wavelength of the light source was 1.54 Å. The data were recorded by a two-dimensional image plate detector of MAR 345 from marXperts, Germany. The grazing incidence angle was 0.2°. The film used in 2D-GIWAXS tests was prepared by drop-casting (2 mg /ml).

Materials and reagents. All commercially available chemicals were used without further purification unless otherwise stated. Alkyl iodide compounds 19-(3-iodopropyl)heptatriacontane and 19-(4-iodobutyl)heptatriacontane were commercially available from Jiujiang Desi Photoelectric

Material Co., Ltd. (<http://www.jjdesi.com/>). Tetrahydrofuran (THF) and toluene (Tol) were dried using sodium before use. All reactions were carried out under Ar atmosphere. Monomer BNPB-Br and BBTz-Tin was synthesized according to our reported procedure.^{[1][2][3]}

Device Fabrication and Characterizations. 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 deionized 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 then treated through UV-Ozone instrument for 15 min. First, Au source/drain electrodes (~30 nm) were deposited on cleaned bare Si/SiO₂ wafer with W/L = 70 (W = 5.6 mm, L = 80 μm). 80% Ethoxylated polyethylenimine (PEIE) (weight average molecular weight = 70.0 kDa, Aldrich) in H₂O with a concentration of 37 wt % was diluted with 2-methoxyethanol (anhydrous, 99.8%, Aldrich) to a lower concentration of 0.07 wt%, and spin coated as an electrode modification layer. After drying at 100 °C for 10 min in glovebox, the polymer film was prepared by bar-coating (coating speed: 60 mm/s; substrates temperature: 100 °C) the preheated (100 °C) polymer solution in *o*-DCB (4 mg/mL) into the pre-patterned substrates in air, followed by thermal annealing at 150 °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 (~600 nm) as dielectric was deposited by spin coating at 1300 rpm for 90 s and then annealed at 100 °C for 40 min. Finally, Al (~80 nm) was vacuum-deposited as gate electrode. The electrical measurements of OFET devices were conducted with KEYSIGHT B1500A semiconductor device analyzer in ambient condition with a probe station. Field-effect mobility was extracted in the saturation and linear regime by using the equation: $I_D^{sat} = (\mu C_i W/2L)(V_G - V_T)^2$ and $I_D^{lin} = (\mu C_i W/L) [(V_G - V_T) V_D - V_D^2/2]$, respectively. 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 (600 nm thickness, 4.6 nF/cm²)), V_G and V_T are the gate voltage and threshold voltage, respectively.

2. Syntheses and characterizations



General Procedure for the Synthesis of three Polymers: Starting materials of **BNBP-Br** (1 equiv), **BBTz-Tin** (1 equiv) and $\text{Pd(PPh}_3)_4$ (0.04 equiv) were added in a microwave vial. The tube was sealed with a cap after dry toluene (0.05 or 0.1 M) was added in a glovebox. The reaction vessel was placed in a CEM microwave reactor and heated to 120 °C using microwave irradiation (220 W) for 1 h. After cooling, the solvent was dispersed in methanol and then the precipitate was collected. The crude polymers was purified by Soxhlet extraction using acetone, hexane and chloroform. The most residue was dissolved in hot chlorobenzene solution, then dispersed in methanol. All the polymers were filtrated and dried in a vacuum to afford the desired polymers as dark red solids.

PBN27-C2 (yield 98%): GPC: $M_n=143\text{k}$, PDI=2.37. $^1\text{H NMR}$ (500 MHz, $\text{C}_6\text{D}_4\text{Cl}_2$, ppm): δ 9.22-9.33 (br), 8.83-8.92 (br), 8.71-8.82 (br), 8.50-8.61 (br), 3.90-4.30 (br), 2.33-2.49 (br), 2.02-2.29 (br), 1.40-2.01 (br), 1.30-1.40 (br), 1.01-1.21 (br). Anal. Calcd for $\text{C}_{82}\text{H}_{138}\text{B}_2\text{F}_4\text{N}_6\text{S}_2$ (%): C, 71.90; H, 10.16; B, 1.58; F, 5.55; N, 6.14; S, 4.68. Found: C, 71.55; H, 9.98; N, 6.00.

PBN27-C4 (yield 95%): GPC: $M_n=145\text{k}$, PDI=2.40. $^1\text{H NMR}$ (500 MHz, $\text{C}_6\text{D}_4\text{Cl}_2$, ppm): δ 8.71-8.82 (br), 3.90-4.30 (br), 1.24-2.56 (br), 0.90-1.24 (br). Anal. Calcd for $\text{C}_{98}\text{H}_{168}\text{B}_2\text{F}_4\text{N}_6\text{S}_2$ (%): C, 73.93; H, 10.64; N, 5.28. Found: C, 73.02; H, 10.54; N, 5.24.

PBN27-C5 (yield 91%): GPC: $M_n=101\text{k}$, PDI=2.50. $^1\text{H NMR}$ (500 MHz, $\text{C}_6\text{D}_4\text{Cl}_2$, ppm): δ 8.71-8.82 (br), 3.90-4.30 (br), 1.24-2.56 (br), 0.90-1.24 (br). Anal. Calcd for $\text{C}_{100}\text{H}_{172}\text{B}_2\text{F}_4\text{N}_6\text{S}_2$ (%): C, 74.13; H, 10.70; N, 5.19. Found: C, 73.21; H, 10.56; N, 5.22.

Molecular weights and molecular weight distribution

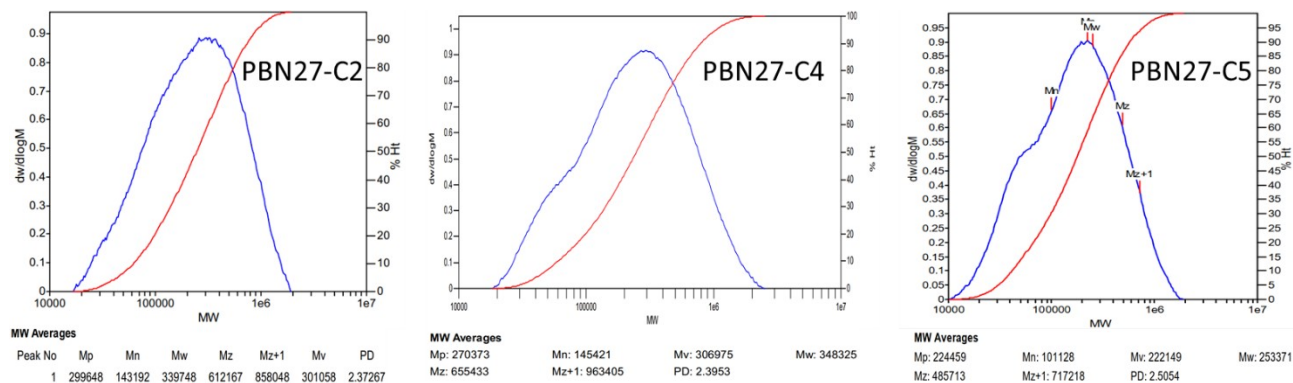


Figure S1. Gel permeation chromatography (GPC) elution curves of the three polymers with trichlorobenzene as the eluent at 150 °C.

3. Thermal properties

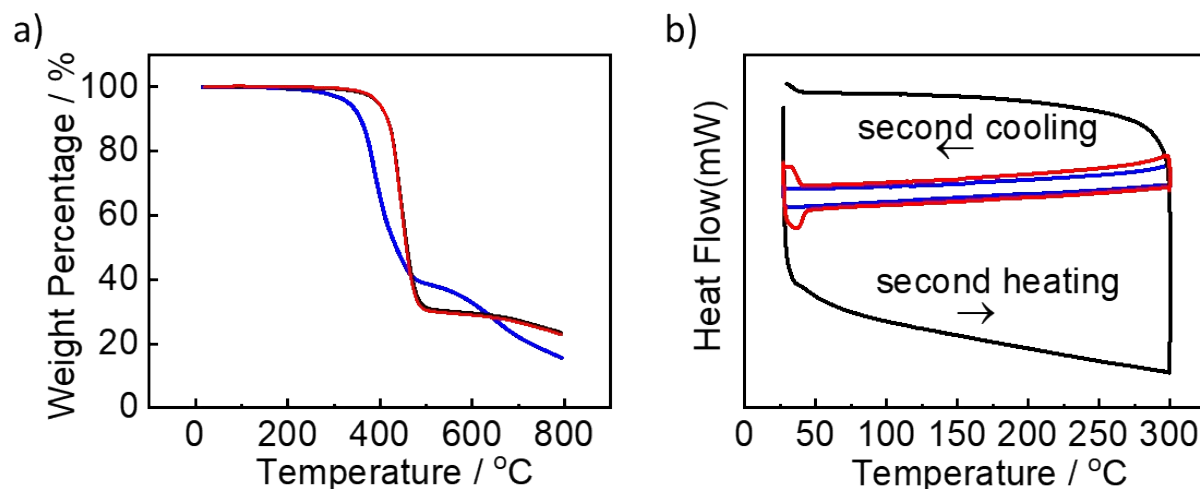


Figure S2. a) Thermogravimetric analysis (TGA) curves of **PBN27-C2** (blue), **PBN27-C4** (black) and **PBN27-C5** (red). b) Differential scanning calorimetry (DSC) curves of **PBN27-C2** (blue), **PBN27-C4** (black) and **PBN27-C5** (red).

4. Cyclic voltammograms

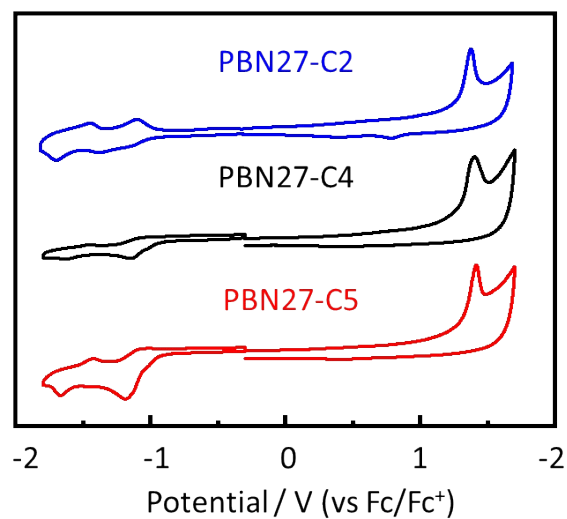


Figure S3. The cyclic voltammograms of the polymers.

5. Polarized UV-vis absorption spectra

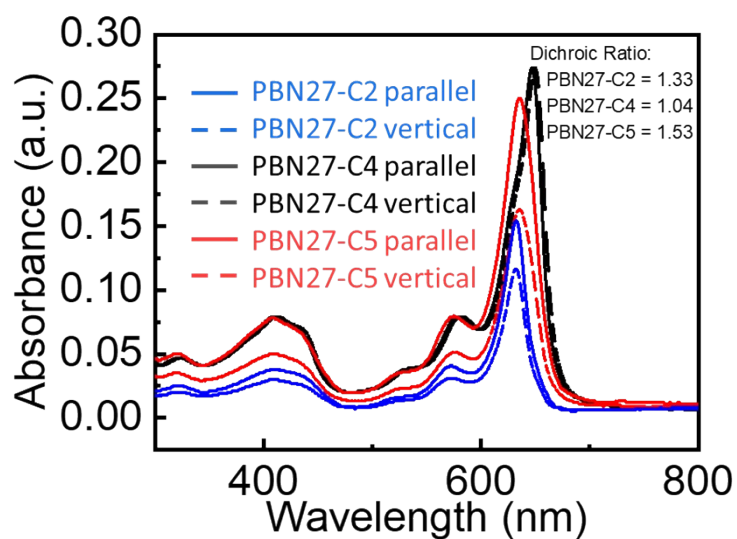


Figure S4. Polarized UV-vis absorption spectra of the bar-coated thin films processed from *o*-DCB solution.

6. AFM phase images

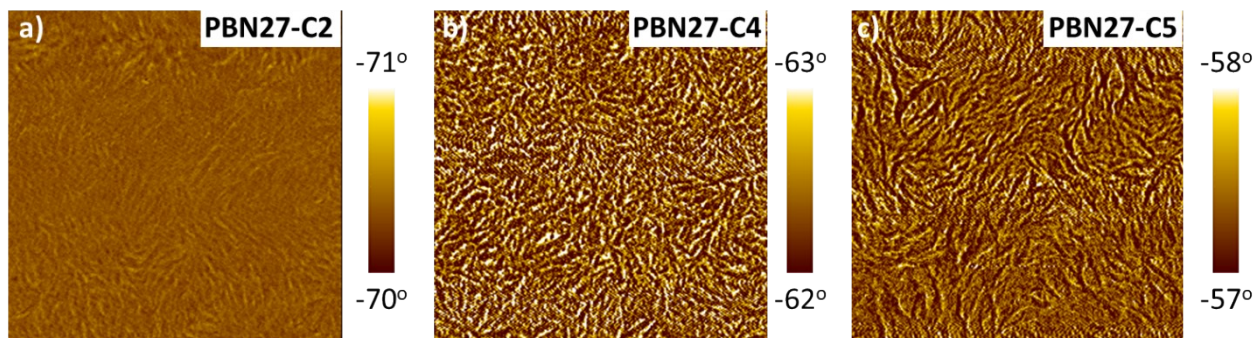


Figure S5. AFM phase images ($2 \mu\text{m} \times 2 \mu\text{m}$) of bar-coated thin films of a) PBN27-C2, b) PBN27-C4 and c) PBN27-C5.

7. Repeatability of OFETs

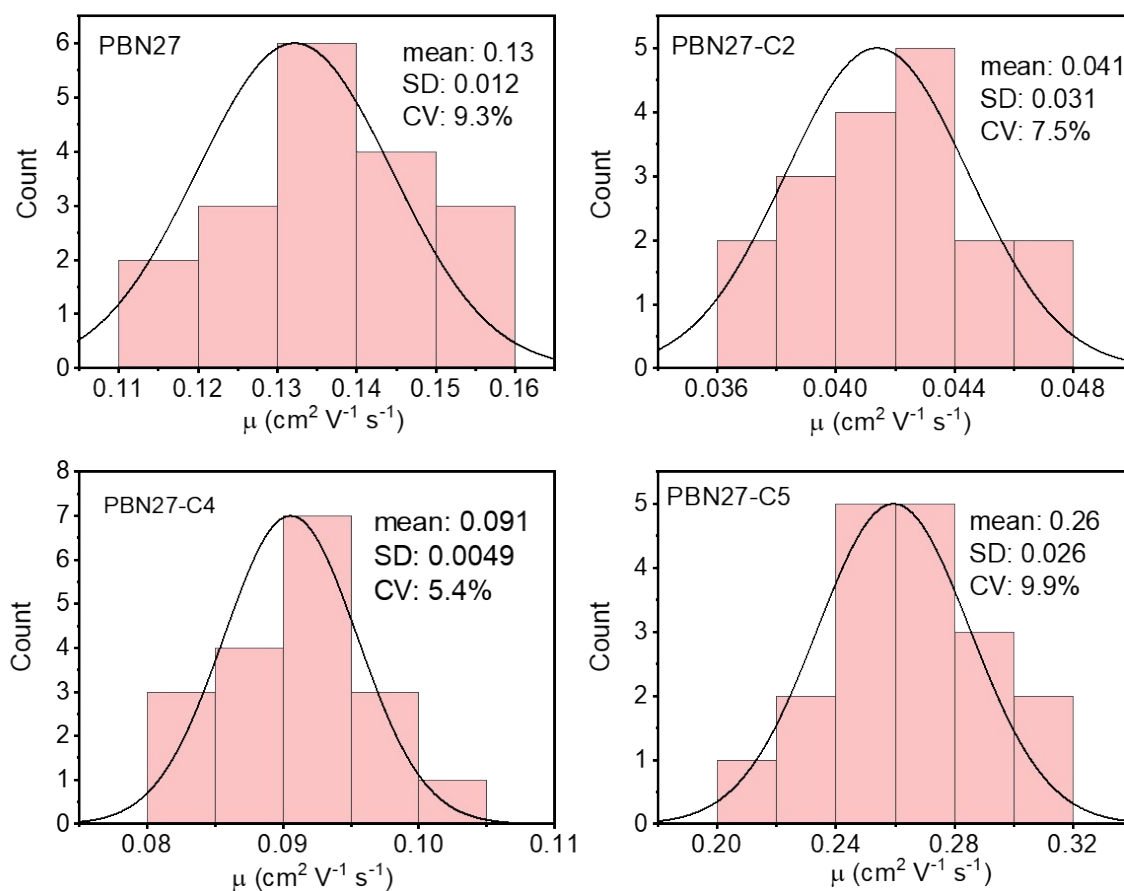


Figure S6. The histograms of mobility for each polymer OFETs and corresponding statistical data, including mean, standard deviation (SD) and coefficient of variance (CV).

8. Temperature-dependent absorption spectra

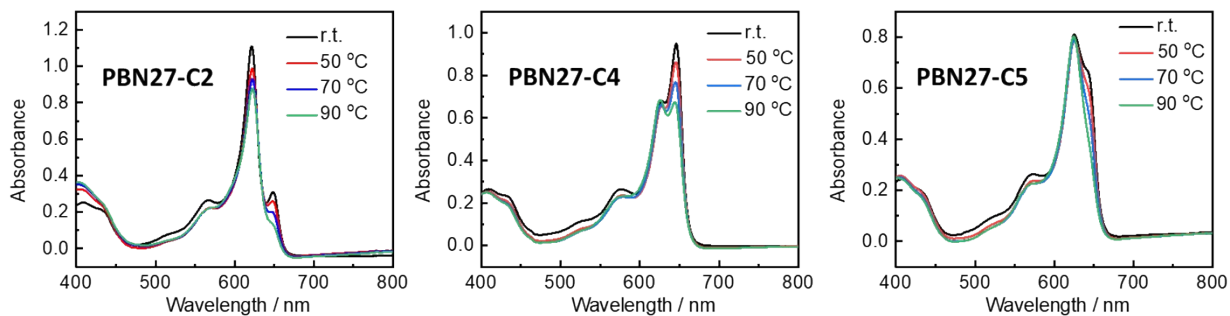


Figure S7. Temperature-dependent absorption spectra of three polymers in diluted *o*-DCB solutions (10^{-5} M).

9. OFET device based on PBN-27

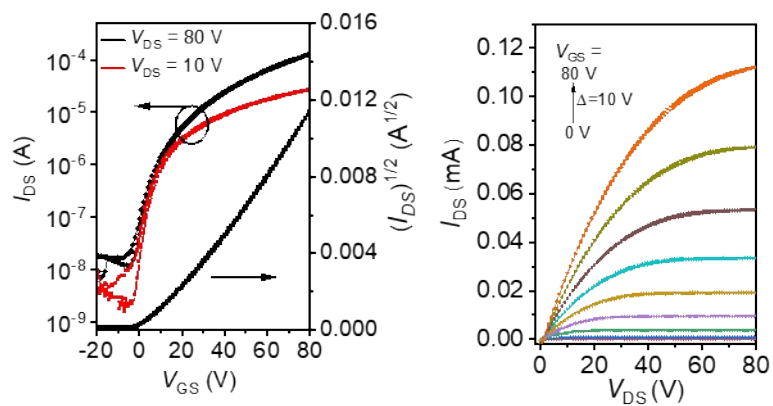


Figure S8. Transfer and output curves of the OFET devices based on **PBN-27**.

10. ¹H and ¹³C NMR spectra

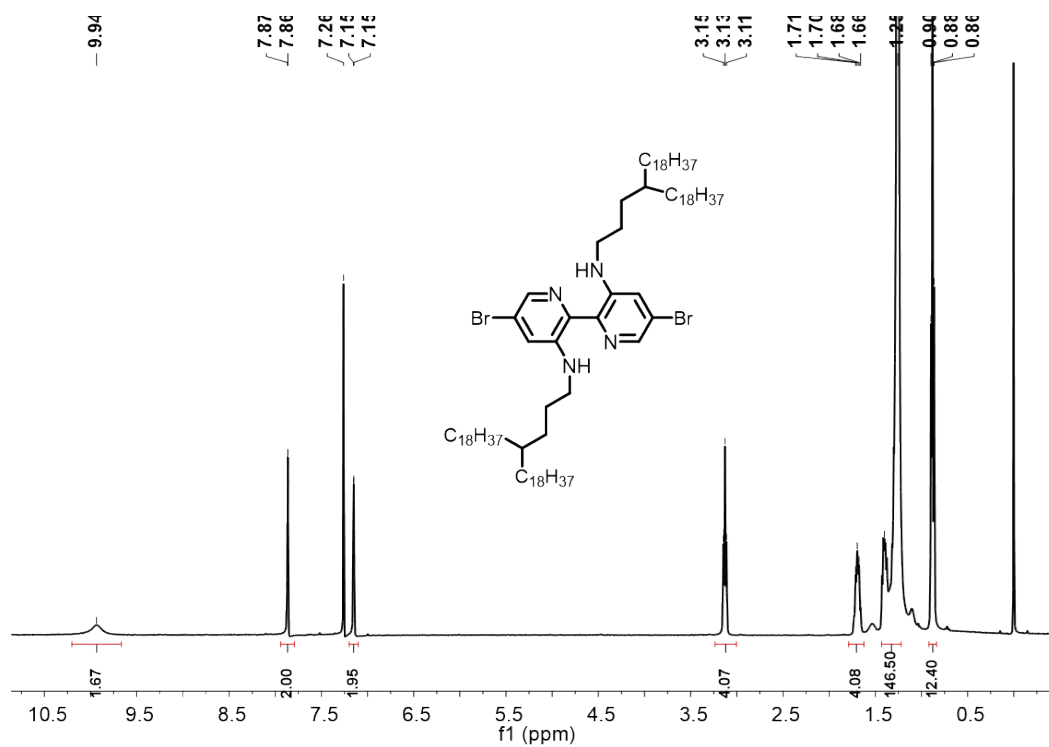


Figure S9. ¹H NMR spectrum of compound 2-C4.

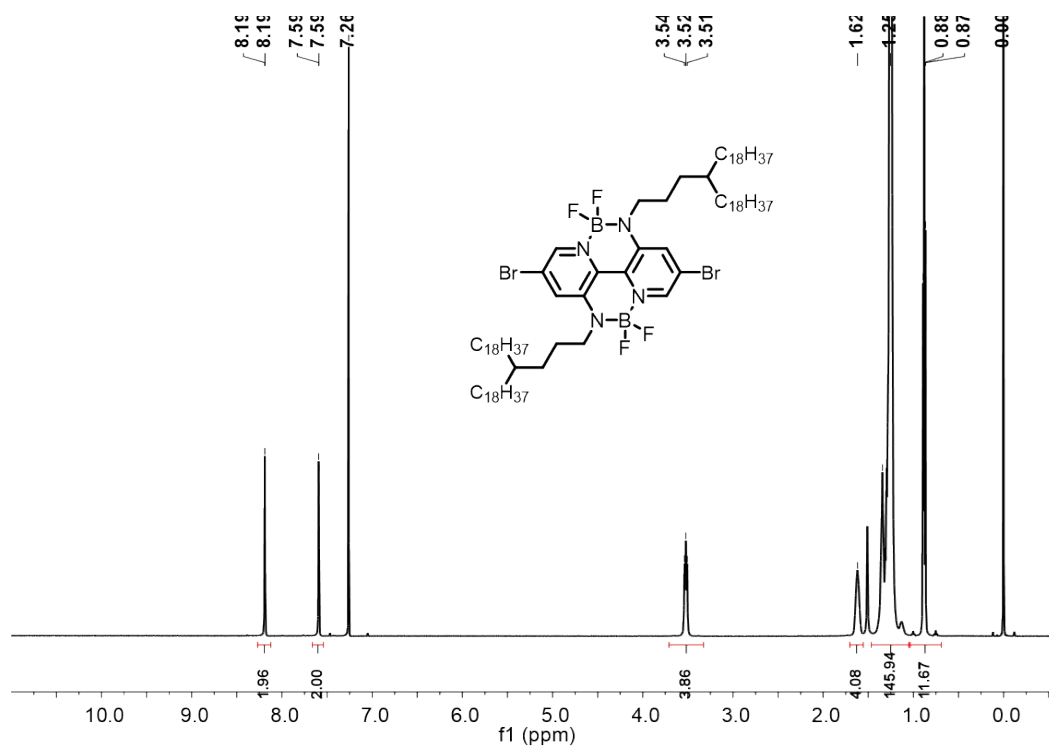


Figure S10. ¹H NMR spectrum of BNP-C4-Br.

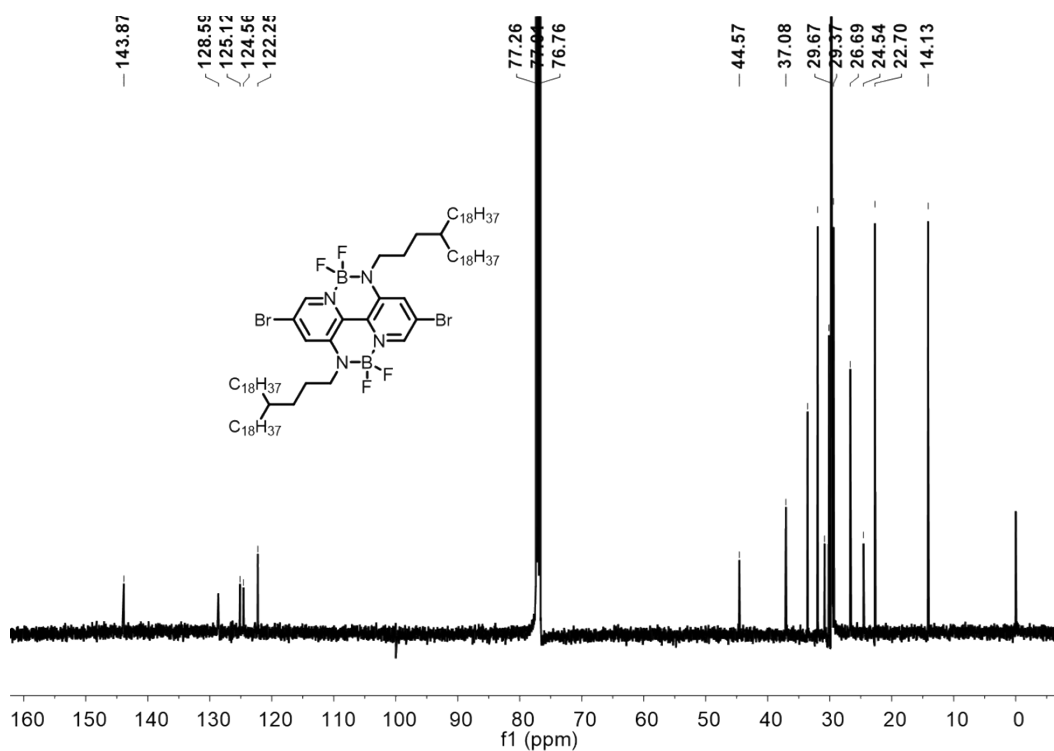


Figure S11. ^{13}C NMR spectrum of **BNP-C4-Br**.

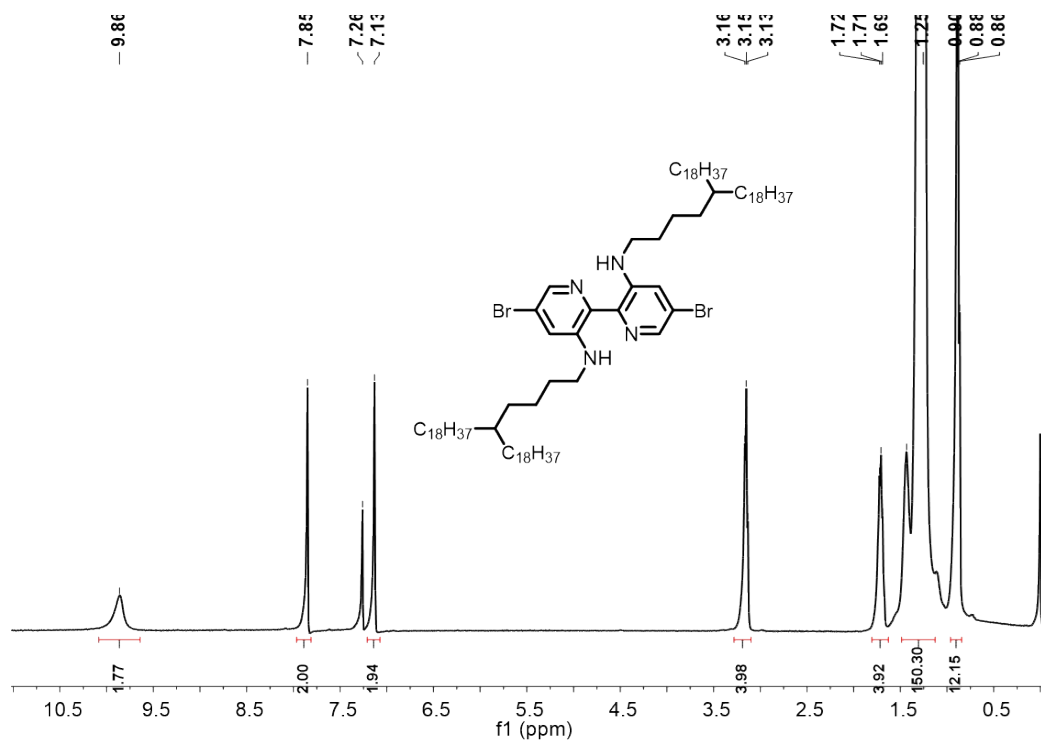


Figure S12. ^1H NMR spectrum of compound **2-C5**.

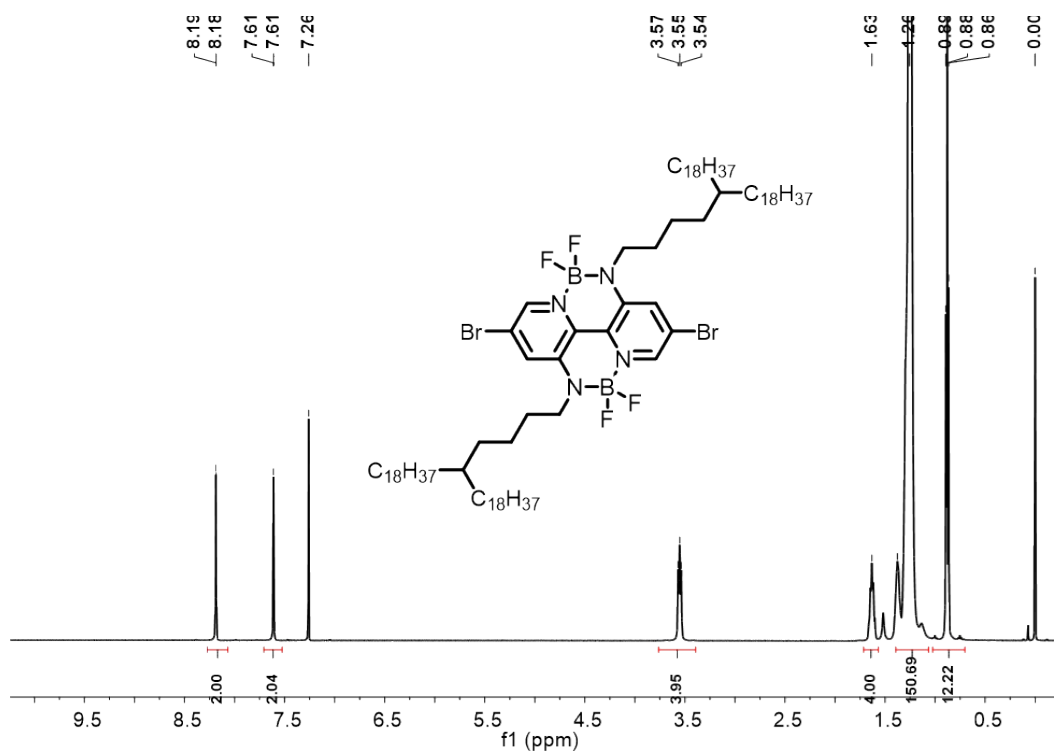


Figure S13. ¹H NMR spectrum of BNP-C5-Br.

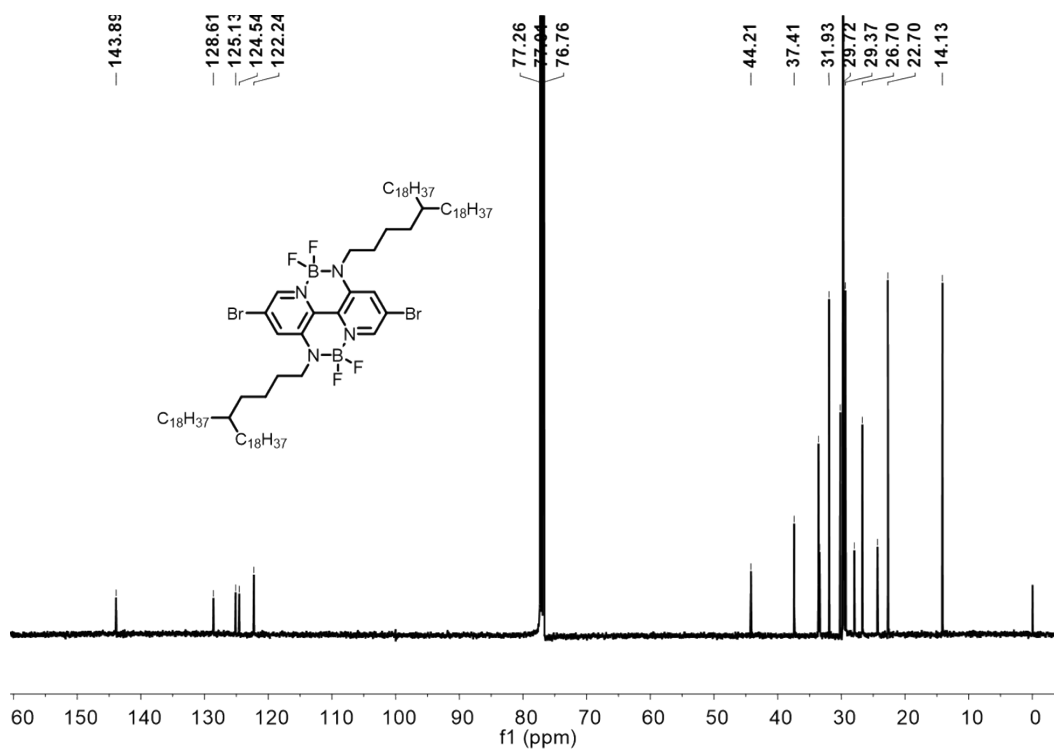


Figure S14. ¹³C NMR spectrum of BNP-C5-Br.

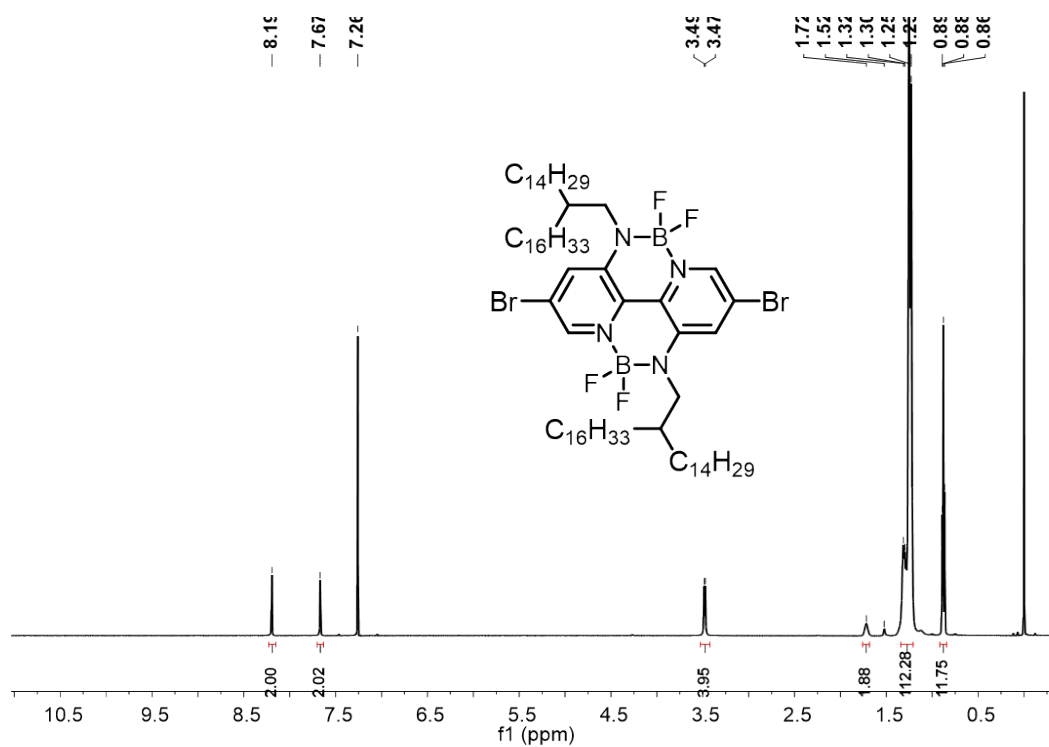


Figure S15. ^1H NMR spectrum of BNP-C2-Br.

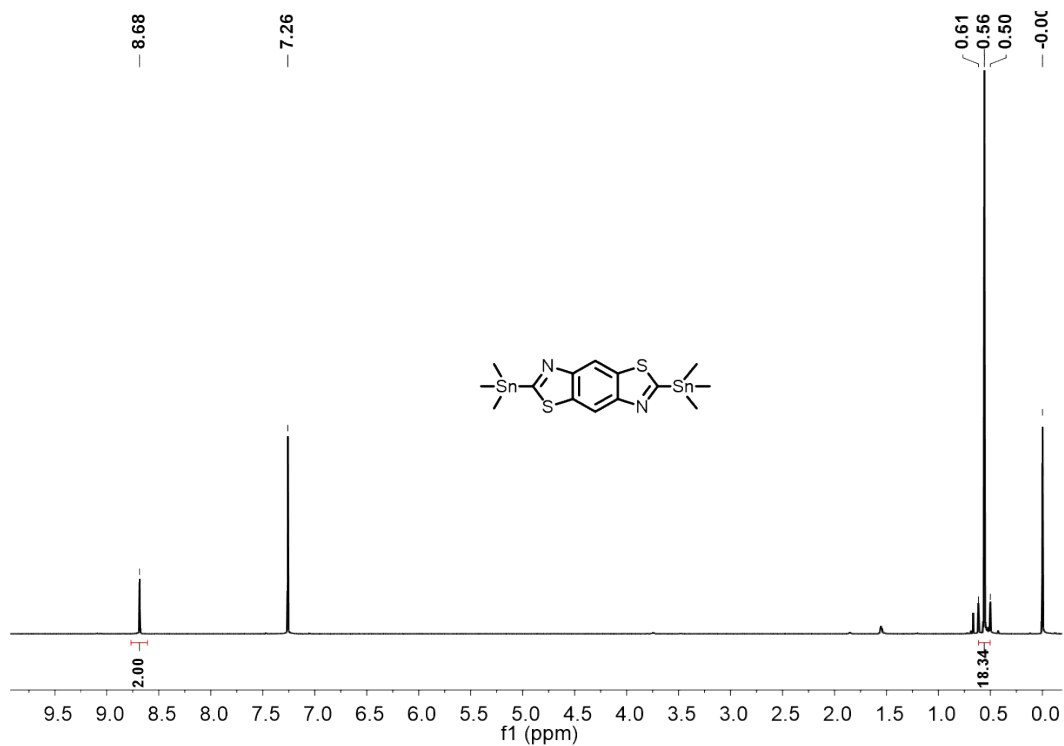


Figure S16. ^1H NMR spectrum of BBTz-Tin.

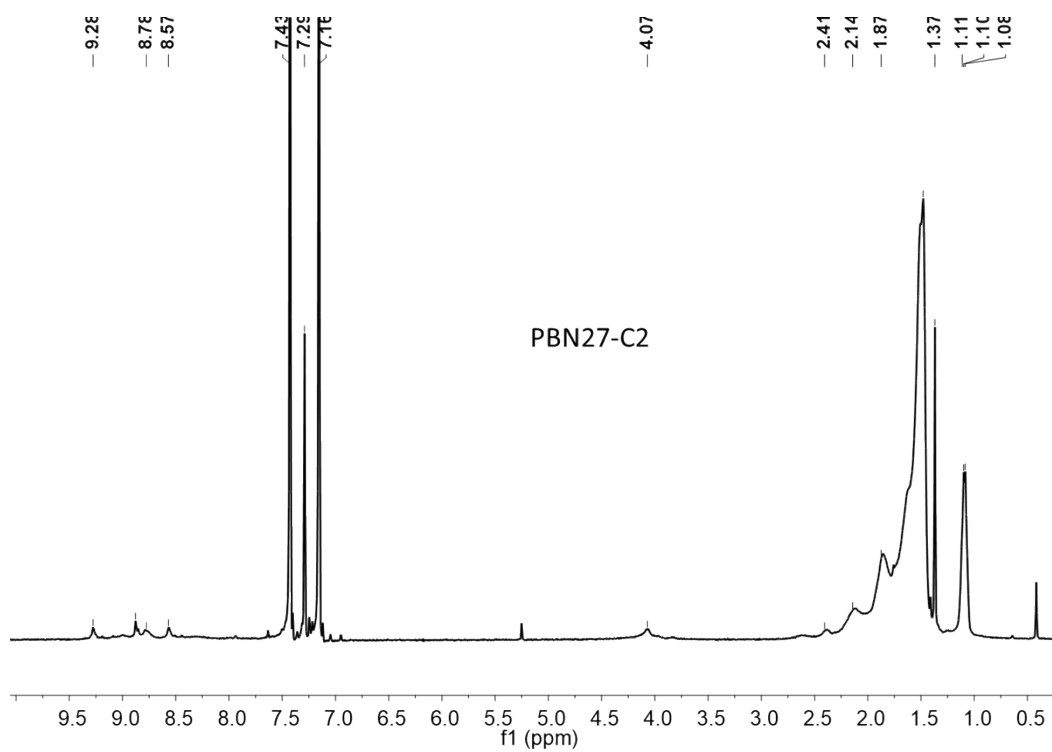


Figure S17. ^1H NMR spectrum of PBN27-C2.

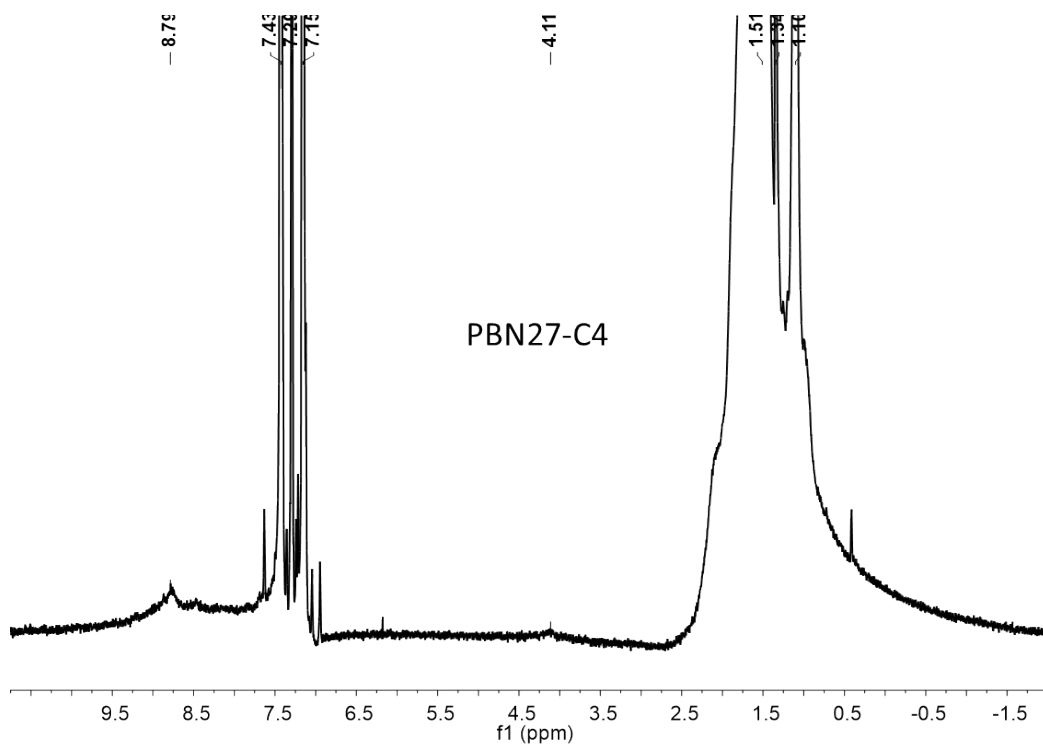


Figure S18. ^1H NMR spectrum of PBN27-C4.

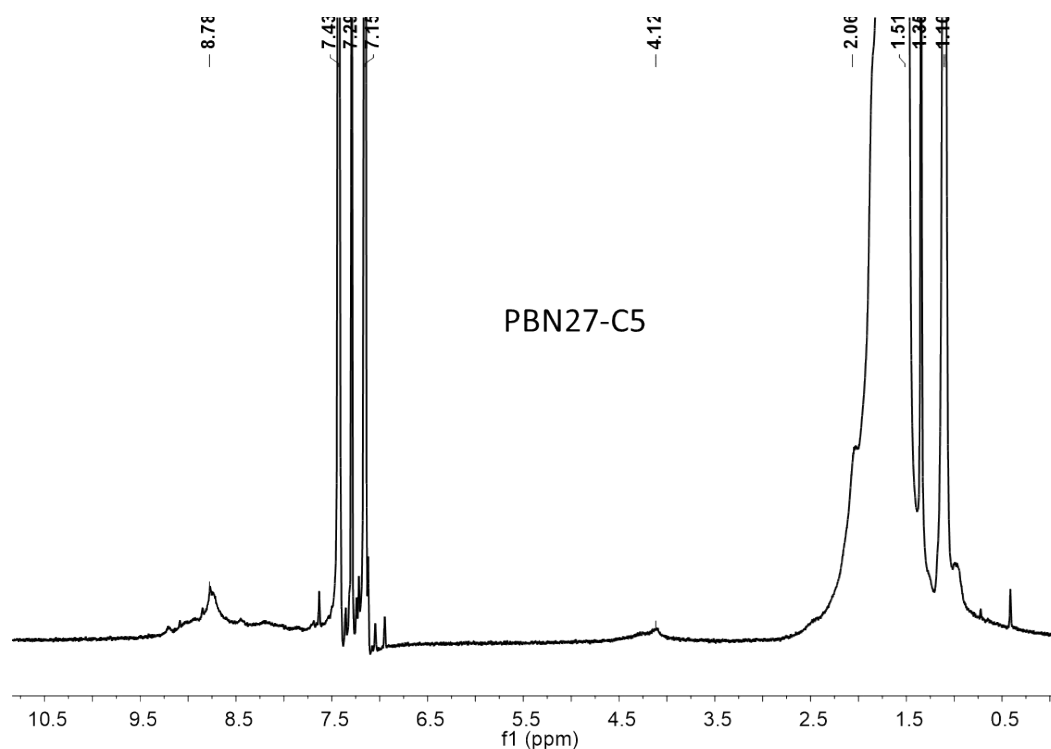


Figure S19. ^1H NMR spectrum of **PBN27-C5**.

11. Reference

1. X. Cao, Y. Min, H. Tian and J. Liu*, Incorporating Cyano Groups to a Conjugated Polymer Based on Double B←N-Bridged Bipyridine Units for Unipolar n-Type Organic Field-Effect Transistors. *Org. Mater.*, **2021**, 3, 469–476
2. C. Dou, X. Long, Z. Ding, Z. Xie, J. Liu and L. Wang, An Electron-Deficient Building Block Based on the B←N Unit: An Electron Acceptor for All-Polymer Solar Cells. *Angew. Chem., Int. Ed.*, **2016**, 55, 1436–1440.
3. X. Cao, H. Li, J. Hu*, H. Tian*, Y. Han, B. Meng, J. Liu* and L. Wang, An Amorphous n-Type Conjugated Polymer with an Ultra-Rigid Planar Backbone. *Angew. Chem.Int. Ed.* **2023**, 62, e202212979