

Electronic supplementary information

Rare solvent annealing effective benzo(1,2-*b*:4,5-*b'*)dithiophene-based low band-gap polymer for bulk heterojunction organic photovoltaics

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S1. Synthesis and Characterization

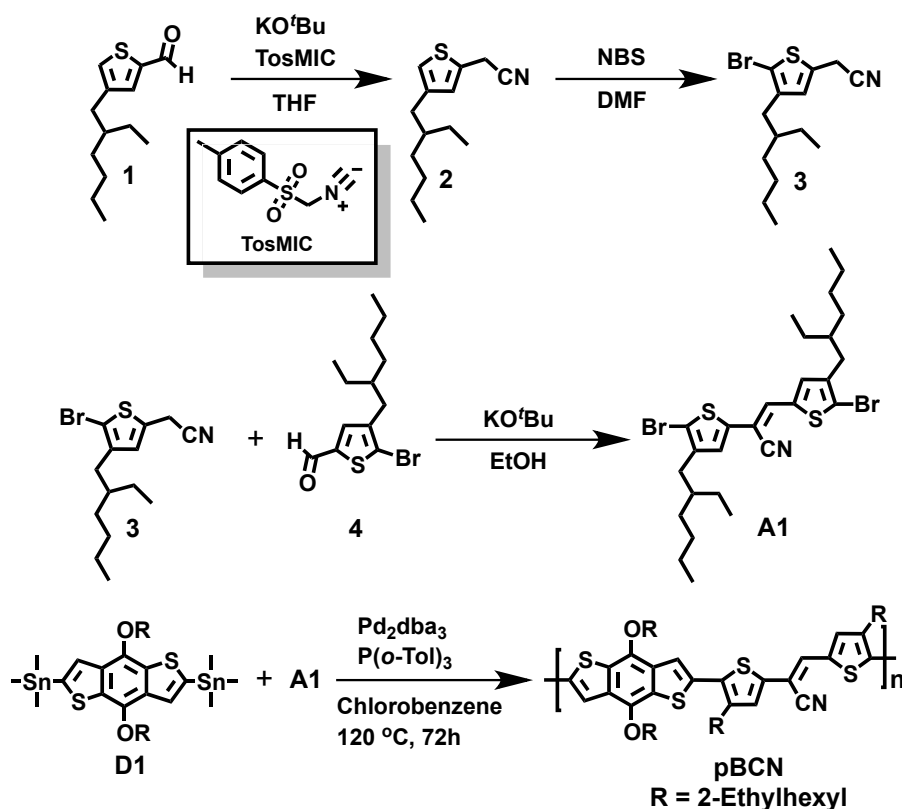
S2. Photovoltaic Device Fabrication and Characterization

S3. OFET Device Fabrication and Characterization

S4. References

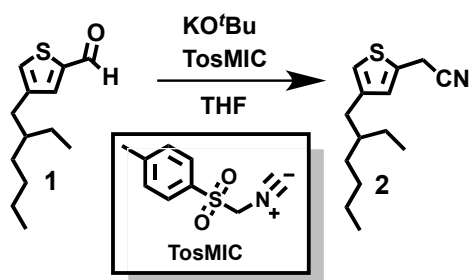
S1. Synthesis and characterization

4-(2-ethylhexyl)thiophene-2-carbaldehyde (1)¹, 5-bromo-4-(2-ethylhexyl)thiophene-2-carbaldehyde (4)² and bis(trimethylstannane) derivative of benzo(1,2-*b*:4,5-*b'*)dithiophene (D1)³ were synthesized according to the procedure reported in the literatures.



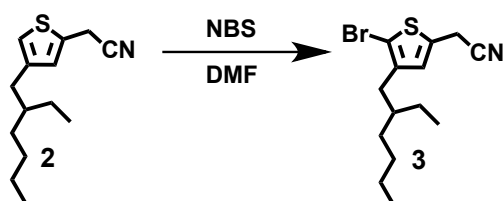
Scheme S1. Synthetic route of cyanovinylene acceptor A1 and copolymer pBCN.

2-(4-(2-Ethylhexyl)thiophen-2-yl)acetonitrile (2)



To a suspension of potassium *tert*-butoxide (8.55 g, 76.2 mmol) in THF (85 mL), tosylmethylisocyanide (7.02 g, 36.0 mmol) in THF (127 mL) was added dropwise under nitrogen atmosphere. The brown suspension was cooled to -50 °C. 4-(2-ethylhexyl)thiophene-2-carbaldehyde (1) (7.13 g, 31.8 mmol) in THF (127 mL) was added slowly and the reaction mixture was stirred at -50 °C for 1 hour. Freshly distilled methanol (105 mL) was added and the brown reaction mixture was then heated at 80 °C for 30 minutes. The solvent of the cooled reaction mixture was removed. The brown mixture was extracted with dichloromethane and the combined organic layers were washed with 10% aqueous sodium hydrogen carbonate solution and water. The organic layers were then dried over magnesium sulfate and the solvent was removed under reduced pressure. The mixture was purified by column chromatography using 3% ethyl acetate/hexanes as eluent to afford the desired product as a brown liquid (4.42 g, 59%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.84 (s, 1H), 6.79 (s, 1H), 3.85 (s, 2H), 2.47 (d, 2H, *J* = 6.8 Hz), 1.48-1.53 (m, 1H), 1.19-1.29 (m, 8H), 0.83-0.88 (m, 6H). HRMS (*m/z*): [M+H]⁺ calcd for C₁₄H₂₂NS 236.1473; found 236.1467.

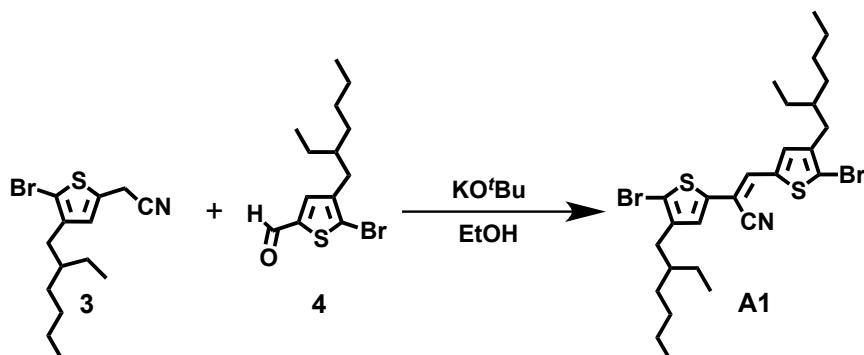
2-(5-Bromo-4-(2-ethylhexyl)thiophen-2-yl)acetonitrile (3)



In a 150 mL two-neck round bottom flask, NBS (0.89 g, 5.0 mmol) was added to a solution of 2-(4-(2-Ethylhexyl)thiophen-2-yl)acetonitrile (2) (1.18 g, 5.0 mmol) in DMF (20 mL). The reaction mixture was then stirred overnight at room temperature. The resulting mixture was extracted with dichloromethane and washed by water and brine, and then dried over magnesium sulfate. After filtering and removing of the solvent, a dark-brown liquid was obtained by column chromatography (1.19 g, 76%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.72 (s, 1H), 3.78 (s, 2H), 2.42 (d, 2H, *J* = 7.2

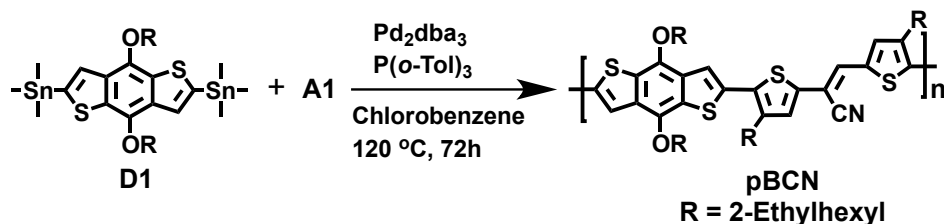
Hz), 1.50-1.56 (m, 1H), 1.21-1.31 (m, 8H), 0.84-0.88 (m, 6H). HRMS (m/z): [M^+] calcd for $C_{14}H_{20}BrNS$ 313.0500; found 313.0494.

Synthesis of A1



To a stirred solution of 2-(5-Bromo-4-(2-ethylhexyl)thiophen-2-yl)acetonitrile (**3**) (0.94 g, 3.0 mmol), 5-bromo-4-(2-ethylhexyl)thiophene (**4**) (0.91 g, 3.0 mmol) and dry ethanol (20 mL) in a 50 mL round bottom flask under ice-bath, a catalytic amount of potassium *tert*-butoxide (*t*-BuOK) was added. The reaction mixture was stirred overnight at room temperature and then water was added. Dichloromethane was added to extract the product. The organic layer was washed with water and dried over magnesium sulfate. After the removal of the solvent, the mixture was purified by column chromatography to afford yellow viscous oils. (1.49 g, 83%). 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.15 (s, 1H), 7.13 (s, 1H), 6.96 (s, 1H), 2.48 (d, 2H, $J = 7.20$ Hz), 2.44 (d, 2H, $J = 7.20$ Hz), 1.56-1.62 (m, 2H), 1.20-1.33 (m, 16H), 0.86-0.89 (t, 12H, $J = 6.4$ Hz). HRMS (m/z): [M^+] calcd for $C_{27}H_{37}NBr_2S_2$ 597.0734; found 597.0731.

Synthesis of pBCN



To a 25 mL two-neck round bottom flask, **D1** (193.1 mg, 0.25 mmol), **A1** (149.9 mg, 0.25 mmol), and dry chlorobenzene (13 mL) were added. The reaction mixture was deoxygenated through three freeze-pump-thaw cycles. Then, Pd_2dba_3 (9.2 mg, 0.01 mmol) and $P(o-Tol)_3$ (12.2 mg, 0.04 mmol) were added under nitrogen and the reaction mixture was reacted for 72 hours at 120 °C. After cooled to room temperature, the mixture was poured into methanol (200 mL). A dark-blue precipitate was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with

methanol, hexane, ethyl acetate, dichloromethane, and chloroform. The chloroform fraction was concentrated and re-precipitated with methanol to obtain a plastic dark-green solid (110 mg, 78%). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.56-7.59 (m, 2H), 7.29 (br, 1H), 7.03 (br, 1H), 6.54 (br, 1H), 4.12-4.30 (m, 4H), 2.73-2.88 (m, 4H), 1.04-1.83 (m, 36H), 0.85-0.98 (m, 24H). Anal. Found (Calcd): C, 71.88 (71.81); H, 8.56 (8.53); N 1.52 (1.58). GPC (40 °C using THF as eluent): $M_w = 91.7$ kg/mol, $M_n = 39.6$ kg/mol, PDI = 2.32.

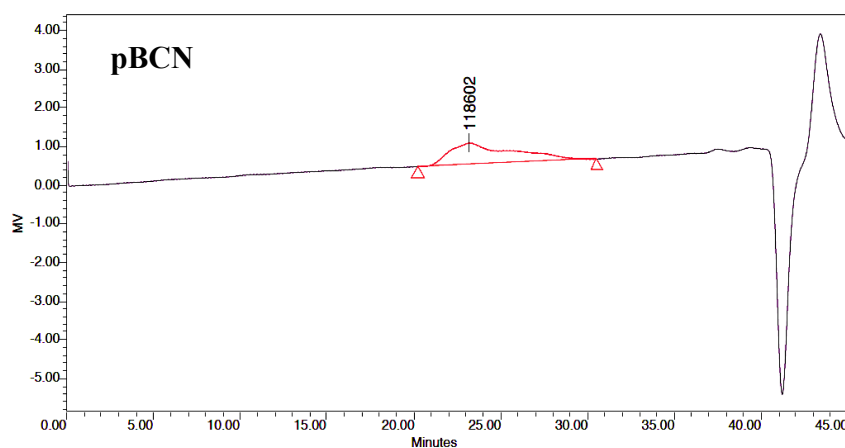
Characterization of Polymer Molecular Weights

In order to further confirm the molecular weight of pBCN due to its rather high value, three P3HT samples purchased from three different companies (UR, Merck, and Aldrich) marked with respective molecular weights (Table S1) were also measured by our GPC (see Figure S1 for GPC eluting profile). From the results summarized in Table S1, pBCN exhibits a much higher molecular weight than P3HT with the highest molecular weight ($M_w = 41.5$ K). This result confirms the high molecular weight for pBCN.

Table S1 GPC results of pBCN and three different molecular weights P3HT.

Polymer	Measured Molecular Weights		Company Marked Molecular Weights ^a	
	M_w	M_n	M_w	M_n
pBCN	91,672	39,562	-	-
P3HT (UR)	41,459	17,924	50,000 ^a	N.A.
P3HT (Merck)	22,809	13,717	N.A.	57,100 ^a
P3HT (Aldrich)	20,456	13,586	17,500 ^a	N.A.

^a Molecular weights provided by the company where the P3HT purchased.



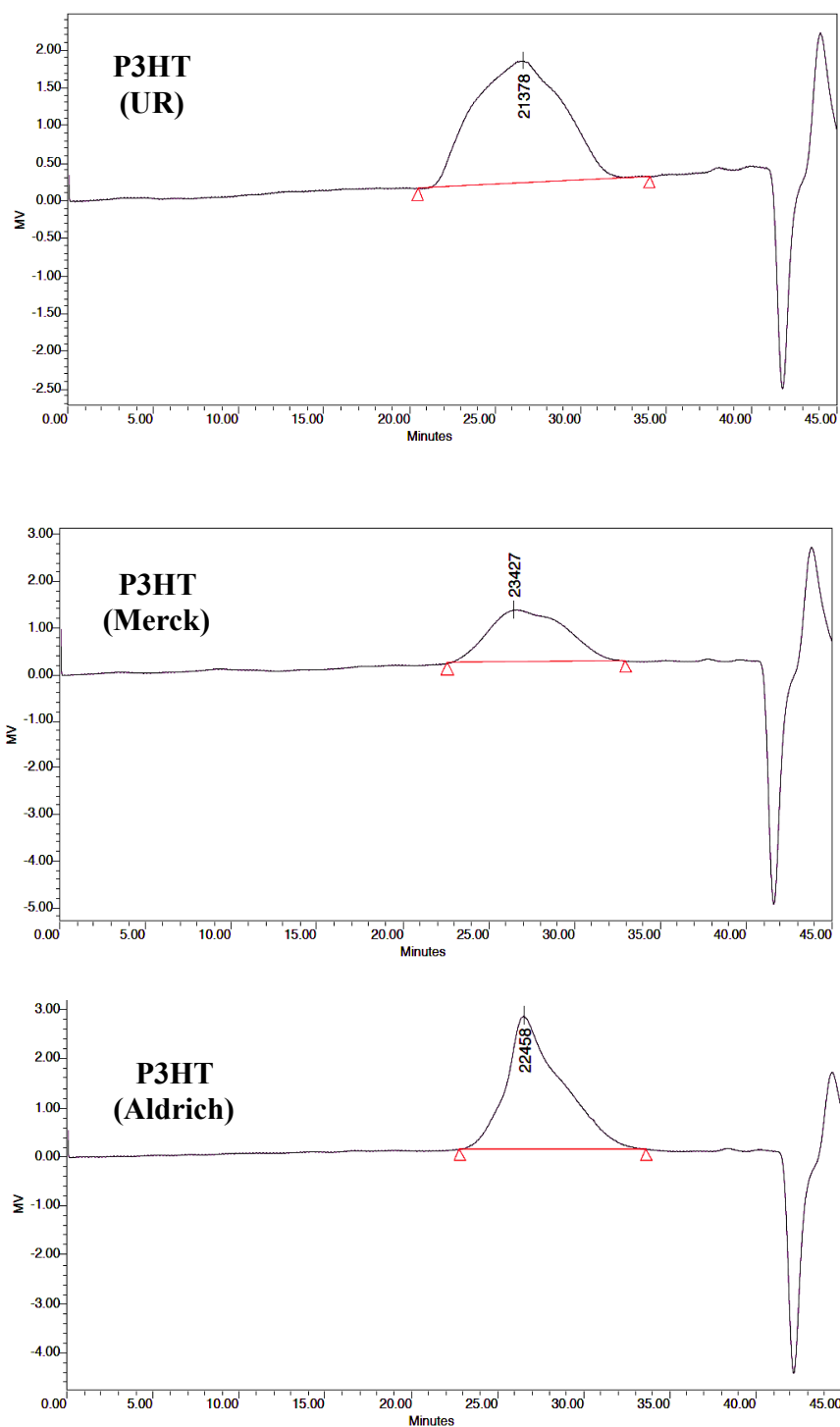


Fig. S1 Comparison of gel permeation chromatograms of pBCN and three different molecular weights poly(3-hexylthiophene) (P3HT).

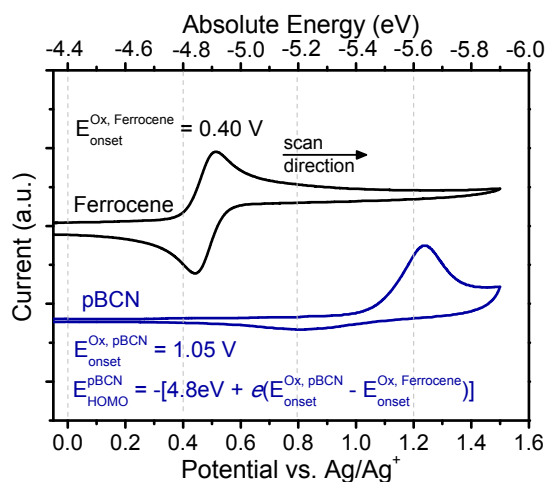


Fig. S2 The oxidation portion of the cyclic voltammogram for pBCN and the ferrocene/ferrocenium redox couple measured in 0.1 M $n\text{Bu}_4\text{NPF}_6$ acetonitrile solution. All curves are shifted up the Y-axis for clarity. The ferrocene/ferrocenium redox couple is used as a standard (-4.8 eV) to calculate the absolute energy (eV) of pBCN.

S2. Photovoltaic Device Fabrication and Characterization

Photovoltaic devices were fabricated on patterned ITO glass substrate. The active layer of each solar cell device is 0.04 cm^2 . ITO glass substrates were sonicated sequentially in detergent, DI water, acetone, and isopropanol. The ITO substrates were then baked on the hot plate at $150\text{ }^\circ\text{C}$ for 10 minutes. A poly(3,4-ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS) thin film was spin-coated (2000 rpm, 60s) and then baked at $150\text{ }^\circ\text{C}$ for 10 minutes. Next, an active layer was spin coated on top of the PEDOT:PSS layer from a 1,2-dichlorobenzene (1,2-DCB) solution of the pBCN:Fullerene blends (1:1, by weight). In the case of the device using the solvent annealing treatment, the spin coated active layer was slow dried inside a covered Petri dish for 60 minutes. Finally, 20 nm of Ca and 80 nm of Al were deposited on the top of the active layer in a vacuum of about $1\text{-}8 \times 10^{-6}$ torr to complete the photovoltaic device fabrication. All devices were encapsulated inside a nitrogen-filled glove box.

The current density–voltage (J – V) characteristics of OPVs were measured in the dark and under AM 1.5G solar illumination from a class A solar simulator (Oriel 300 W), controlled by a programmable source meter (Keithley 2400). The light intensity was calibrated using a Si photodiode (PVM 172; area = 3.981 cm^2) from Nation Renewable Energy Laboratory. For the incident photon-to-electron conversion efficiency (IPCE) measurement, an AM 1.5G solar simulator was used to generate the bias light. A monochromator (Newport Model 74100), which was calibrated with a National Institute of Standards and Technology calibrated photodiode and chopped at 250 Hz, was used to select the wavelengths between 400–750 nm for illuminating the

OPV. The photocurrent from the OPV was measured through the lock-in amplifier (Signal Recovery 7265), which was in turn referenced to the chopper frequency. All electrical measurements were carried out in air.

S3. OFET Device Fabrication and Characterization

The hole mobility of pBCN was measured on organic field-effect transistors (OFETs) with a bottom-gate, top-contact structure. The channel width (W) and length (L) of the transistors are 2 mm and 50 μm , respectively. The device was built on a heavily doped Si wafer with a layer of thermally grown SiO_2 (~ 300 nm) with a capacitance of 12 nF/cm^2 . The Si wafer functioned as the gate electrode while the OTS-modified SiO_2 layer acted as the gate dielectric. The substrate was cleaned and modified with octyltrichlorosilane (OTS) prior to use. A solution of pBCN (10 mg/mL) or pBCN/ PC_{61}BM (10 mg/mL , 1:1, w/w) blends in 1,2-dichlorobenzene solution was filtered through a 0.45 μm syringe filter and spin-coated on the substrate at 1500 rpm for 60s at room temperature in a glove box. Subsequently, the gold (Au) source/drain electrode pairs (70 nm) were deposited on top of the polymer thin film by high vacuum thermal evaporation through a shadow mask to define the channel length (L , 50 μm) and width (W , 2mm).

The electrical measurements were carried out in air using a semiconductor parameter analyzer (Keithley 2636). The saturation mobility (μ_{sat}) was extracted from the slope of the square root of the drain current plot vs. V_G from the following equation,

$$I_{\text{D,sat}} = \frac{W}{2L} C_i \mu_{\text{sat}} (V_G - V_T)^2$$

where $I_{\text{D,sat}}$ is the drain-to-source saturated current; W/L is the channel width to length ratio; C_i is the capacitance of the insulator per unit area ($C_i = 12$ nF/cm^2), and V_G and V_T are the gate voltage and threshold voltage, respectively.

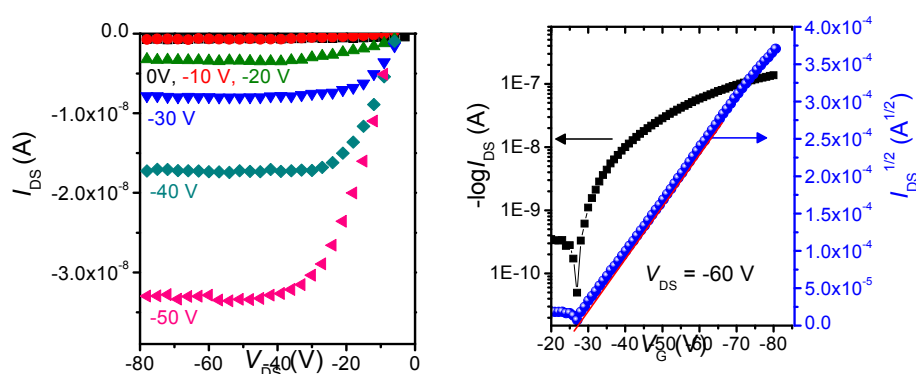


Fig. S3 Left: Output curves at various gate voltages V_G and Right: transfer curve at drain-source voltage V_{DS} at -30 V for the pBCN/ PC_{61}BM (1:1) blend based OFET devices.

S4. References

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- 2 J. Zhang, G. Wu, C. He, D. Deng and Y. Li; *J. Mater. Chem.*, 2011, **21**, 3768.
- 3 (a) J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang; *Macromolecules*, 2008, **41**, 6012. (b) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu; *J. Am. Chem. Soc.* 2009, **131**, 7792.