

Impact of Alkyl Side Chains on the Photovoltaic and Charge Mobility

Properties of Naphthodithiophene–Benzothiadiazole Copolymers

Bao Wang,^a Ji Zhang,^c Hoi Lam Tam,^b Bo Wu,^b Weifeng Zhang,^c Miu Shan Chan,^a Feng Pan,^d
Gui Yu,^{c,*} Furong Zhu,^{b,*}, and Man Shing Wong^{a,*}

^a*Institute of Molecular Functional Materials[#], Department of Chemistry and Institute of Advanced Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China*

^b*Department of Physics and Institute of Advanced Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China*

^c*Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China*

^d*School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen University Town, Xili, Nanshan District, Shenzhen, 518055, P.R. China*

[#]*Areas of Excellence Scheme, University Grants Committee (Hong Kong)*

E-mail: mshwong@hkbu.edu.hk; frzhu@hkbu.edu.hk; yugui@iccas.ac.cn

Materials Characterization

All reagents and starting materials were purchased from commercial sources and used as received, unless otherwise noted. The Pd(PPh₃)₄ was purchased from Sigma-Aldrich. The synthetic routes of monomers are shown in **Schemes 1** and **2**, respectively. The key intermediates are prepared according to reported procedures with modification. All the solvents were dried by the standard methods wherever needed. ¹H NMR spectra were recorded using a Bruker-400 NMR spectrometer and referenced to the residual CHCl₃ 7.26 ppm. ¹³C NMR spectra were recorded using a Bruker-400 NMR spectrometer and referenced to the CDCl₃ 77 ppm. Thermal stabilities were determined by thermal gravimetric analyzer (PE-TGA6) with a heating rate of 10 °C /min under N₂. All absorption measurements were performed with Varian Cary 100-UV-vis spectrophotometer. Cyclic voltammetry (CV) were carried out on a CH

Instrument 630C using platinum wires as working electrode and counter-electrode at a scan rate of 100 mV/s. The reference electrode was Ag/AgNO₃ and the electrolyte was a solution of 0.1 M hexafluorophosphate (Bu₄NPF₆) in dry acetonitrile. Under these conditions, the half wave potential of oxidation of ferrocene was 0.07 V versus Ag/Ag⁺. The HOMO energy level was determined from the oxidation onset from the cyclic voltammograms and reported values were calculated with reference to ferrocene (4.8 eV vs vacuum), the LUMO energy level was determined by $LUMO = (HOMO + E_g^{opt})$ eV. The molecular weight and polydispersity index (PDI) of the polymer were determined by gel permeation chromatography (GPC) using Agilent 1050 HPLC system with VWD and waters 515 HPLC pump. THF was used as eluent and commercial polystyrenes were used as standards.

Fabrication of Field – Effect Transistor Devices

Polymer field effect transistor (PFET) devices were fabricated in a bottom-gate bottom-contact (BGBC) configuration (gold electrode on Si/SiO₂ substrates). Before the deposition of organic semiconductors, octadecyltrichlorosilane (OTS) treatment was performed on the gate dielectrics, which were placed in a vacuum oven with OTS at a temperature of 120 °C for 3 hours to form an OTS self-assembled monolayer. Then the polymer thin films were spin-coated on the OTS modified SiO₂/Si substrates from the solutions (In chlorobenzene, 10 mg/ml, spin-coated at 1500 rpm, for 60 s). The PFETs devices were annealed successively different temperature for 6 min in air. The PFET devices were measured at room temperature in air by using a Keithley 4200 SCS semiconductor parameter analyzer. As contrast, the characteristics of as-prepared devices were also measured. The mobility of the devices was calculated in the saturation regime. The equation is listed as follows:

$$I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$$

where W/L is the channel width / length, C_i is the insulator capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively.

Fabrication of Photovoltaic Devices

The conventional BHJ PV cells with a device structure of ITO/PEDOT:PSS (30 nm)/Polymer:PC₇₁BM (100 nm)(1:2)/Al (100nm) were fabricated by spin-coating of a PEDOT:PSS layer and then a blend of the polymer:PC₇₁BM layer in chlorobenzene (with 0%, 1% or 3% DIO) followed by vacuum deposition of Al as the cathode, after post annealing at 80 °C for 10 min, the device was completed. The concentration of the polymer/PC₇₁BM blend solution for spin coating was 6 mg/ml (polymer/chlorobenzene), and the thickness of the active layer is ~ 100 nm. The performance of PV cells was measured under AM 1.5 simulated solar illumination at an irradiation intensity of 100 mW/cm². The devices were tested under glove-box (filled with Nitrogen) environment and the device active area is 3 mm × 3 mm.

Experimental Procedures:

1,2-bis(2-ethylhexyloxy)benzene (**1**).¹ A mixture of catechol (3.3 g, 30 mmol), KOH (6.7 g, 120 mmol) and 3-(bromomethyl)heptane (19.3 g, 100 mmol) in DMSO (60 mL) was refluxed overnight under N₂. After being cooled to room temperature, the reaction mixture was poured to water and then extracted with hexane. The organic phase was washed with water, brine, dried over anhydrous Na₂SO₄, and evaporated to dryness. The residue was purified by silica gel column chromatography using petroleum ether as eluent affording the desired product as a colorless oil (8.9 g, 88 %). ¹H NMR (400 MHz, CDCl₃) δ: 6.88 (s, 4H), 3.87-3.85 (m, 4H), 1.77-

1.73 (m, 2H), 1.56-1.30 (m, 16H), 0.95-0.88 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 149.5, 120.8, 113.8, 71.5, 39.5, 30.6, 29.1, 23.9, 23.0, 14.0, 11.1.

1,2-dibromo-4,5-bis(2-ethylhexyloxy)benzene (2).¹ To a stirred solution of compound **1** (7.0 g, 21 mmol) in $\text{AcOH}/\text{CHCl}_3$ (25 mL/25 mL) at room temperature, NBS (8.9 g, 50 mmol) was added in portions. After complete addition, the mixture was stirred for 10 h. The reaction was quenched with water and extracted with hexane. The organic phase was separated and washed with brine, dried over anhydrous Na_2SO_4 . The crude was purified by silica gel column chromatography using petroleum ether as eluent affording the desired product as a colorless oil (9.7 g, 88 %). ^1H NMR (400 MHz, CDCl_3) δ : 7.05 (s, 2H), 3.82-3.80 (m, 4H), 1.77-1.71 (m, 2H), 1.52-1.25 (m, 16H), 0.94-0.88 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 149.3, 117.6, 114.3, 71.8, 39.3, 30.4, 29.0, 23.8, 22.9, 13.9, 11.0.

1,2-Bis(2-ethylhexyloxy)-4,5-bis(3-thienyl)benzene (3).¹ To a 100 mL two-neck round-bottom flask was added 3-thiopheneboronic acid, (3.8 g, 30 mmol), 1,2-dibromo-4,5-bis(2-ethylhexyloxy)benzene (4.9 g, 10 mmol), $\text{Pd}(\text{PPh}_3)_4$ (100 mg), THF (100 mL) and 2 M K_2CO_3 (30 mL). The solution mixture was heated to 80 °C overnight under N_2 . After being cooled to room temperature, the mixture was poured into water and extracted with dichloromethane (3 \times 50 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography eluting with petroleum ether/dichloromethane affording the desired product (3.5 g, 84%). ^1H NMR (400 MHz, CDCl_3) δ : 7.17 (dd, $J = 3.0, 4.96$ Hz, 2H), 7.02 (dd, $J = 1.28$ Hz, 3.0 Hz, 2H), 6.78 (dd, $J = 1.24, 4.96$ Hz, 2H), 3.93-3.91 (m, 4H), 1.81-1.78 (m, 2H), 1.56-1.33 (m, 16H), 0.97-0.92 (m, 12 H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 148.7, 142.2, 129.1, 127.8, 124.5, 122.2, 71.8, 39.6, 30.6, 29.1, 23.9, 23.1, 14.1, 11.1.

Synthesis of compound (4).¹ A solution of iron(III) chloride (953 mg, 5.88 mmol) in nitromethane (20 mL) was added dropwise to a solution of 1,2-*bis*(2-ethylhexyloxy)-4,5-*bis*(3-thienyl)benzene **3** (1.0 g, 2 mmol) in DCM (200 mL) under N₂. After complete addition in 30 min, methanol (10 mL) was added and the reaction was stirred for another 30 min. The solvent was removed and the residue was purified by silica gel column chromatography giving the desired product (940 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ: 7.89 (d, *J* = 5.36 Hz, 2H), 7.68 (s, 2H), 7.47 (d, *J* = 5.32 Hz, 2H), 4.11-4.04 (m, 4H), 1.90-1.87 (m, 2H), 1.60-1.36 (m, 16H), 1.00 (t, *J* = 7.44 Hz, 6H), 0.93 (t, *J* = 7.04 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 149.2, 133.9, 130.3, 123.4, 122.7, 122.6, 106.4, 71.5, 39.6, 30.7, 29.2, 24.1, 23.1, 14.1, 11.3.

Synthesis of compound (5).¹ To a 100 mL two-neck round bottom flask was added 5,6-*bis*(2-ethylhexyloxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene **4** (400 mg, 0.8 mmol) and anhydrous THF (10 mL). After deoxygenating with nitrogen three times, the solution was cooled to -78 °C and 1.6 M of *n*-BuLi (1.3 mL, 2.0 mmol) was added dropwise. The resulting white suspension was stirred at -78 °C for 1 h and *tri-n*-butyltin chloride (651 mg, 2.0 mmol) was added in one portion. Upon complete addition, the reaction mixture was stirred at -78 °C for 10 min, and then warmed to room temperature stirring for 3 h. The reaction mixture was poured into ethyl acetate (100 mL), washed with H₂O (2 × 30 mL), brine (2 × 30 mL), and dried over anhydrous Na₂SO₄. After removal of solvent, the residue was purified by silica gel column chromatography (silica gel was immersed in hexane containing 15% triethylamine for 1 h before use) using hexane as the eluent affording the desired product as a colorless liquid (810 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (s, 2H), 7.81 (s, 2H), 4.22-4.15 (m, 4H), 1.99-1.93(m, 2H), 1.80-1.26 (m, 52H), 0.96-0.88 (m, 30H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.5, 136.1, 135.4, 134.6, 130.3, 122.5, 107.3, 69.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.0, 27.3, 26.2, 22.7, 14.1, 13.7, 10.9. MS (MALDI-TOF),

m/z 1077.4831 (M^+).

2,1,3-Benzothiadiazole (**6**).¹ A 1000 mL round-bottom flask was added *o*-phenylene-diamine (10.0 g, 92.5 mmol), CH_2Cl_2 (300 mL), and triethylamine (37.4 g, 370 mmol). The solution mixture was stirred until total dissolution of diamine was observed. Thionyl chloride (13.6 mL, 184.9 mmol) was added dropwise very slowly and the solution mixture was heated at reflux for 5 h. The solvent was removed under reduced pressure and water (700 mL) was added. Concentrated HCl was added to achieve a final pH of 1. Water was added to the reaction mixture and the product was purified by direct steam distillation. The steam-distilled mixture was extracted with CH_2Cl_2 (5×200 mL), dried with $MgSO_4$, and filtered. The solvent was removed to afford pure product (19.6 g, 76%). 1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, J = 3.2 Hz, 5.7 Hz, 2 H), 7.57 (dd, J = 3.2 Hz, 5.7 Hz, 2 H).

4,7-Dibromo-2,1,3-benzothiadiazole (**7**).¹ To a 500 mL two-necked round-bottomed flask were added 2,1,3-benzothiadiazole (10.0 g, 73.4 mmol) and 48% HBr (150 mL). A solution containing Br_2 (35.2 g, 220.3 mmol) in 48% HBr (100 mL) was added dropwise very slowly. If necessary, an additional 100 mL of 48% HBr can be added to the solution. After complete addition of Br_2 , the solution was heated at reflux for 6 h. Precipitation of a dark orange solid was noted. The mixture was cooled to room temperature, and a sufficient amount of a saturated solution of $NaHSO_3$ was added. The mixture was filtered under vacuum and washed exhaustively with water. The solid was then washed once with cold Et_2O and dried under vacuum for 20 h to afford dibrominated product in 95% yield (20.5 g, 69.8 mmol). 1H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 152.9, 132.3, 113.9.

3-Octylthiophene (**8a**).²

To a mixture of magnesium turnings (1.02 g, 42 mmol), anhydrous ether (100 mL) and a small

amount of iodine in a 250 mL round-bottom flask, a solution of 3-(bromomethyl)heptane (7.9 g, 41 mmol) was added slowly at 0 °C under N₂. After refluxing for 1 h, the reaction mixture was added dropwise to a mixture of 3-bromothiophene (5 g, 31 mmol), Ni(dppp)Cl₂ (170 mg, 0.3 mmol) placed in a 500 mL flask at 0 °C. After being stirred overnight at room temperature, the reaction was quenched with cold HCl aq. (2 M). The solution was extracted with CHCl₃ and dried over anhydrous Mg₂SO₄. The crude product was further purified by column chromatography using hexane as eluent to give a clear liquid (5.1 g, 86% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.28-7.26 (m, 1H), 6.98-6.95 (m, 2H), 2.67 (t, *J* = 7.6Hz, 2H), 1.69-1.65 (m, 2H), 1.36-1.32 (m, 10H), 0.95-0.92 (m, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 143.3, 128.3, 125.0, 119.8, 32.0, 30.7, 30.4, 29.5, 29.4, 29.4, 22.8, 14.2.

3-Decylthiophene (8b).³

This material was synthesized following the same procedure as for **8a**. After purification by column chromatography, the product was obtained as colorless oil (6.1 g, 88% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.23-7.21 (m, 1H), 6.93-6.90 (m, 2H), 2.63 (t, *J* = 5.7 Hz, 2H), 1.65-1.57 (m, 2H), 1.30-1.26 (m, 14H), 0.89 (t, *J* = 5.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 143.3, 128.3, 124.9, 119.7, 31.9, 30.6, 30.3, 29.6, 29.5, 29.3, 22.7.

3-Dodecylthiophene (8c).⁴

This material was synthesized following the same procedure as for **8a**. After purification by column chromatography, the product was obtained as colorless oil (6.4 g, 82% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.26 (m, 1H), 6.96 - 6.94 (m, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.64 (m, 2H), 1.31 (m, 18H), 0.93 (t, *J* = 5.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ143.5, 128.5, 125.2, 120.00, 32.1, 30.8, 30.5, 29.9, 29.8, 29.7, 29.6, 22.9, 14.4.

3-Tetradecylthiophene (8d).⁴

This material was synthesized following the same procedure as for **8a**. After purification by column chromatography, the product was obtained as colorless oil (7.66 g, 88% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.26-7.22 (m, 1H), 6.94-6.91 (m, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.62~1.54 (m, 2H), 1.30~1.26 (m, 22H), (0.88, t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 143.3, 128.3, 125.0, 119.8, 31.94, 30.6, 30.3, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1.

3-Hexadecylthiophene (8e).⁴

This material was synthesized following the same procedure as for **8a**. After purification by column chromatography, the product was obtained as colorless oil (7.7 g, 81% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.26-7.22 (m, 1H), 6.94-6.92 (m, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.64-1.60 (m, 2H), 1.31-1.26 (m, 26H), 0.89 (t, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 143.3, 128.3, 125.0, 119.8, 32.0, 30.6, 30.3, 29.7, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1.

*(4-(2-ethylhexyl)thiophen-2-yl)boronic acid (9a)*¹

To a mixture of 3-(2-ethylhexyl)thiophene (1.96 g, 10 mmol) and anhydrous THF (20 mL) cooled in a liquid nitrogen/acetone bath was added 2.5 M *n*-butyl lithium (10 mmol, 4 mL) dropwise over 15 min. After stirring for 2 h at -78 °C, trimethyl borate (1.04 g, 10 mmol) was added in one portion. The solution mixture was stirred for 1 h at -78 °C and then at room temperature overnight. The reaction was quenched with cold HCl (2 M) and the solution was adjusted to pH = 1. The product was extracted with ethyl acetate and dried over anhydrous Mg₂SO₄. After removal of the solvent under reduced pressure, the corresponding boronic acid was used directly in the next step without further purification.

The synthetic procedure of **9a** was followed to prepare **9b**, **9c**, **9d**, and **9e**.

*4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (10a)*.² To a mixture of (4-(2-ethylhexyl)thiophen-2-yl)boronic acid (2.40 g, 10 mmol), 4,7-dibromo-2,1,3-benzothiadiazole

(0.88 g, 3 mmol), potassium carbonate (4.14 g, 30 mmol) in THF (15 mL) and water (15 mL) under N₂ was added Pd(PPh₃)₄ (30 mg, 0.025 mmol). The mixture was heated at reflux overnight with vigorous stirring. After cooling to room temperature, the reaction mixture was quenched with water (50 mL) and extracted with DCM and dried over anhydrous Mg₂SO₄. The crude product was purified by silica gel column chromatography to give an orange solid (1.38 g, 88% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.94 (s, 2H), 7.82 (s, 2H), 7.02 (s, 2H), 2.63 (d, *J* = 6.8 Hz, 2H), 1.65-1.57 (m, 2H), 1.38-1.25 (m, 16H), 0.93-0.90 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.6, 143.1, 138.8, 129.5, 126.0, 125.5, 122.5, 40.3, 34.7, 32.49, 28.9, 25.6, 23.1, 14.2, 10.9. MS (MALDI-TOF): *m/z* 524.23 (M⁺).

4,7-Bis(4-decylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (10b).³

This material was synthesized following the same procedure as for **10a**. After purification by column chromatography, the product was obtained as a solid (1.61 g, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (d, *J* = 1.2 Hz, 2H), 7.76 (s, 2H), 7.01 (d, *J* = 1.2 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 4H), 1.73-1.65 (m, 4H), 1.38-1.26 (m, 28H), 0.89 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.5, 144.3, 138.9, 128.9, 125.9, 125.4, 121.4, 31.9, 30.6, 30.5, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1. MS (MALDI-TOF): *m/z* 580.30 (M⁺).

4,7-Bis(4-dodecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (10c).⁴

This material was synthesized following the same procedure as for **10a**. After purification by column chromatography, the product was obtained as a solid (1.51 g, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.91 (s, 2H), 7.81 (s, 2H), 7.03 (s, 2H), 2.69 (t, *J* = 7.6 Hz, 4H), 1.74-1.66 (m, 4H), 1.39-1.26 (m, 38H), 0.88 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.7, 144.3, 139.0, 129.0, 126.0, 125.5, 121.5, 31.9, 30.7, 30.5, 29.7, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1. MS (MALDI-TOF): *m/z* 636.18 (M⁺).

*4,7-Bis(4-tetradecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (10d).*⁴

This material was synthesized following the same procedure as for **10a**. After purification by column chromatography, the product was obtained as a solid (1.51 g, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.97 (s, 2H), 7.82 (s, 2H), 7.03 (s, 2H), 2.68 (t, *J* = 7.6 Hz, 4H), 1.73-1.65 (m, 4H), 1.39-1.35 (m, 44H), 0.87 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.7, 144.4, 139.0, 129.0, 126.0, 125.6, 121.5, 31.9, 30.7, 30.5, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1. MS (MALDI-TOF): *m/z* 693.43 (M⁺).

*4,7-Bis(4-hexadecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (10e).*⁴

This material was synthesized following the same procedure as for **10a**. After purification by column chromatography, the product was obtained as a solid (1.85 g, 82% yield). ¹H NMR (400 MHz, CDCl₃) δ: 8.01 (s, 2H), 7.86 (s, 2H), 7.07 (s, 2H), 2.72 (t, *J* = 7.6 Hz, 4H), 1.77-1.70 (m, 4H), 1.44-1.39 (m, 52H), 0.91 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.7, 144.4, 139.0, 129.0, 126.1, 125.5, 121.5, 31.9, 30.7, 30.5, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1. MS (MALDI-TOF): *m/z* 749.50 (M⁺).

Synthesis of compound (11a).² To a solution of 4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2.63 g, 5 mmol) (**10 a**) in CHCl₃/AcOH (10 mL/10 mL) at 0 °C was added NBS (2.7 g, 15 mmol) in small portions. The mixture was stirred at room temperature overnight. The reaction was quenched with a solution of 2 M Na₂SO₃. The product was extracted with DCM and dried with anhydrous MgSO₄. The crude product was purified by silica gel column chromatography affording the desired product as a solid (3.1 g, 90% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.79 (s, 2H), 7.77 (s, 2H), 2.60 (d, *J* = 7.2 Hz, 4H), 1.77-1.72 (m, 2H), 1.44-1.28 (m, 16H), 0.97-0.91 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.2, 142.2, 138.3, 128.6, 125.3, 124.8, 112.3, 40.0, 33.9, 32.5, 28.8, 25.7, 23.1, 14.2, 10.9. MS (MALDI-

TOF): m/z 682.05 (M^+).

*4,7-Bis(5-bromo-4-decylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (11b).*³

This material was synthesized following the same procedure as for **11a**. After purification by column chromatography, the product was obtained as a solid (3.2 g, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ : 7.75 (s, 2H), 7.71 (d, $J = 0.8$ Hz, 2H), 2.64 (t, $J = 7.8$ Hz, 4H), 1.70-1.62 (m, 4H), 1.39-1.26 (m, 28H), 0.89 (t, $J = 6.8$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 149.9, 135.9, 135.4, 134.7, 130.4, 122.4, 106.8, 71.6, 39.7, 30.8, 29.3, 29.1, 27.5, 24.1, 23.2, 14.2, 13.8, 11.4, 11.0. MS (MALDI-TOF): m/z 738.12 (M^+).

*4,7-Bis(5-bromo-4-dodecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (11c).*⁴

This material was synthesized following the same procedure as for **11a**. After purification by column chromatography, the product was obtained as a solid (3.5 g, 87% yield). ¹H NMR (400 MHz, CDCl₃) δ : 7.75 (s, 2H), 7.71 (d, $J = 6.8$ Hz, 2H), 2.63 (t, $J = 7.6$ Hz, 4H), 1.68-1.63 (m, 4H), 1.36-1.26 (m, 36H), 0.88 (t, $J = 6.4$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.2, 143.1, 138.5, 128.1, 125.3, 124.8, 111.6, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1. MS (MALDI-TOF): m/z 794.18 (M^+).

*4,7-Bis(5-bromo-4-tetradecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (11d).*⁴

This material was synthesized following the same procedure as for **11a**. After purification by column chromatography, the product was obtained as a solid (3.65 g, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ : 7.76 (s, 2H), 7.73 (s, 2H), 2.63 (t, $J = 7.2$ Hz, 4H), 1.70-1.63 (m, 4H), 1.37-1.25 (m, 44H), 0.88 (t, $J = 6.4$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.3, 143.1, 138.5, 128.1, 125.3, 124.9, 111.6, 31.9, 29.8, 29.7, 29.6, 29.4, 29.4, 29.3, 22.7, 14.1. MS (MALDI-TOF): m/z 850.25 (M^+).

*4,7-Bis(5-bromo-4-hexadecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (11e).*⁴

This material was synthesized following the same procedure as for **11a**. After purification by column chromatography, the product was obtained as a solid (4.02 g, 89% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.77 (s, 2H), 7.75 (s, 2H), 2.64 (t, $J = 7.6$ Hz, 4H), 1.68-1.63 (m, 4H), 1.37-1.25 (m, 56H), 0.87 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 152.2, 143.1, 138.5, 128.1, 125.3, 124.9, 111.6, 31.9, 29.8, 29.7, 29.7, 29.6, 29.4, 29.4, 29.3, 22.7, 14.1. MS (MALDI-TOF): m/z 906.30 (M^+).

Synthesis of PNB-C10.

This polymer was synthesized following the same procedure as for **PNB-C2,6**. After purification by Soxhlet extraction, the desired polymer was precipitated as a black solid (69 mg, 64%). GPC: M_n (45 kDa), PDI (1.9).

Synthesis of PNB-C12.

This polymer was synthesized following the same procedure as for **PNB-C2,6**. After purification by Soxhlet extraction, the desired polymer was precipitated as a black solid (70 mg, 62%). GPC: M_n (47 kDa), PDI (1.8).

Synthesis of PNB-C14.

This polymer was synthesized following the same procedure as for **PNB-C2,6**. After purification by Soxhlet extraction, the desired polymer was precipitated as a black solid (66 mg, 55%). GPC: M_n (44 kDa), PDI (1.6).

Synthesis of PNB-C16.

This polymer was synthesized following the same procedure as for **PNB-C2,6**. After purification by Soxhlet extraction, the desired polymer was precipitated as a black solid (80 mg, 65%). GPC: M_n (47 kDa), PDI (1.8).

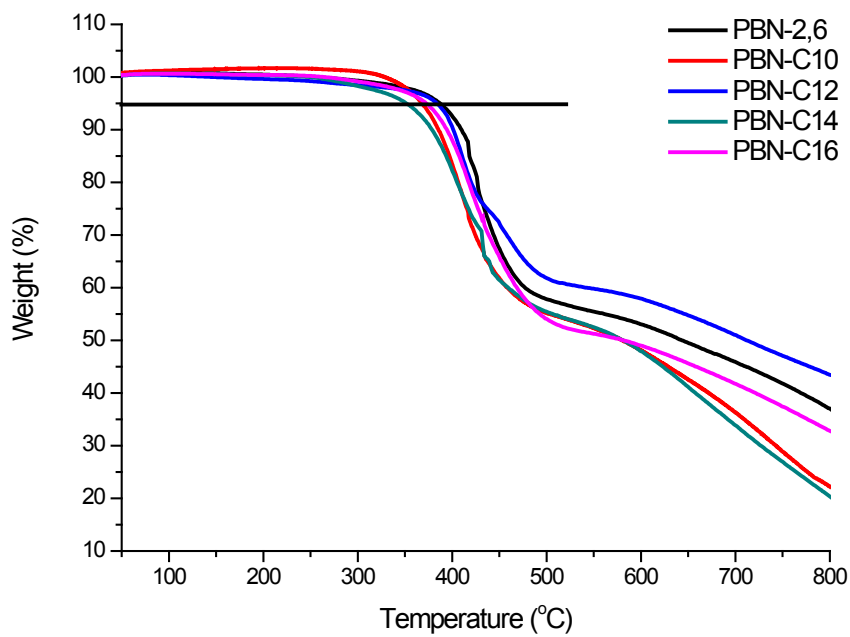


Figure S1. TGA plots of polymers with a heating rate of 10 °C / min under an inert atmosphere.

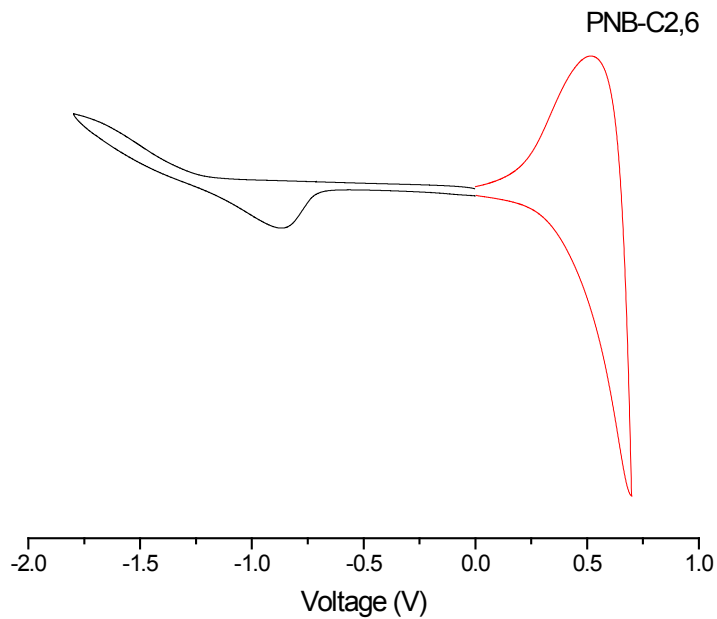


Figure S2. CV traces of PNB-C2,6.

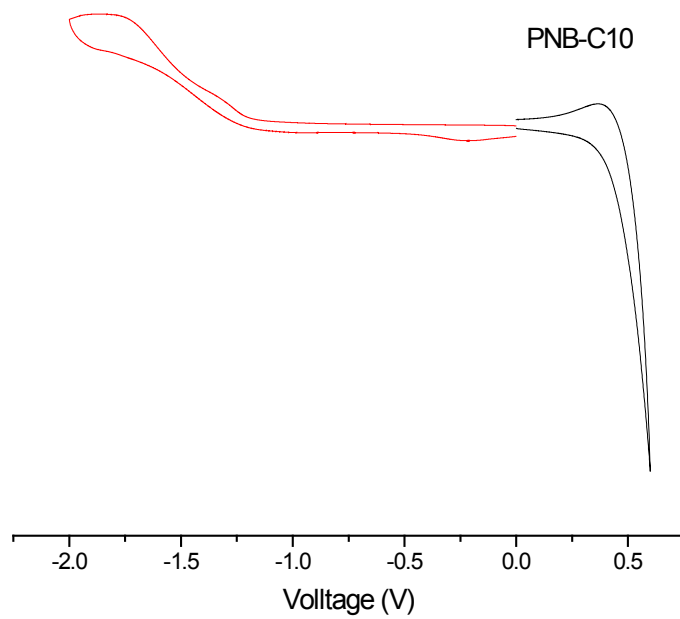


Figure S3. CV traces of PNB-C10.

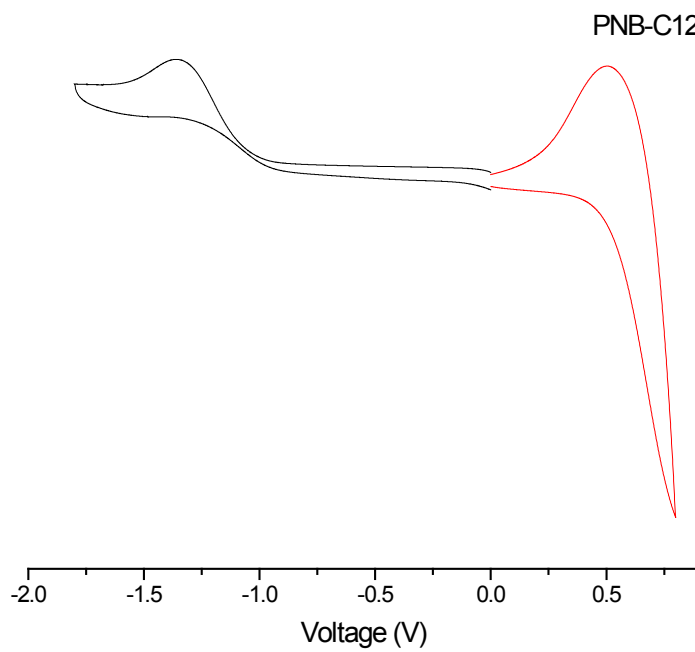


Figure S4. CV traces of PNB-C12.

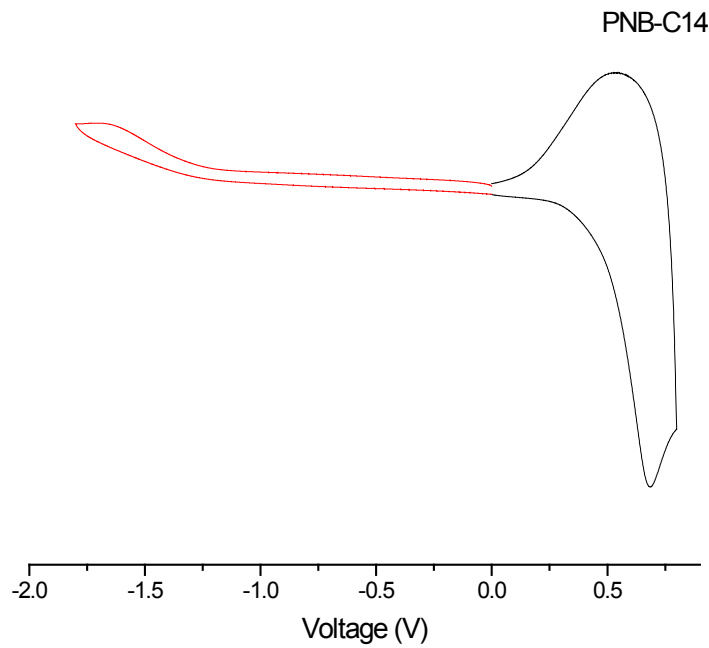


Figure S5. CV traces of PNB-C14.

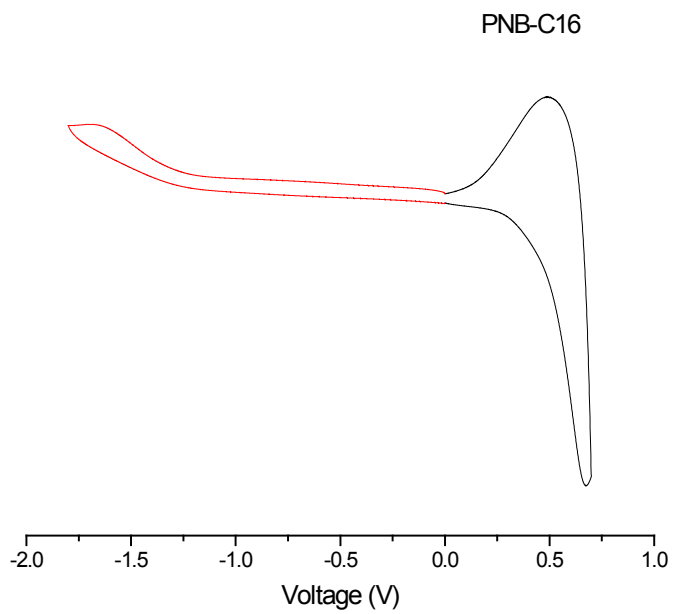


Figure S6. CV traces of PNB-C16.

Table S1. Characteristics of the PNB-C2,6 based OTFTs devices with a channel width of 1400 μm .

Channel length		Annealing temperature ($^{\circ}\text{C}$)						
		RT	80	120	160	200	240	280
8 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	5.0E-03	8.5E-03	7.9E-03	1.6E-02	1.9E-02	2.9E-02	1.3E-03
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	5-6	5	6	5-6	3	5-6	3-4
	$V_{\text{threshold}}/\text{V}$	13	8	-4	-3	20	1	-18
18 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	2.5E-03	4.4E-03	4.8E-03	9.1E-03	1.2E-02	1.7E-02	9.5E-04
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	5	5	5-6	5-6	3	5-6	3-4
	$V_{\text{threshold}}/\text{V}$	4	3	-3	3	18	-6	-21
28 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.6E-03	3.0E-03	4.6E-03	7.1E-03	1.2E-02	1.5E-02	8.6E-04
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	4	4	5	4-5	2-3	4-5	3-4
	$V_{\text{threshold}}/\text{V}$	14	3	-4	-2	30	-4	-20
38 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.8E-03	3.1E-03	4.4E-03	6.6E-03	1.0E-02	1.5E-02	7.7E-04
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	4-5	4	5-6	5-6	3	5	3-4
	$V_{\text{threshold}}/\text{V}$	6	8	-7	-4	25	-5	-21
48 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.6E-03	2.9E-03	4.2E-03	7.0E-03	1.1E-02	1.6E-02	7.0E-04
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	4-5	4-5	5-6	5	3	5	3-4
	$V_{\text{threshold}}/\text{V}$	2	8	-2	-4	25	-8	-24

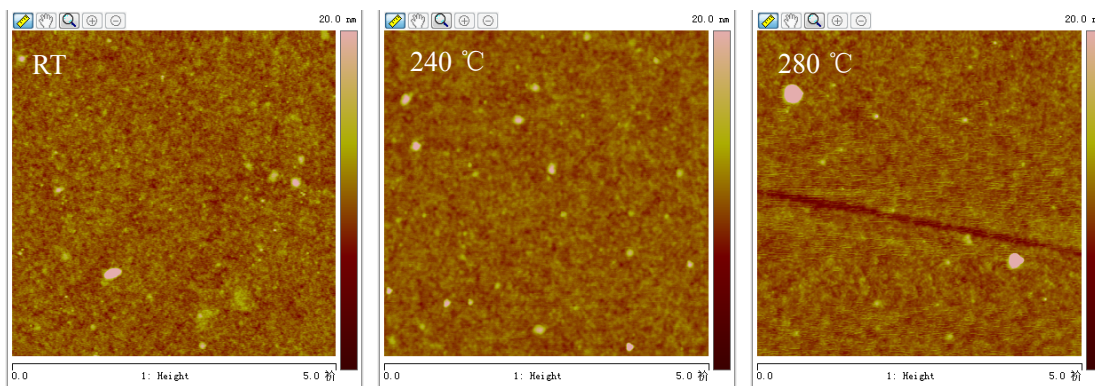


Figure S7. AFM images of the PNB-C2,6 based OTFTs devices (From RT to 280 $^{\circ}\text{C}$).

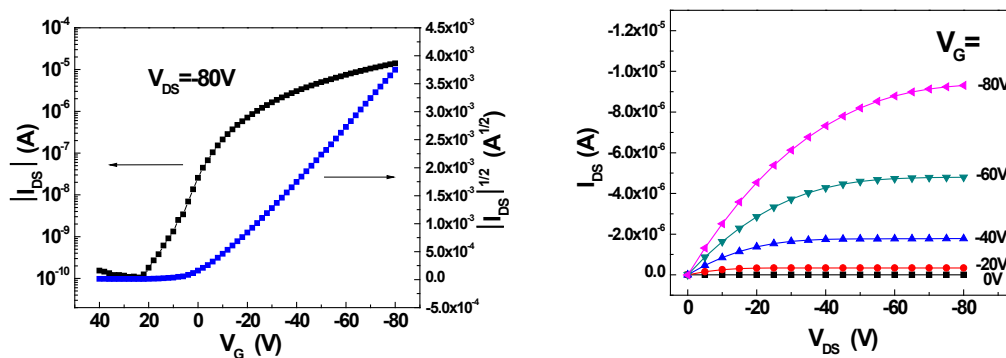


Figure S8. Transfer (left) and output (right) characteristics of the OTFTs based on **PNB-C2,6** (48 μm , 240 $^{\circ}\text{C}$).

Table S2. Characteristics of the **PNB-C10** based OTFTs devices with a channel width of 1400 μm .

Channel length		Annealing temperature ($^{\circ}\text{C}$)						
		RT	80	120	160	200	240	280
8 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.9E-03	4.2E-03	5.7E-03	6.8E-03	1.3E-02	1.5E-02	1.8E-05
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	2-3	3	3-4	2	3	2-3
	$V_{\text{threshold}}/\text{V}$	8	16	10	11	22	7	-31
18 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.7E-03	3.5E-03	4.0E-03	8.0E-03	1.0E-02	1.1E-02	9.5E-06
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	2-3	3-4	4	2	3-4	2
	$V_{\text{threshold}}/\text{V}$	12	17	12	9	32	8	-31
28 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.3E-03	2.6E-03	3.2E-03	6.5E-03	9.1E-03	8.7E-03	6.6E-06
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	3	3-4	4	2	3-4	2
	$V_{\text{threshold}}/\text{V}$	9	13	11	6	32	4	-27
38 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.3E-03	4.1E-03	3.1E-03	6.9E-03	1.0E-02	9.2E-03	5.5E-06
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	3	3-4	4-5	2	3-4	2-3
	$V_{\text{threshold}}/\text{V}$	8	13	13	6	33	8	-26
48 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.1E-03	3.0E-03	3.3E-03	6.6E-03	9.7E-03	8.3E-03	8.3E-06
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	3	3-4	4	2	4	2
	$V_{\text{threshold}}/\text{V}$	6	14	10	5	31	5	-30

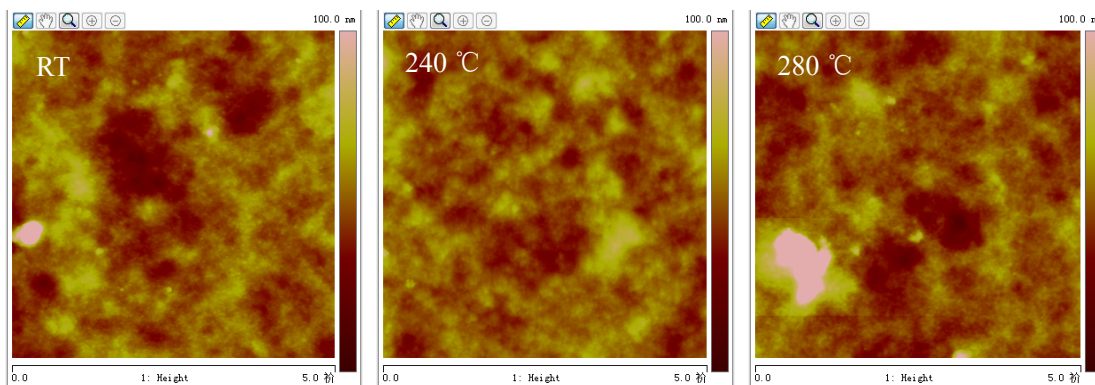


Figure S9. AFM images of the **PNB-C10** based OTFTs devices (From RT to 240 $^{\circ}\text{C}$).

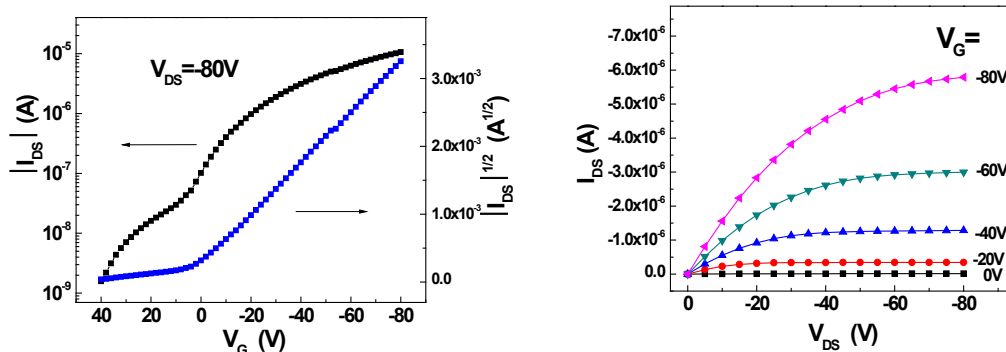


Figure S10. Transfer (left) and output (right) characteristics of the OTFTs based on **PNB-C10** (48 μm , 240 $^\circ\text{C}$).

Table S3. Characteristics of the **PNB-C12** based **OTFTs** devices with a channel width of 1400 μm .

Channel length		Annealing temperature ($^\circ\text{C}$)						
		RT	80	120	160	200	240	280
8 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	3.1E-03	8.3E-03	1.2E-02	2.3E-02	2.3E-02	2.2E-02	4.7E-05
	$\lg (I_{\text{on}}/I_{\text{off}})$	3	2-3	3	2-3	2	2-3	2-3
	$V_{\text{threshold}}/\text{V}$	3	11	4	5	16	6	-31
18 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.7E-03	5.0E-03	7.3E-03	1.3E-02	1.4E-02	1.6E-02	3.6E-04
	$\lg (I_{\text{on}}/I_{\text{off}})$	2-3	2-3	3	2-3	2	2-3	2-3
	$V_{\text{threshold}}/\text{V}$	4	14	7	10	26	6	-31
28 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.6E-03	5.1E-03	5.9E-03	1.2E-02	1.2E-02	1.4E-02	5.4E-05
	$\lg (I_{\text{on}}/I_{\text{off}})$	3	2-3	3	3	2	3	2-3
	$V_{\text{threshold}}/\text{V}$	5	11	7	7	27	6	-27
38 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.6E-03	4.7E-03	6.9E-03	1.4E-02	1.3E-02	1.4E-02	8.8E-05
	$\lg (I_{\text{on}}/I_{\text{off}})$	3	2-3	3	3	2	3	2-3
	$V_{\text{threshold}}/\text{V}$	6	12	6	3	26	6	-29
48 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.7E-03	3.9E-03	6.6E-03	1.3E-02	1.2E-02	1.3E-02	5.2E-05
	$\lg (I_{\text{on}}/I_{\text{off}})$	3	2-3	3	3-4	2	3	2-3
	$V_{\text{threshold}}/\text{V}$	5	13	5	4	26	8	-28

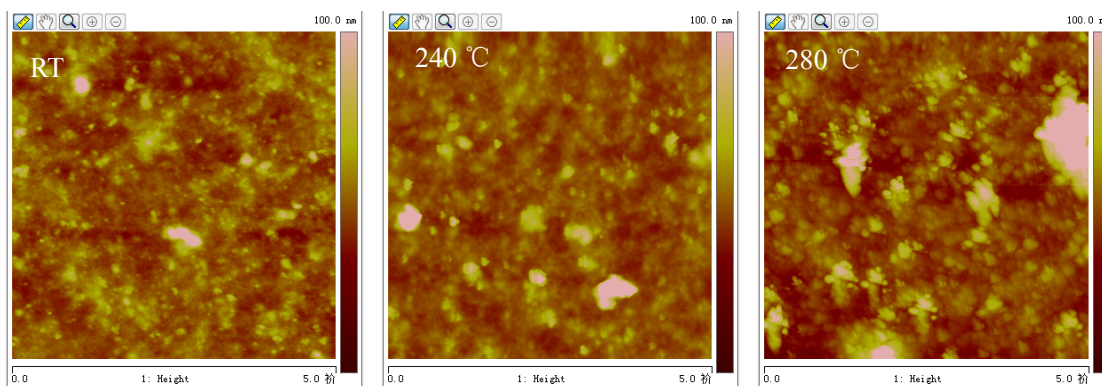


Figure S11. AFM images of the PNB-C12 based OTFTs devices (From RT to 240 °C).

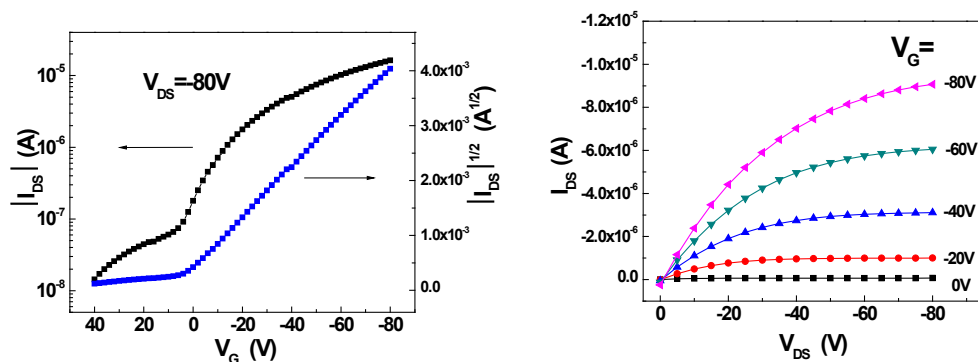


Figure S12. Transfer (left) and output (right) characteristics of the OTFTs based on PNB-C12(48 μm, 240 °C).

Table S4. Characteristics of the PNB-C14 based OTFTs devices with a channel width of 1400 μm.

Channel length		Annealing temperature (°C)						
		RT	80	120	160	200	240	280
8 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.8E-03	6.6E-03	1.4E-02	1.9E-02	2.4E-02	2.6E-02	4.2E-06
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	3-4	3	3-4	3	2-3	6-7	2-3
	$V_{\text{threshold}}/\text{V}$	2	10	11	15	18	-14	-34
18 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.5E-03	4.8E-03	1.0E-02	1.3E-02	1.9E-02	2.0E-02	4.9E-06
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	3-4	3-4	4	3	2-3	5-6	2-3
	$V_{\text{threshold}}/\text{V}$	-3	9	11	13	25	-19	-36
28 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	6.6E-04	2.8E-03	5.1E-03	7.4E-03	1.1E-02	1.1E-02	1.7E-06
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	3-4	3-4	4	3-4	2-3	5-6	2-3
	$V_{\text{threshold}}/\text{V}$	-5	7	10	15	24	-20	-25
38 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	8.9E-04	3.6E-03	5.3E-03	8.4E-03	1.4E-02	1.4E-02	2.0E-06
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	3-4	3-4	4-5	3-4	2-3	5-6	2-3
	$V_{\text{threshold}}/\text{V}$	-3	7	8	15	24	-15	-25
48 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.3E-03	5.2E-03	7.9E-03	1.2E-02	1.7E-02	2.1E-02	3.7E-06
	$\lg \langle I_{\text{on}}/I_{\text{off}} \rangle$	3-4	3-4	4-5	3-4	2-3	6	2-3
	$V_{\text{threshold}}/\text{V}$	-2	7	11	15	24	-15	-26

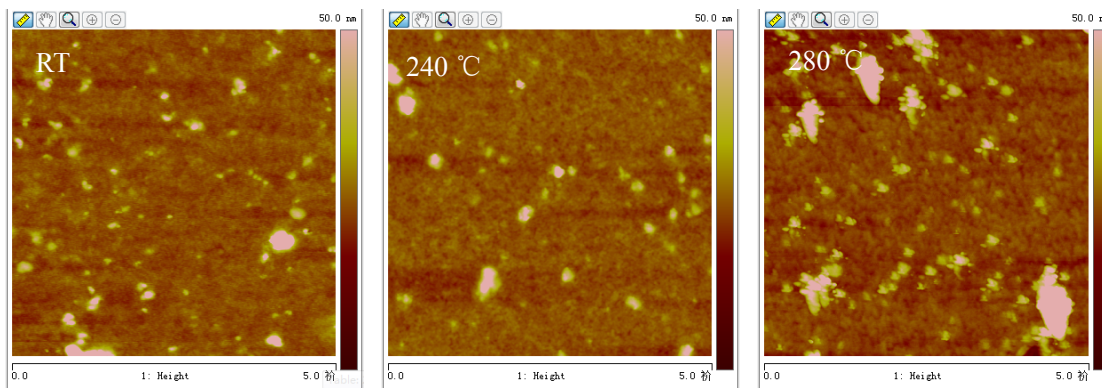


Figure S13. AFM images of the PNB-C14 based OTFTs devices (From RT to 240 °C).

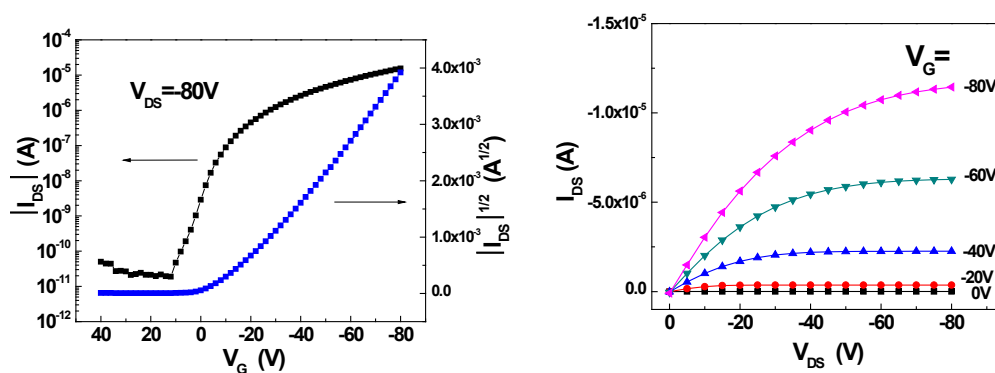


Figure S14. Transfer (left) and output (right) characteristics of the OTFTs based on PNB-C14 (48 μm , 240 °C).

Table S5. Characteristics of the PNB-C16 based OTFTs devices with a channel width of 1400 μm .

Channel length		Annealing temperature (°C)						
		RT	80	120	160	200	240	280
8 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	3.7E-03	1.0E-02	1.7E-02	2.3E-02	3.4E-02	1.9E-02	1.5E-05
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	3	3	2-3	6	4-5	2-3
	$V_{\text{threshold}}/\text{V}$	-10	9	9	10	-10	-14	-34
18 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	2.2E-03	8.3E-03	1.5E-02	1.9E-02	2.5E-02	1.6E-02	1.1E-05
	$\lg(I_{\text{on}}/I_{\text{off}})$	4	3-4	3-4	3	5-6	5	2-3
	$V_{\text{threshold}}/\text{V}$	-17	8	6	11	-11	-15	-32
28 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.9E-03	8.1E-03	1.4E-02	1.8E-02	2.6E-02	1.7E-02	1.5E-05
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	3-4	3-4	2-3	5-6	4-5	2-3
	$V_{\text{threshold}}/\text{V}$	-18	9	7	12	-14	-15	-31
38 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	2.0E-03	8.4E-03	1.3E-02	1.8E-02	2.2E-02	1.5E-02	7.7E-06
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	3	3-4	2-3	5-6	4-5	2-3
	$V_{\text{threshold}}/\text{V}$	-13	7	7	12	-17	-18	-28

48 μm	$\mu/\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	1.7E-03	1.0E-02	1.3E-02	1.7E-02	2.4E-02	1.4E-02	5.8E-06
	$\lg(I_{\text{on}}/I_{\text{off}})$	3-4	4-5	3-4	3	5-6	4-5	2-3
	$V_{\text{threshold}}/\text{V}$	-7	-4	7	12	-14	-18	-31

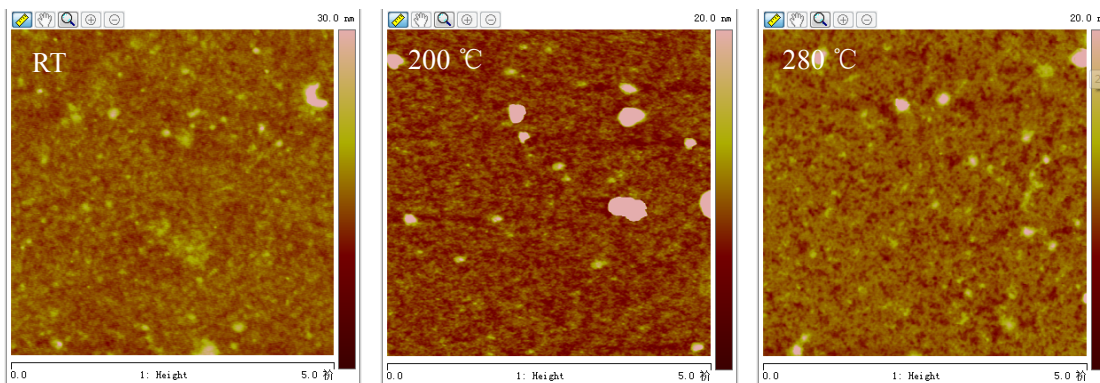


Figure S15. AFM images of the PNB-C16 based OTFTs devices (From RT to 240 °C).

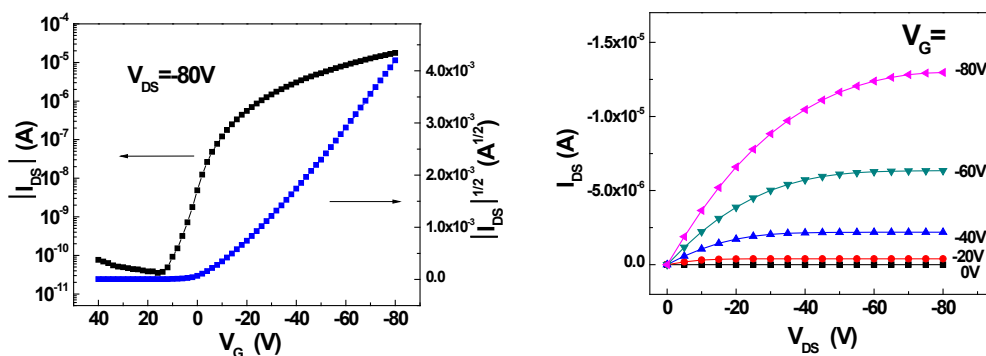


Figure S16. Transfer (left) and output (right) characteristics of the OTFTs based on PNB-C16 (48 μm , 200 °C).

PNB-C n :PC $_{71}$ BM (1:2) in CB w/o DIO

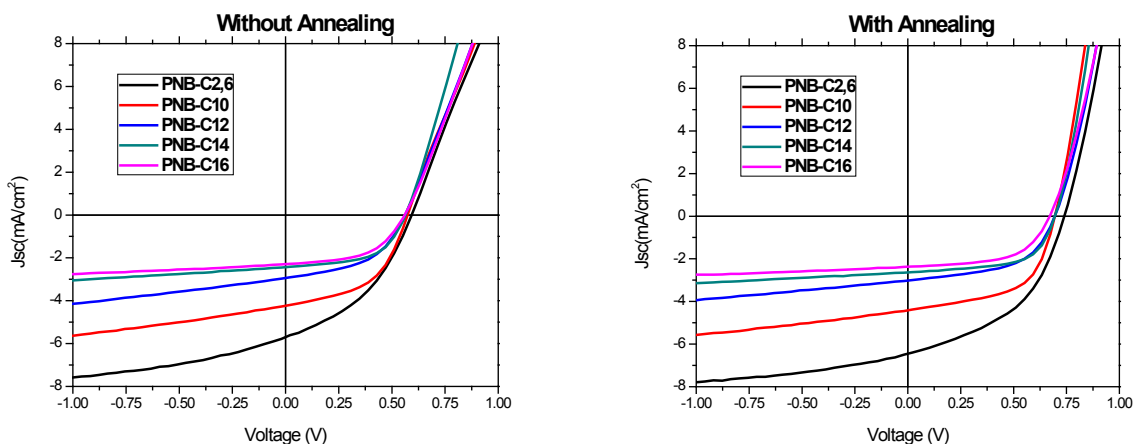


Figure S17. *J-V* curves without (left) and with annealing (right) of BHJ PV devices with PNB-*C_n*:PC₇₁BM (1:2) in CB w/o DIO.

Table S6. PV performance of polymer based devices without annealing and DIO.

No annealing	V_{oc}	J_{sc}	J_{sc} (IPCE)	FF	PCE	PCE (IPCE)
PNB-C2,6	0.59	5.7	5.99	40.4	1.37	1.44
PNB-C10	0.57	4.2	4.41	50.4	1.22	1.28
PNB-C12	0.56	2.9	3.05	48.8	0.81	0.85
PNB-C14	0.57	2.4	2.52	56.1	0.77	0.81
PNB-C16	0.55	2.3	2.42	57.3	0.68	0.71

Table S7. PV performance of polymer based devices with annealing and without DIO.

Post annealing	V_{oc}	J_{sc}	J_{sc} (IPCE)	FF	PCE	PCE (IPCE)
PNB-C2,6	0.74	6.45	6.78	46.0	2.2	2.31
PNB-C10	0.67	4.40	4.62	56.3	1.73	1.82
PNB-C12	0.69	3.02	3.17	53.5	1.12	1.18
PNB-C14	0.70	2.64	2.77	60.5	1.11	1.17
PNB-C16	0.67	2.37	2.49	60.5	0.92	0.97

PNB-C_n:PC₇₁BM(1:2) in CB+DIO(1%)

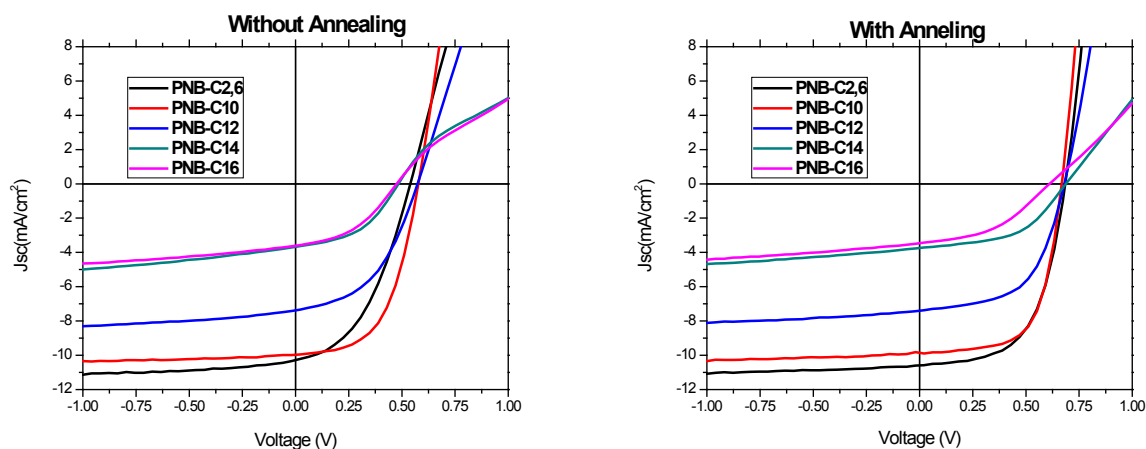


Figure S18. *J-V* curves without (left) and with annealing (right) of BHJ PV devices with PNB-C_n:PC₇₁BM (1:2) in CB+DIO (1%).

Table S8. PV performance of polymer based devices without annealing and with DIO (1%).

No annealing	V_{oc}	J_{sc}	J_{sc} (IPCE)	FF	PCE	PCE (IPCE)
PNB-C2,6	0.54	10.28	10.80	43.3	2.4	2.52
PNB-C10	0.58	9.97	10.47	54.8	3.16	3.32
PNB-C12	0.57	7.38	7.75	46.47	1.97	2.07
PNB-C14	0.48	3.67	3.85	45.9	0.82	0.86
PNB-C16	0.47	3.61	3.79	41.3	0.71	0.75

Table S9. PV performance of polymer based devices with annealing and DIO (1%).

Post annealing	V_{oc}	J_{sc}	J_{sc} (IPCE)	FF	PCE	PCE (IPCE)
PNB-C2,6	0.68	10.6	11.13	58.4	4.2 (4.12)	4.45 (4.33)
PNB-C10	0.67	9.85	10.34	64.7	4.27 (4.51)	4.48 (4.75)
PNB-C12	0.68	7.4	7.77	56.3	2.84	2.98
PNB-C14	0.68	4.12	4.33	51.5	1.45	1.52

PNB-C16	0.65	3.79	3.98	45.7	1.12	1.18
----------------	------	------	------	------	------	------

PNB-C_n:PC₇₁BM(1:2) in CB+DIO (3%)

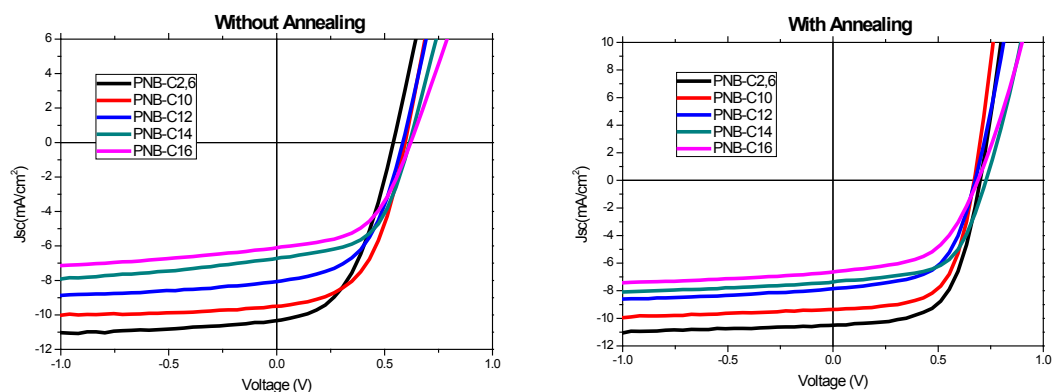


Figure S19. *J-V* curves without (left) and with annealing (right) of BHJ PV devices with PNB-C_n:PC₇₁BM (1:2) in CB+DIO (3%).

Table S10. PV performance of polymer based devices without annealing but with DIO (3%).

No annealing	V_{oc}	J_{sc}	J_{sc} (IPCE)	FF	PCE	PCE (IPCE)
PNB-C8	0.54	10.33	10.95	47.3	2.64	2.8
PNB-C10	0.59	9.5	10.07	51.7	2.92	3.1
PNB-C12	0.58	8.06	8.54	51.33	2.41	2.55
PNB-C14	0.613	6.72	7.12	54.8	2.26	2.4
PNB-C16	0.62	6.1	6.47	51.8	1.96	2.1

Table S11. PV performance of polymer based devices with annealing and DIO (3%).

Post annealing	V_{oc}	J_{sc}	J_{sc} (IPCE)	FF	PCE	PCE (IPCE)
PNB-C2,6	0.7	10.5	11.13	61	4.5	4.8
PNB-C10	0.68	9.36	9.92	62.5	3.93	4.2

PNB-C12	0.68	7.85	8.32	58	3.3	3.5
PNB-C14	0.73	7.35	7.79	59.2	3.2	3.4
PNB-C16	0.67	6.64	7.04	62.5	2.8	2.97

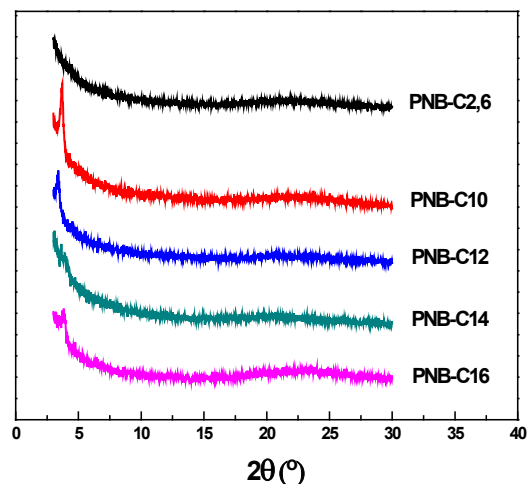


Figure S20. The X-ray diffraction (XRD) patterns of the polymer thin films annealed at temperature of 200 to 240 °C.

References:

1. B. Wang, S.-W. Tsang, W. Zhang, Y. Tao, M. S. Wong, *Chem. Commun.*, **2011**, 47, 9471.
2. L. Biniek, S. Fall, C. L. Chochos, D. V. Anokhin, D. A. Ivanov, N. Leclerc, P. Lévêque, T. Heiser, *Macromolecules*, **2010**, 43, 9779.
3. L. Yang, H. Zhou, W. You, *J. Phys. Chem. C*, **2010**, 114, 16793.
4. S. P. Mishre, A. K. Palai, R. Srivastava, M. N. Kamalasanan, M. Patri, *J. Poly. Sci. Part A: Polym. Chem.*, **2009**, 47, 6514.