

Supplementary Information

A Donor Polymer Based on 3-Cyanothiophene with Superior Batch-to-Batch Reproducibility for High-Efficiency Organic Solar Cells

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1. Synthesis

General information: 3-Cyano-2,5-dibromothiophene (2) and 2-(tri-*n*-butylstannyl)-4-octylthiophene were synthesized according to the procedures reported in literatures.^[1] (4,8-Bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (compound 5) was purchased from Suna Tech Inc, Y6 was purchased from Derthon Optoelectronic Materials Science Technology Co LTD, and PNDIT-F3N was purchased from eFlexPV. The other chemicals and solvents were purchased from commercial sources (Sigma Aldrich, Acros, Stream, S2 or Alfa Aesar) and used as received unless otherwise indicated.

4,4''-Dioctyl-[2,2':5',2''-terthiophene]-3'-carbonitrile (3): A mixture of 2-(tri-*n*-butylstannyl)-4-octylthiophene (8.51 g, 17.53 mmol), and compound 2 (1.56 g, 5.84 mmol) was dissolved in 80 mL *N,N*-dimethylformamide. After being purged by argon twice, Pd(PPh₃)₄ (337 mg, 0.34 mmol) was added into the solution and then the reaction mixture was purged by argon twice again. The reaction was stirred at 80 °C overnight. After removing the solvent, the product was purified by column chromatography of silica gel using dichloromethane:petroleum ether (1:4) solvent mixture as eluent to afford the crude product, which was further purified by recrystallization from the solvent mixture of methanol and tetrahydrofuran to give the title compound 3 (2.59 g, yield = 89%). ¹H NMR (500 MHz, CDCl₃, δ): 7.43 (s, 1H), 7.17 (s, 1H), 7.03 (s, 1H), 7.00 (s, 1H), 6.89 (s, 1H), 2.64-2.57 (m, 4H), 1.66-1.60 (m, 4H), 1.32-1.28 (m, 20H), 0.90-0.87 (t, 6H). ¹³C NMR (125 MHz, CDCl₃, δ): 145.08, 144.83, 144.54, 136.39, 134.35, 132.73, 128.40, 126.46, 124.91, 122.44, 120.72, 115.57, 105.01, 31.89, 30.44, 30.41, 30.39, 29.41, 29.29, 29.26, 22.69, 14.13.

5,5''-Dibromo-4,4''-dioctyl-[2,2':5',2''-terthiophene]-3'-carbonitrile (4): A mixture of compound 3 (967 mg, 1.94 mmol), and *N*-bromosuccinimide (NBS) (691 mg, 2.00 mmol) in the solvent mixture of chloroform (50 mL) and acetate acid (25 mL) was stirred at 60 °C for 18 hours. The reaction was cooled to room temperature, quenched by deionized water, and then extracted with dichloromethane. The organic layer was dried over magnesium sulfate. After removing the solvent, the crude product was subjected to column chromatography of silica gel using dichloromethane:petroleum ether (1:5) solvent mixture as eluent to afford a yellow solid, which was further purified by recrystallization from the solvent mixture of methanol and tetrahydrofuran to give the title compound 4 (1.19 g, yield = 94%). ¹H NMR (500 MHz, CDCl₃, δ): 7.27 (s, 1H), 7.11 (s, 1H), 6.89 (s, 1H), 2.59-2.52 (m, 4H), 1.64-1.57 (m, 4H), 1.33-1.28 (m, 20H), 0.90-0.87 (t, 6H). ¹³C NMR (125

MHz, CDCl₃, δ): 144.12, 143.75, 143.47, 135.70, 133.87, 132.28, 128.05, 126.08, 125.07, 115.11, 112.17, 109.91, 105.38, 31.87, 29.62, 29.54, 29.34, 29.29, 29.22, 22.67, 14.12.

Synthesis of PBCT-2F (18, 40, and 57 kDa): To a degassed solution of compound 4 (98.34 mg, 0.15 mmol) and compound 5 (141.08 mg, 0.15 mmol) in mixture solution of anhydrous *o*-xylene (4 mL) and *N,N*-dimethylformamide (0.5 mL) under argon protection, Pd(PPh₃)₄ (3.47 mg, 0.003 mmol) were added. The mixture was then stirred at 120 °C for 3, 5.5 and 8 hours, respectively. After that, 2-(tributylstannyl) thiophene and 2-bromothiophene were sequentially added to the reaction with a two hours interval. After another two hours, the reaction was refluxed with an aqueous solution of sodium *N,N*-diethylcarbamodithioate trihydrate for 2 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform under argon protection. The chloroform fraction was concentrated under reduced pressure and precipitated in methanol to obtain the resulting polymer batches.

PBCT-2F (18 kDa) (CF fraction, yield = 88%): M_n = 18 kDa, D_M = 2.4;

PBCT-2F (40 kDa) (CF fraction, yield = 94%): M_n = 40 kDa, D_M = 2.2;

PBCT-2F (57 kDa) (CF fraction, yield = 95%): M_n = 57 kDa, D_M = 2.3.

Synthesis of PBCT-2F (64 kDa): To a degassed solution of compound 4 (98.34 mg, 0.15 mmol) and compound 5 (141.08 mg, 0.15 mmol) in mixture solution of anhydrous *o*-xylene (4 mL) and *N,N*-dimethylformamide (0.5 mL) under argon protection, Pd₂(dba)₃ (2.33 mg, 0.0023 mmol) and P(*o*-tol)₃ (5.48 mg, 0.018 mmol) were added. The mixture was then stirred at 120 °C for 24 hours. After that, 2-(tributylstannyl) thiophene and 2-bromothiophene were sequentially added to the reaction with a two hours interval. After another 2 hours, the reaction was refluxed with an aqueous solution of sodium *N,N*-diethylcarbamodithioate trihydrate for 2 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, trichloromethane under argon protection. The residue was dissolved in hot chlorobenzene and then filtered. The chlorobenzene fraction was concentrated under reduced pressure and precipitated in methanol to obtain the polymer.

PBCT-2F (64 kDa) (CB fraction, yield = 93%): M_n = 64 kDa, D_M = 2.0.

Synthesis of PBCT-2F (26, and 74 kDa): To a degassed solution of compound 4 (98.34 mg, 0.15 mmol) and compound 5 (141.08 mg, 0.15 mmol) in mixture solution of anhydrous *o*-xylene (4 mL) and *N,N*-dimethylformamide (0.5 mL) under argon protection, Pd(PPh₃)₄ (3.47 mg, 0.003 mmol) were added. The mixture was then stirred at 120 °C for 40 hours. After that, 2-(tributylstannyl) thiophene and 2-bromothiophene were sequentially added to the reaction with a two hours interval. After another 2 hours, the reaction was refluxed with an aqueous solution of sodium *N,N*-diethylcarbamodithioate trihydrate for 2 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform under argon protection. The residue was dissolved in hot chlorobenzene and then filtered. The chloroform and chlorobenzene fractions were concentrated under reduced pressure and precipitated into methanol, and the precipitates were dried under vacuum to obtain resulting polymers.

PBCT-2F (26 kDa) (CF fraction, yield = 35%): M_n = 26 kDa, D_M = 2.6;

PBCT-2F (74 kDa) (CB fraction, yield = 63%): $M_n = 74$ kDa, $D_M = 2.2$.

2. Measurements and characterization

Nuclear magnetic resonance (NMR): ^1H and ^{13}C NMR were measured on a Bruker AV-500 MHz spectrometer in deuterated solvents at room temperature. Chemical shifts were recorded with tetramethylsilane (TMS) as the internal reference.

Gel permeation chromatography (GPC): The molecular weights of PBCT-2F were determined using a PL-GPC 220 high-temperature chromatography in 1,2,4-trichlorobenzene (TCB) at 150 °C and using a calibration curve of polystyrene standards.

Thermogravimetric analysis (TGA): TGA measurements were conducted on a NETZSCH (DSC200F3) apparatus at a heating rate of 20 °C min⁻¹ under nitrogen atmosphere.

Differential scanning calorimetry (DSC): DSC measurements were performed on a NETZSCH (DSC200F3) apparatus under a nitrogen atmosphere with a heating/cooling rate of 10/20 °C min⁻¹ for the first cycle and a heating/cooling rate of 10/40 °C min⁻¹ for the second cycle, respectively.

UV-vis absorption spectra: UV-vis absorption of the polymers in chlorobenzene solutions and in films were recorded on a SHIMADZU UV-3600 spectrophotometer.

Cyclic voltammetry (CV): Cyclic voltammetry was carried out on a CHI660A electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a platinum plate as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. A ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as internal standard and was assigned an absolute energy of - 4.8 eV vs vacuum. The HOMO energies of materials were determined according to the equation $E_{\text{HOMO}} = -e (E_{\text{ox onset}} + 4.8 - E_{1/2}^{(\text{Fc}/\text{Fc}^+)})$, where $E_{\text{ox onset}}$ is the onset of oxidation potential relative to the measured Fc/Fc^+ redox couple. And the LUMO energies of materials were determined according to the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$. The Fc/Fc^+ redox couple was found at 0.42 V relative to the Ag/Ag^+ electrode.

Single crystal X-ray diffraction: Single-crystal of compound 4 was grown by slow evaporation method. The powder material samples were completely dissolved by in chloroform and ethanol mixing solution with concentrations of around 3 mg mL⁻¹, then the solvent was evaporated over the following days, and finally the needle-like crystals grew on the inner wall of glass vial. A suitable crystal was selected and measured on Rigaku XtaLAB P2000 diffractometer. The crystal was kept at 150 K during data collection. After data reduction, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

Density functional theory (DFT) calculation: The optimized molecular geometry with DFT at B3LYP/6-31G(d) level. The calculation of frontier orbitals was performed by using Gaussian 16 package. All the alkyl chains were replaced with methyl for calculation.

Grazing incidence wide-angle X-ray scattering (GIWAXS) for the comparison of PBCT-2F (64 kDa) and PM6: The grazing incidence wide-angle X-ray scattering (GIWAXS) was carried out at the PLS-II 6D U-SAXS beamline of the Pohang Accelerator Laboratory. The X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength $\lambda = 1.07220$ Å) using a double crystal monochromator and focused both horizontally and vertically (450 (H) × 60 (V) μm² in FWHM @ the sample position) using K-B type mirrors. The GIWAXS sample stage was equipped with a 7-axis motorized stage for the fine alignment of the sample, and the incidence angles of the X-ray beam were set to be 0.12° for the blend films. The GIWAXS patterns were recorded with a

2D CCD detector (Rayonix SX165) and an X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21, $a = 10.8631 \text{ \AA}$, $b = 8.7044 \text{ \AA}$, $c = 7.7624 \text{ \AA}$, and $\beta = 102.938^\circ$) and the sample-to-detector distance was $\approx 227 \text{ mm}$.

GIWAXS for the comparison of various PBCT-2F batches (18, 26, 40, 57, 64, and 74 kDa):

2D-GIWAXS experiments were carried out on a GANESHA 300XL+ system from JJ X-ray. The instrument is equipped with a Pilatus 300K detector, with pixel size of $172 \times 172 \text{ }\mu\text{m}$. The X-ray source is a Genix 3D Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (multilayer optic “3D version” optimized for SAXS) (30 W). The wavelength used is $\lambda = 1.5418 \text{ \AA}$. The detector moves in a vacuum chamber with sample-to-detector distance varied between 0.115 m and 1.47 m depending on the configuration used, as calibrated using silver behenate ($d_{001} = 58.380 \text{ \AA}$). The minimized background scattering plus high-performance detector allows for a detectable q -range varying from 3E^{-3} to $3 \text{ \AA}^{-1}$ (0.2 to 210 nm). The sample was placed vertically on the goniometer and tilted to a glancing angle of 0.2° with respect to the incoming beam. A small beam was used to get a better resolution. The primary slits have a size of $0.3 \text{ (horizontal)} \times 0.5 \text{ mm}$ (vertical), and the guard slits have a size of $0.1 \text{ (horizontal)} \times 0.3 \text{ (horizontal)} \text{ mm}$. The accumulation time was 2 h for each measurement. In plane and out of plane line cuts were obtained using SAXSGUI program.

Atomic force microscopy (AFM): AFM images were acquired from a Bruker Multimode 8 Microscope AFM in tapping-mode.

Transmission electron microscope (TEM): TEM images were obtained from a JEM-2100F transmission electron microscope operated at 200 kV.

Contact angle measurements: The contact angle tests were conducted on a Dataphysics OCA40 Micro surface contact angle analyzer. The surface tension of the materials was characterized and calculated by the contact angles of the water and ethylene glycol via the Owens-Wendt & Kaelble (OW) method, where γ^d and γ^p are the dispersion and polarity components, respectively. The samples were cast on PEDOT:PSS-coated ITO substrates, and the contact angle images were taken when the liquids had been dropped on the sample films for 60s.

3. Device fabrication and characterization

Fabrication of solar cells: Patterned indium tin oxide (ITO) glass substrates were precleaned sequentially by sonicating in a detergent bath, then with deionized water, acetone, and isopropanol at room temperature and in a boiled isopropanol bath, each for 10 minutes. The substrates were subjected to oxygen plasma treatment at room temperature for 20 minutes. Then PEDOT:PSS was spin-coated on the ITO glass substrates at 3000 rpm for 30 seconds to give a thickness of 40 nm, followed by baking at 140°C for 15 minutes. The substrates were transferred to a nitrogen-filled glove box. The active layer solution of the PBCT-2F:Y6 blend was prepared in chloroform with a concentration of 16 mg mL^{-1} . The active layers were spin-coated on substrates in a nitrogen-filled glovebox at 2000 rpm to give a thickness of 100 nm. The films were then annealed at 100°C for three minutes. Afterwards, a layer of PNDIT-F3N (10 nm) was spin-coated from a methanol solution (1.0 mg mL^{-1}) at a speed of 3000 rpm for 30 seconds. Finally, a 100 nm Ag was deposited by thermal evaporation through a shadow mask in a vacuum chamber with a pressure of $4 \times 10^{-4} \text{ Pa}$.

Characterization of solar cells: The solar cells were measured under AM1.5G illumination derived from a class solar simulator (Enlitech, Taiwan). The current density–voltage (J – V) curves were recorded with a Keithley 2400 source meter. The light intensity was 100 mW cm^{-2} in the test, which

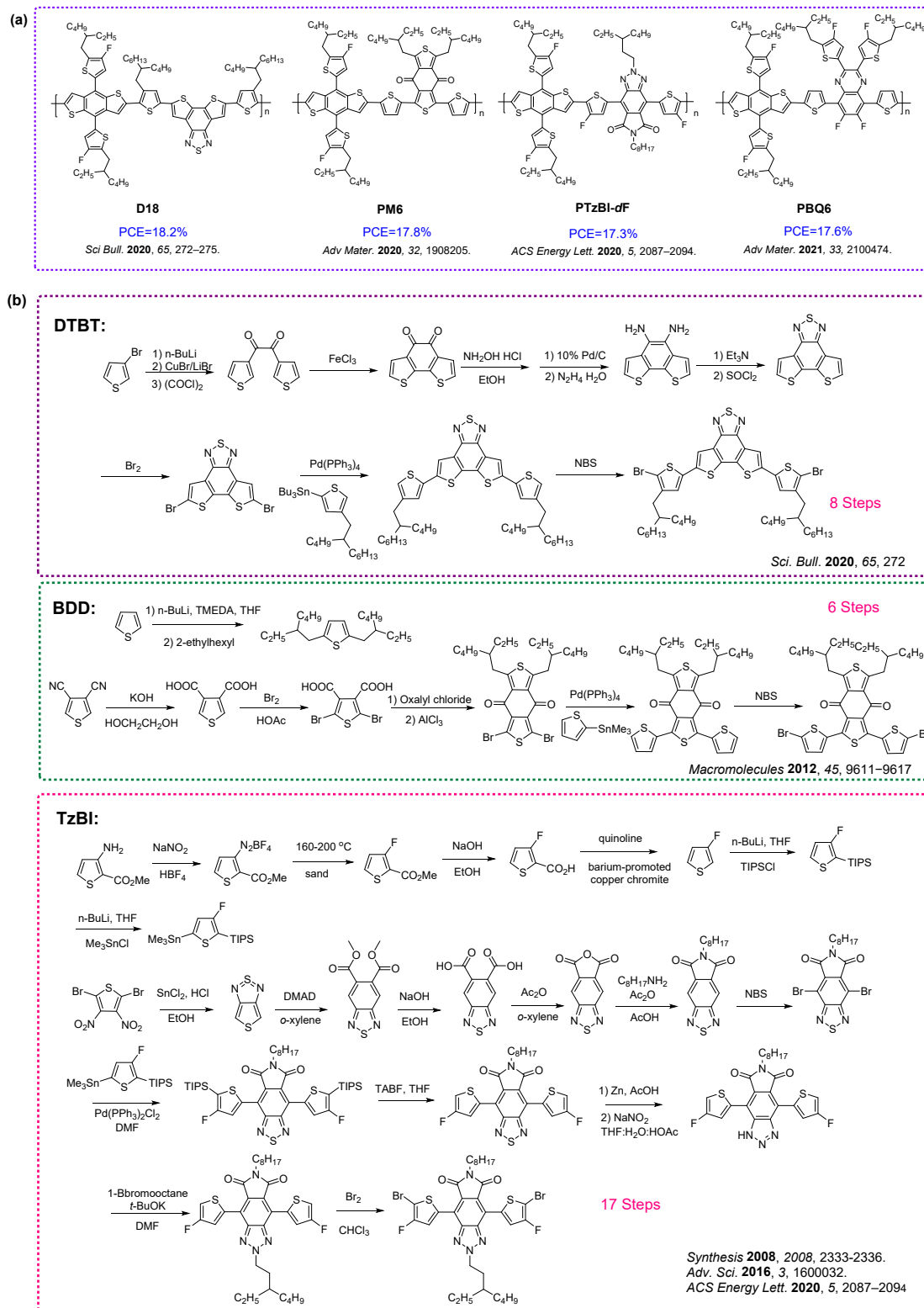
was calibrated by a China General Certification Center certified reference monocrystal silicon cell (Enlitech).

External quantum efficiencies (EQEs): EQEs were recorded on a commercial EQE measurement system (Enlitech, QE-R3011, Taiwan).

Fabrication and characterization of single-carrier devices: The electron and hole mobility were measured in single carrier devices with a structure of ITO/ZnO/active layer/ PDNIT-F3N/Ag for electron only devices and a structure of ITO/PEDOT:PSS/active layers/MoOx/Ag for hole-only devices. The dark current densities of the polymer:Y6 blends were measured by applying a voltage between 0 and 5 V using a computer-controlled Keithley 2400 source meter under an N₂ atmosphere. The data were analyzed according to the Mott–Gurney law that considers a Poole–

Frenkel-type dependence of mobility on the electric field, given by $J = \frac{9}{8\epsilon_r\epsilon_0\mu_0} \exp(0.89\gamma\sqrt{V/d})$, where ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant of the polymer which is assumed to be 3 for organic semiconductors, μ_0 is the zero-field mobility, V is the voltage drop across the device, d is the film thickness of the active layer, and γ is a parameter that describes the strength of the field-dependence effect. The applied voltage is used without correcting for series resistance or built-in voltage, which offers the best fitting of the experimental data following the protocol reported in the literature.¹ The hole and electron mobilities are extracted with the fit parameters at an electric field (E) of $1 \times 10^5 \text{ V cm}^{-1}$ by the Murgatroyd equation $\mu = \mu_0 \exp(\gamma\sqrt{E})$.

4. Additional figures and tables



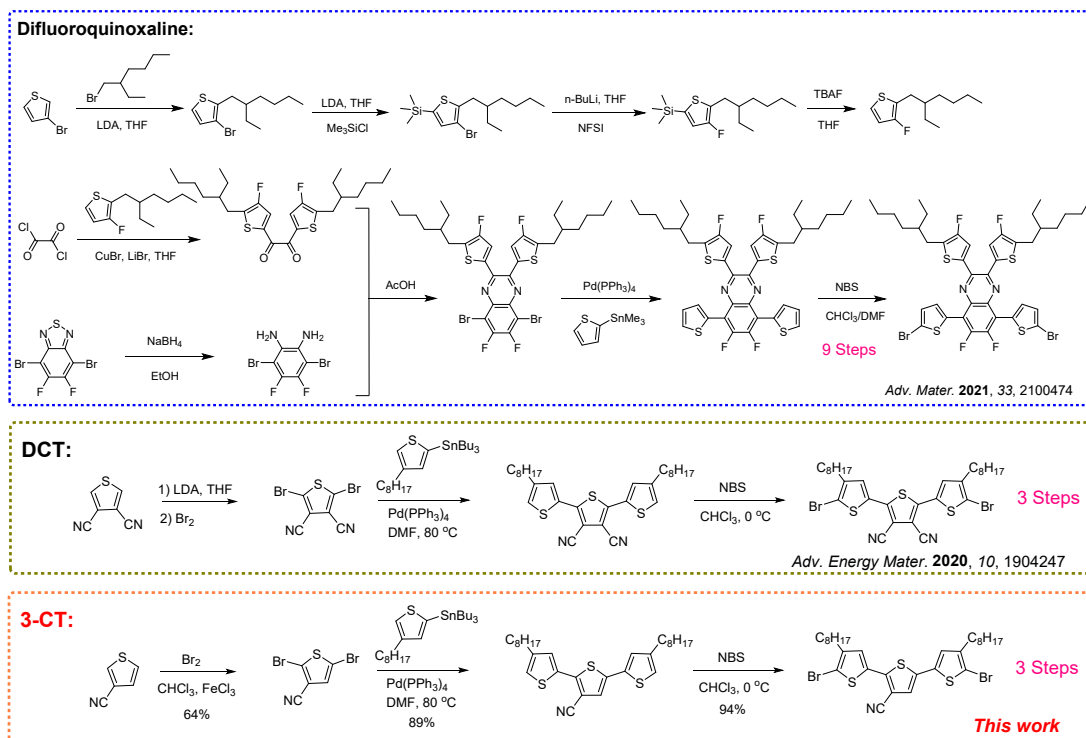


Figure S1. (a) Chemical structure of the representative polymers mentioned in this paper. (b) Synthetic routes of the representative monomers mentioned in this paper.

Table S1. Crystal data and structure refinement parameters for the compound 4.

Name	Compound 4
Empirical formula	C ₂₉ H ₃₇ Br ₂ NS ₃
Formula weight	655.59
Temperature/K	149.98(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.9722(7)
b/Å	17.5232(8)
c/Å	19.1562(9)
α /°	94.993(4)
β /°	108.440(4)
γ /°	91.696(4)
Volume/Å ³	4424.4(4)
Z	6
ρ_{calc} /cm ³	1.476
μ /mm ⁻¹	5.603
F(000)	2016
Crystal size/mm ³	0.058 × 0.052 × 0.039
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	4.888 to 134.156
Index ranges	-16 ≤ h ≤ 16, -13 ≤ k ≤ 20, -22 ≤ l ≤ 21
Reflections collected	43246
Independent reflections	15307 [R _{int} = 0.0891, R _{sigma} = 0.1061]
Data/restraints/parameters	15307/24/952
Goodness-of-fit on F ²	0.948
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0857, wR ₂ = 0.2003
Final R indexes [all data]	R ₁ = 0.1726, wR ₂ = 0.2572
Largest diff. peak/hole / e Å ⁻³	4.68/-0.83

Table S2. Dihedral angles between the thiophene units in the compound 4.

Conformational molecule	θ_1	θ_2
I	0.58	3.66
II	0.73	8.34
III	2.91	3.36

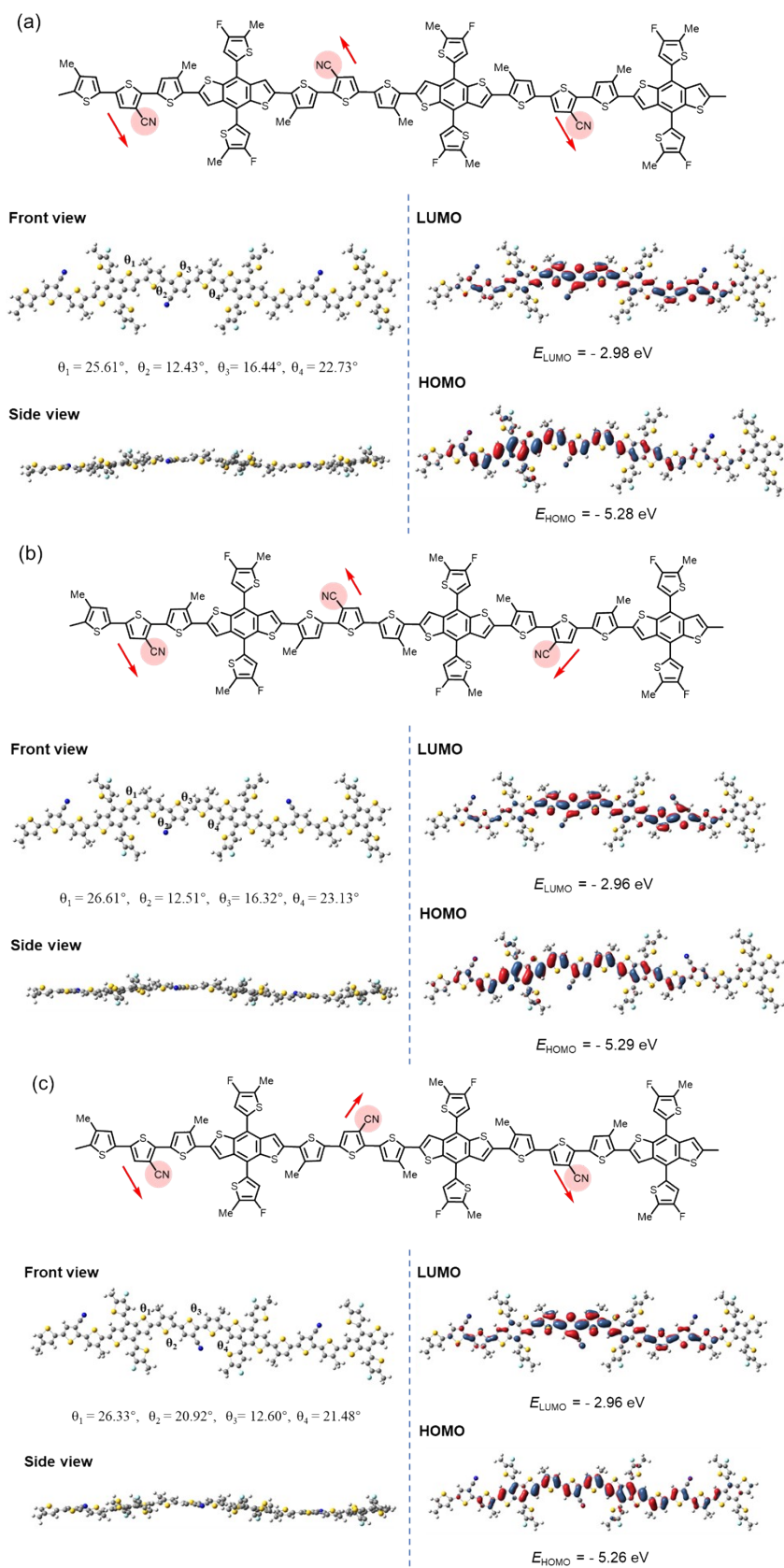


Figure S2. Calculated molecular geometries and frontier molecular orbitals of PBCT-2F trimers at B3LYP/6-31G(d) level. Three possible configurations were used for the calculations.

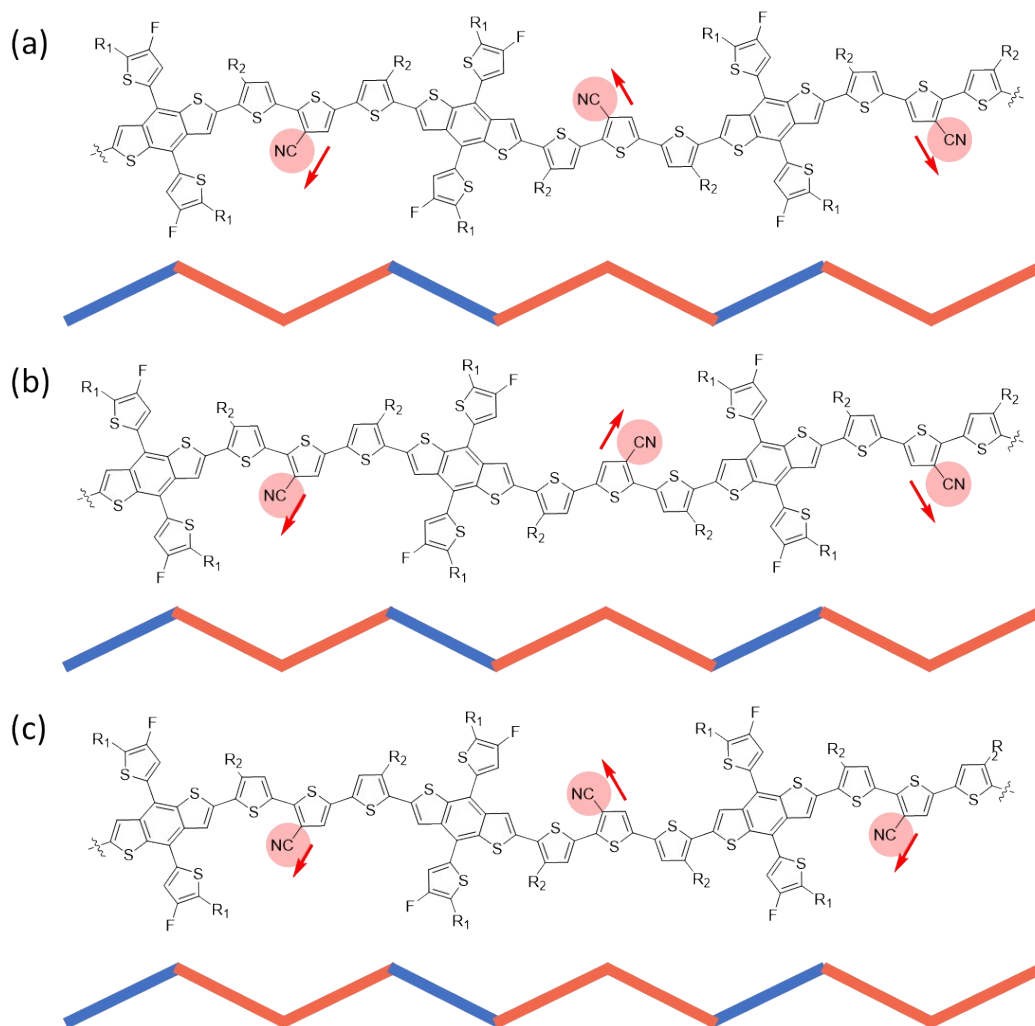


Figure S3. Proposed conformation of the polymer backbone with three repeat units for PBCT-2F. Similar conformation can be proposed for all the three possible orientations of the cyano-group.

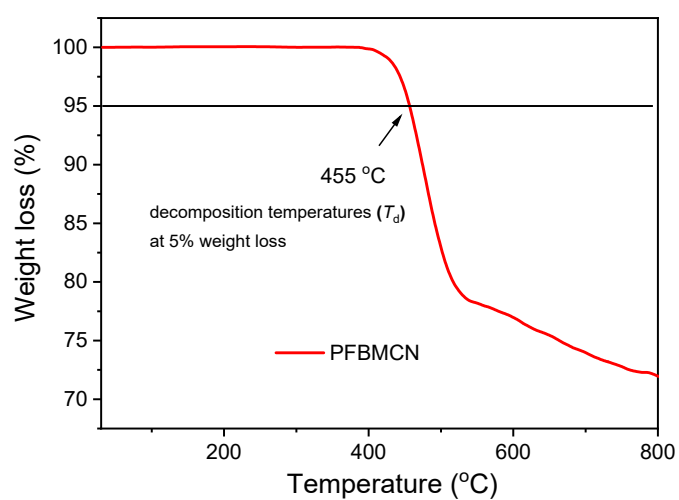


Figure S4. The TGA curve of PBCT-2F.

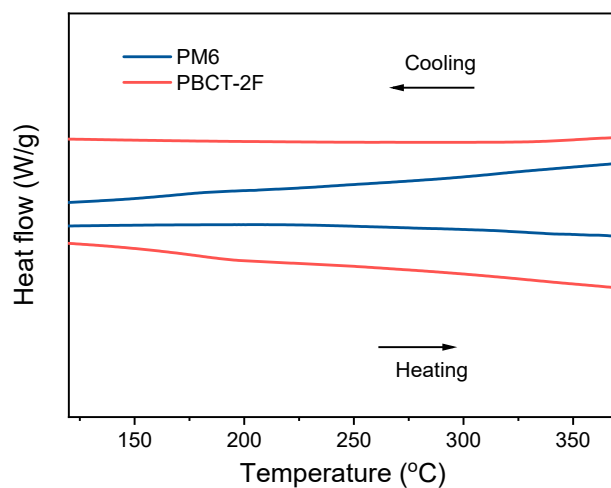


Figure S5. DSC traces of PBCT-2F and PM6 with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ and a cooling rate of $40\text{ }^{\circ}\text{C min}^{-1}$.

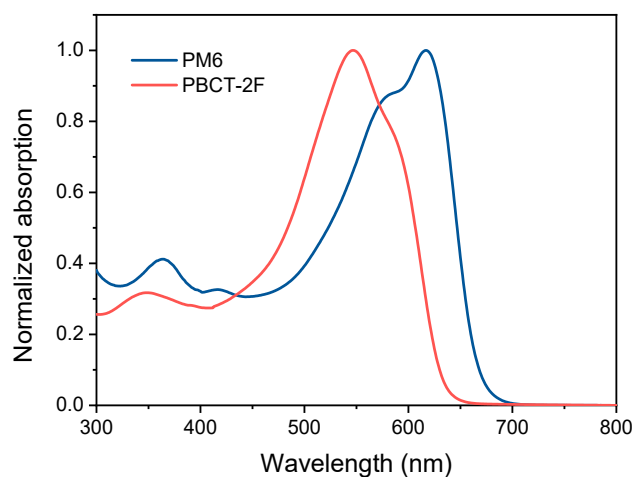


Figure S6. UV-vis absorption spectra of PBCT-2F and PM6 in chlorobenzene solutions at room temperature.

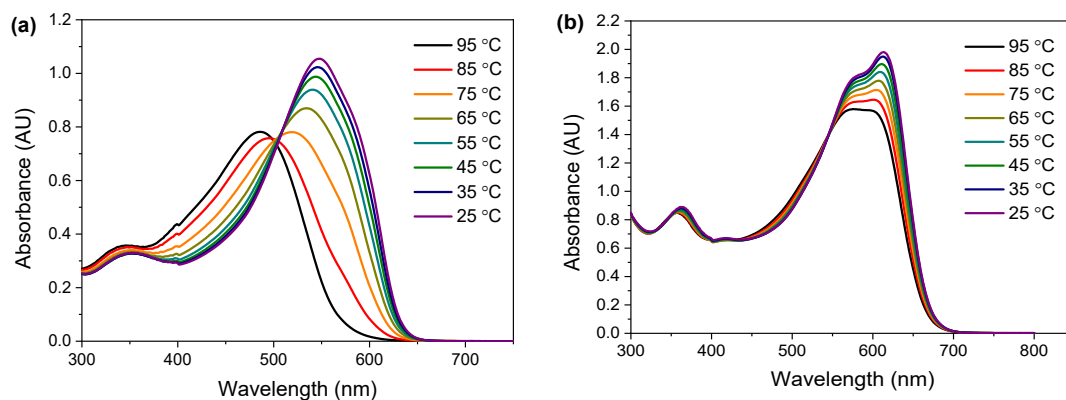


Figure S7. The UV-vis absorption spectra of (a) PBCT-2F and (b) PM6 under different temperatures in chlorobenzene solutions.

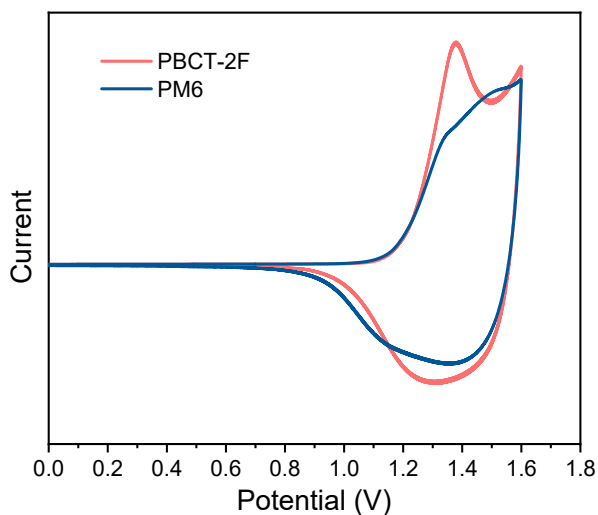


Figure S8. Cyclic voltammograms of PBCT-2F and PM6 measured in acetonitrile.

Table S3. Optical and electrochemical properties of polymers.

Polymer	solvent		film		E_g^{opt} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	λ_{onset} (nm)			
PBCT-2F	548	640	552, 584	647	1.92	-5.58	-3.66
PM6	582, 619	704	580, 618	674	1.84	-5.54	-3.70

Table S4. Device performance of the PBCT-2F (64 kDa):Y6 solar cells with a device architecture of ITO/PEDOT:PSS/PBCT-2F:Y6/PNDIT-F3N/Ag (100nm) with different D/A ratio under AM1.5G illumination (100 mW cm⁻²). The active layers were deposited from CF with 0.25% PN as solvent additive and annealed at 100 °C for 3 minutes.

D:A	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
1:1.20	0.85	26.30	0.75	16.65
1:1.35	0.85	27.22	0.74	17.12
1:1.50	0.84	27.53	0.73	16.99
1:1.65	0.84	26.30	0.74	16.43

Table S5. Device performance of the PBCT-2F (64 kDa):Y6 solar cells with a device architecture of ITO/PEDOT:PSS/PBCT-2F:Y6/ETL/cathode with different cathode and ETL under AM1.5G illumination (100 mW cm⁻²). The active layers were deposited from CF with 0.25% DPE and 0.25% CN as solvent additives and annealed at 100 °C for 3 minutes. The weight ratio of PBCT-2F:Y6 is 1:1.5.

Cathode	ETL	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
Al	PFNBr	0.84	21.93	0.73	13.40
	PDINO	0.84	23.17	0.73	14.23
	PDINN	0.84	22.88	0.71	13.62
	PDNIT-F3N	0.84	23.44	0.72	14.07
	ZrAcac	0.83	24.29	0.68	13.72
Ag	PFNBr	0.84	24.61	0.72	14.92
	PDINO	0.84	25.28	0.71	15.09
	PDINN	0.84	23.55	0.69	13.59
	PDNIT-F3N	0.84	25.66	0.73	15.83
	ZrAcac	0.84	26.27	0.70	15.46

Table S6. Device performance of the PBCT-2F (64 kDa):Y6 solar cells with a device architecture of ITO/PEDOT:PSS/PBCT-2F:Y6/PNDIT-F3N/Ag (100nm) with different solvent additives and ETL under AM1.5G illumination (100 mW cm⁻²). The active layers were deposited from CF and annealed at 100 °C for 3 minutes. The weight ratio of PBCT-2F:Y6 is 1:1.5.

Additive	ETL	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
0.25%DPE+	PFNBr	0.85	25.41	0.74	15.84
0.25%CN		0.86	26.54	0.69	15.71
0.25%PN		0.84	26.68	0.71	16.01
0.25%DBE		0.85	26.26	0.68	15.14
0.25%NMP		0.84	25.69	0.69	14.85
0.25%ODT		0.84	25.79	0.68	14.83
NO		0.86	25.72	0.71	15.82
0.25%DPE+	PNDIT-F3N	0.85	25.12	0.76	16.01
0.25%CN		0.85	26.71	0.72	16.30
0.125%PN		0.84	27.38	0.73	16.75
0.25%PN		0.83	26.45	0.73	15.99
0.5%PN		0.84	26.86	0.73	16.43
0.25%PN+					
0.25%DPE					

Table S7. Device performance of the PBCT-2F (64 kDa):Y6 solar cells with a device architecture of ITO/PEDOT:PSS/PBCT-2F:Y6/PNDIT-F3N/Ag (100nm) with different solution delay time before spin-coating under AM1.5G illumination (100 mW cm^{-2}). The active layers were deposited from CF with 0.25% PN as solvent additives and annealed at 100°C for 3 minutes. The weight ratio of PBCT-2F:Y6 is 1:1.5.

Delay time (minutes)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
2	0.84	26.39	0.74	16.50
10	0.84	26.37	0.74	16.31
30	0.84	26.54	0.73	16.27
90	0.83	25.79	0.72	15.41

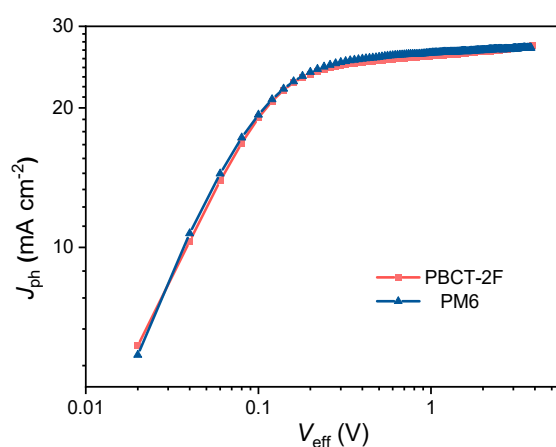


Figure S9. J_{ph} as a function of V_{eff} of the solar cells based on PBCT-2F:Y6 and PM6:Y6 blends.

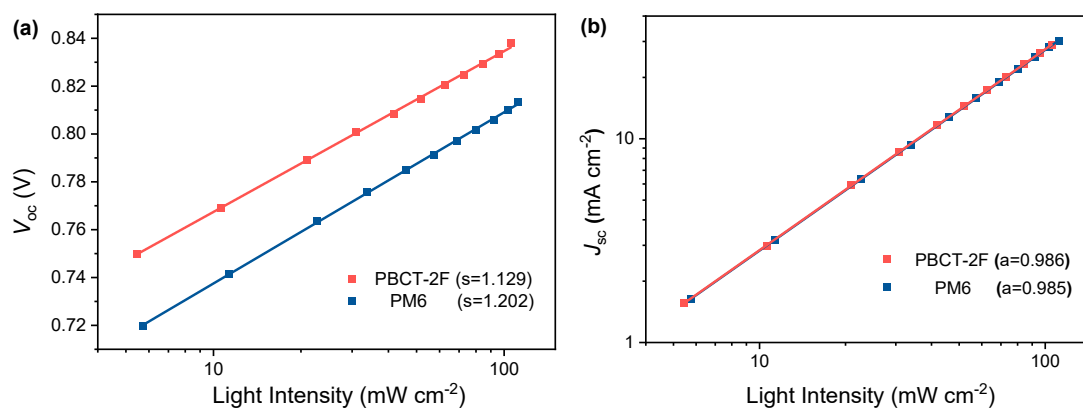
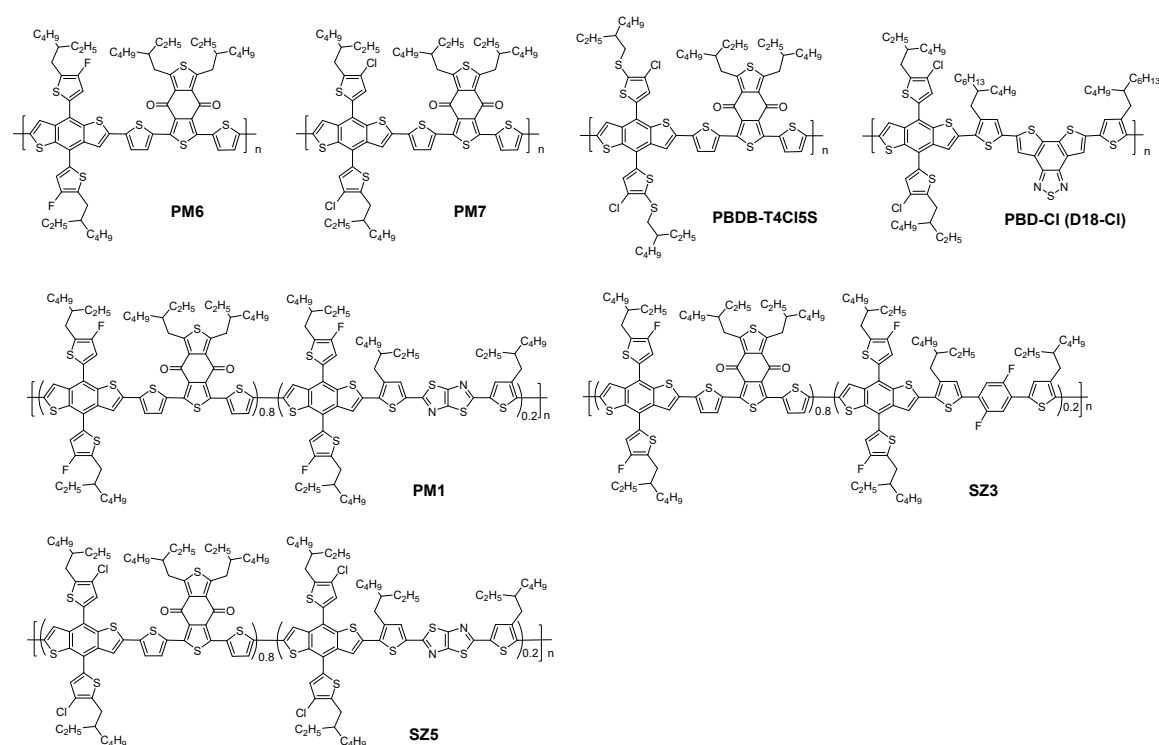


Figure S10. (a) V_{oc} and (b) J_{sc} as a function of the illumination intensity of the solar cells based on PBCT-2F:Y6 and PM6:Y6 blends.

Table S8. GIWAXS parameters of the pure films and the corresponding blend films.

Sample	OOP (010)			IP (100)		
	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	CCL ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	CCL ($\text{\AA}$)
PBCT-2F	1.665	3.77	30.4	0.291	21.6	53.3
PM6	1.662	3.78	22.8	0.293	21.4	48.7
Y6	1.706	3.68	28.6	0.287	21.9	60.0
PBCT-2F:Y6	1.686	3.73	31.3	0.288	21.8	79.5
PM6:Y6	1.684	3.73	26.1	0.301	20.9	66.2

**Figure S11.** Chemical structure of several reported polymers mentioned in this paper.**Table S9.** Photovoltaic data of the PM6:Y6 solar cells with different M_n of PM6 under AM1.5G illumination (100 mW cm^{-2}).

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	reference
10.5	0.87	24.9	64.9	14.1	[2]
16.8	0.85	25.0	72.0	15.3	
30.0	0.83	25.5	74.2	15.7	
34.2	0.82	26.0	74.7	16.0	
38.0	0.82	26.0	74.9	16.1	

47.0	0.82	26.1	75.7	16.2	
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Table S10. Photovoltaic data of the PM7:Y6 solar cells with different M_n of PM7 under AM1.5G illumination (100 mW cm⁻²).

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	reference
36.0	0.87	23.1	61.8	12.4	
45.0	0.86	21.6	68.9	12.9	
57.0	0.85	24.5	64.0	13.3	
60.7	0.85	24.1	77.2	15.8	[3]
61.1	0.86	24.1	76.0	15.7	
66.7	0.84	23.2	66.8	13.1	
77.0	0.85	21.1	73.4	13.3	

Table S11. Photovoltaic data of the PBDB-T4Cl5S:Y6 based OSCs with different M_n of PBDB-T4Cl5S under the illumination of AM 1.5G, 100 mW cm⁻²

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	reference
17.0	0.88	22.4	56.8	11.2	
30.0	0.86	23.8	75.5	15.3	[4]
53.0	0.84	25.6	76.1	16.3	
98.0	0.82	25.9	76.2	13.2	

Table S12. Photovoltaic data of the PBD-Cl:N3 based OSCs with different M_n of PBD-Cl under the illumination of AM 1.5G, 100 mW cm⁻²

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	reference
23.9	0.85	19.6	72.4	12.1	
48.0	0.85	23.3	72.8	14.5	
58.7	0.86	24.1	77.5	16.1	[5]
60.3	0.86	25.7	77.9	17.2	
76.2	0.84	16.0	66.8	9.0	

Table S13. Photovoltaic data of the D18-Cl:Y6 based OSCs with different M_n of D18-Cl under the illumination of AM 1.5G, 100 mW cm⁻²

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	reference
45	0.87	26.8	77.0	18.0	
48	0.87	27.4	73.1	17.4	[6]
52	0.87	26.0	77.1	17.4	
58	0.86	27.3	75.6	17.8	

62	0.86	27.2	76.2	17.8
73	0.85	26.4	77.0	17.3

Table S14. Photovoltaic data of the PM1:Y6 based OSCs with different M_n of PM1 under AM1.5G illumination (100 mW cm⁻²).

M_n (kDa)	PCE (%)	reference
21.2	17.1	[7]
23.5	17.1	
24.1	17.3	
25.6	17.2	
26.7	17.5	
28.7	17.6	
31.5	17.0	
33.0	17.4	

Table S15. Photovoltaic data of the SZ3:N3 based OSCs with different M_n of SZ3 under AM1.5G illumination (100 mW cm⁻²).

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	reference
43.2	0.84	26.0	76.7	16.6	[3]
44.1	0.84	25.6	77.7	16.7	
50.8	0.83	26.0	74.3	16.0	

Table S16. Photovoltaic data of the SZ5:BPT-4F based OSCs with different M_n of SZ5 under AM1.5G illumination (100 mW cm⁻²).

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	reference
49.8	0.85	24.9	78.0	16.6	[3]
50.2	0.84	25.2	78.5	16.5	
56.2	0.84	24.8	77.4	16.0	
56.8	0.84	25.0	76.3	16.1	
74.6	0.82	25.2	76.8	16.0	
84.1	0.84	25.0	78.1	16.5	

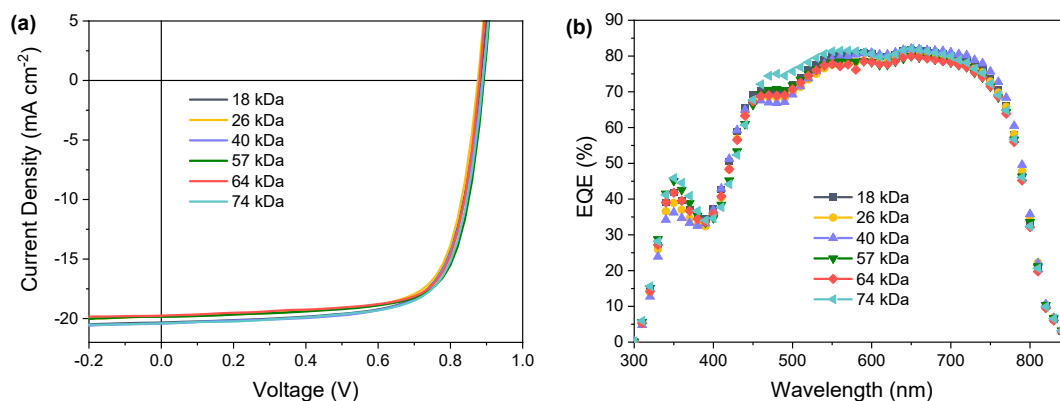


Figure S12. (a) J - V characteristics and (b) EQE spectra of the PBCT-2F:IT-4F solar cells with different PBCT-2F batches.

Table 17. Photovoltaic data of the PBCT-2F:IT-4F solar cells with different M_n of PBCT-2F under AM1.5G illumination (100 mW cm⁻²).

M_n (kDa)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
18	0.88 (0.88±0.01)	20.3 (20.0±0.4)	0.720 (0.717±0.005)	12.9 (12.6±0.3)
26	0.88 (0.88±0.01)	19.8 (19.8±0.2)	0.730 (0.725±0.005)	12.7 (12.5±0.2)
40	0.89 (0.89±0.01)	20.4 (19.9±0.5)	0.713 (0.720±0.007)	13.0 (12.8±0.2)
57	0.89 (0.89±0.01)	19.9 (20.0±0.2)	0.739 (0.733±0.007)	13.1 (12.9±0.2)
64	0.88 (0.88±0.01)	19.8 (19.6±0.2)	0.743 (0.739±0.006)	12.9 (12.7±0.2)
74	0.89 (0.89±0.01)	20.4 (20.2±0.3)	0.724 (0.720±0.005)	13.2 (12.8±0.4)

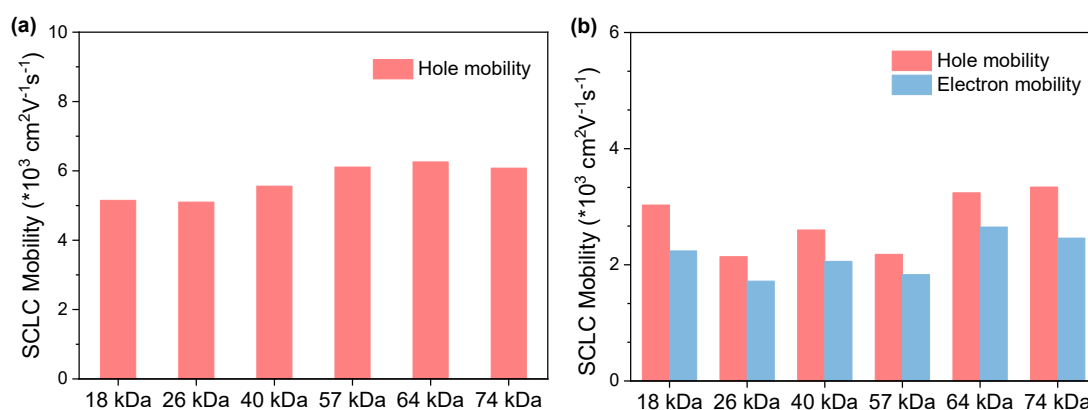


Figure S13. (a) The hole mobilities of the PBCT-2F with different molecular weights acquired from single-carrier devices; (b) The hole and electron mobilities of the PBCT-2F with different molecular weights and Y6 blends acquired from single-carrier devices.

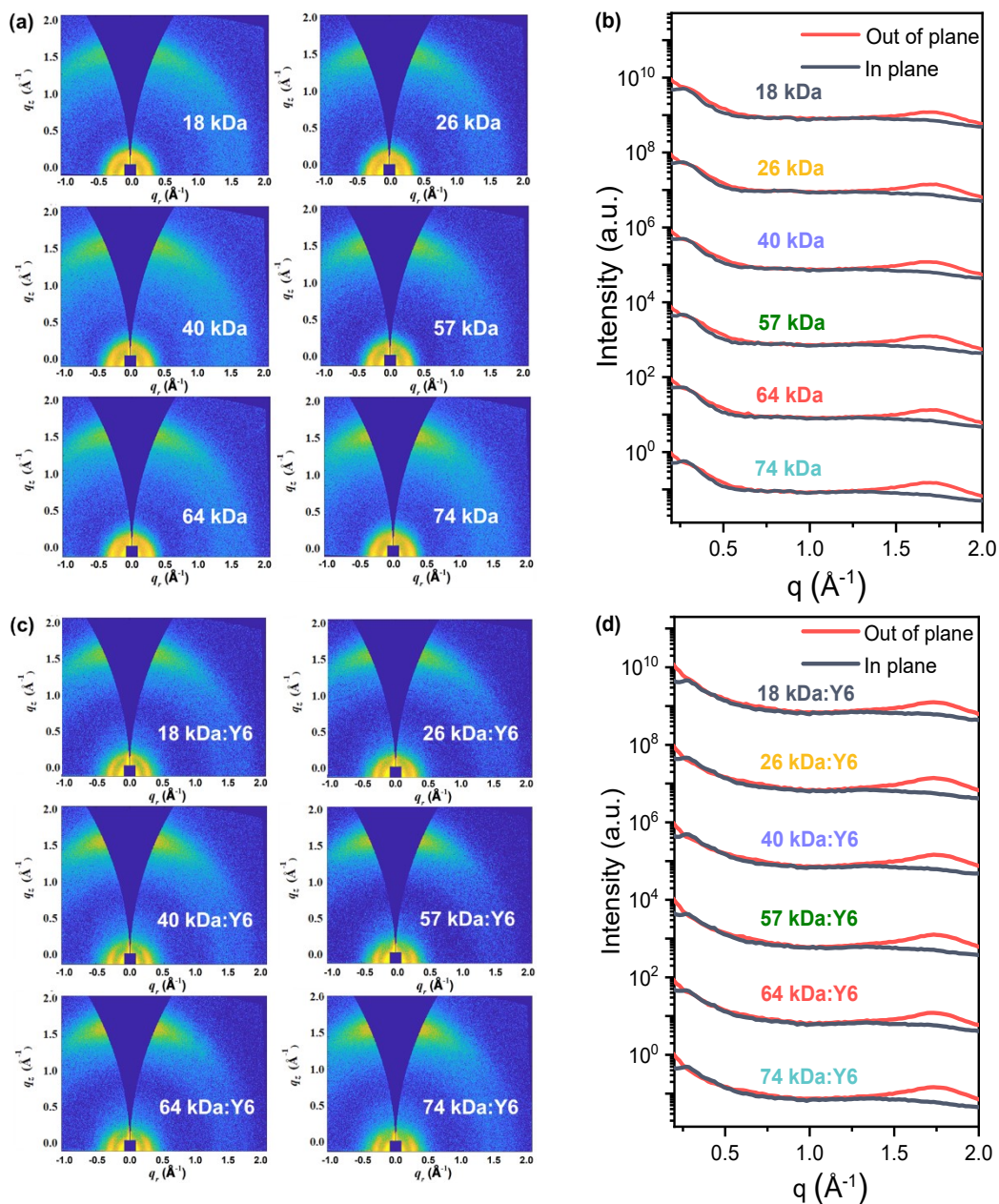


Figure S14. The 2D-GIWAXS pattern (a and c) and 1D-GIWAXS line-cut profiles (b and d) of the pure polymers (a and b) and polymer:Y6 blends (c and d) of PBCT-2F with different M_n

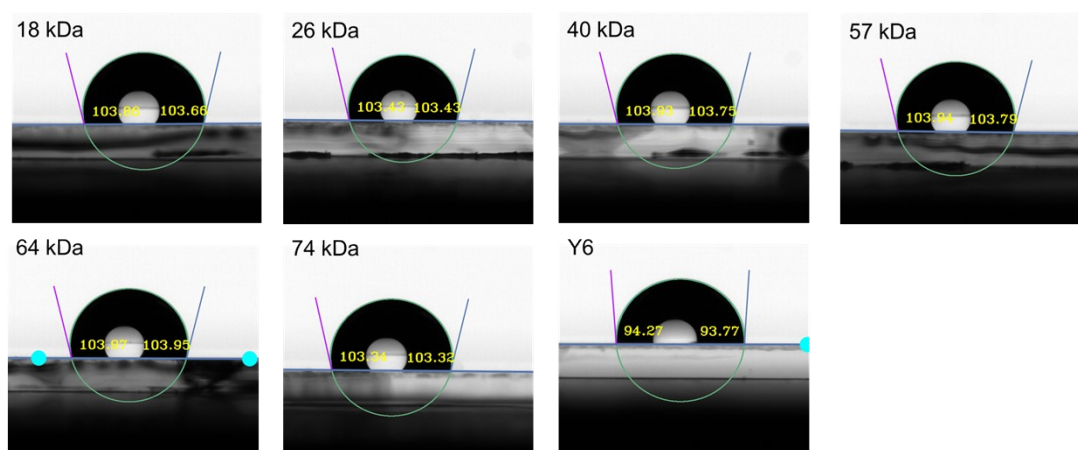
Table S18. GIWAXS parameters of the pure films of PBCT-2F with different M_n .

Polymer	OOP (010)			IP (100)		
	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	CCL ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	CCL ($\text{\AA}$)
18 kDa	1.673	3.76	21	0.269	23.4	41
26 kDa	1.674	3.75	22	0.269	23.4	38
40 kDa	1.673	3.76	22	0.272	23.0	39
57 kDa	1.677	3.75	24	0.269	23.4	40
64 kDa	1.680	3.74	25	0.267	23.5	39
74 kDa	1.680	3.74	25	0.270	23.3	41

Table S19. GIWAXS parameters of the blend films of PBCT-2F:Y6 with different M_n .

Polymer	OOP (010)			IP (100)		
	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	CCL ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	CCL ($\text{\AA}$)
18 kDa	1.730	3.63	24	0.272	23.0	44
26 kDa	1.731	3.63	25	0.275	22.9	42
40 kDa	1.737	3.62	26	0.272	23.0	45
57 kDa	1.738	3.62	27	0.274	22.9	44
64 kDa	1.737	3.62	27	0.272	23.0	43
74 kDa	1.740	3.61	28	0.278	22.6	45

(a) Water



(b) Ethylene glycol

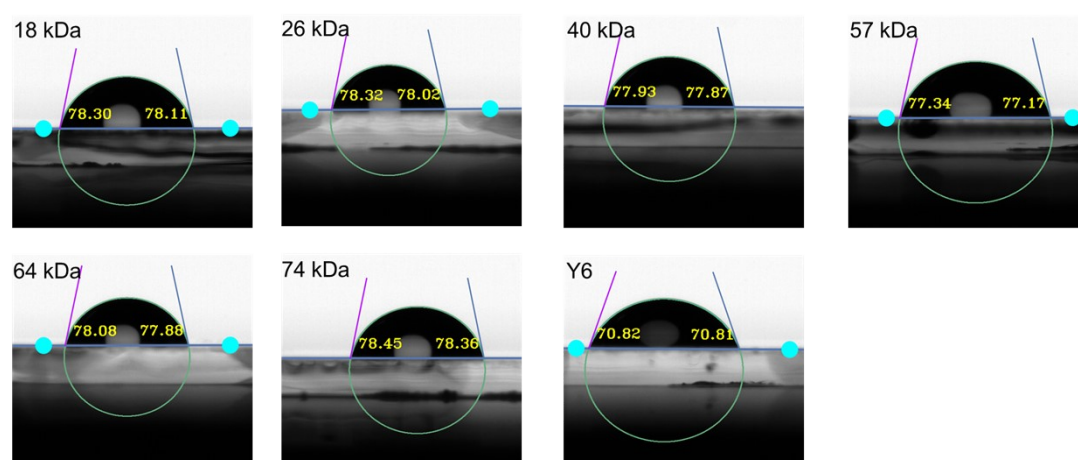


Figure S15. Contact angles of water (a) and ethylene glycol (b) on the neat films of PBCT-2F with different molecular weights and Y6.

Table S20. Contact angles and surface energy of the neat films, and the Flory-Huggins interaction parameters (χ) between various polymer donor and Y6.

Material	Contact angle		γ^d (mN/m) ^b	γ^p (mN/m) ^b	γ (mN/m)	relative χ^c with Y6
	[Water] (°)	[EG] ^a (°)				
18 kDa	103.8±0.2	78.2±0.4	13.44	2.33	15.77	0.21 K
26 kDa	103.4±0.3	78.2±0.2	13.51	2.14	15.65	0.22 K
40 kDa	103.8±0.2	78.0±0.4	13.58	2.15	15.73	0.21 K
57 kDa	103.8±0.1	77.6±0.5	13.59	2.15	15.74	0.21 K
64 kDa	103.9±0.2	78.0±0.3	13.52	2.17	15.69	0.22 K
74 kDa	103.3±0.3	78.4±0.3	13.51	2.14	15.65	0.22 K
Y6	94.5	70.8	14.63	5.01	19.64	-

a) EG represents the contact angle of ethylene glycol; b) γ^d and γ^p represent the dispersion and polarity components of surface tensions, respectively; c) The Flory–Huggins interaction parameters ($\chi_{\text{donor-acceptor}}$) were calculated using the empirical relation $\chi = K(\sqrt{\gamma^d} - \sqrt{\gamma^p})^2$

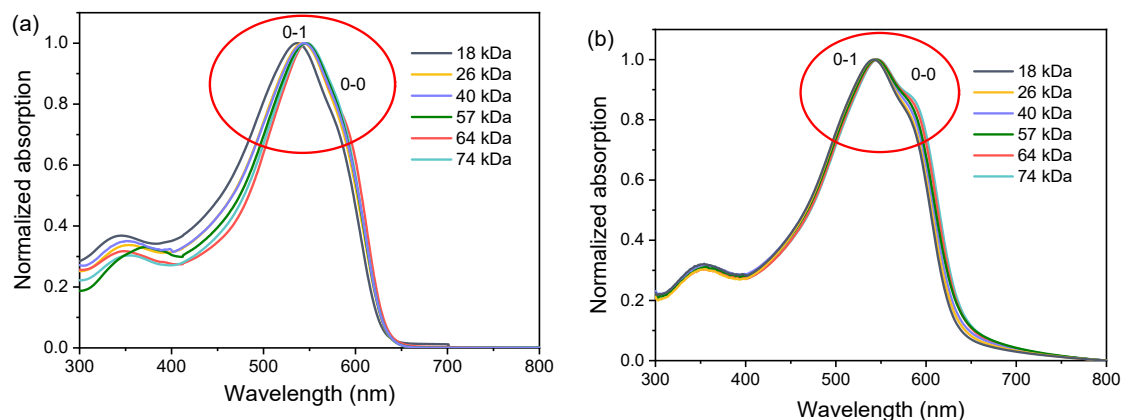


Figure S16. UV-vis absorption spectra of PBCT-2F with different M_n (a) in chlorobenzene solutions and (b) as thin films.

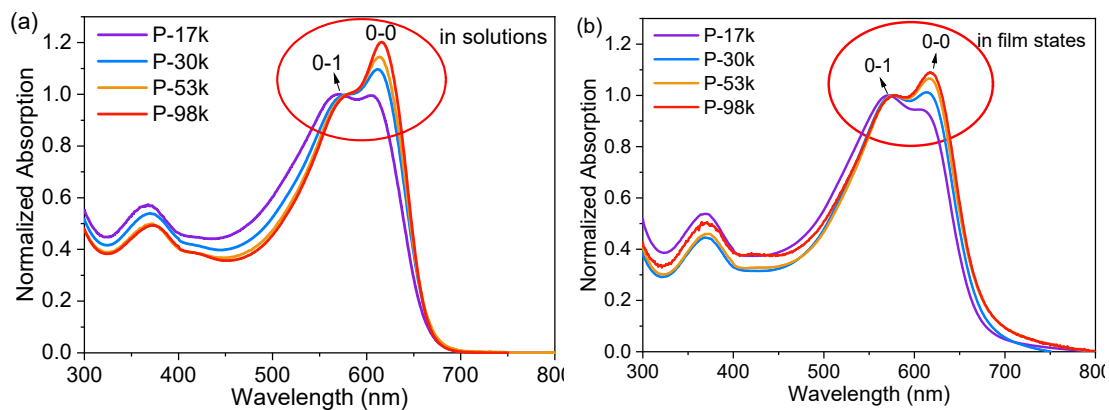


Figure S17. UV-vis absorption spectra of PBDB-T4Cl5S with different M_n (a) in chlorobenzene solutions and (b) as thin films.^[4]

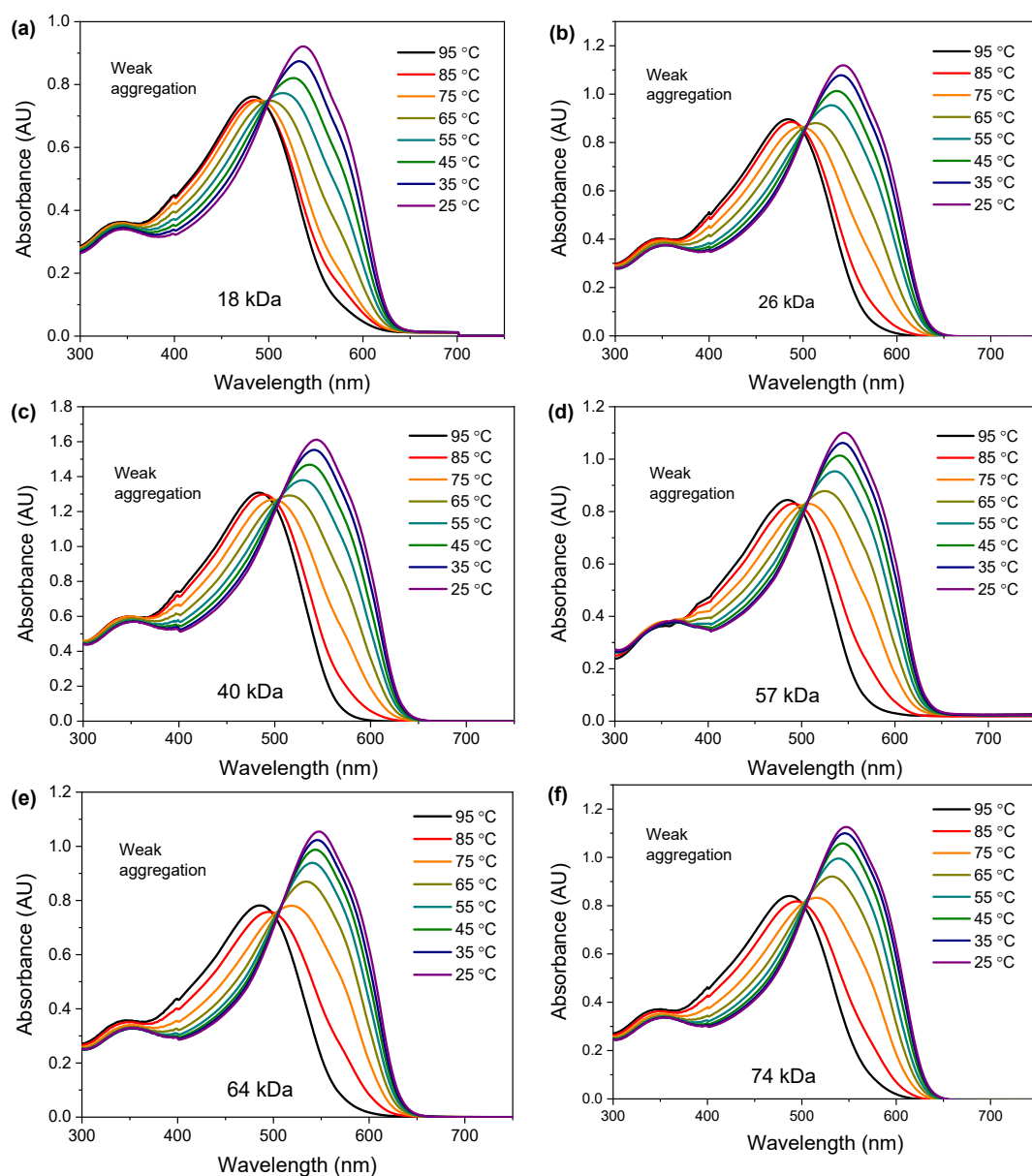


Figure S18. Temperature-dependent absorption spectra of PBCT-2F with different M_n in chlorobenzene solutions: (a) 18 kDa, (b) 26 kDa, (c) 40 kDa, (d) 57 kDa, (e) 64 kDa, and (f) 74 kDa.

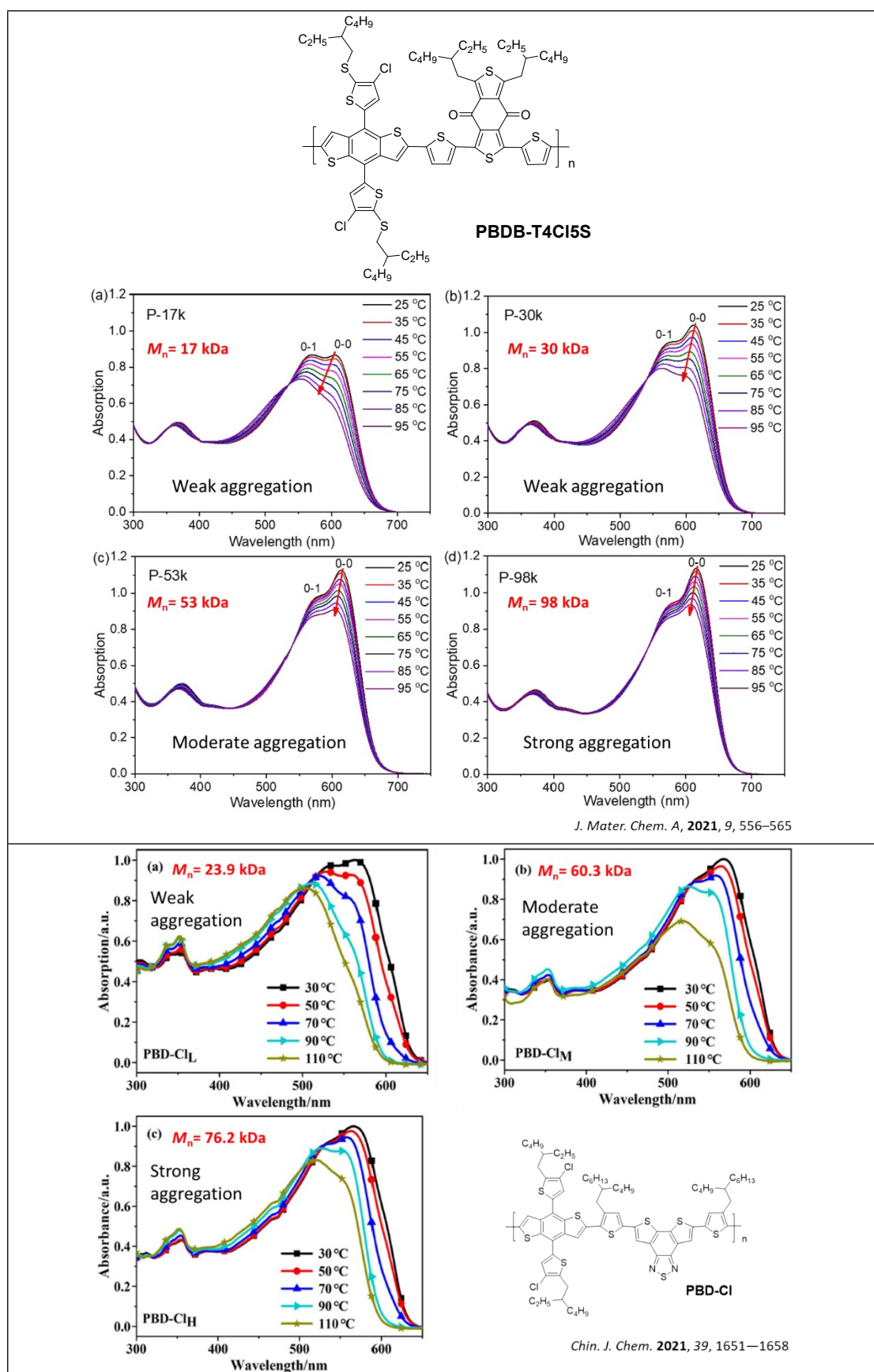


Figure S19. Temperature-dependent absorption spectra of (a) PBDB-T4Cl5S ^[4] and (b) PBD-Cl ^[5] in dilute chlorobenzene solutions.

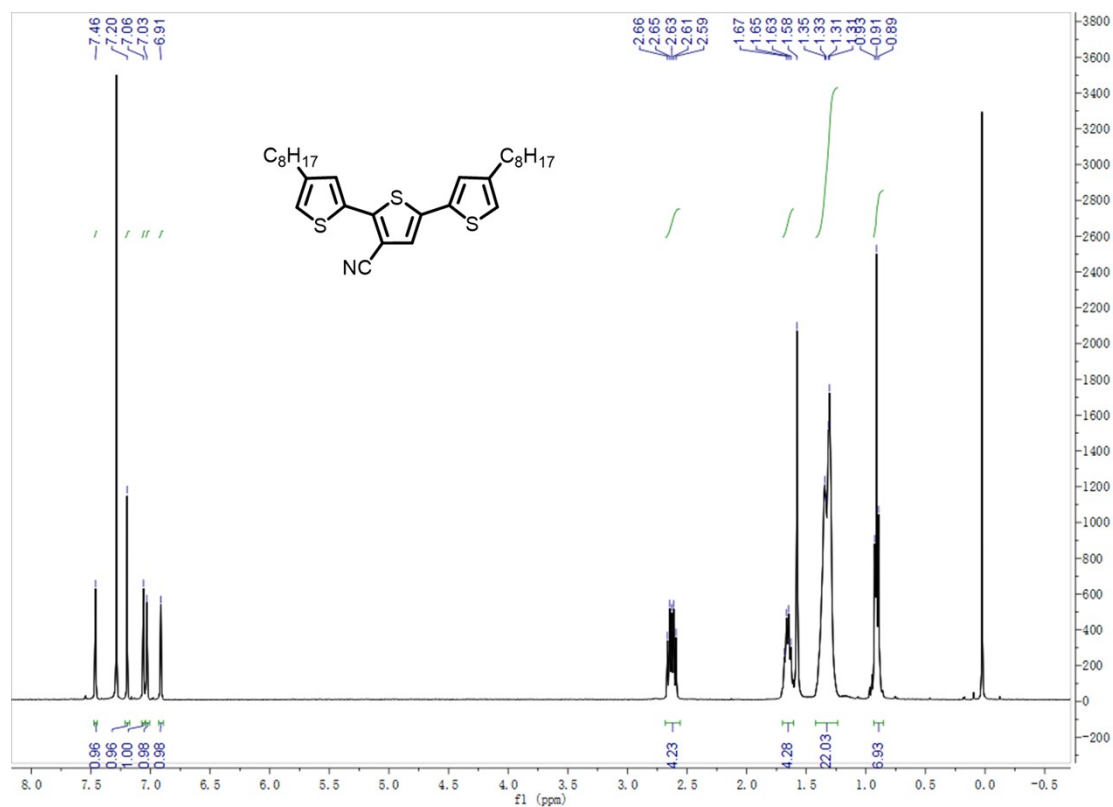


Figure S20. ¹H NMR spectrum of the compound 3.

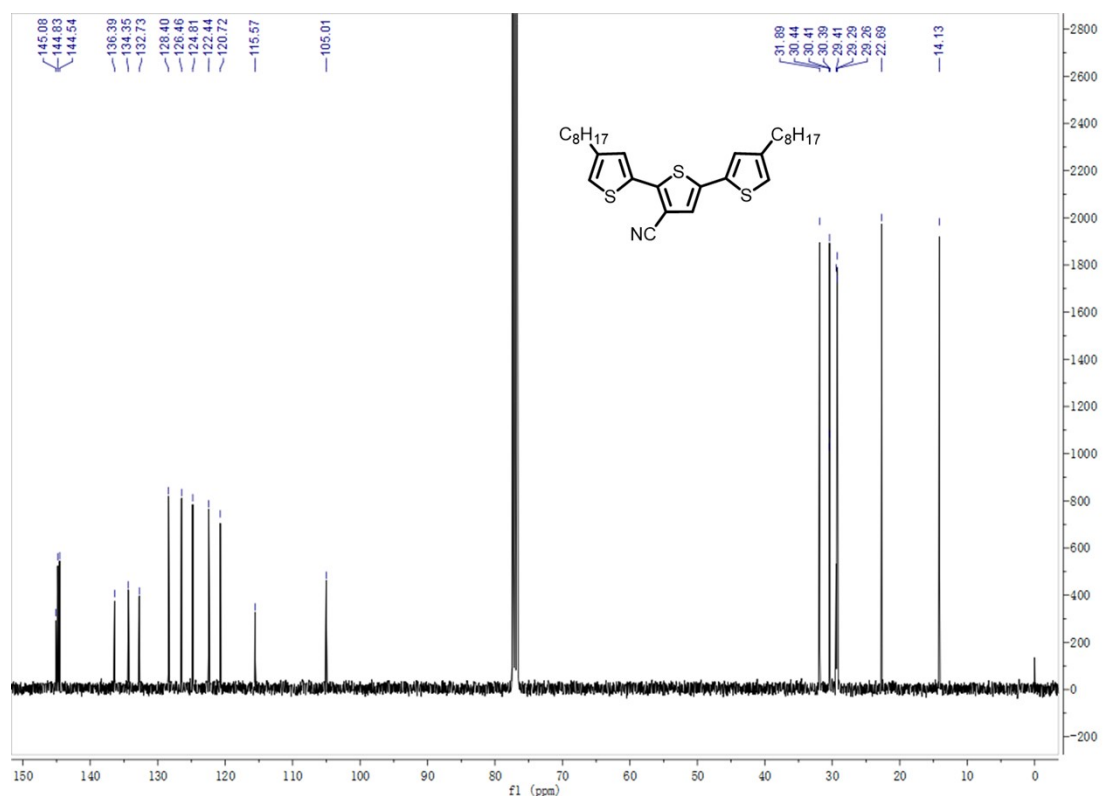


Figure S21. ¹³C NMR spectrum of the compound 3.

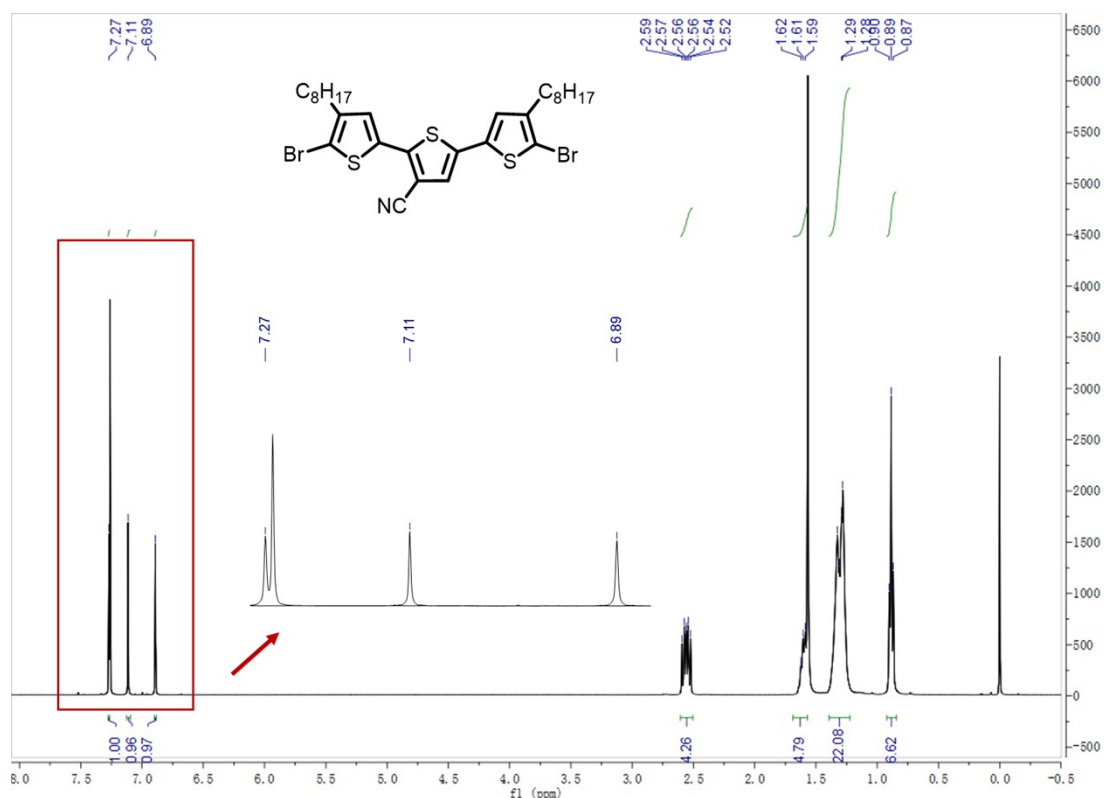


Figure S22. ¹H NMR spectrum of the compound 4.

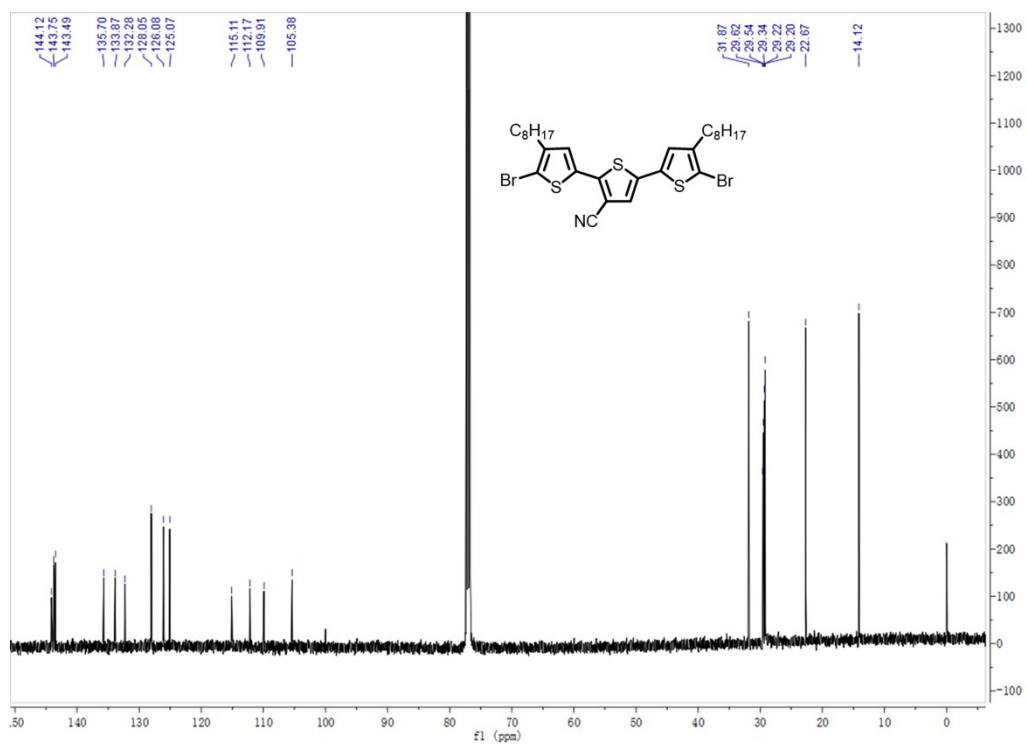
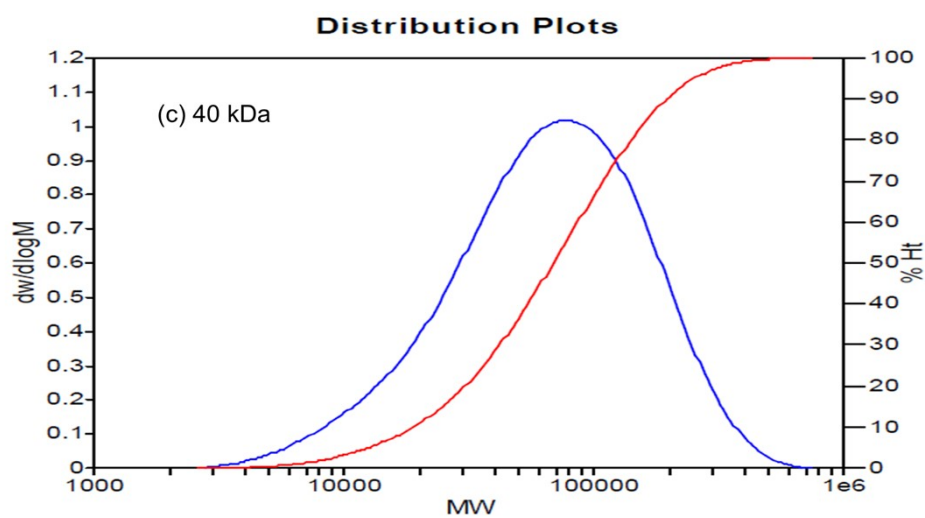
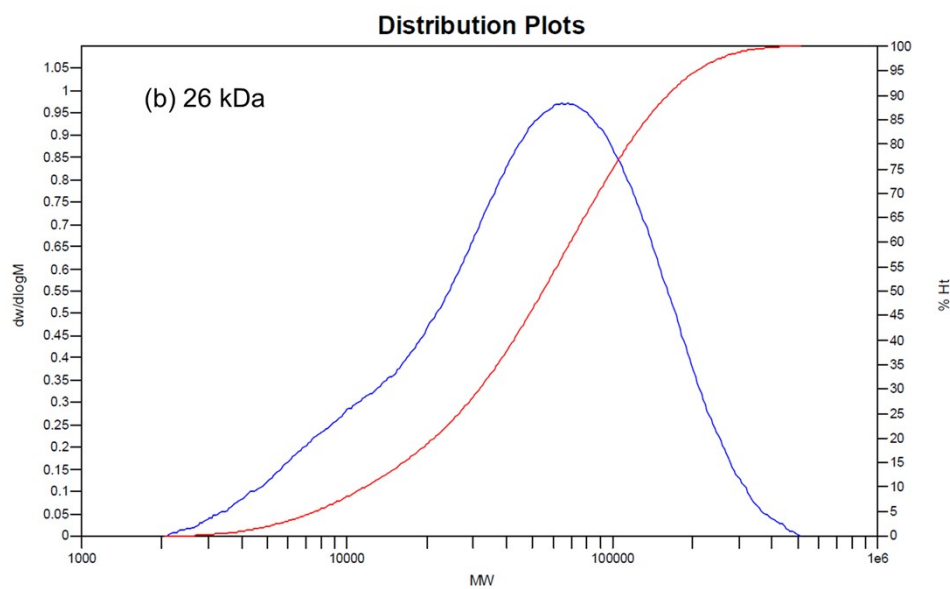
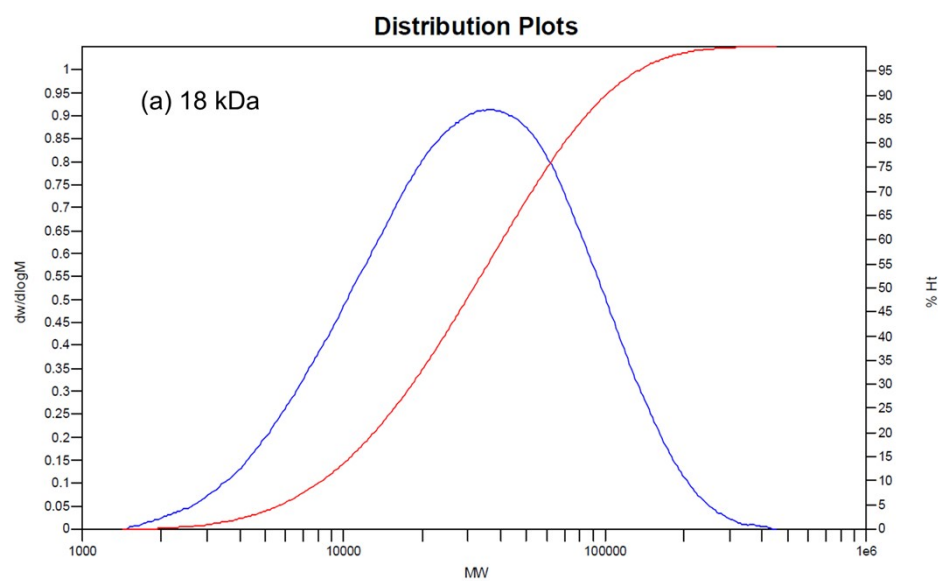


Figure S23. ¹³C NMR spectrum of the compound 4.



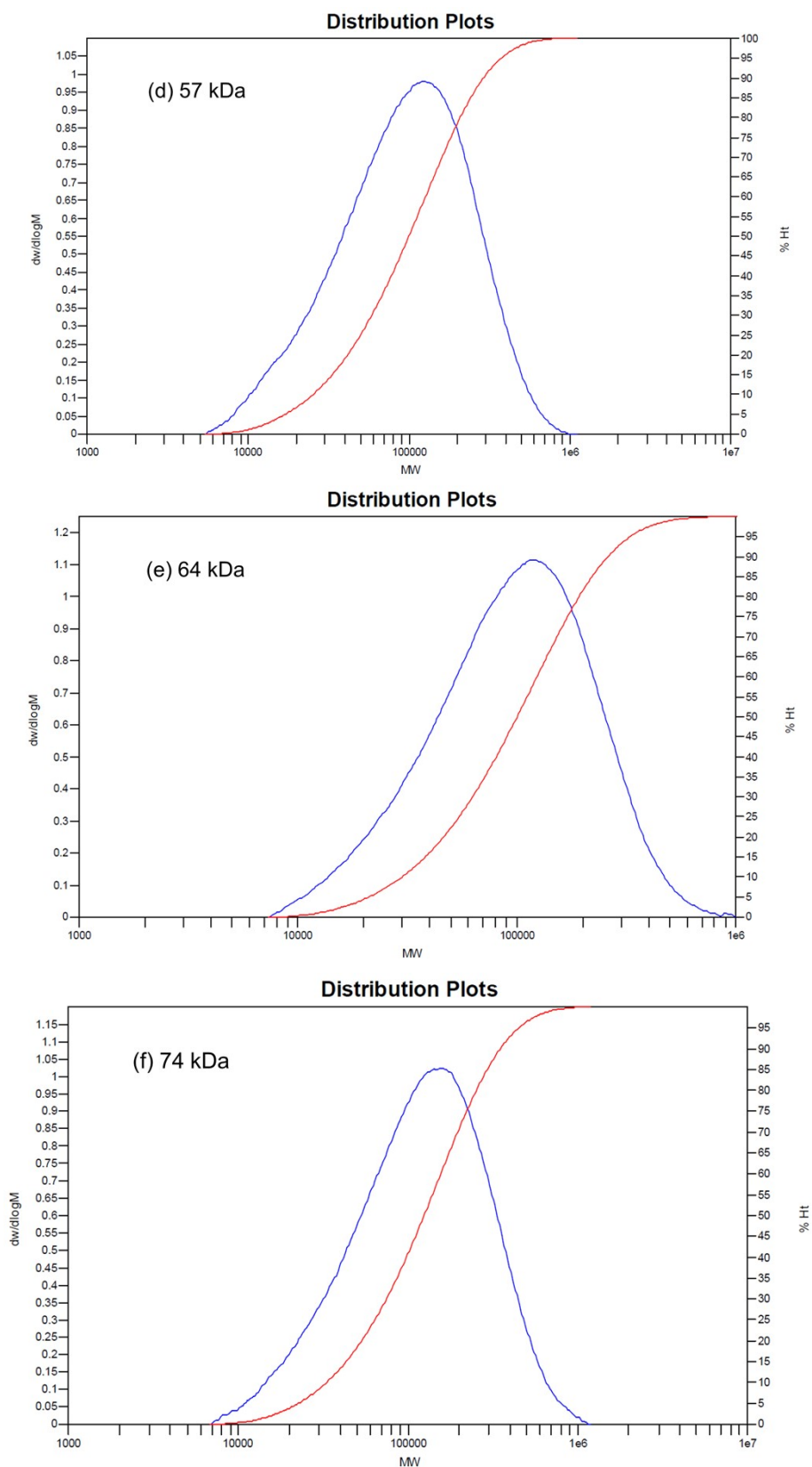


Figure S24. GPC traces of the different PBCT-2F batches measured with 1,2,4-trichlorobenzene as the eluent and polystyrene as a standard at 150 °C: (a) 18 kDa, (b) 26 kDa, (c) 40 kDa, (d) 57 kDa, (e) 64 kDa, (f) 74 kDa.

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