Supporting Information

Tailoring the side chain of imide-functional benzotriazole based polymers to achieve internal quantum efficiency approaching 100%

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Experimental Section

Materials synthesis.

All the solvents and reagents were obtained commercially and were used without further purification unless stated otherwise. TzBI-EHp-2Br was synthesized according to the reported methods[1], BDT-HT-2Sn, BDT-FT-2Sn, BDT-ClT-2Sn, and Y6 were purchased from Derthon Optoelectronic Materials Science Technology Co Ltd. Y6DT were synthesized according to previous reports and the corresponding NMR showed in the Fig. S12 and Fig. S13[2].

Poly{(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-alt-2-(3-ethylheptyl)-6-octyl-4,8-di(thiophen-2-yl)-[1,2,3]triazolo[4,5-*f*]isoindole-5,7(2*H*,6*H*)-dione)} **(PHT-EHp)**. Under an argon atmosphere, a mixture of monomer BDT-HT-2Sn (90.45 mg, 0.1 mmol), monomer TzBI-EHp-2Br (74.86 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (7 mg, 0.006 mmol) was dissolved in anhydrous chlorobenzene (CB) (1.4 mL). The mixture was heated to 140 ^oC and stirred for 48 h. After cooling to room temperature, the mixtures were precipitated into methanol (150 mL) and filtered off. The collected solids were further purified through Soxhlet extraction by *n*-hexane, acetone, and chloroform (CF) in succession. The CF fraction was concentrated and dried under vacuum to give 112.4 mg PHT-EHp (Yield = 94 %). The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured to be 19.5 KDa and 56.9 KDa, respectively (Fig. S17). The elemental analysis calcd (%) for PHT-EHp: C 69.30, H 7.25, N 4.69, S 16.09; found: C 68.53, H 7.36, N 4.79, S 15.41.

The procedure of poly{4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-alt-2-(3-ethylheptyl)-6-octyl-4,8-di(thiophen-2-yl)-[1,2,3]triazolo[4,5-*f*]isoindole-5,7(2*H*,6*H*)-dione)} **(PFT-EHp)** and poly{ 4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-alt-2-(3-ethylheptyl)-6-octyl-4,8-di(thiophen-2-yl)-[1,2,3]triazolo[4,5-*f*]isoindole-5,7(2*H*,6*H*)-dione)} **(PClT-EHp)** were analogous to that described for PHT-EHp except using BDT-FT-2Sn and BDT-ClT-2Sn to replace BDT-HT-2Sn, respectively. The CF fraction was concentrated and dried under vacuum to give 118.9 mg (96.5 %) PFT-EHp and 122.3 mg (97.2 %) PClT-EHp. The number average molecular weight (M_n) and weight average molecular weight (M_w) of PFT-EHp were measured to be 23.8 KDa and 61.3 KDa, respectively (Fig. S18). The M_n and M_w of PClT-EHp were measured to be 24.6 KDa and 69.2 KDa, respectively (Fig. S19). The elemental analysis calcd (%) for PFT-EHp: C 67.28, H 6.87, N 4.55, S 15.62; found: C 67.13, H 7.16, N: 4.63, S 15.57. The elemental analysis calcd (%) for PClT-EHp: C 65.53, H 6.69, N 4.43, S 15.21; found: C 64.98, H 6.57, N 4.38. S, 15.12.

Solar cells fabrication.

The conventional structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios P VP AI 4083)/photoactive layer/PFNDI-Br/Ag was used to fabricate all the solar cell devices. ITO substrates were cleaned by sequent sonication with detergent, deionized water, and isopropanol. After an oxygen plasma of 2 min, ~40 nm PEDOT:PSS was cast onto the substrates and annealed at 150 ^oC for 20 min in air. The substrates were then transferred into nitrogen protected glovebox, where blends of polymer:Y6 (1:1, wt:wt, 5.2 mg/mL in CF, w and w/o 1.0 vol% dibenzylether) were spin-coated on them to give ~100 nm photoactive layers. After thermal annealed (TA) at 110 ^oC for 10 min, ~5 nm PFNDI-Br was spin-coated atop. Silver of 100 nm was thermally deposited on the top through a shadow mask in a vacuum chamber (1×10^{-6} mbar). The effective device area was 0.0516 cm^2, which was further defined as 0.04 cm^2 aperture via a non-refractive mask.

Instruments and Characterizations

EQE and *J-V* Characteristics.

The EQE spectra were performed on a commercial EQE measurement system (Taiwan, Enlitech, QE-R3011) and the light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell. Photovoltaic performance was measured under an AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The *J–V* characteristics were recorded by using a Keithley 2400 source meter. The light intensity of the light source was calibrated by using a standard silicon solar cell with a KG5 filter, calibrated by a National Renewable Energy Laboratory (NREL) certified silicon photodiode to give a value of 100 mW cm^{-2}.

GPC, CV, AC-3, UV-vis, PL, and TEM Measurements.

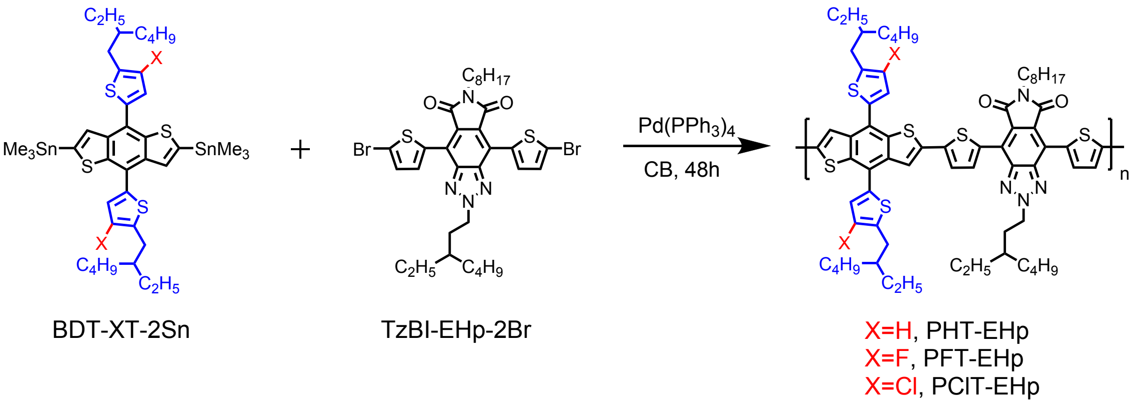
The molecular weight was evaluated by high-temperature gel permeation chromatography (GPC) at 150 °C with 1,2,4-trichorobenzene as the eluent on PL-GPC 220. Cyclic voltammetry (CV) was measured on a CHI660A Electrochemical Workstation equipped with a glass carbon working electrode, a Ag/AgCl reference electrode, and a platinum wire counter electrode. HOMO levels of donor polymers were determined by photoelectron yield spectra under vacuum (10^{-3} Pa). Ultraviolet-visible (UV-vis) absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence (PL) spectra were recorded on a FLS920 spectrofluorimeter (Edinburgh Instruments) by using a 150W, Ozone-free xenon arc lamp. TEM image were obtained by using a JEM 2100F Microscope.

Grazing incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS measurements was performed at beamline 7.3.3 of Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL). The X-ray beam energy was 10 keV. The sample to detector distance was ~280 mm calibrated with AgB and the incidence angle was 0.16^{o} normalized by a photodiode. All the GIWAXS signals were recorded in Helium atmosphere with exposure time of 2 s per image using a 2D charge-coupled device (CCD) detector (Pilatus 2M) with a pixel size of 0.172 mm by 0.172 mm. The film samples were spin-coated on PEDOT:PSS/silicon wafer substrates.

Resonant soft X-ray scattering (RSoXS)

RSoXS was performed at beamline 11.0.1.2 of Advanced Light Source, LBNL. Sample preparation was the same as that of GIWAXS samples. The thin films were floated in deionized water and transferred on silicon nitrile (Si_3N_4) windows. The samples then were loaded onto a holder. After the films were dried in air, the holder was moved into the vacuum chamber for the measurement. The beam energy was screened ranging from 280 to 290 eV, with exposure time of 5 s per energy. The scattering patterns were collected using Princeton Instrument PI-MTE CCD camera with a pixel size of 0.027 mm by 0.027 mm.



Scheme S1. The synthetic routes for polymers PHT-EHp, PFT-EHp and PClT-EHp.

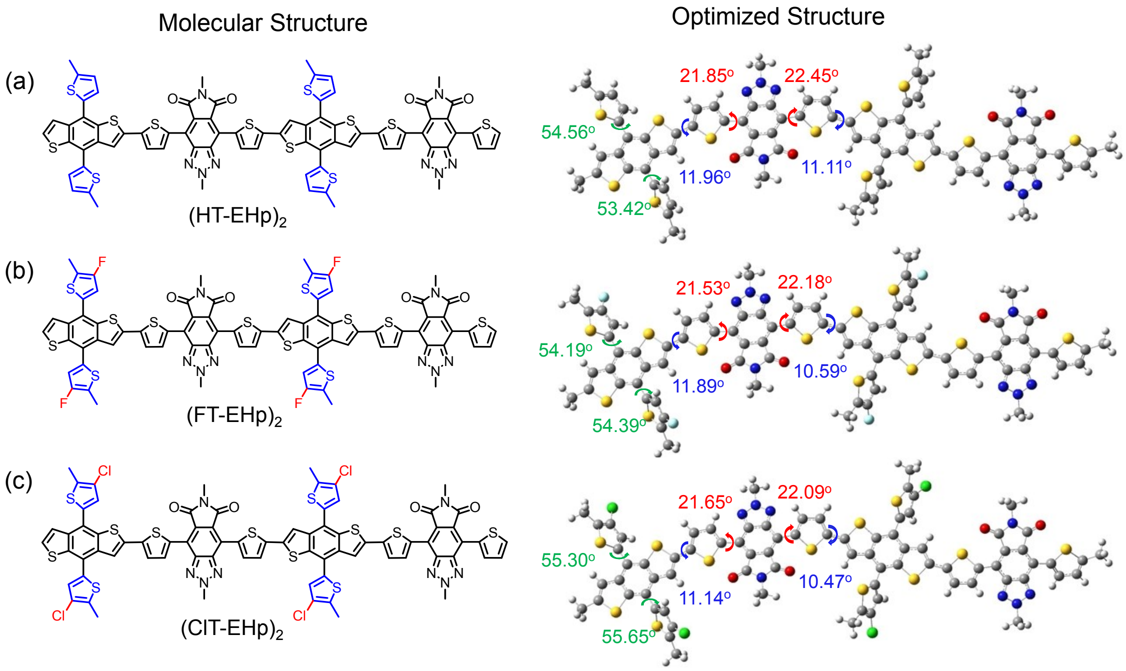


Fig. S1. Dihedral angle for the optimized structure of the dimer $(HT\text{-}EHp)_2$ (a), $(FT\text{-}EHp)_2$ (b), and $(ClT\text{-}EHp)_2$ (c), obtained from DFT calculations at B3LYP/6-13G(d) level.

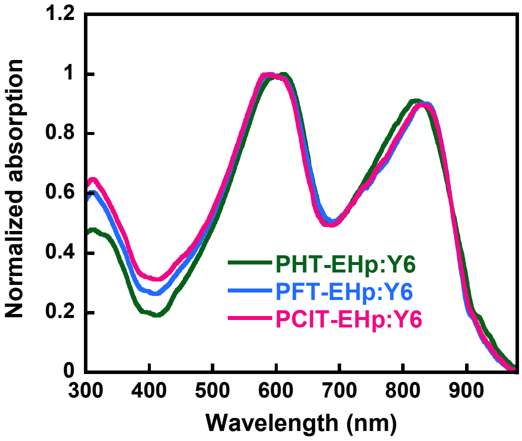


Fig. S2. Normalized absorption profiles of the PHT-EHp:Y6, PFT-EHp:Y6 and PClT-EHp:Y6 blends with 1% DBE.

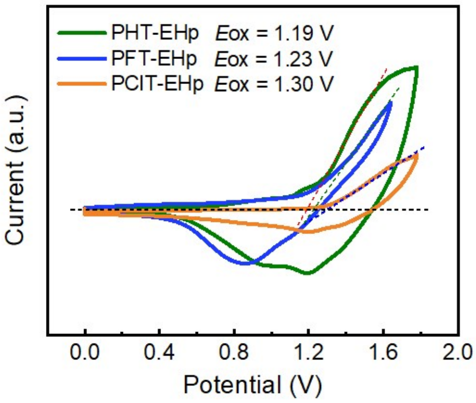


Fig. S3. Cyclic voltammetry characteristics of PHT-EHp, PFT-EHp and PClT-EHp.

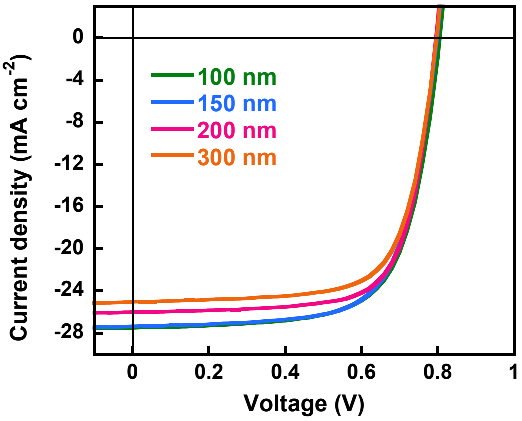


Fig. S4 *J–V* characteristics for PClT-EHp:Y6 devices treated with different film thickness.

Table S1. Photovoltaic parameters for OSCs based on PClT-EHp:Y6 treated with different thickness, measured under simulated AM 1.5G (100 mW cm^{-2}) illumination.

D:A	Thickness (nm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PClT-EHp:Y6[a]	100	0.795	27.31	72.60	15.76
	150	0.791	27.13	71.22	15.28
	200	0.795	26.02	71.80	14.86
	300	0.792	25.16	71.75	14.29

[a] With 1% DBE.

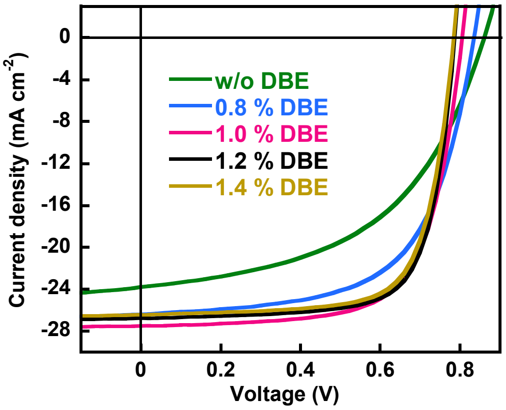


Fig. S5. *J–V* characteristics for PClT-EHp:Y6 devices treated with different amount of DBE.

Table S2. Photovoltaic parameters for OSCs based on PClT-EHp:Y6 treated with different amount of DBE, measured under simulated AM 1.5G (100 mW cm^{-2}) illumination.

Blend	DBE amount	TA	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PClT-EHp:Y6	w/o	w/o	0.91	19.24	48.71	8.5
		110 °C/10min	0.86	23.8	50.1	10.3
	0.8%	110 °C/10min	0.84	26.4	61.5	13.6
	1.0%	110 °C/10min	0.80	27.3	72.6	15.8
	1.2%	110 °C/10min	0.79	26.8	72.6	15.3
	1.4%	110 °C/10min	0.78	26.4	72.1	14.9

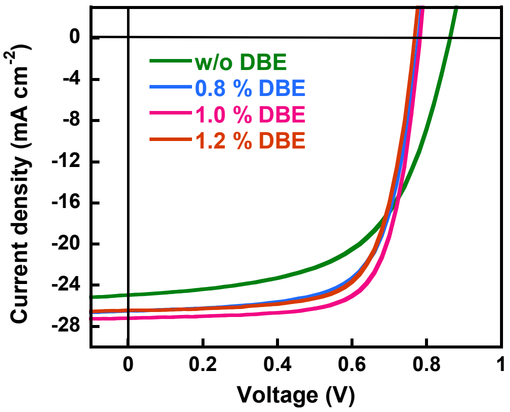


Fig. S6. *J–V* characteristics for PFT-EHp:Y6 devices treated with different amount of DBE.

Table S3. Photovoltaic parameters for OSCs based on PFT-EHp:Y6 treated with different amount of DBE, measured under simulated AM 1.5G (100 mW cm^{-2}) illumination.

Blend	DBE amount	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PFT-EHp:Y6	w/o	0.86	23.96	57.68	12.38
	0.8%	0.78	26.47	68.32	14.04
	1.0%	0.78	26.92	72.68	15.37
	1.2%	0.77	26.43	70.01	14.18

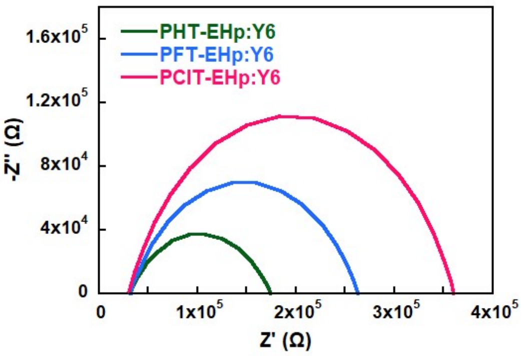


Fig.S7. Impedance spectra of devices.

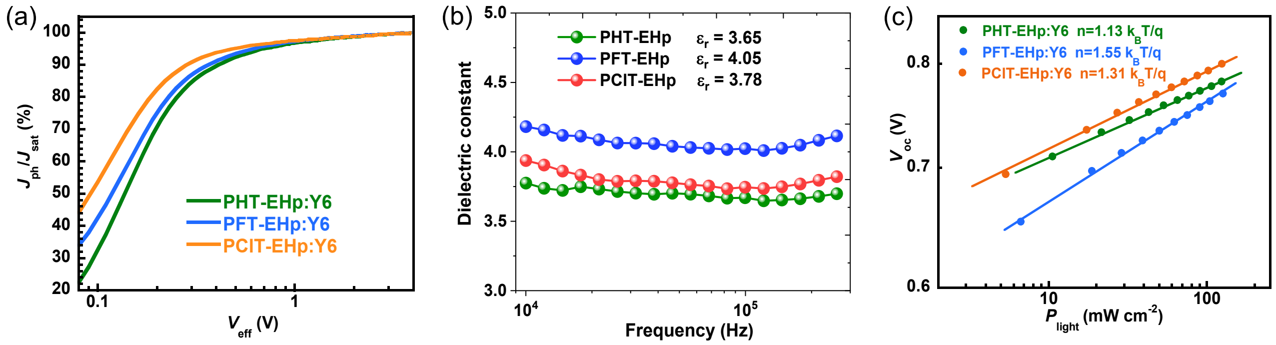


Fig. S8. J_{ph}/J_{sat}–V_{eff} characteristics (a), dielectric constant (b), and V_{oc}-P_{light} curves (c) for OSCs based on polymer:Y6.

Table S4. Charge dynamics parameters for devices based on various donors.

Blend	V_{bi} (V)	J_{sat} (mA cm^{-2})	G_{max} (m^{-3} s^{-1})	$P(E,T)_{SC}$ (%)	L (nm)
PHT-EHp:Y6	0.77	23.0	1.41×10^{28}	95.46	102
PFT-EHp:Y6	0.79	27.3	1.56×10^{28}	96.24	109
PClT-EHp:Y6	0.81	27.6	1.57×10^{28}	97.02	110

$G_{max} = J_{sat}/qL$, J_{sat} named the saturated photo current density, q and L are electrical charge and thickness of active layer, respectively.

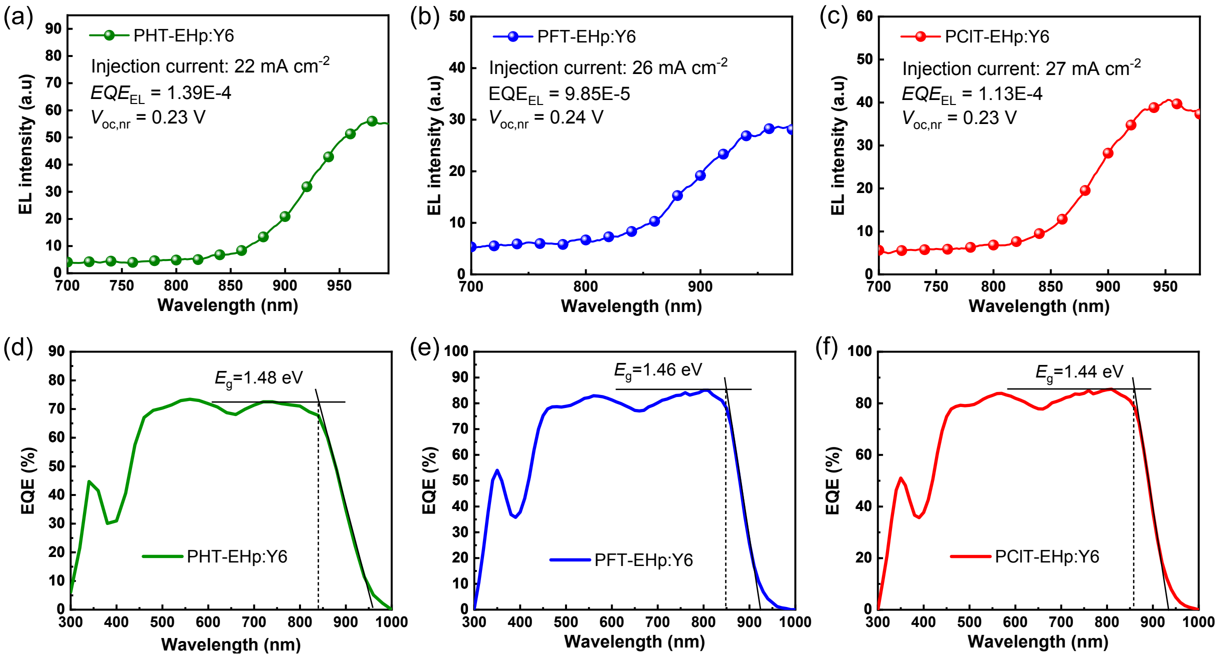


Fig. S9. EL (a-c) and PV (d-f) quantum efficiencies for OSCs based on different donors.

Table S5. Parameters obtained from V_{OC} loss analysis.

Blend	E_g [a] (eV)	$V_{OC,\ SQ}$ (V)	$V_{OC,\ rad}$ [c] (V)	$V_{OC,\ meas}$ (V)	E_g/q-$V_{OC,\ meas}$ (V)	$\Delta V_{OC,\ nr}$ [b] (V)	λ (eV)
PHT-EHp:Y6	1.48	1.23	1.00	0.77	0.71	0.23	0.13
PFT-EHp:Y6	1.46	1.21	1.02	0.78	0.68	0.24	0.15
PClT-EHp:Y6	1.44	1.19	1.03	0.80	0.64	0.23	0.22

[a] Determined by EQE edge and the local EQE maximum at the edge of the EQE spectrum. [b] Calculated according to: $\Delta V_{OC,\ nr} = -(kT/q)\ \ln(EQE_{EL})$. [c] Calculated according to: $V_{OC,\ rad} = V_{OC,\ meas.} + \Delta V_{OC,\ nr}$.

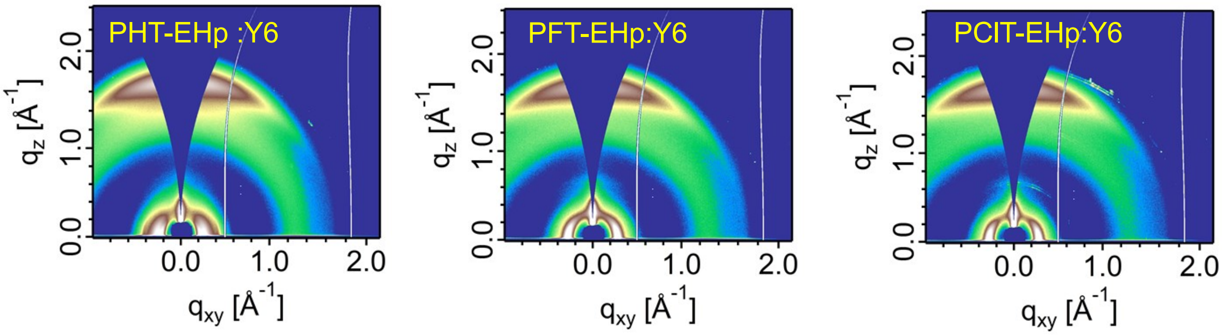


Fig. S10. 2D GIWAXS patterns for blend films of PHT-EHp:Y6 (a), PFT-EHp:Y6 (b), and PClT-EHp:Y6 (c), processed under optimal conditions.

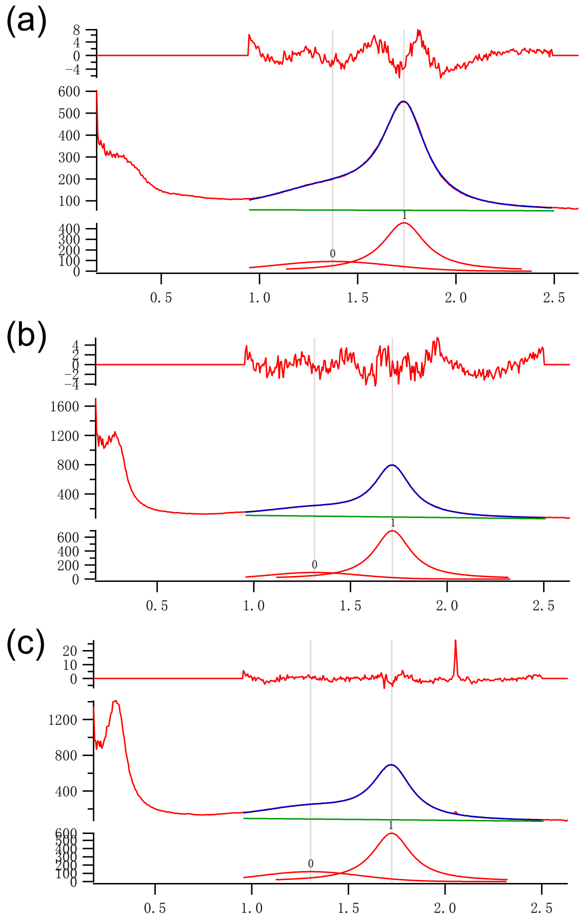


Fig. S11. GIWAXS (010) peak fitting for PHT-EHp:Y6 (a), PFT-EHp:Y6 (b) and PClT-EHp:Y6 (c), processed under optimal conditions.

Table S6. Parameters extracted from the GIWAXS (010) peak fitting.

Blend	Type	Location (Å^{-1})	FWHM (Å^{-1})	CCL (Å)
PHT-EHp	Gauss	1.37	0.70	/
	Lorentzian	1.74	0.26	2.4
PFT-EHp	Gauss	1.30	0.60	/
	Lorentzian	1.72	0.24	2.6
PClT-EHp	Gauss	1.31	0.55	/

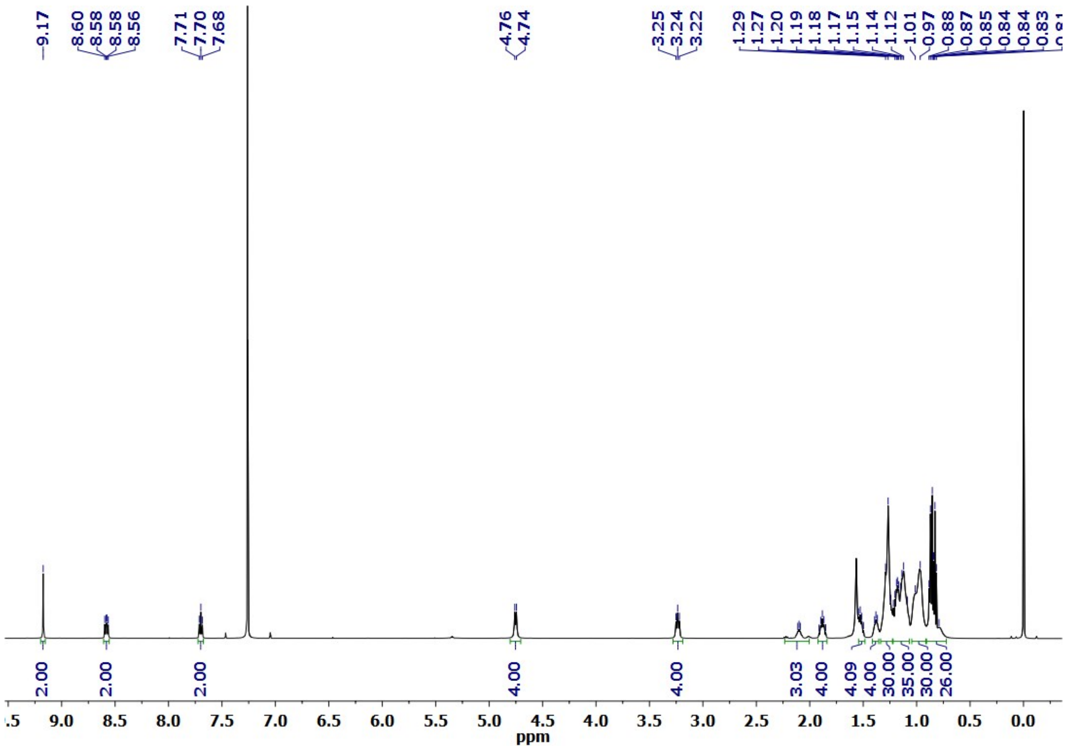


Fig. S12. ^{1}H NMR spectrum of the Y6DT, measured at room temperature with $CDCl_3$ as solvent.

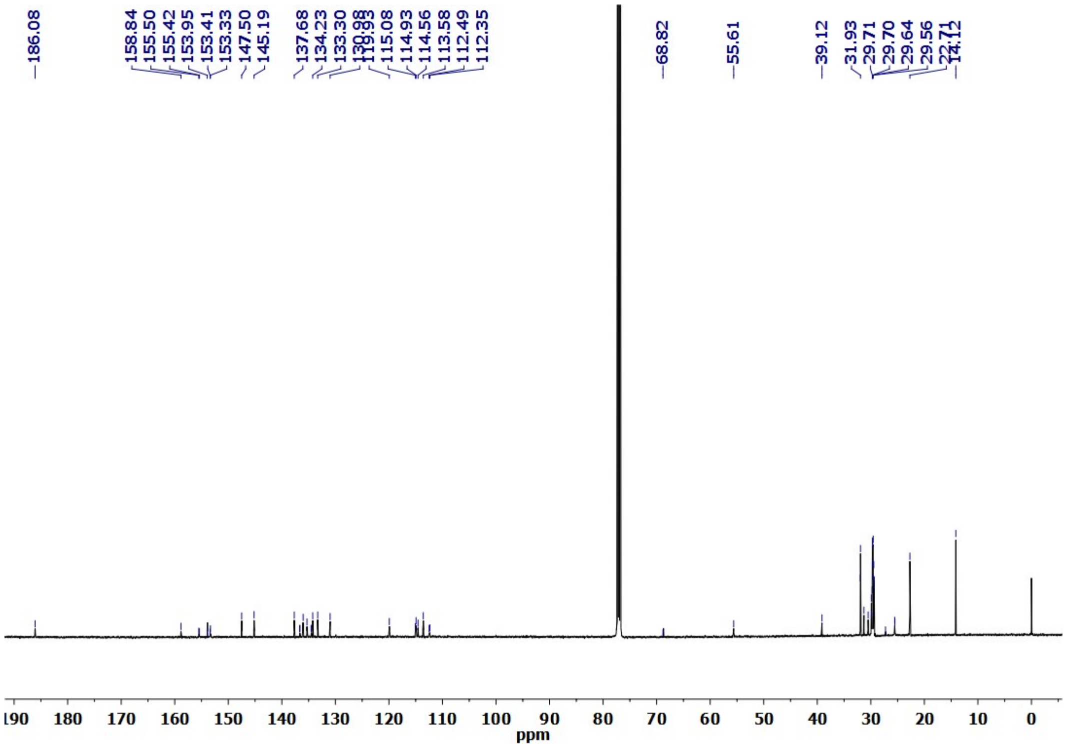


Fig. S13. ^{13}C NMR spectrum of the Y6DT, measured at room temperature with $CDCl_3$ as solvent.

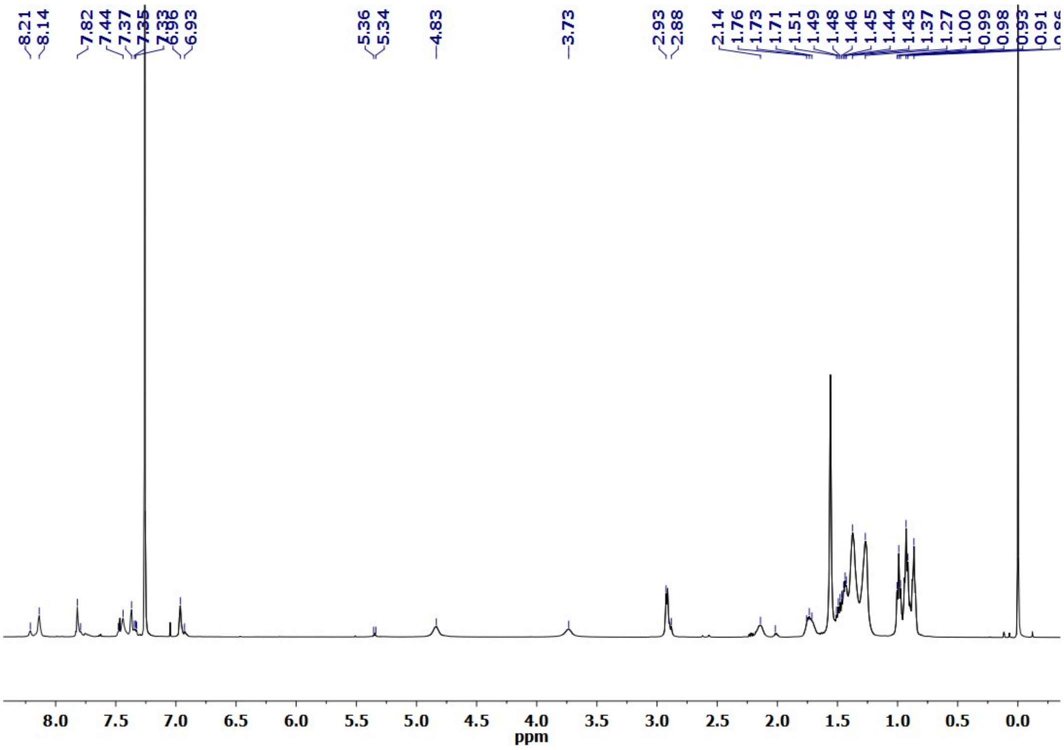


Fig.S14 ^{1}H NMR spectrum of the polymer PHT-EHp, measured at room temperature with $CDCl_3$ as solvent.

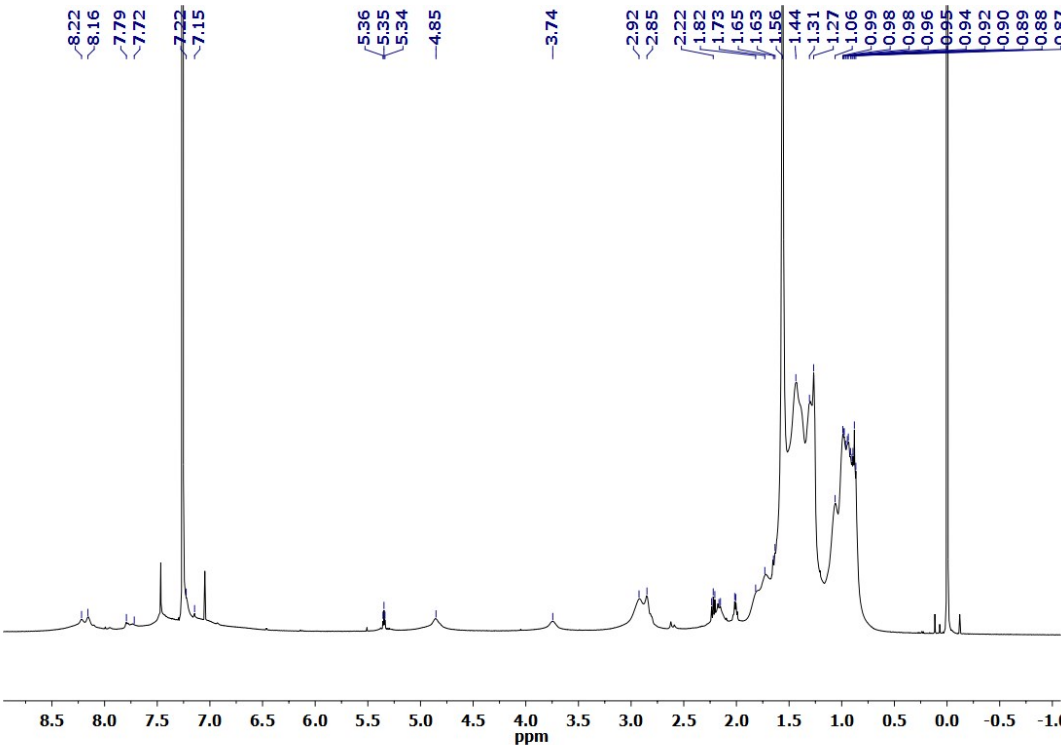


Fig.S15 ^{1}H NMR spectrum of the polymer PFT-EHp, measured at room temperature with $CDCl_3$ as solvent.

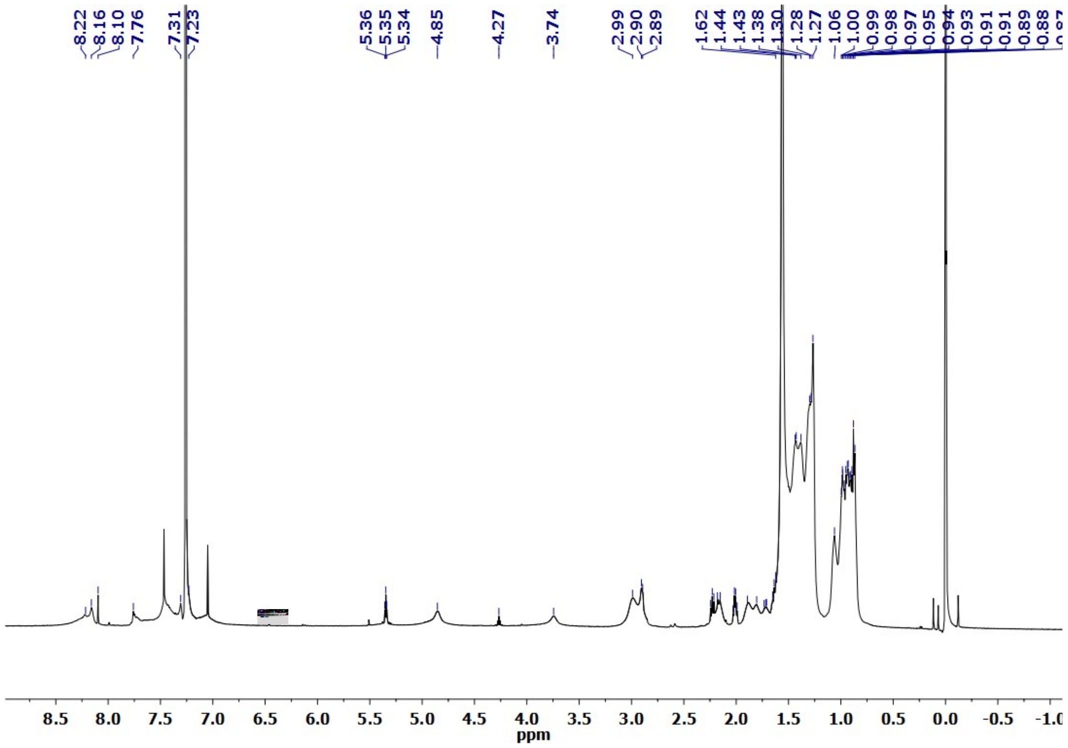


Fig.S16 ^{1}H NMR spectrum of the polymer PClT-EHp, measured at room temperature with $CDCl_3$ as solvent.

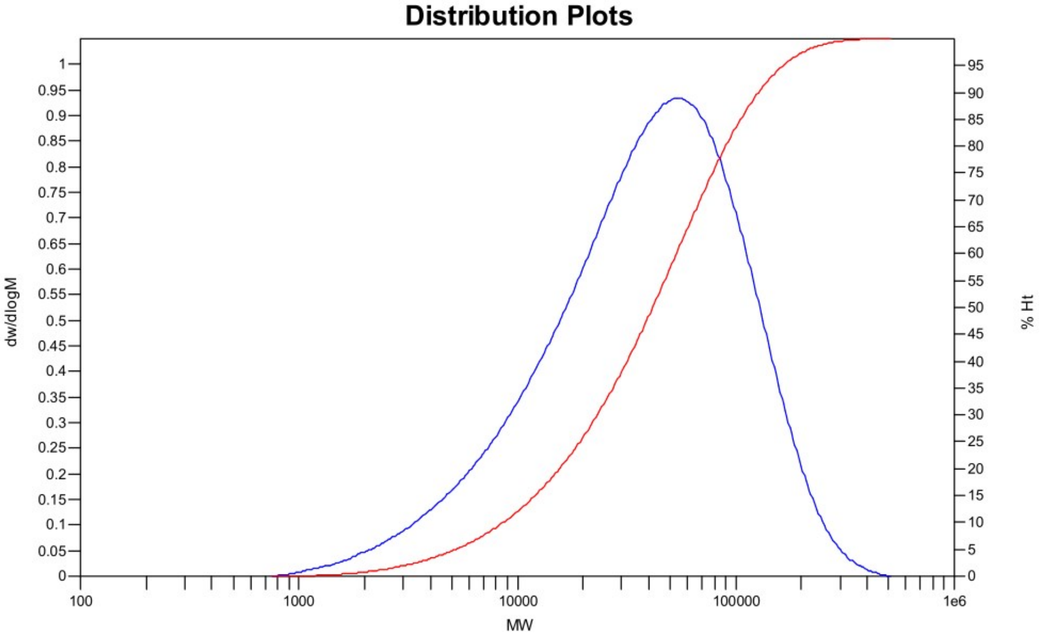


Fig. S17 The GPC trace of the polymer PHT-EHp.

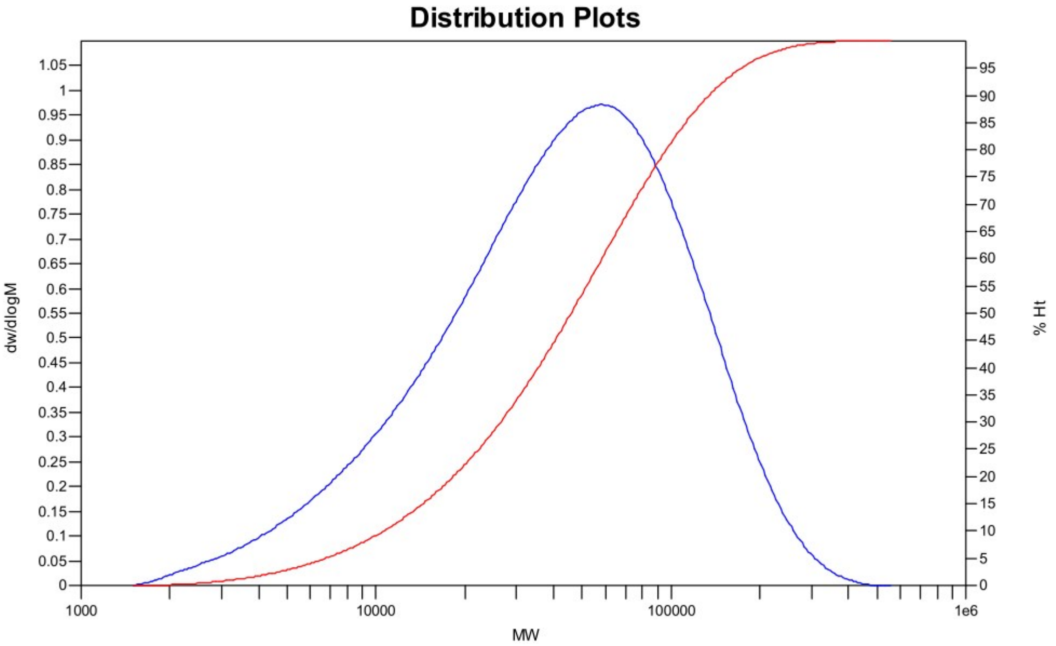


Fig. S18 The GPC trace of the polymer PFT-EHp.

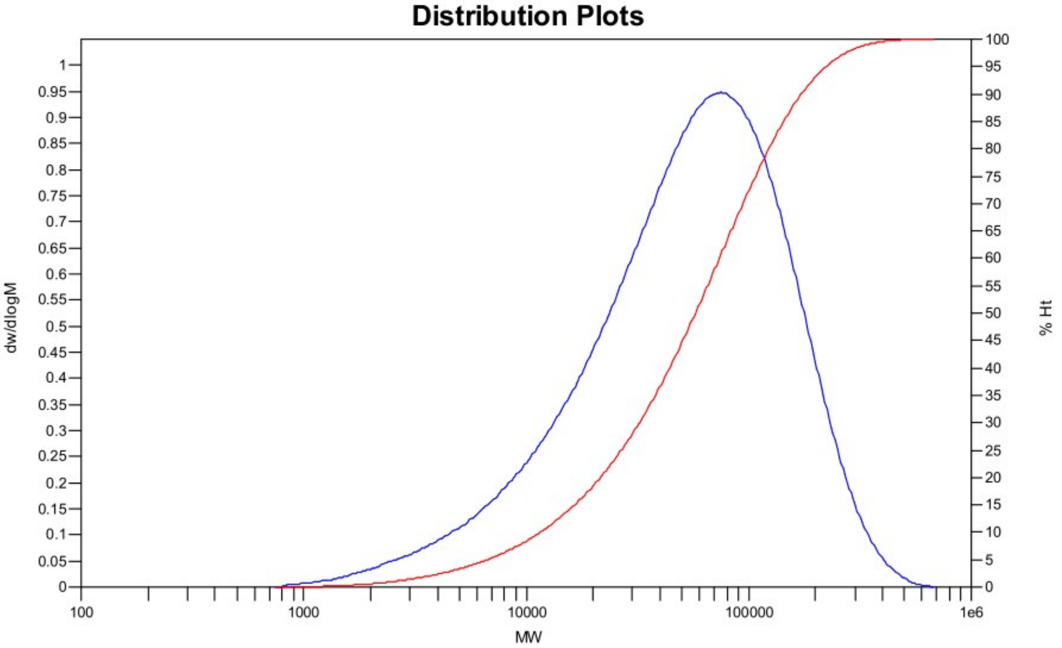


Fig. S19 The GPC trace of the polymer PClT-EHp.

References

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