Supplementary Information (SI) for Materials Horizons.

Supporting Information

Polyethylene Glycol-decorated n-Type Conducting Polymers with Improved Ion Accessibility for High-performance Organic Electrochemical Transistors

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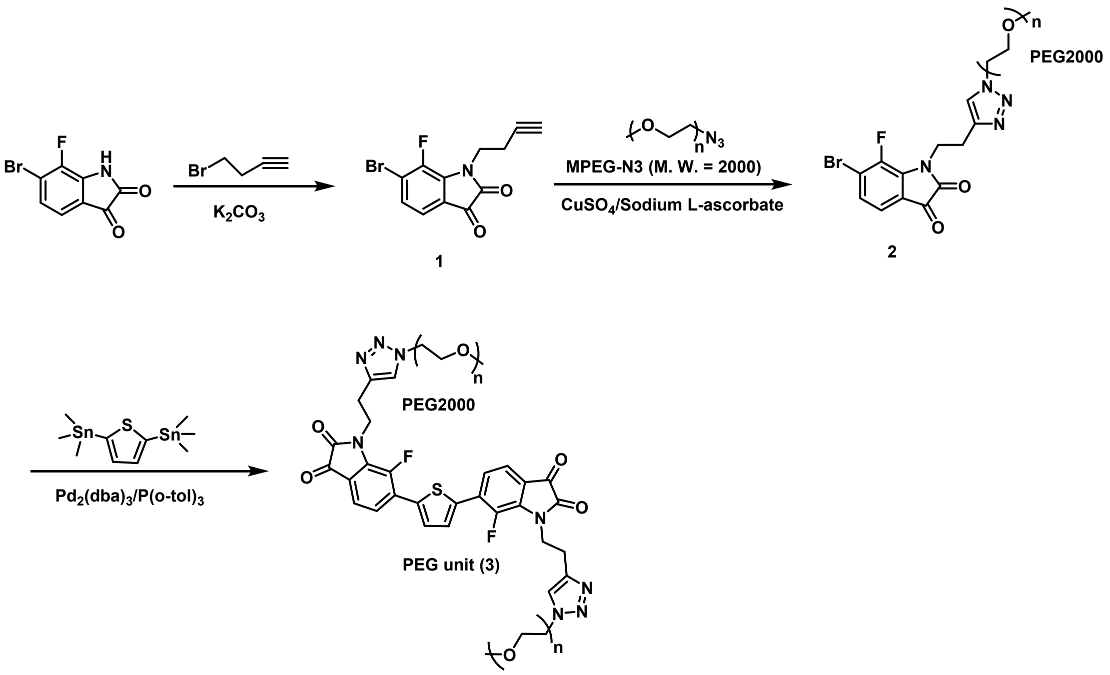


Figure S1. The Synthetic route to PEG copolymerization units.

Synthesis of 6-bromo-1-(but-3-yn-1-yl)-7-fluoroindoline-2,3-dione (1)

In a 100 mL two-necked flask, 6-bromo-7-fluoro-2,3-dihydro-1H-indole-2,3-dione (500 mg, 2.05 mmol) and anhydrous potassium carbonate (311.5 mg, 2.255 mmol) were added. Subsequently, anhydrous *N*, *N*-dimethylformamide (35 ml) was added, and the mixture was subjected to vacuum evacuation and argon refilling for three cycles to maintain an inert atmosphere. The reaction mixture was initially stirred at 80 °C for 30 minutes. Then, 4-bromo-1-butyne (408.9 mg, 8.2 mmol) was injected by syringe, and the mixture was heated under 80 °C overnight. After cooling to room temperature, the solvent was removed by rotary evaporation. The crude product was purified by silica column chromatography with dichloromethane: hexane (1: 1, vol%) as eluent to give resulting product (414 mg, yield: 68%).

^{1}H NMR (400 MHz, Chloroform-*d*, ppm): 7.40-7.29 (m, 2H), 4.14-4.06 (td, 2H), 2.70-2.61 (m, 2H), 1.99-1.97 (t, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*, ppm): 181.17, 157.70, 146.23, 143.76, 137.53, 128.53, 121.80, 119.25, 79.35, 71.15, 41.02, 18.70.

Synthesis of compound 2

Compound 1 (365.7 mg, 1.235 mmol), MPEG-N$_3$ (M. W. = 2000) (2.5 g, 1.25mmol), copper sulfate (12 mg, 0.07 mmol) and sodium L-ascorbate (25 mg, 0.12 mmol) were added to a 250 mL two-necked flask. The reactants were dissolved in tetrahydrofuran (100 mL) and water (10 mL) under argon protection. The resulting reaction mixture was stirred at room temperature overnight. The product was then extracted using water and dichloromethane, and the organic phase was collected. After removal of solvent by rotary evaporation, the crude product was purified by silica column chromatography with dichloromethane: methanol (20: 1, vol%) as eluent to obtain the compound 2 as orange solid (2.67 g, yield: 94%).

^{1}H NMR (400 MHz, Chloroform-*d*, ppm): 7.62 (s, 1H), 7.34-7.25 (m, 2H), 4.50-4.42 (t, 2H), 4.20-

4.10 (m, 2H), 3.68-3.54 (m, ~194H), 3.46-3.38 (m, 2H), 3.36-3.31 (s, 3H), 3.18-3.10 (t, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*, ppm): 181.33, 157.74, 146.17, 143.70, 143.22, 137.61, 128.40, 122.91, 121.74, 119.31, 71.90, 70.53, 69.50, 59.01, 50.23, 42.21, 25.04.

Synthesis of PEG unit (3)

Compound 2 (1000 mg, 0.434 mmol), 2,5-bis(trimethylstannyl)thiophene (89 mg, 0.217 mmol) and tri(o-tolyl)phosphine (80 mg) were introduced into the Schlenk reaction tube. Subsequently, dioxane (67 ml) was added to dissolve the reactants. The mixture was subjected to vacuum evacuation and argon replenishment three times. Following this, tris(dibenzylideneacetone)dipalladium (40 mg, 0.043 mmol) was added to the reaction mixture under argon protection. The reaction was conducted at 100 °C for 24 hours. After the reaction, the solvent was removed by rotary evaporation and the product was purified by column chromatography with dichloromethane: methanol (10: 1, vol%) as eluent. The product was then washed by hexane and dried under vacuum to obtain PEG unit as red solid (810 mg, yield: ~83%).
^{1}H NMR (400 MHz, Chloroform-*d*, ppm): 7.74-7.60 (m, 4H), 7.52-7.40 (m, 4H), 4.56-4.44 (m, 4H), 4.34-4.22 (m, 4H), 3.88-3.42 (m, ~394H), 3.39-3.35 (m, 6H), 3.30-3.12 (m, 4H).

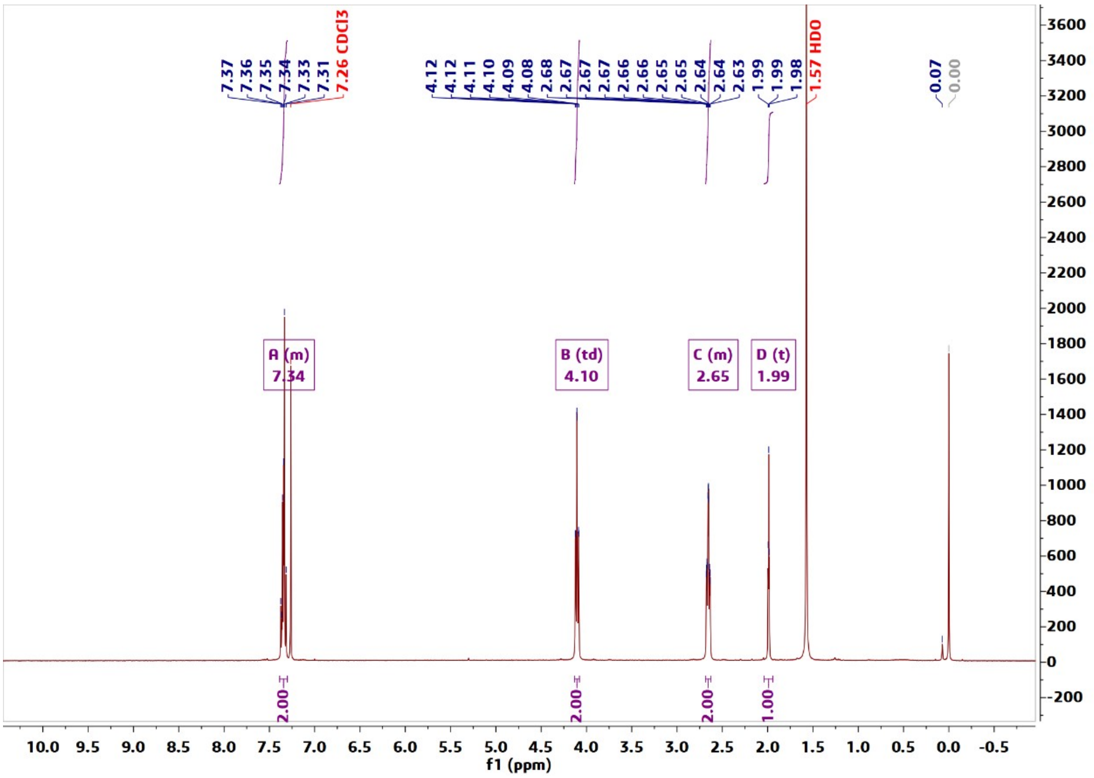


Figure S2. ^{1}H NMR spectrum of 6-bromo-1-(but-3-yn-1-yl)-7-fluoroindoline-2,3-dione (1).

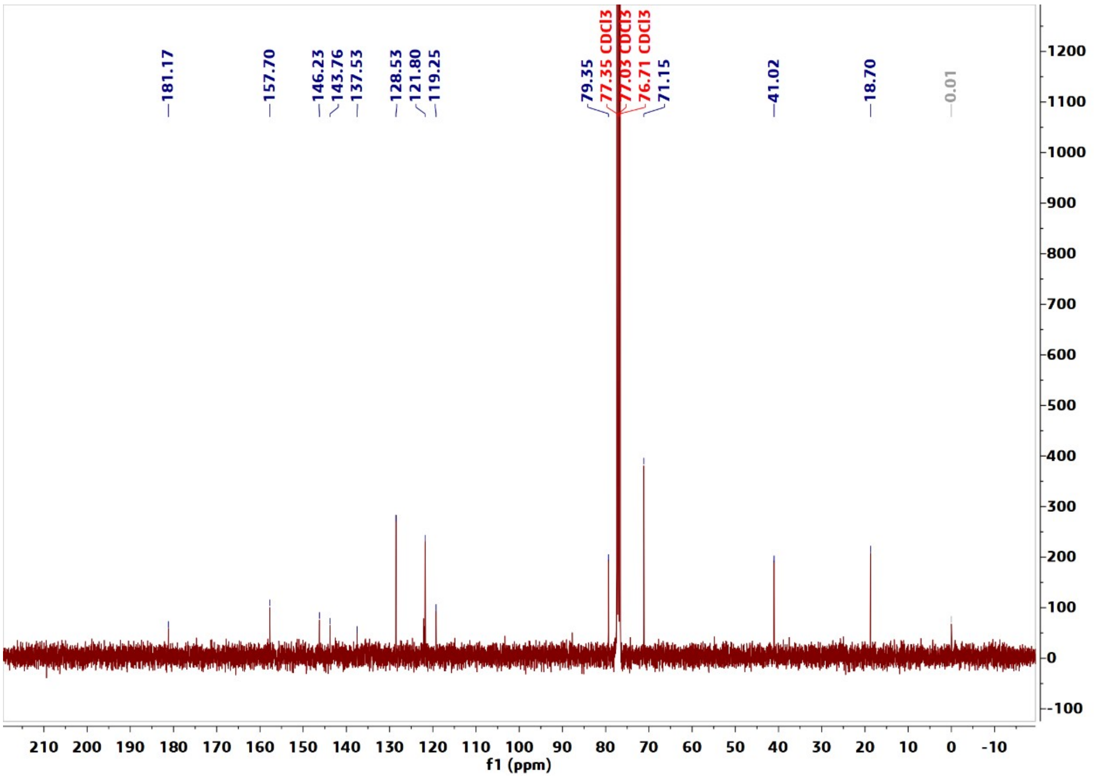


Figure S3. ^{13}C NMR spectrum of 6-bromo-1-(but-3-yn-1-yl)-7-fluoroindoline-2,3-dione (1).

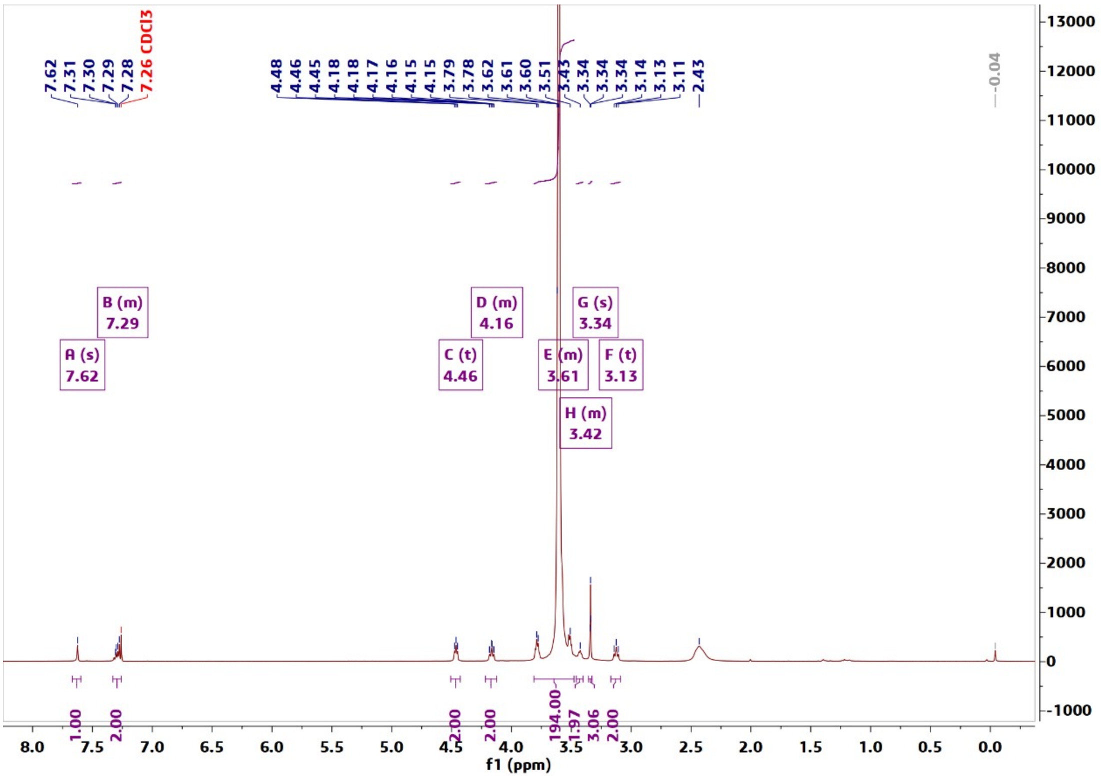


Figure S4. ^{1}H NMR spectrum of compound 2.

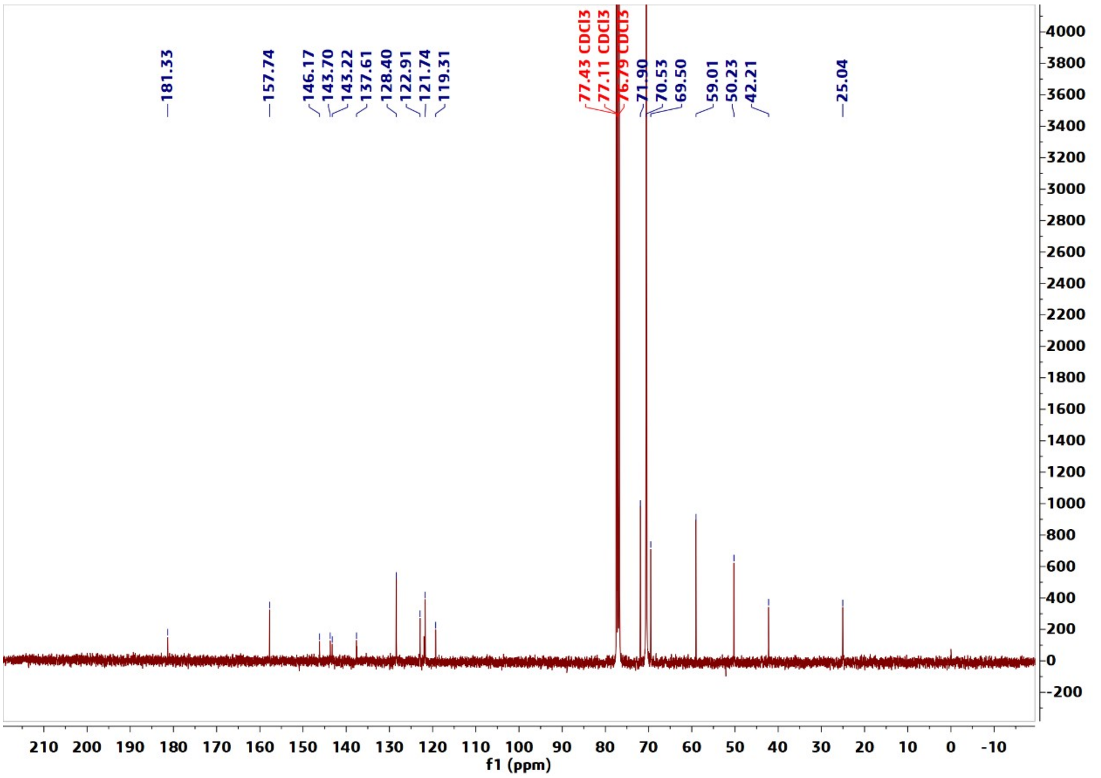


Figure S5. ^{13}C NMR spectrum of compound 2.

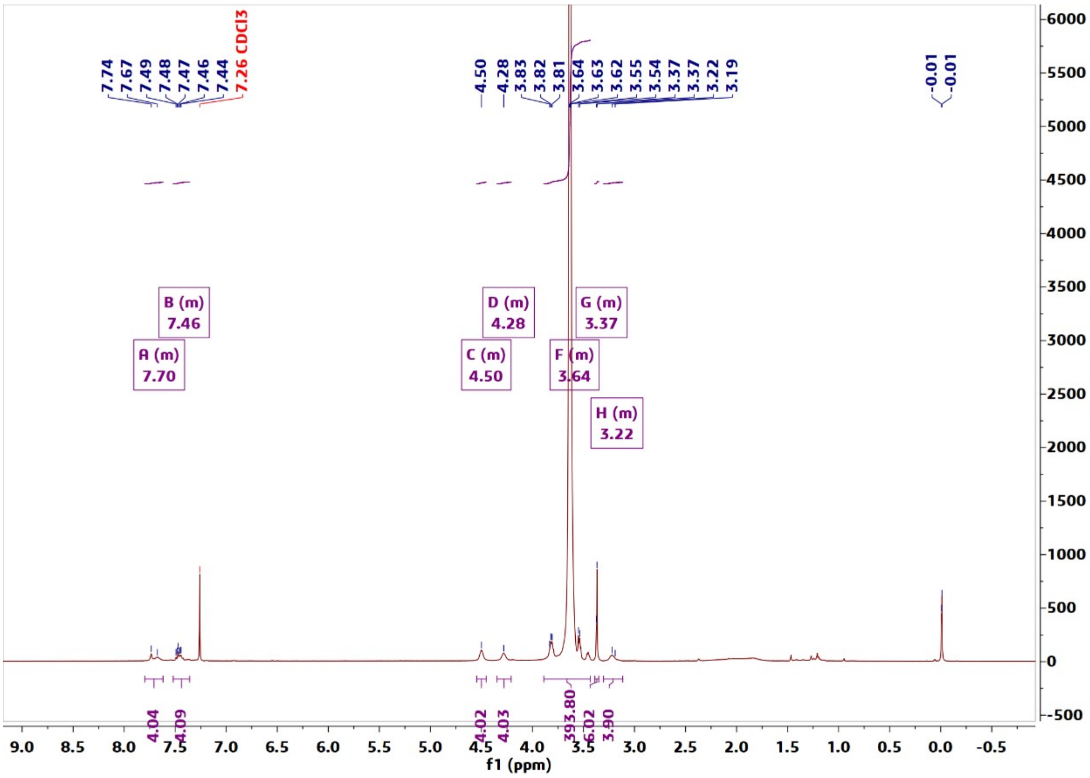


Figure S6. ^{1}H NMR spectrum of PEG unit (compound 3).

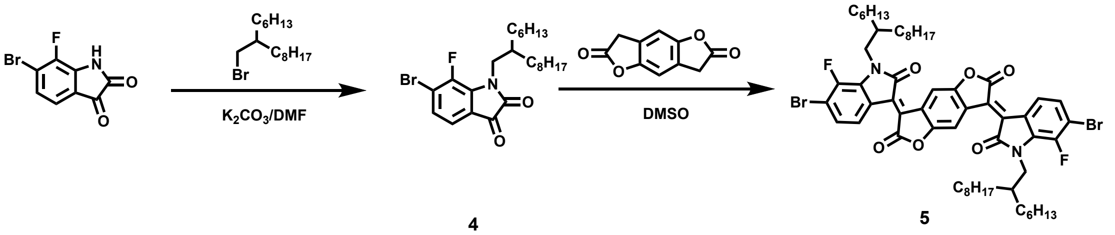


Figure S7. The Synthetic route to model small molecule demonstrating occurrence of aldol condensation.

Synthesis of 6-bromo-7-fluoro-1-(2-hexyldecyl)indoline-2,3-dione (4)

In a 100 mL two-necked flask, 6-bromo-7-fluoro-2,3-dihydro-1H-indole-2,3-dione (500 mg, 2.05 mmol) and anhydrous potassium carbonate (311.5 mg, 2.255 mmol) were added. Subsequently, anhydrous *N*, *N*-dimethylformamide (35 ml) was added, and the mixture was subjected to vacuum evacuation and argon refilling for three cycles to maintain an inert atmosphere. The reaction mixture was initially stirred at 80 °C for 30 minutes. Then, 1-bromo-2-hexyldecane (1.88 g, 6.15 mmol) was injected by syringe, and the mixture was heated under 80 °C overnight. After cooling to room temperature, the solvent was removed by rotary evaporation. The crude product was purified by silica column chromatography with dichloromethane: hexane (1: 1, vol%) as eluent to give resulting product (610 mg, yield: 62%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 2H), 3.77 – 3.74 (dd, 2H), 1.91 – 1.77 (m, 1H), 1.34 – 1.23 (m, 24H), 0.91 – 0.85 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.79, 158.02, 146.13, 143.66, 138.14, 138.04, 128.27, 122.17, 121.97, 121.64, 121.60, 119.33, 119.30, 47.03, 46.99, 37.40, 37.38, 31.87, 31.77, 31.17, 29.97, 29.71, 29.65, 29.51, 29.29, 26.15, 26.12, 22.68, 22.64, 14.12, 14.09.

Synthesis of 3,7-bis((*E*)-6-bromo-7-fluoro-1-(2-hexyldecyl)-2-oxoindolin-3-ylidene)-3,7-dihydrobenzo[1,2-*b*:4,5-*b*']difuran-2,6-dione (5)

3,7-Dihydrobenzo[1,2-*b*:4,5-*b*']difuran-2,6-dione (H-BFDO) monomer (100 mg, 0.53 mmol) and 6-bromo-7-fluoro-1-(2-hexyldecyl)indoline-2,3-dione (4) (515.3 mg, 1.10 mmol) were introduced into the Schlenk reaction tube. Subsequently, dimethyl sulfoxide (20 ml) was added to dissolve the reactants. The mixture was subjected to vacuum evacuation and argon replenishment three times. The reaction was conducted at 85 °C for 24 hours. After the reaction, the solvent was removed by rotary evaporation and the product was purified by column chromatography with dichloromethane: hexane (2: 1, vol%) as eluent to give resulting product (393.2 mg, yield: 68%).

^{1}H NMR (400 MHz, Chloroform-d) δ 9.07 (s, 2H), 8.78 (d, 2H), 7.23 (dd, 2H), 3.84 (d, 4H), 1.92 – 1.82 (m, 2H), 1.45 – 1.17 (m, 48H), 0.93 – 0.79 (m, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.93, 166.82, 151.95, 142.62, 133.59, 127.67, 127.17, 126.74, 126.42, 122.69, 116.90, 116.71, 111.27, 46.71, 37.60, 31.88, 31.80, 31.30, 31.27, 30.03, 29.71, 29.54, 29.31, 26.25, 26.19, 22.68, 22.65, 14.12, 14.09.

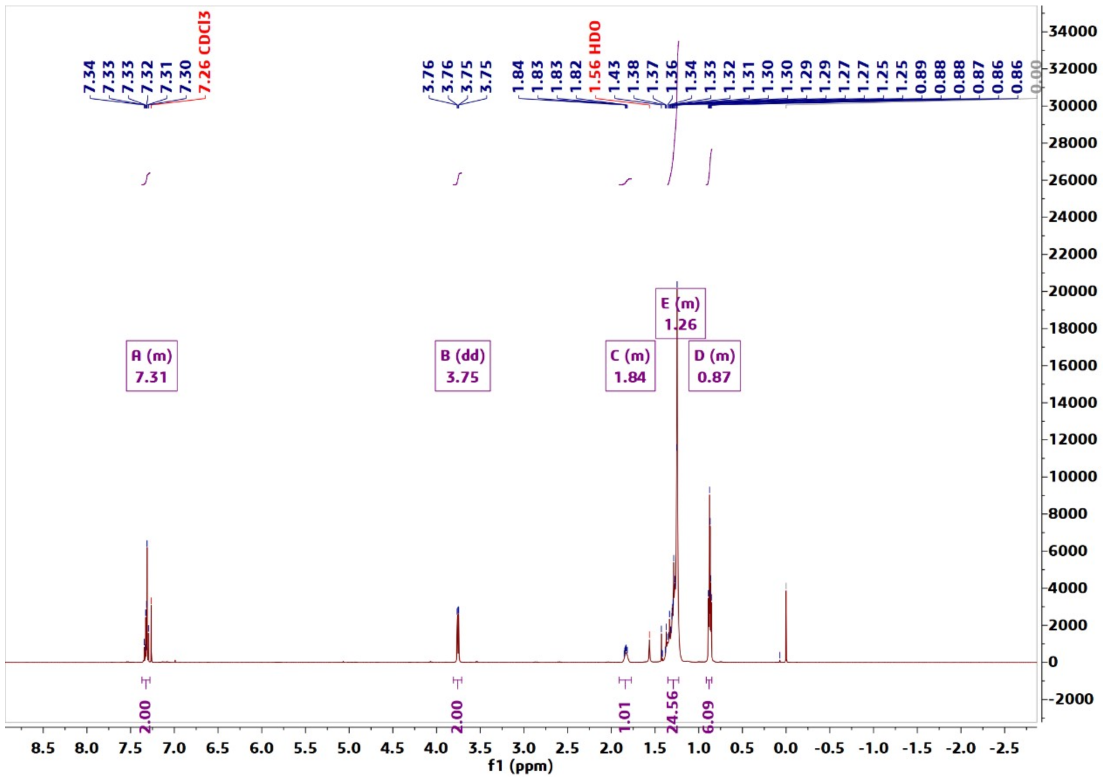


Figure S8. ^{1}H NMR spectrum of 6-bromo-7-fluoro-1-(2-hexyldecyl)indoline-2,3-dione (4).

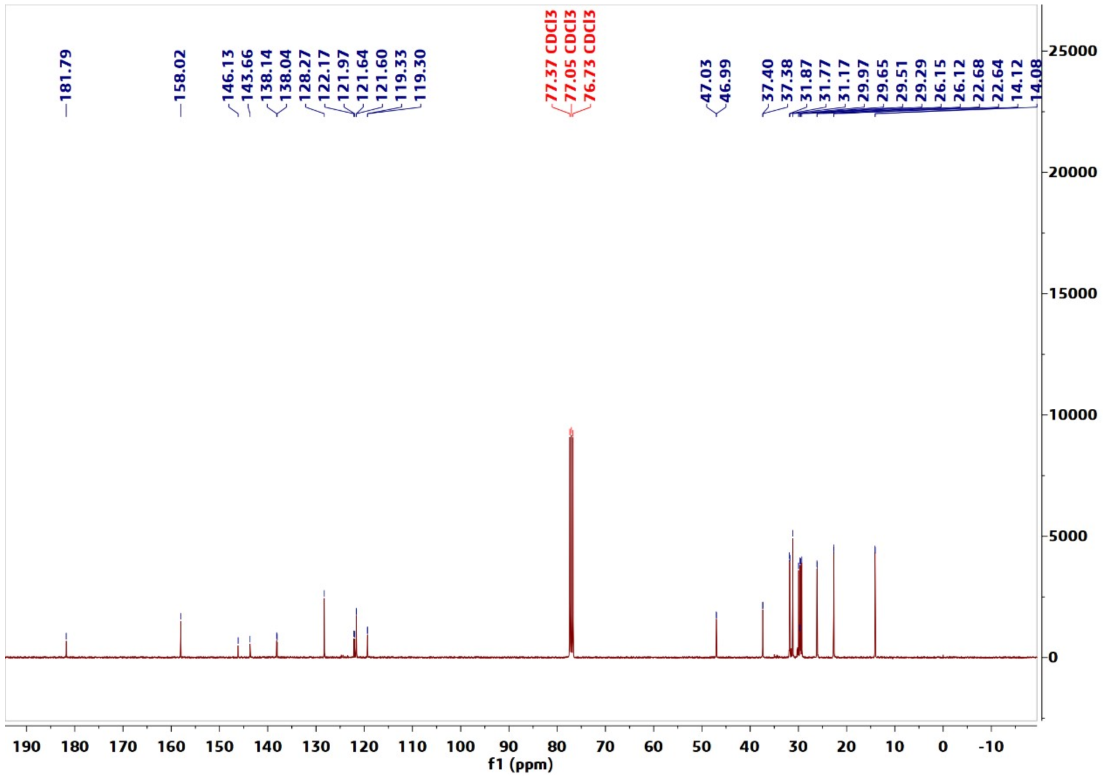


Figure S9. ^{13}C NMR spectrum of 6-bromo-7-fluoro-1-(2-hexyldecyl)indoline-2,3-dione (4).

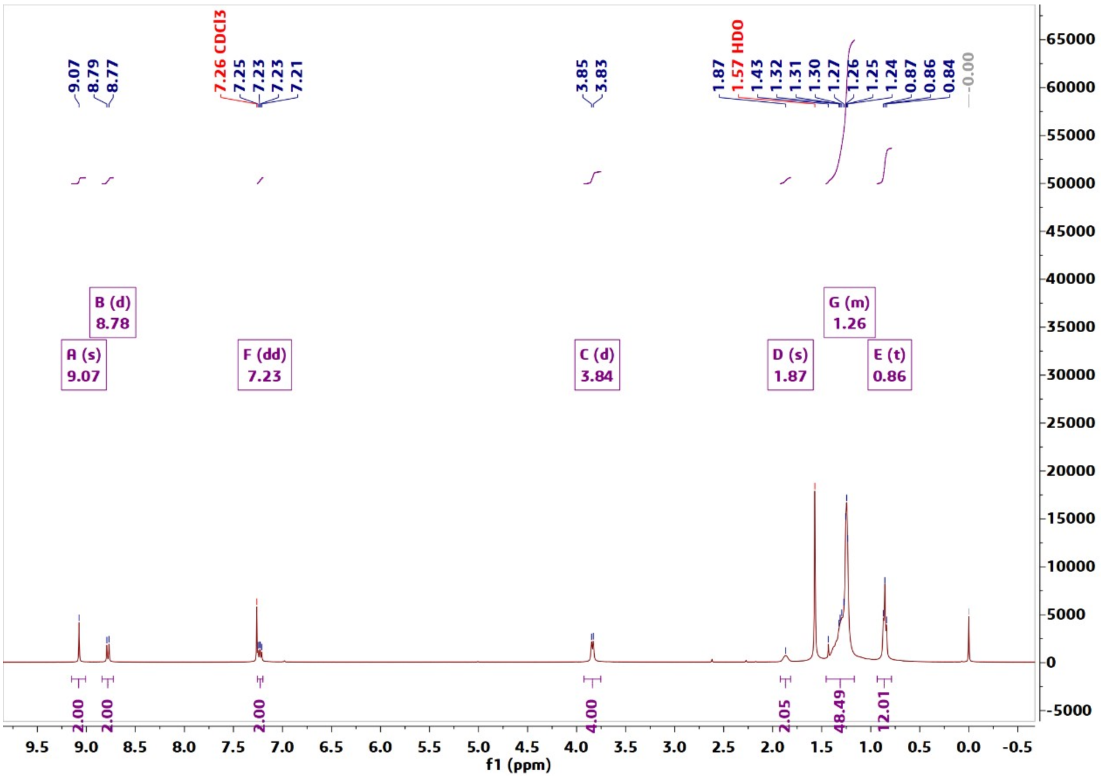


Figure S10. ^{1}H NMR spectrum of 3,7-bis((*E*)-6-bromo-7-fluoro-1-(2-hexyldecyl)-2-oxoindolin-3-ylidene)-3,7-dihydrobenzo[1,2-*b*:4,5-*b*']difuran-2,6-dione (5).

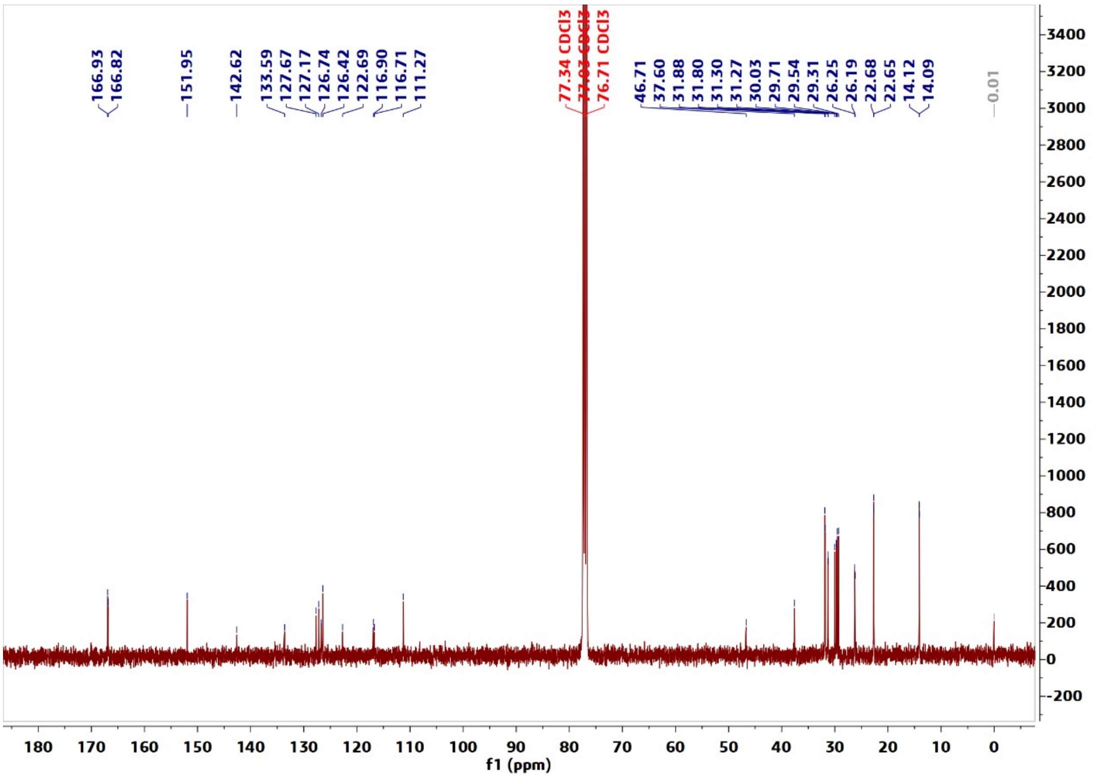


Figure S11. ^{13}C NMR spectrum of 3,7-bis((*E*)-6-bromo-7-fluoro-1-(2-hexyldecyl)-2-oxoindolin-3-ylidene)-3,7-dihydrobenzo[1,2-*b*:4,5-*b*']difuran-2,6-dione (5).

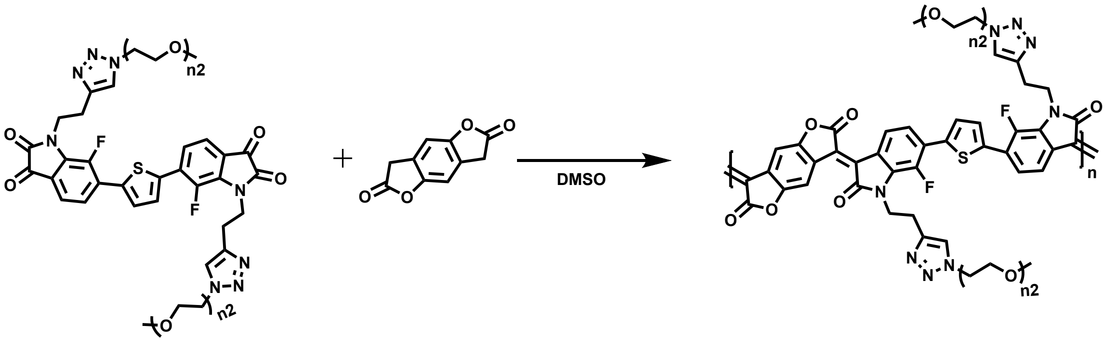
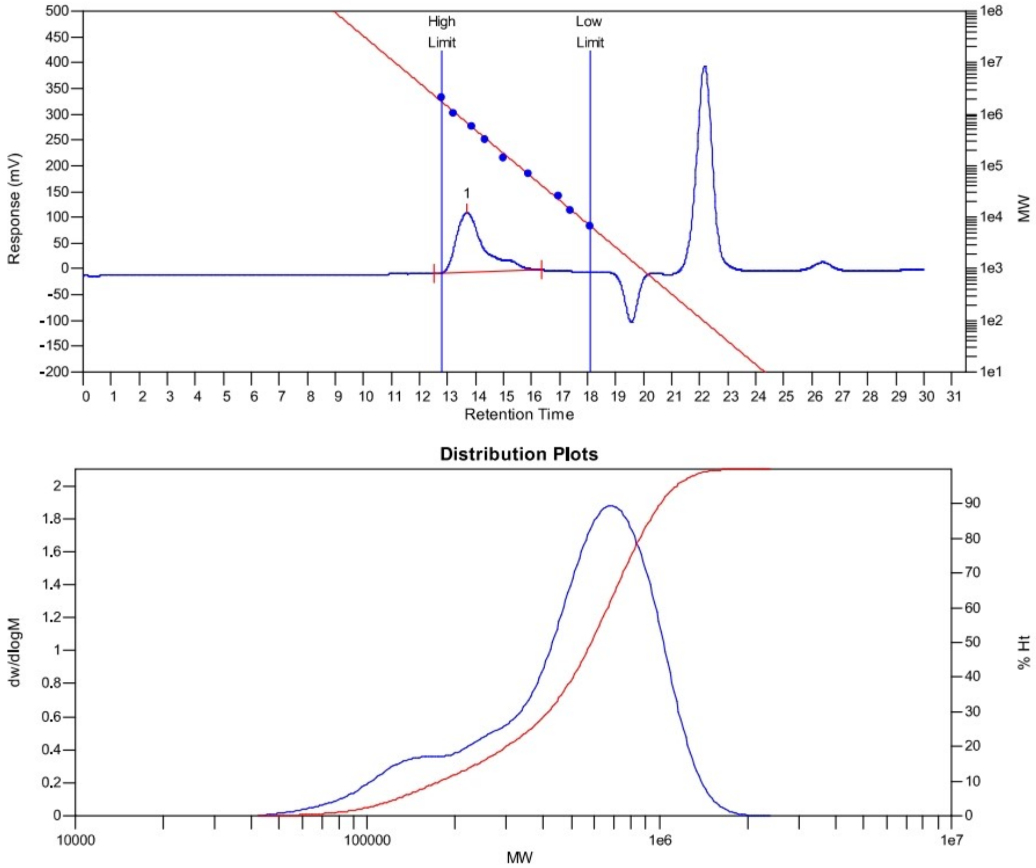


Figure S12. The Synthetic route to model polymer demonstrating occurrence of aldol polycondensation.

Synthesis of model polymer of H-BFDO monomer and PEG unit

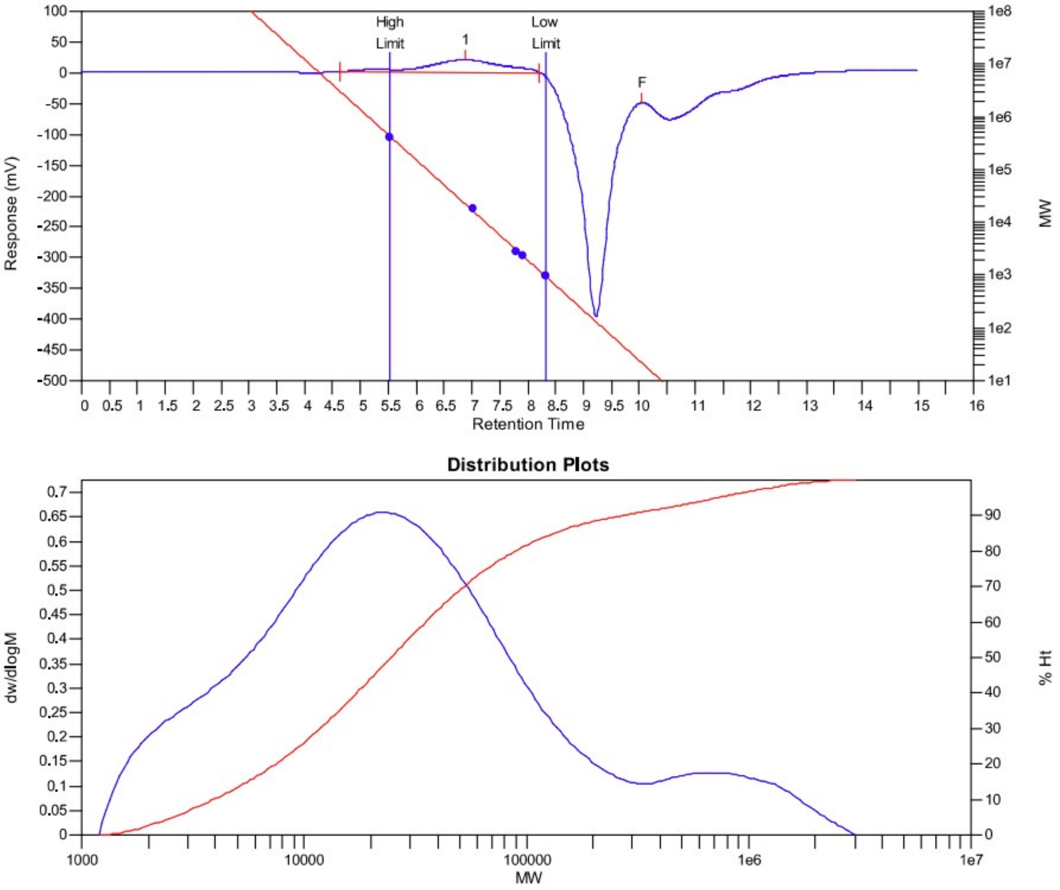
The monomer 3,7-dihydrobenzo[1,2-*b*:4,5-*b*']difuran-2,6-dione (H-BFDO) (10 mg, 0.0526 mmol) and PEG unit (242 mg, ~0.0526 mmol) were introduced into the Schlenk reaction tube. Dimethyl sulfoxide (DMSO, 18 ml) was then added to dissolve the reactants, followed by three cycles of vacuum evacuation and argon replenishment. The mixture was heated at 85 °C for 12 hours. Subsequently, dialysis against DMSO was carried out using dialysis bags with a cut-off molecular weight of 10 kDa. After approximately one week of dialysis, the polymer solution in the dialysis bag was collected for further characterization.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	678430	381764	591995	752550	872551	565630	1.55068

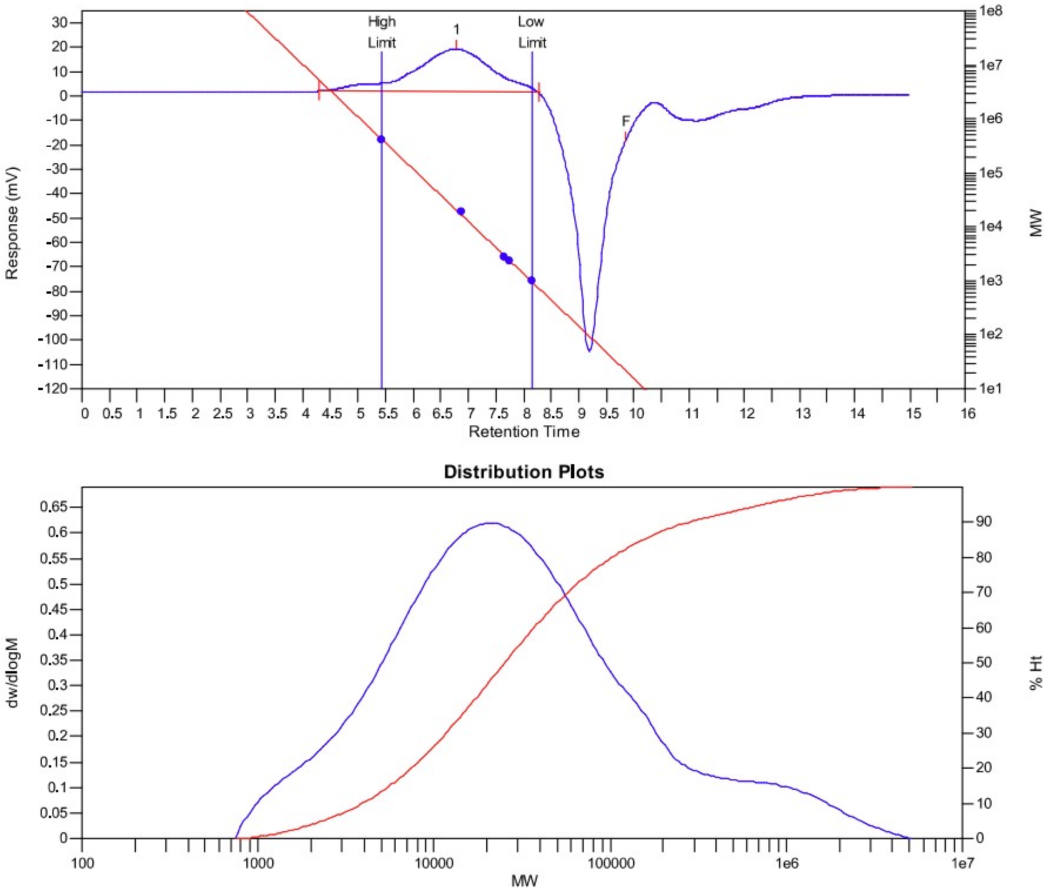
Figure S13. GPC measurement of model polymer obtained through aldol polycondensation of PEG unit and H-BFDO monomer.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	22080	10755	118822	871080	1445602	76645	11.0481
2	0	0	0	0	0	0	0

Figure S14. GPC measurement of PBFDO-PEG50wt%.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	20330	9905	133234	1153905	2143883	83736	13.4512
2	0	0	0	0	0	0	0

Figure S15. GPC measurement of PBFDO-PEG100wt%.

Table S1. The elemental analysis (EA) of PBFDO-PEG series polymers.

Name	N [%]	C [%]	H [%]	S [%]	Estimated Copolymerization Weight Ratio[a]
PBFDO-PEG50wt%	0.72	60.45	4.04	0.44	54 wt%
PBFDO-PEG100wt%	1.25	59.07	4.80	0.43	100 wt%
PEG unit	2.25	54.54	7.99	0.76	-

[a] The actual copolymerization weight ratio of PEG units was estimated by ensuring the absolute error between the measured values of C, H, and N element contents and their corresponding theoretical values remained below 0.4%. The theoretical element contents were estimated using equation $(([E]_{\text{PBFDO block}}+[E]_{\text{PEG unit}}\times x)/(1+x) = [E]_{\text{polymer}})$, which ignored the removal of oxygen due to the high molecular weight of PEG units. 64.2% for C and 1.5% for H were estimated for PBFDO copolymerization block.

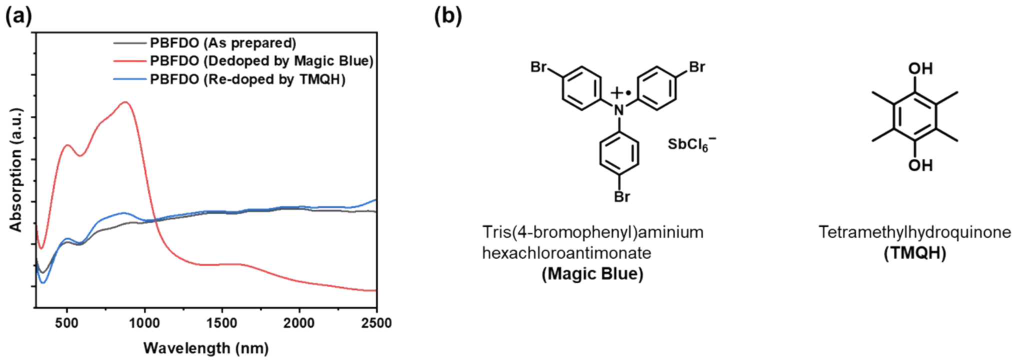


Figure S16. a) The absorption spectra of PBFDO and de-doped/re-doped films. The as-prepared film was immersed in an acetonitrile solution of magic blue (5 mg/ml) for 30 seconds to achieve de-doping. After being washed with acetonitrile, the de-doped film was immersed in the acetonitrile solution of TMQH (5 mg/ml) for 30 seconds to achieve re-doping. b) The chemical structures of Magic Blue and TMQH.

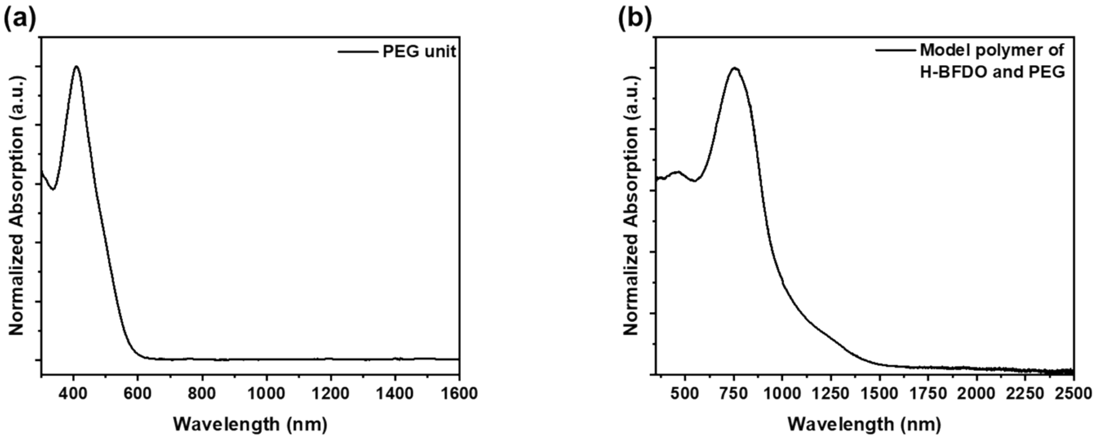


Figure S17. The absorption spectra of PEG unit and model polymer of H-BFDO monomer and PEG unit.

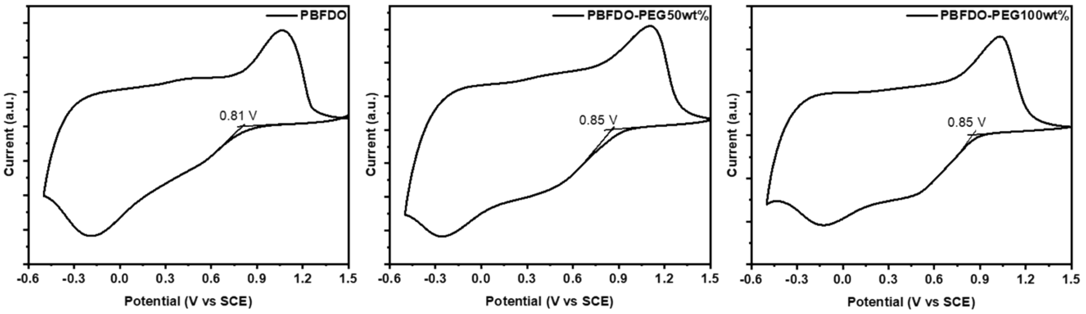


Figure S18. Cyclic voltammetry (CV) measurements of PBFDO-PEG-based OMIECs in 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) anhydrous acetonitrile solution with ferrocene/ferrocenium (Fc/Fc^+) redox couple as the external reference.

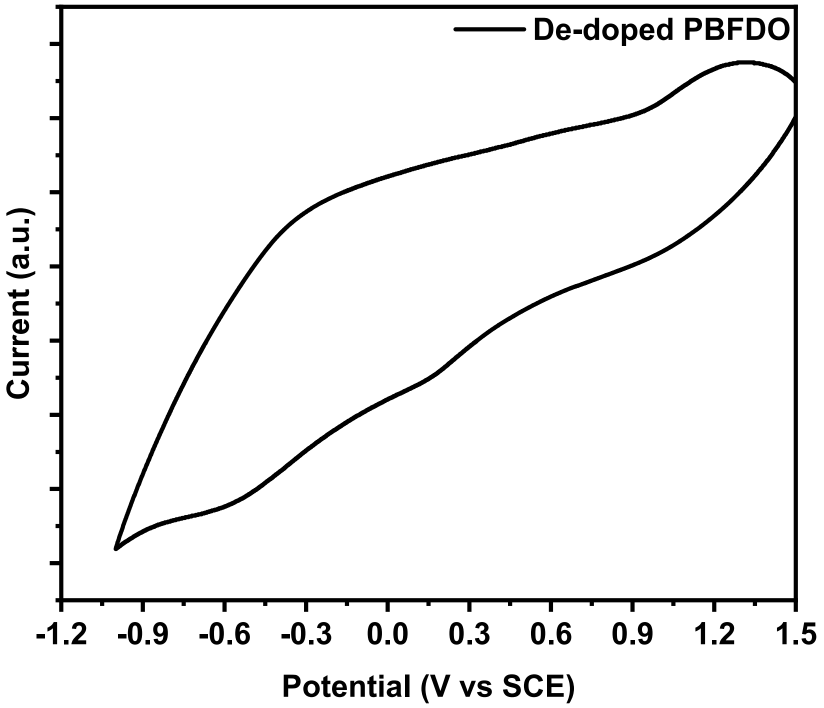


Figure S19. Cyclic voltammetry (CV) measurements of de-doped PBFDO film. The as-prepared PBFDO film was first immersed into the acetonitrile solution of magic blue (5 mg/ml) for 30 seconds to achieve de-doping.

Estimation of surface energy:[1]

The surface free energy of liquid could be written as:

$\gamma_l = \gamma_l^d + \gamma_l^h$

Where the superscripts *d* and *h* refer to the hydrogen bonding and dispersion force components. The relevant parameters for water and diiodomethane are listed as below:

Water (γ_l = 72.8 mN/m, γ_l^d = 21.8 mN/m, γ_l^h = 51.0 mN/m)

Diiodomethane (γ_l = 50.8 mN/m, γ_l^d = 49.5 mN/m, γ_l^h = 1.3 mN/m)

When the liquid is present on the surface of a solid film, the contact angles typically adhere to the following equation:

$\gamma_l(1 + cos\theta) = 2\sqrt{\gamma_s^d\gamma_l^d} + 2\sqrt{\gamma_s^h\gamma_l^h}$

Therefore, By selecting two distinct liquids to measure their contact angles on the identical solid surface, it is possible to estimate the values of γ_s^d and γ_s^h for the solid. The total surface energy

$\gamma_s = \gamma_s^d + \gamma_s^h$.

Table S2. The estimation of surface energy for PBFDO-PEG series polymers.

Name	Contact angle (°)		Surface energy (mN m^{-1})		
	Water	Diiodomethane	γ_s^d	γ_s^h	γ_s
PBFDO	79.3	39.8	36.54	4.37	40.91
PBFDO-PEG50wt%	69.4	39.3	34.97	9.14	44.11
PBFDO-PEG100wt%	64.0	32.4	37.44	11.09	48.53

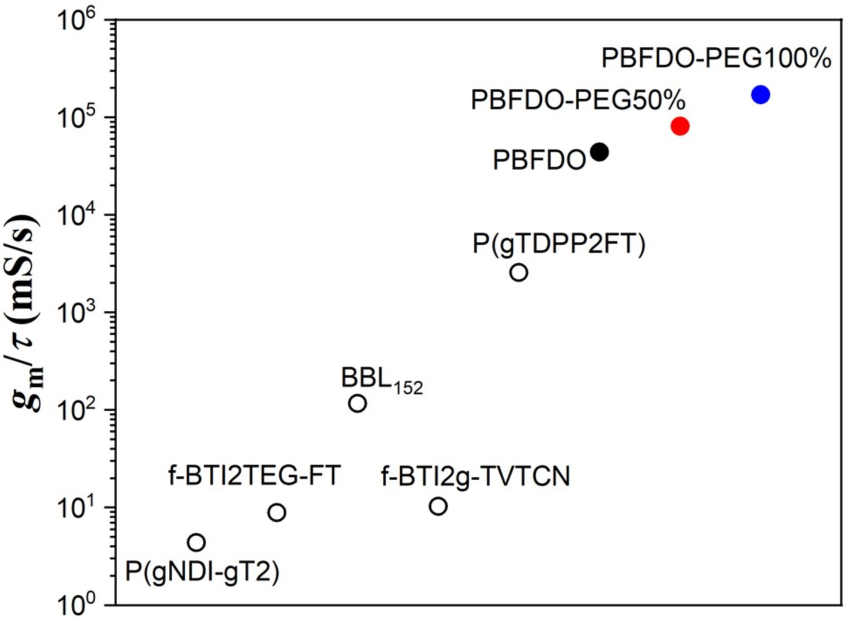


Figure S20. Ratio of transconductance to transient time for different n-type OMIECs-based OECTs.[2-6]

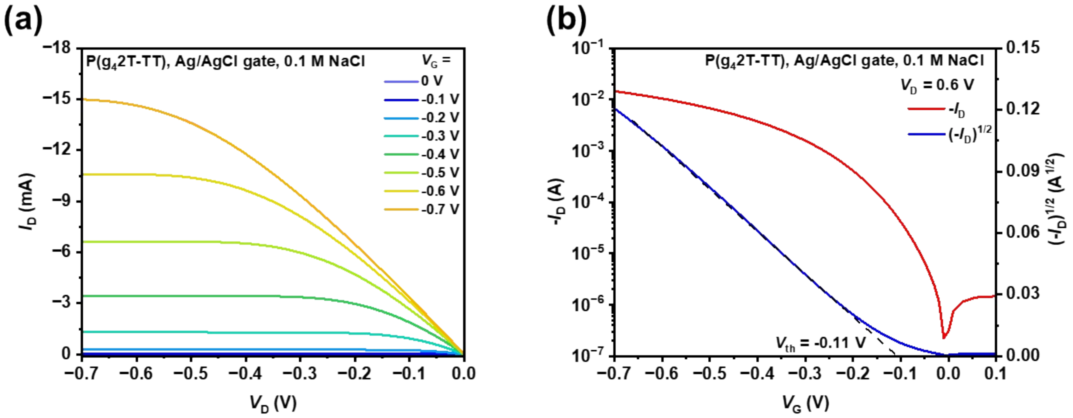


Figure S21. Transfer characteristics of the p-type OMIEC P($g_4$2T-TT)-based OECT.

References

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