

Electronic Supporting Information (ESI)

Study of Carbonyl and Ester Group on Regulating the Optical and Electrical Characteristics of Wide Bandgap Polymers for Organic Solar Cells

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Reagents and measurements

The solvents used in the experiment are reagent grade, deuterated chloroform (CDCl₃), HPLC grade acetonitrile (CH₃CN), chlorobenzene, 1,8-diiodooctane (DIO) are purchased from sigma Aldrich and do not need further treatment. Before use, dry solvents such as ether, dichloromethane and toluene should be distilled from appropriate desiccants. Commercially available reagents bromomethyl cyclohexane, iodine, 2,5-dibromo-3-cyanothiophene, 2,5-dibromothiophene-3-carboxylic acid, cyclohexanol, dicyclohexylcarbodiimide, 4-dimethylaminopyridine, [1,1'-bis(diphenylphosphine)ferrocene]nickel dichloride (II), (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophenyl)benzo[1,2-b:4,5-b']dithiophenyl)bis(trimethyltin), tetra(*n*-butyl)ammonium hexafluorophosphate (*n*-Bu₄NPF₆), tris(dibenzylideneacetone)palladium (Pd₂(dba)₃) and tris(*o*-tol)phosphorus (P(*o*-tol)₃) are purchased from sigma Aldrich or Aladdin, and no further purification is required during use. In the experiment, all reactions were monitored by thin layer chromatography (TLC) of Merck precoated chromatographic aluminum plate, and the reaction system and compounds were observed under UV irradiation of 254 nm and 365 nm. The nuclear magnetic resonance (NMR) spectrum in CDCl₃ was measured on Bruker AVANCE III HD 400 MHz NMR spectrometer in Germany, and the

chemical shift relative to the internal standard tetramethylsilane was quoted. The absorption spectrum was measured with tu-1901 dual beam UV-vis spectrophotometer. The molecular weight of the polymer was measured by gel permeation chromatography (GPC) using ELEOS system, and polystyrene was used as standard (room temperature, tetrahydrofuran (THF) as eluent). Cyclic voltammetry (CV) measurement is carried out on CHI660E electrochemical workstation, which is equipped with a three-electrode battery, which is composed of glassy carbon working electrode, platinum wire counter electrode and saturated calomel electrode (SCE) reference electrode. Measurements were made in anhydrous acetonitrile containing 0.1M *n*-Bu₄NPF₆ as an auxiliary electrolyte in argon atmosphere at a scanning rate of 100 mV/s. Before measurement, the film was deposited from the chlorobenzene solution onto the working electrode and dried under nitrogen. Compared with SCE, the redox potential of Fe/Fe⁺ internal reference is 0.41 V. The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are determined by calculating the empirical formulas of $E_{HOMO} = e(E_{ox} - 4.8 - E_{1/2}^{(Fe/Fe^+)})$ and $E_{LUMO} = E_{HOMO} - E_g$, where E_{ox} and E_g are the initial oxidation potential and optical band gap, respectively. Grazing incidence wide-angle X-ray scattering (GIWAXS) mode is obtained by beamline BL16B1 (Shanghai Synchrotron Radiation Facility). The X-ray wavelength is 0.124 nm ($e=10$ keV), and the incident angle is set to 0.2 degree.

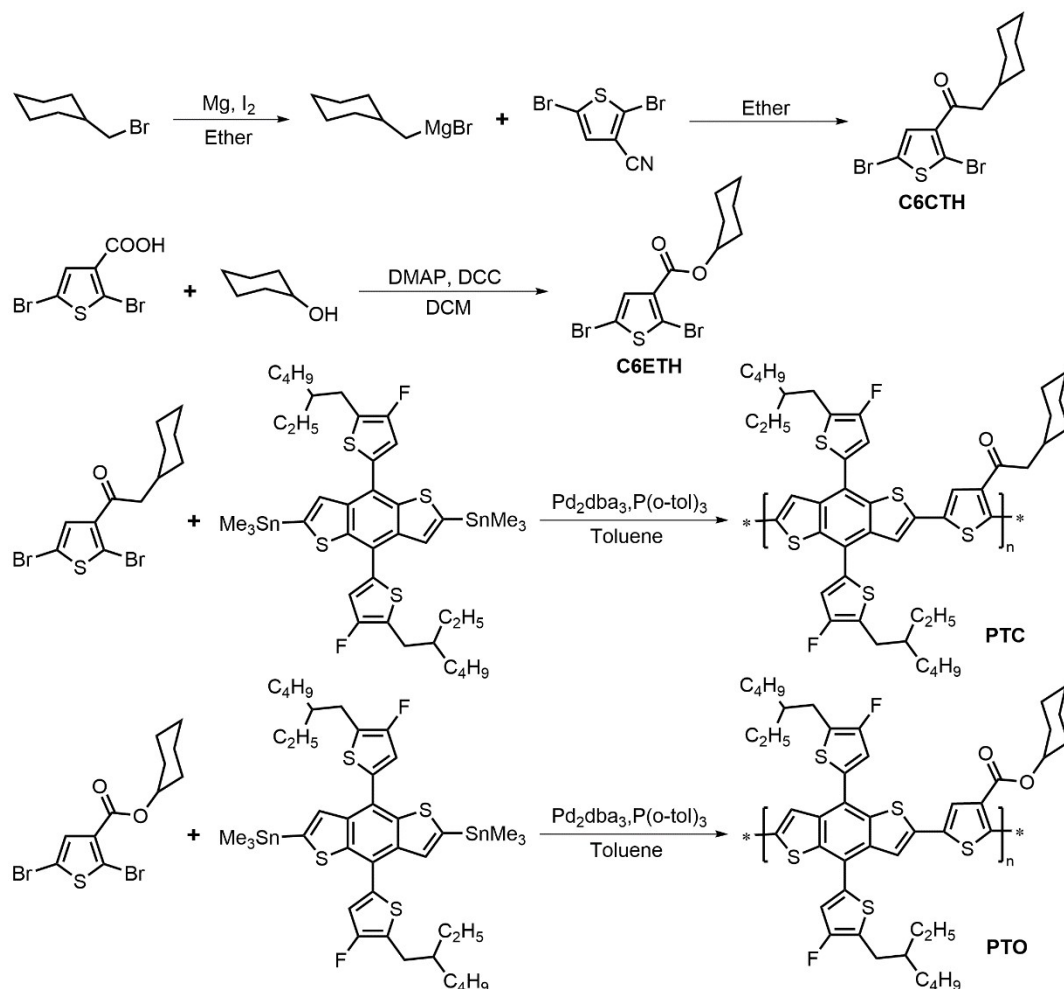
Fabrication and measurement of polymer solar cells (PSCs)

All PSCs in this paper are manufactured with the conventional device structure of ITO/PEDOT:PSS/polymer:IT-F4/PDINO/Al. In solvents such as detergent, deionized water, acetone and isopropanol, ITO coated substrates were cleaned in an ultrasonic bath for 15 minutes, dried with ultra-pure N₂, and then treated with O₂ plasma (Plasma Preen II-862 Cleaner) for 6 minutes. Then, at 4000 rpm, 40 nm PEDOT:PSS was rotationally cast on the ITO glass coating, annealed in an oven at 80 °C for 10 minutes, and then the glass substrate was transferred to a glove box filled with N₂. Dissolve PTO (or PTC) and IT-4F in *o*-dichlorobenzene with or without DIO solvent

and stir overnight at room temperature (the optimal polymer concentration of PTO and PTC is 22 mg/mL). The solution was spin coated on the ITO/PEDOT:PSS substrate to form an active layer. Using Veeco-Dektak 150 surface profiler, the optimized thickness of PTO/IT-4F and PTC/IT-4F films is about 100 nm. Then, a layer of ultra-thin PDINO was cast on the active layer at 3000 rpm for 20 s. Finally, The Al (82 nm) metal electrode is thermally evaporated at about 4×10^{-4} Pa, and the device area is 0.1 cm^2 , which is defined by the shadow mask.

Current density–voltage (J – V) characteristics of the devices were recorded using Keithley 2420 source measurement unit under the illumination of AM 1.5G (100 mW cm^{-2} , Newport solar simulator). Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. The hole only device employed a device architecture of ITO/PEDOT:PSS/BHJ/MoOx/Ag and the electron-only device employed a device architecture of ITO/ZnO/BHJ/PDINO/Al. The mobility was measured using the space-charge-limited current (SCLC) method¹, which uses the space charge limited form to fit the J - V curve, where the SCLC is described by $J = 9\epsilon_0\epsilon_r\mu_{h(e)}V^2/8d^3$, where ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), ϵ_r is the relative permittivity of the material (assumed to be 3), μ_h is the hole mobility and μ_e is the electron mobility. $V = V_{\text{appl}} - V_{\text{bi}} - V_s$ (V_{appl} is the applied voltage, V_{bi} is the built-in voltage, V_s is the voltage drop from the substrates series resistance) and d is the thickness of the related films.

Synthesis and characterization



Scheme S1. Synthetic route of polymer PTC and polymer PTO.

2-cyclohexyl-1-(2,5-dibromothiophen-3-yl)ethan-1-one (C6CTH):

(Cyclohexylmethyl)magnesium bromide was synthesized according to previous work.² To a stirred solution of 2,5-dibromo-3-cyanothiophene (1.7916 g, 16.4 mmol) in dry ether (20 mL) was added dropwise (cyclohexylmethyl)magnesium bromide (22 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. 5% Hydrochloric acid (30 mL) was added at 0 °C and stirred for another 1 hour, then the mixture was extracted using ether for 3 times, the organic phase was dried using anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: petroleum ether/CH₂Cl₂ = 4:1, v/v). C6CTH is obtained as light-yellow solid (1.1108 g, yield = 18.5%). ¹HNMR (400 MHz, CDCl₃): δ (ppm) 7.29 (s, 1H), 2.74 (d,

$J=8$, 2H), 1.95-1.91 (m, 1H), 1.75-1.64 (t, 4H), 1.34-1.14 (m, 4H), 1.04-0.95 (td, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 193.63, 140.01, 131.29, 116.51, 111.80, 49.28, 34.11, 33.28, 26.22, 26.10.

cyclohexyl 2,5-dibromothiophene-3-carboxylate (C6ETH):

2,5-Dibromo-3-formic acid (0.5719 g, 2 mmol), cyclohexanol (0.80128 g, 8 mmol), DCC (0.5365 g, 2.6 mmol) and DMAP (0.0733 g, 0.6 mmol) were mixed in 10 mL of dichloromethane at 0 °C, and then warm up to room temperature for 12 hours. Water was added and the mixture was extracted with dichloromethane, and dried over magnesium sulfate, then purified by silica gel column chromatography (eluent: petroleum ether/ CH_2Cl_2 = 4:1, v/v) to afford a light-yellow liquid. (0.4932 g, yield \square 67%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.35 (s, 1H), 5.00-4.98 (m, 1H), 1.94-1.89 (m, 2H), 1.80-1.76 (m, 2H), 1.60-1.39 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 160.30, 132.50, 131.84, 118.69, 111.19, 73.78, 31.50, 25.39, 23.52.

Polymer PTC:

C6CTH (0.0442 g, 0.12 mmol), (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (0.1135 g, 0.12 mmol), $\text{Pd}_2(\text{dba})_3$ (0.0018 g, 0.002 mmol) and $\text{P}(o\text{-tol})_3$ (0.0036 g, 0.012 mmol) were dissolved into 6 mL toluene in a 25 mL round bottom flask protected by argon. The flask was purged three times with successive vacuum and argon filling cycles. The oil bath was heated to 110 °C gradually, and the reaction mixture was stirred for 18 h at 110 °C under argon atmosphere. After cooling, the mixture was cooled to room temperature and precipitated in 200 mL methanol. The precipitate was filtered and washed with methanol and hexane successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight. PTC can be readily dissolved into THF, CHCl_3 , etc. The number-average molecular weight (M_n) \square 51.960 KDa, polydispersity index (PDI) \square 3.12. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.91-7.89 (br, ArH), 7.70-7.67 (br, ArH), 7.52 (br, ArH), 7.20 (br, ArH), 7.18 (br, ArH), 2.83-2.81 (br), 2.70-2.68 (br, CO- CH_2), 1.95-0.93 (br).

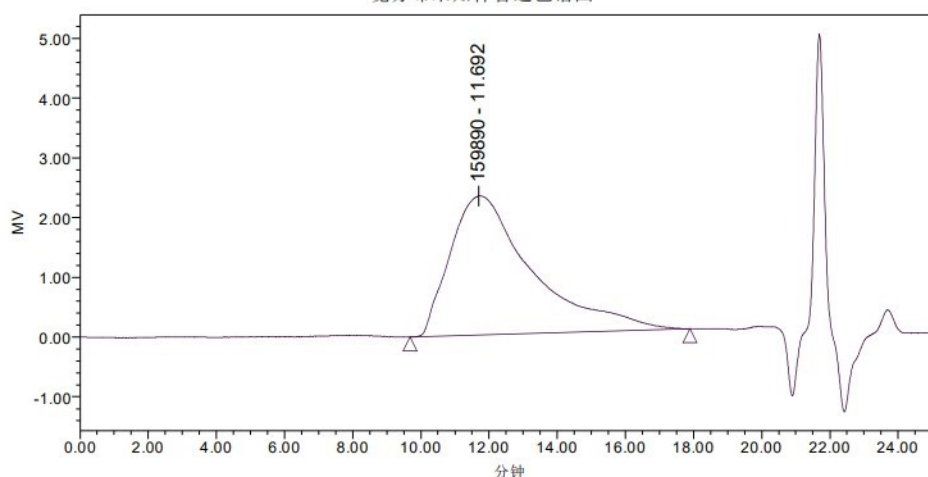
Polymer PTO: PTO was synthesized similar to PTC, C6ETH (0.0451 g, 0.12 mmol) was used instead of C6CTH. The number-average molecular weight (M_n) \square 50.134 KDa, polydispersity index (PDI) \square 2.99. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.04-7.97 (br, ArH), 7.70-7.64 (br, ArH), 7.63-7.58 (br, ArH), 7.23-7.19 (br, ArH), 7.18-7.14 (br, ArH), 5.02-4.81 (br, COO-CH), 2.82-2.79 (br), 1.89-0.92 (br).

项目名称: test
 用户名称: System



样品信息			
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样品类型:	宽分布未知样	样品组名称:	
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进样次数:	1	处理方法:	GPCdata SHY
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宽分布未知样普适色谱图



宽分布未知样普适峰表

分布名	Mv (道尔顿)	k (dl/g)	alpha	固有黏度 (dl/g)	Mn (道尔顿)	Mw (道尔顿)	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性
1					50134	149761	283244	412268	2.987236

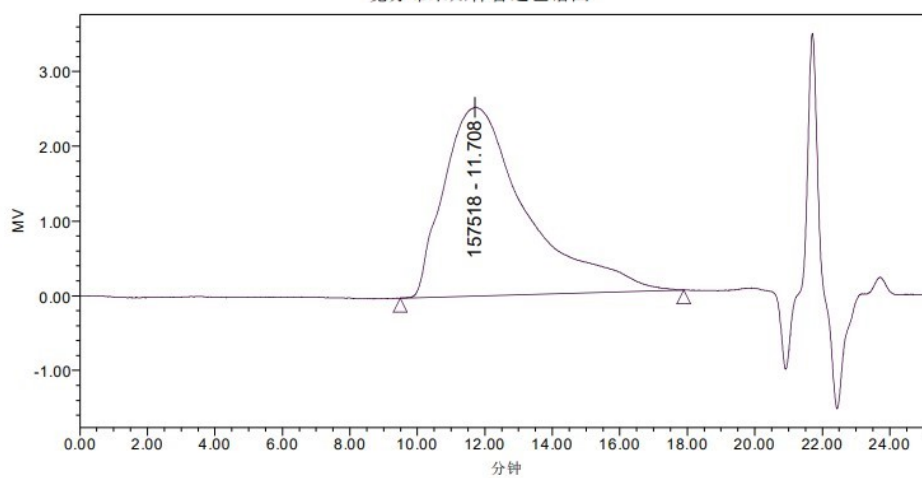
Figure S1. GPC chromatograms of polymer PTO, THF as an eluent at a column temperature at room temperature.

项目名称: test
 用户名称: System



样品信息			
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进样次数:	1	处理方法:	GPCdata SHY
进样体积:	20.00 ul	通道名称:	410
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宽分布未知样普适色谱图



宽分布未知样普适峰表

分布名	Mv (道尔顿)	k (dl/g)	alpha	固有黏度 (dl/g)	Mn (道尔顿)	Mw (道尔顿)	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性
1					51960	162046	316754	471589	3.118653

Figure S2. GPC chromatograms of polymer PTC, THF as an eluent at a column temperature at room temperature.

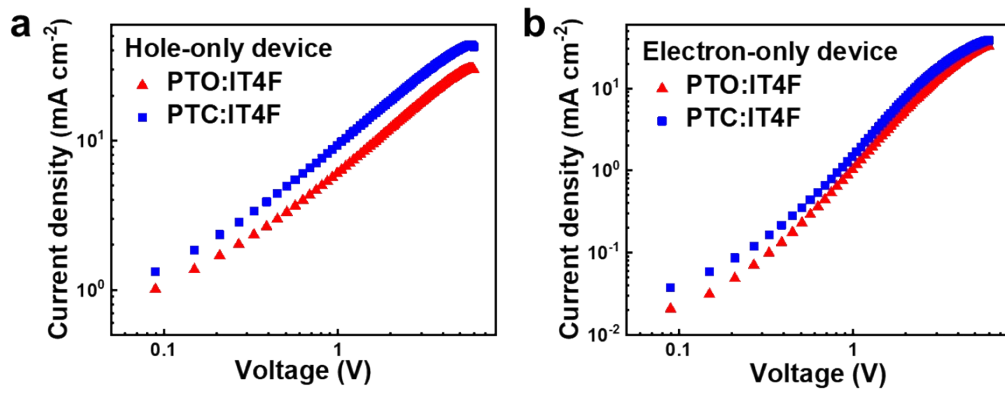


Figure S3. $J^{1/2}$ - V curves for the hole-only (a) and electron-only (b) devices.

Table S1. Hole and electron mobility parameters of PTO and PTC-based devices.

Devices	μ_h (cm ² V ⁻¹ s ⁻¹)	μ_e (cm ² V ⁻¹ s ⁻¹)	μ_h/μ_e
PTO:IT4F	1.78×10^{-4}	1.52×10^{-4}	1.17
PTC:IT4F	3.79×10^{-4}	2.28×10^{-4}	1.66

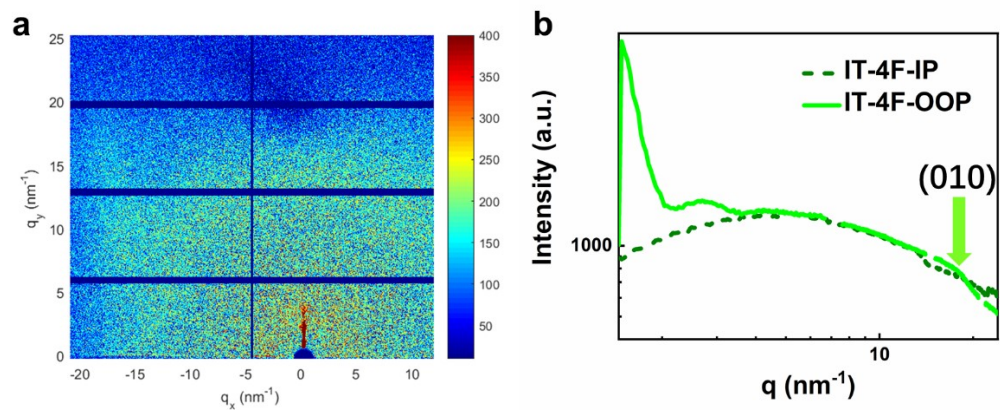


Figure S4. 2D GIWAXS pattern of IT-4F (a). (b) Corresponding IP and OOP wire cutting of pure films.

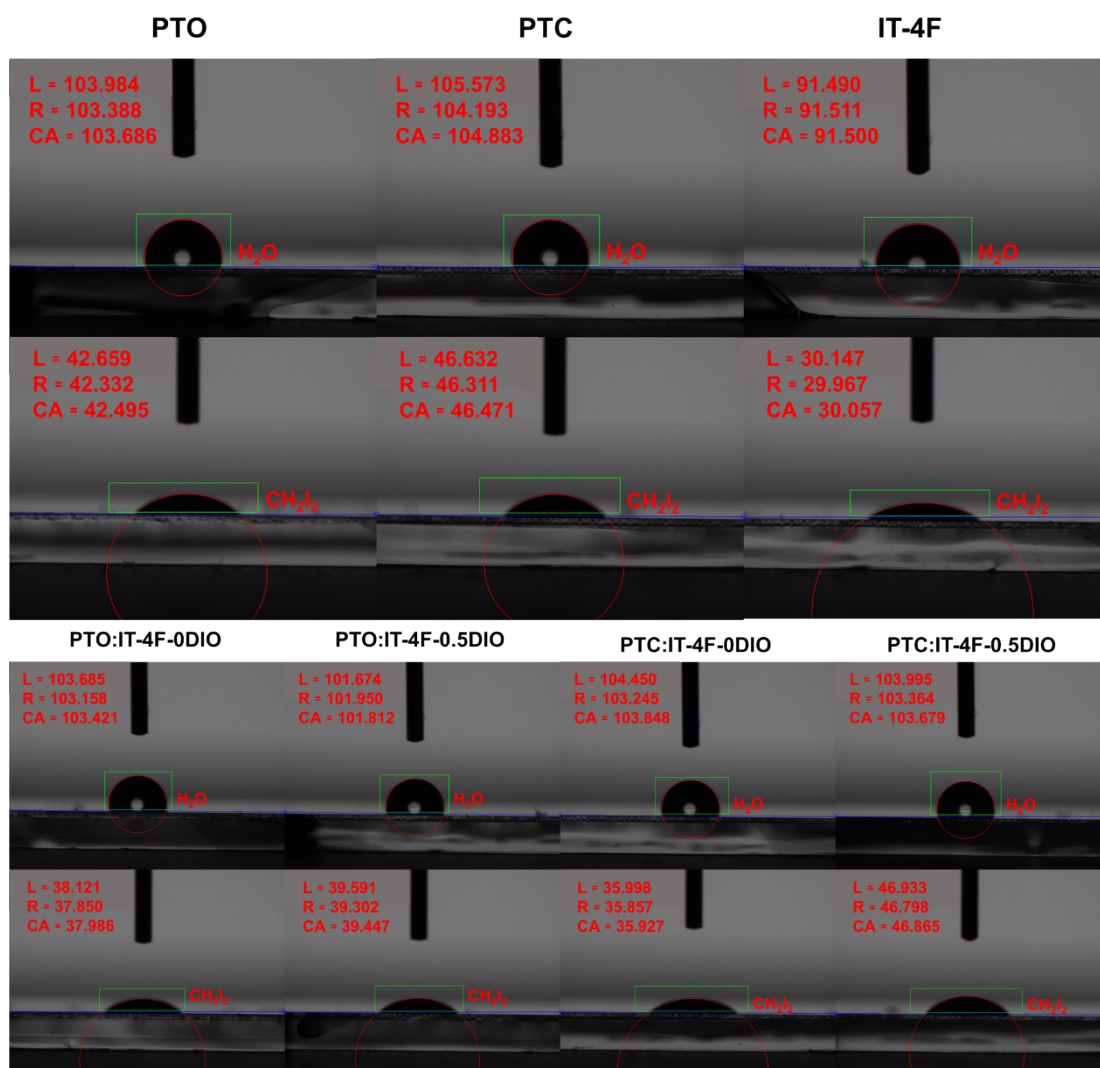


Figure S5. Drop shapes of water and CH_2I_2 on PTO, PTC, IT-4F, PTO:IT-4F-0DIO, PTO:IT-4F-0.5DIO, PTC:IT-4F-0DIO and PTC:IT-4F-0.5DIO thin films.

Table S2. Summary of contact angle data of IT-4F, PTO, PTC and corresponding blend films with different concentrations of DIO.

Materials	CA[H_2O]	CA[CH_2I_2]	γ_d	γ_p	γ	γ_{D-A}	γ_{D-A}
IT-4F	91.5	30.1	45.6	/	45.6	/	/
PTO	103.7	42.4	41.6	1.1	42.7	1.28	0.05 k
PTC	104.9	46.5	39.2	1.0	40.2	1.48	0.18 k
BHJ-PTO ^{a)}	103.4	37.9	44.3	1.4	45.7	/	/
BHJ-PTO ^{b)}	101.8	39.4	43.0	0.9	43.9	/	/
BHJ-PTC ^{c)}	103.8	35.9	45.5	1.7	47.3	/	/
BHJ-PTC ^{d)}	103.6	42.3	41.6	1.1	42.7	/	/

^{a)} PTO:IT-4F blends with 0% DIO. ^{b)} PTO:IT-4F blends with 0.5% DIO. ^{c)} PTC:IT-4F blends with 0% DIO. ^{d)} PTC:IT-4F blends with 0.5% DIO.

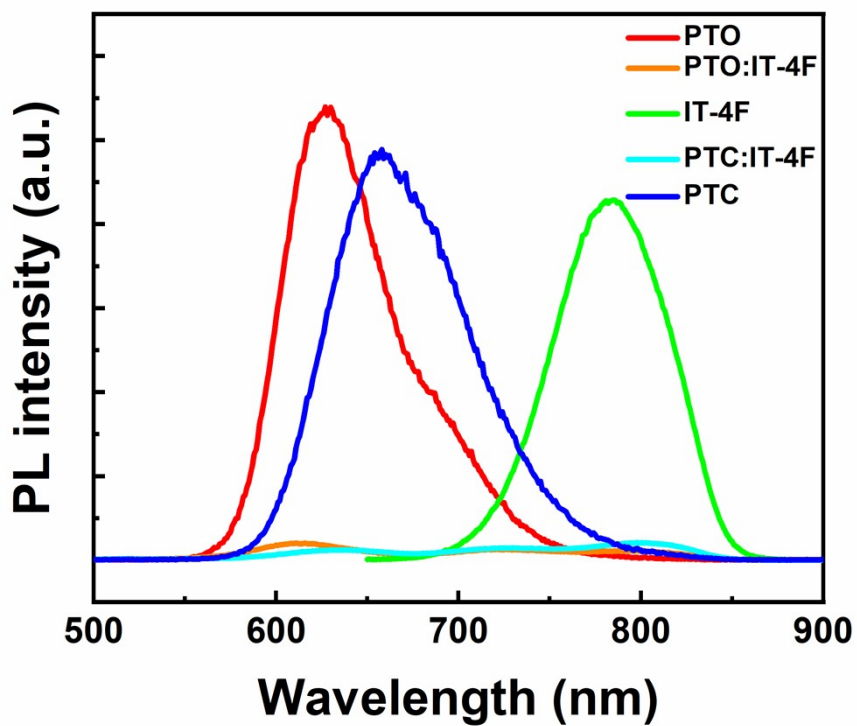


Figure S6. Photoluminescence (PL) spectra of PTO, PTC, IT-4F and corresponding blending films.

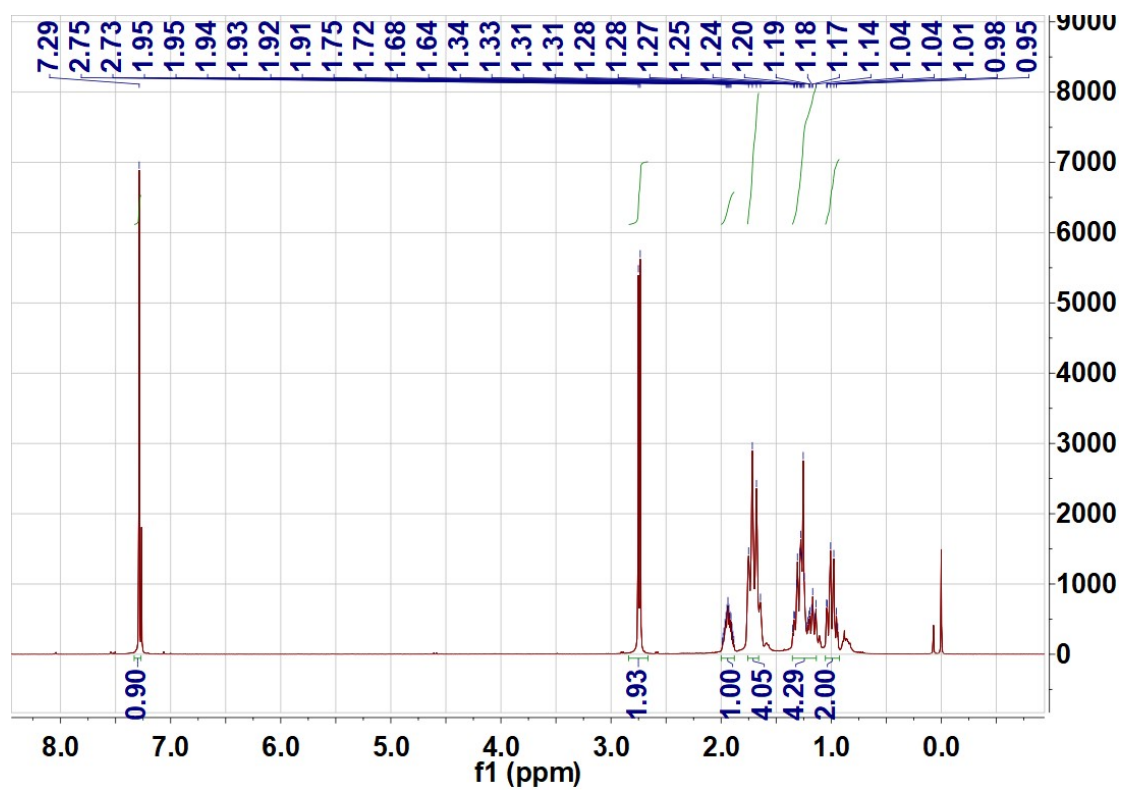


Figure S7. ^1H NMR spectra of monomer C6CTH

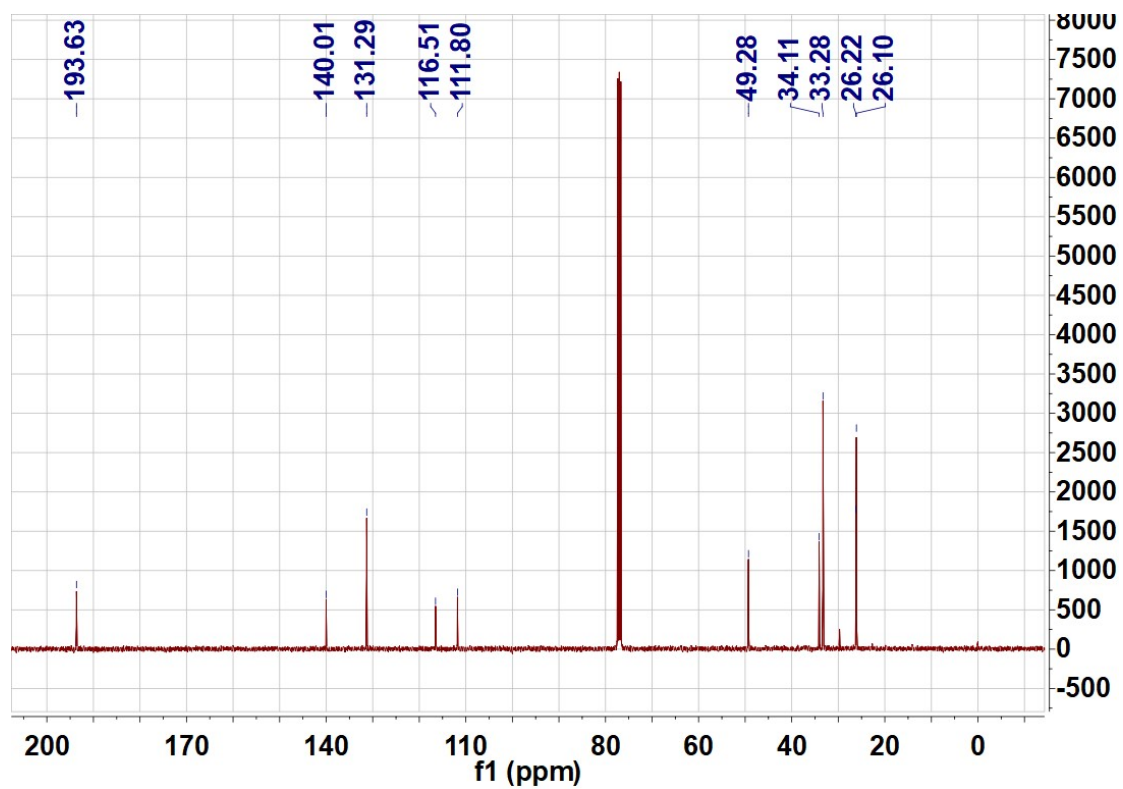


Figure S8. ^{13}C NMR spectra of monomer C6CTH

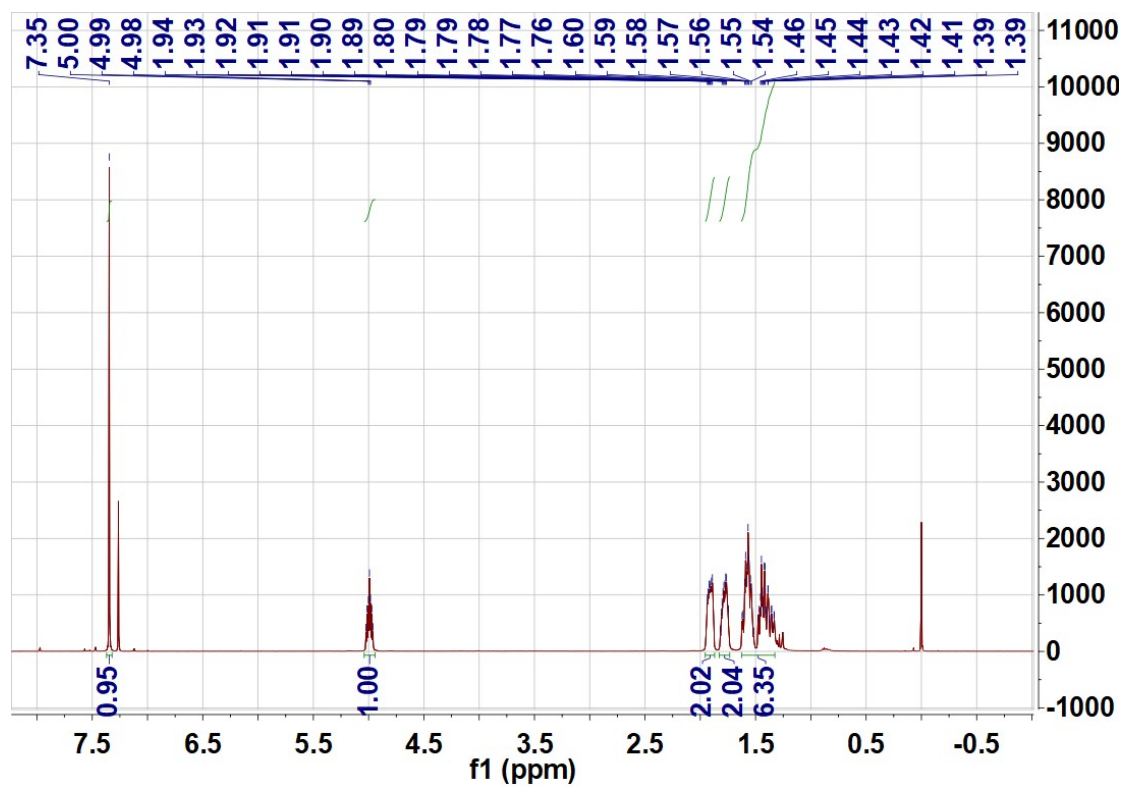


Figure S9. ^1H NMR spectra of monomer C6ETH

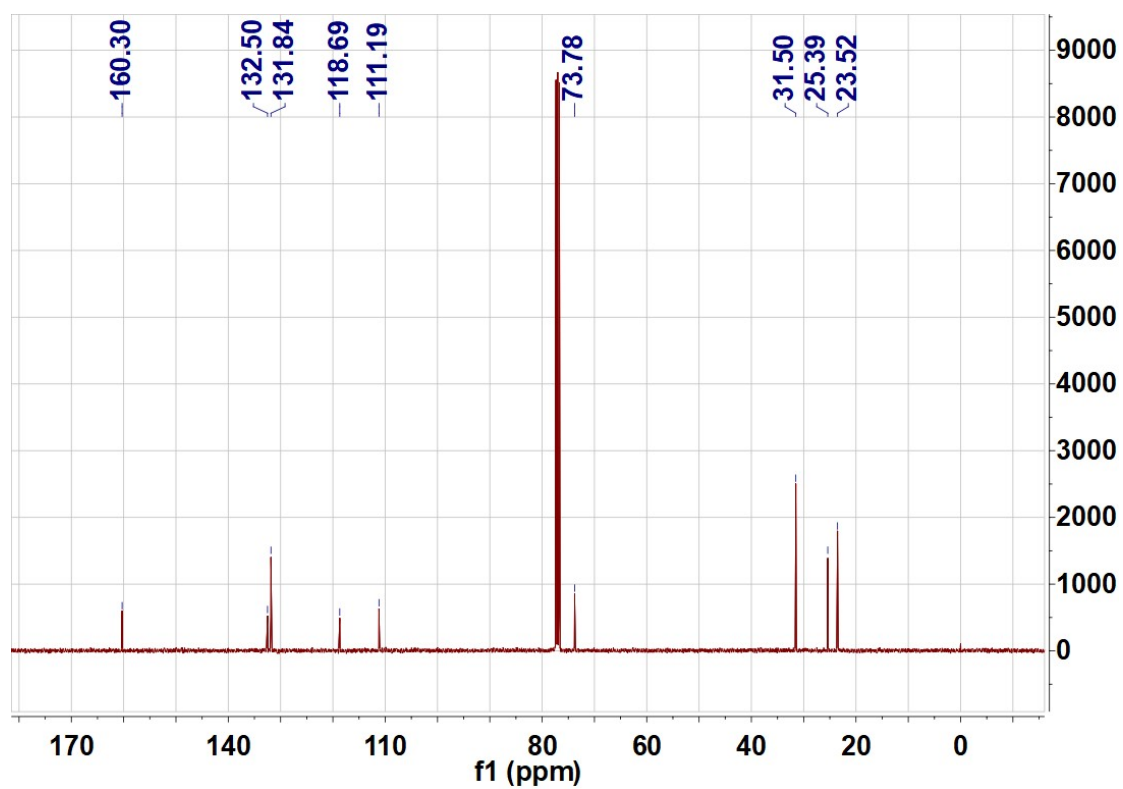


Figure S10. ^{13}C NMR spectra of monomer C6ETH

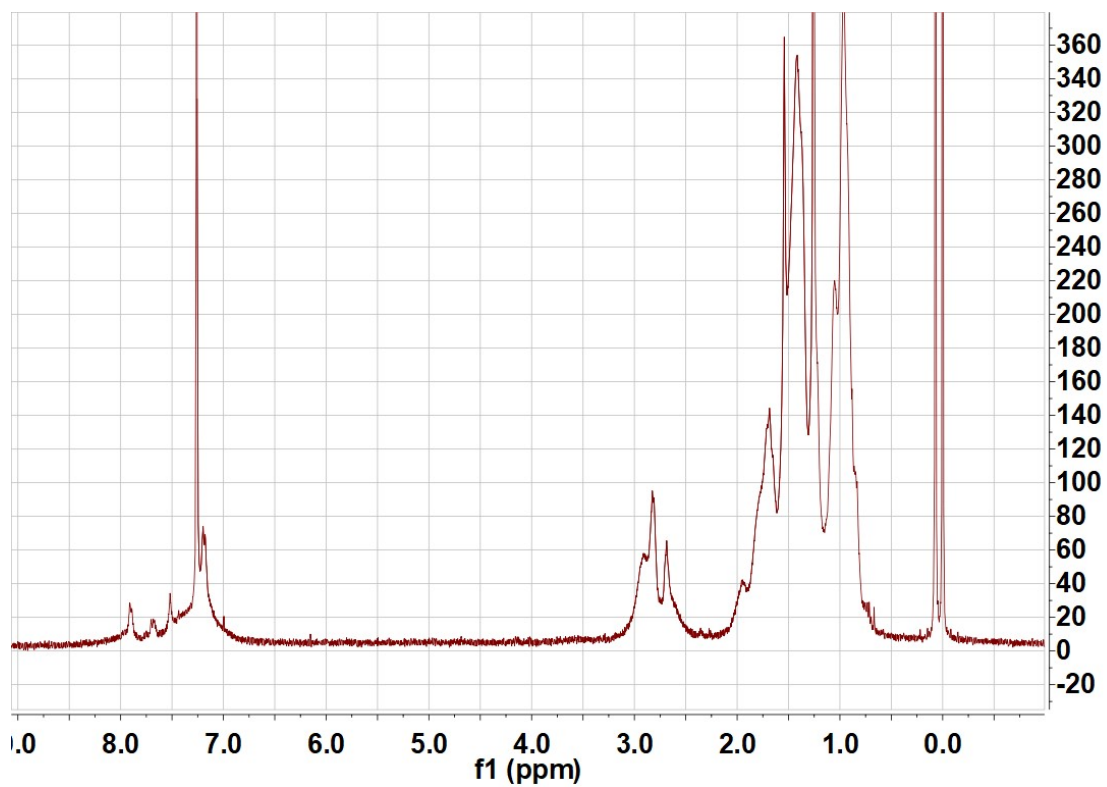


Figure S11. ^1H NMR spectra of polymer PTC

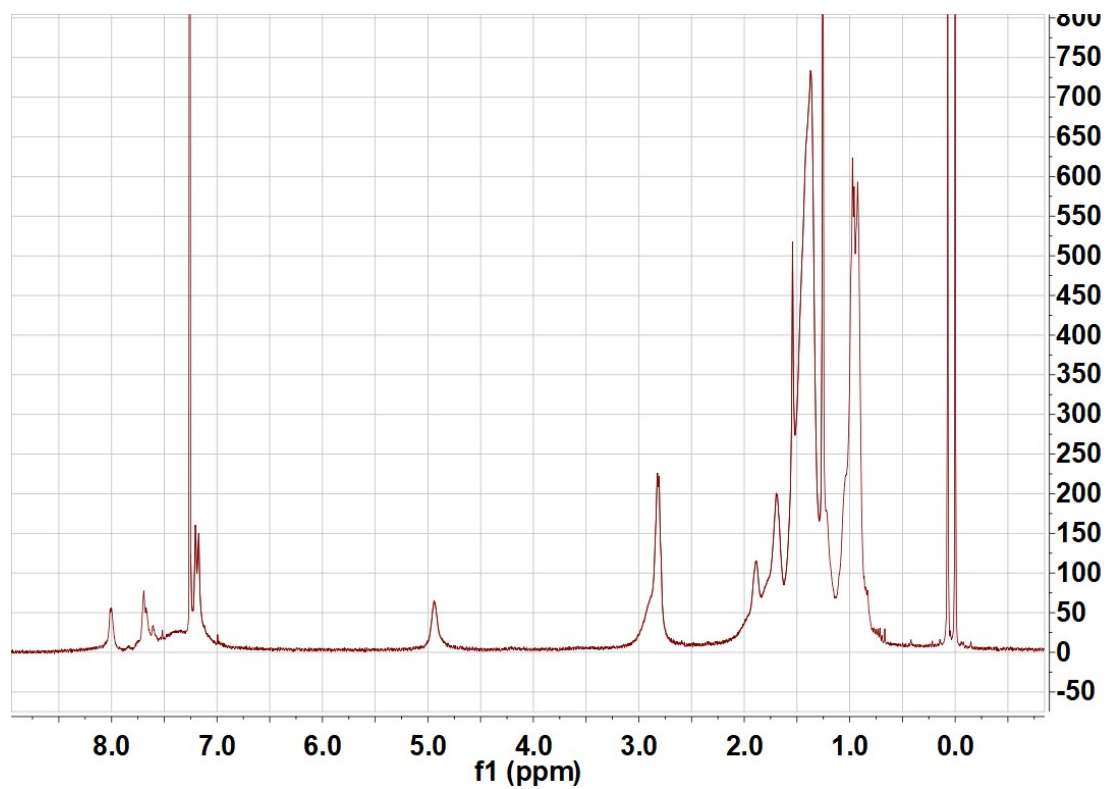


Figure S12. ^1H NMR spectra of polymer PTO

References

1. Y. Chen, L. Yang, J. Wu, G. Wang, W. Huang, F. S. Melkonyan, Z. Lu, Y. Huang, T. J. Marks and A. Facchetti, *Chem. Mater.*, 2018, **30**, 6810-6820.
2. P. Zhang, J. Wang, Z. R. Robertson and T. R. Newhouse, *Angew. Chem. Int. Ed.*, 2022, **61**, e202200602.