Effects of polymer precursor conjugation length on the optoelectronic properties of fluorinated benzothiadiazole-based D-A systems

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1. Material

3-Octylthiophene, tri-*n*-butyltinchloride ((*n*-Bu)$_3$SnCl), *n*-butyllithium (*n*-BuLi), 4-fluoro-1,2-diaminobenzene, thionyl chloride ($SOCl_2$), *N*, *N*-dimethylformamide (DMF), tributyl(thiophen-2-yl) stannane, 3,4-ethylenedioxythiophene (EDOT), hydrobromic acid (HBr), bromine (Br_2), sodium carbonate (Na_2CO_3), tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), and *N*-bromosccinimide (NBS) were purchased from commercial sources and used directly without further purification. Before the reaction, tetrahydrofuran (THF) and toluene were distilled from the sodium/benzophenone under the protection of nitrogen atmosphere.

2. Synthesis of Monomers

Unless otherwise noted, all reagents were obtained from commercial sources and used without further purification. **Scheme 1** shows the synthetic routes of F-BT, F-BT-Th, and F-BT-EDOT. The detailed synthesis procedures are described as following:

Synthesis of F-BT-2Br

To a solution of compound F-BT (0.4 g, 0.93 mmol) in THF (150 mL) was added *N*-bromosuccinimide (NBS, 0.36 g, 2.04 mmol) in a one-neck round flask. The mixture was then stirred overnight at room temperature. After the solvent was distilled, the residue was purified by silica gel column chromatography, using petroleum ether- dichloromethane (v/v, 4/1) as an eluent, to yield F-BT-2Br as a red solid (0.52 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.80 (d, J = 4.0 Hz, 1H), 7.17 (d, J = 4.0 Hz, 1H), 2.66 (t, J = 7.7 Hz, 2H), 1.66 (d, J = 7.7 Hz, 2H), 1.33-

1.26 (m, 10H), 0.88 (d, J = 6.2 Hz, 3H).

Synthesis of F-BT-Th

F-BT-2Br (0.11g, 0.19mmol), tributyl(thiophen-2-yl) stannane (0.174g, 0.47mmol), and $Pd(PPh_3)_4$ (0.009g, 0.007mmol) were added to a 250.0 mL round-bottom flask. The flask was blanked by argon three times and 100 mL of a toluene/DMF (4:1) solution was syringed at once; the reaction was stirred at 120 °C for 24 hours and then allowed to cool to room temperature. The mixture was poured into saturated aqueous brine and then extracted with dichloromethane. The organic layer was washed twice with water, dried over anhydrous Na_2SO_4 and purified by silica column chromatography to yield deed red solid product (55.6 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 3.9 Hz, 1H), 7.75 (d, J = 13.1 Hz, 1H), 7.36 (dd, J = 5.1, 1.2 Hz, 1H), 7.32 (dd, J = 3.6, 1.2 Hz, 1H), 7.29 (d, J = 4.4 Hz, 2H), 7.11 (d, J = 1.5 Hz, 1H), 7.07 (d, J = 1.6 Hz, 1H), 2.87 (d, J = 7.9 Hz, 2H), 1.73 (d, J = 5.9 Hz, 2H), 1.29 (d, J = 7.4 Hz, 10H), 0.87 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.94, 158.26, 153.55, 153.48, 149.84, 140.10, 139.93, 137.12, 136.00, 129.89, 129.27, 128.22, 127.67, 126.33, 125.86, 125.35, 124.75, 124.51, 116.59, 116.38, 111.19, 111.09, 32.04, 30.85, 29.85, 29.75, 29.59, 29.44, 22.83, 14.27.

Synthesis of F-BT-EDOT

F-BT-2Br (0.52 g, 0.88 mmol), tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (0.989 g, 2.29 mmol), and $Pd(PPh_3)_4$ (0.0408 g, 0.035 mmol) were added to a 250.0 mL round-bottom flask. The flask was blanked by argon three times and

100 mL of a toluene/DMF (4:1) solution was syringed at once; the reaction was stirred at 120 °C for 24 hours and then allowed to cool to room temperature. The mixture was poured into saturated aqueous brine and then extracted with dichloromethane. The organic layer was washed twice with water, dried over anhydrous Na_2SO_4 and purified by silica column chromatography to yield deed red solid product (0.34 g, 54.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15-8.07 (m, 2H), 7.74 (d, *J* = 13.1 Hz, 1H), 7.31 (d, *J* = 4.0 Hz, 1H), 6.41 (s, 1H), 6.30 (s, 1H), 4.43-4.26 (m, 8H), 2.87-2.76 (m, 2H), 1.71-1.64 (m, 2H), 1.32-1.26 (m, 10H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.94, 158.27, 153.66, 153.58, 149.92, 142.12, 141.71, 141.10, 138.60, 138.51, 137.63, 132.70, 132.65, 128.92, 123.82, 116.30, 116.08, 112.25, 110.44, 99.47, 98.14, 97.68, 65.32, 65.07, 64.75, 64.68, 32.06, 30.79, 29.81, 29.71, 29.61, 29.46, 22.84, 14.28.

3. Instruments and characterization

^{1}H NMR spectra were tested on a Bruker AV-500 with tetramethylsilane (TMS) as an internal reference. UV-vis spectra of the monomers dissolved in dichloromethane solution were taken by using on the Shimadzu UV-1900i spectrometer. With an F-4500 fluorescence spectrophotometer (Hitachi), the fluorescence spectra of the monomers were determined.

All the electrochemical experiments and polymerization of monomers were performed in a one-compartment cell with the use of CHI 660E potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd. China) under computer control. For electrochemical tests, the working and counter electrodes were

glass carbon (GC) electrode and platinum wire (1 mm diameter), respectively, while the reference electrode (RE) was Ag/AgCl. The Ag/AgCl RE was prepared by chronoamperometry method at potential of 1.5 V for 100 s in hydrochloric acid (6 mol L^{-1}) and calibrated with the SCE system. Bu_4NPF_6 as electrolyte was dissolved in anhydrous CH_2Cl_2 (0.1 mol L^{-1}). The system was calibrated with ferrocene, its oxidation peak and reduction peak are located at 0.53 V and 0.28 V, respectively. The oxidation potential of ferrocene was 0.31 V (**Fig.S8**), while the vacuum energy level of ferrocene/ferrocene$^+$ (Fc/Fc^+) was 4.8 V. Therefore, the HOMO and LUMO levels of polymers after calibration could be obtained, which were calculated by the following equations: E_{HOMO}=-e($E_{ox,\ onset}$(*vs* ferrocene)+4.8)eV, E_{LUMO}=*e*($E_{re,\ onset}$(*vs* ferrocene)+4.8)eV, where $E_{ox,\ onset}$ is the onset oxidation potential and $E_{re,\ onset}$ is the onset reduction potential. Polymer films were obtained by potentiodynamic regime. After polymerization, the films were washed repeatedly with anhydrous DCM to remove the electrolyte and monomer. The solutions used in electrochemical experiments were purified with argon to remove oxygen.

Spectroelectrochemistry and electrochromic studies of fluorinated polymers were systematically investigated on the Shimadzu UV-1900i spectrophotometer and the potentials were controlled using CHI 660E potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd. China). The spectroelectrochemical cell consisted of a quartz cell, an Ag/AgCl electrode as reference electrode, a Pt wire as counter electrode, and an indium tin oxide (ITO) coated glass as the transparent working electrode. All measurements were carried out in ACN containing Bu_4NPF_6 (0.1 mol L^{-}

[1]).

The potentials were alternated between the reduced and oxidized states with a residence time of 5 s. The optical contrast at the specific wavelength (λ) was determined by ΔT% values of polymer films, using the following equation:

$$\Delta T = \left| T_{ox} - T_{red} \right|$$

The coloration efficiency (*CE*) is defined as the relation between the injected/ejected charge as a function of electrode area (Q_d) and the change in optical density (ΔOD) at the specific wavelength (λ) of the sample as illustrated by the following equation:

$$\Delta OD = \log(T_{ox} / T_{red})$$

$$CE = \Delta OD / Q_d$$

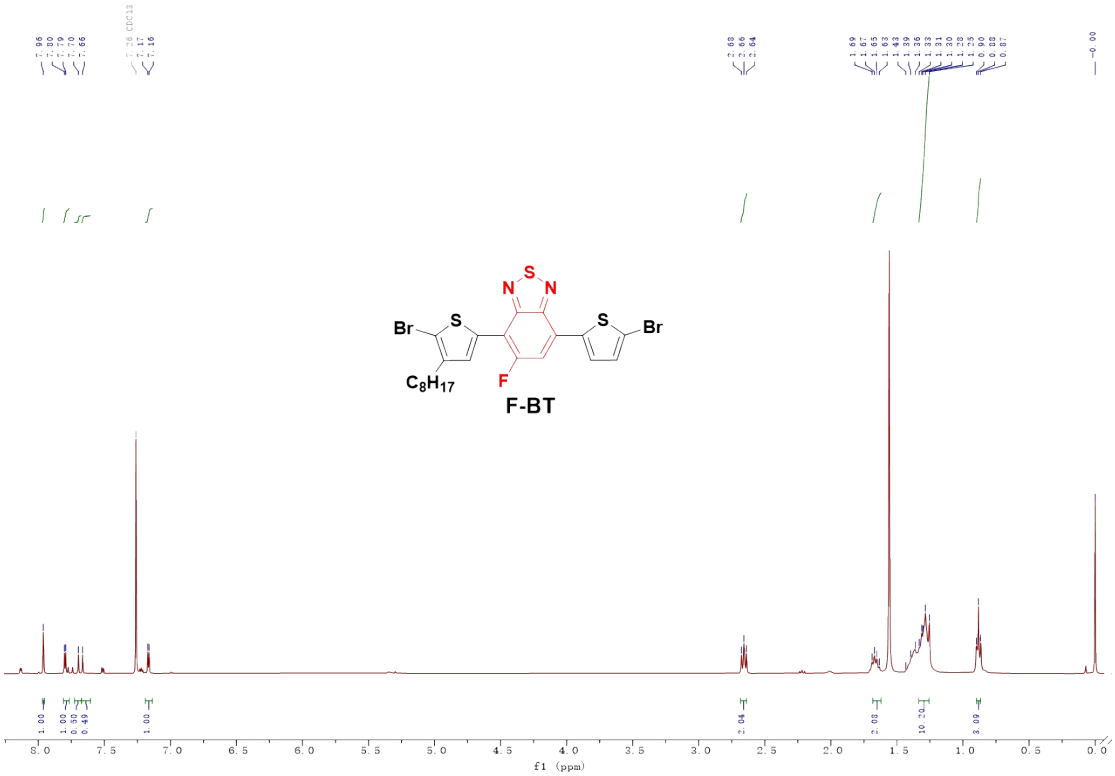

Fig.S1.[1]H NMR spectrum of F-BT-2Br in $CDCl_3$.

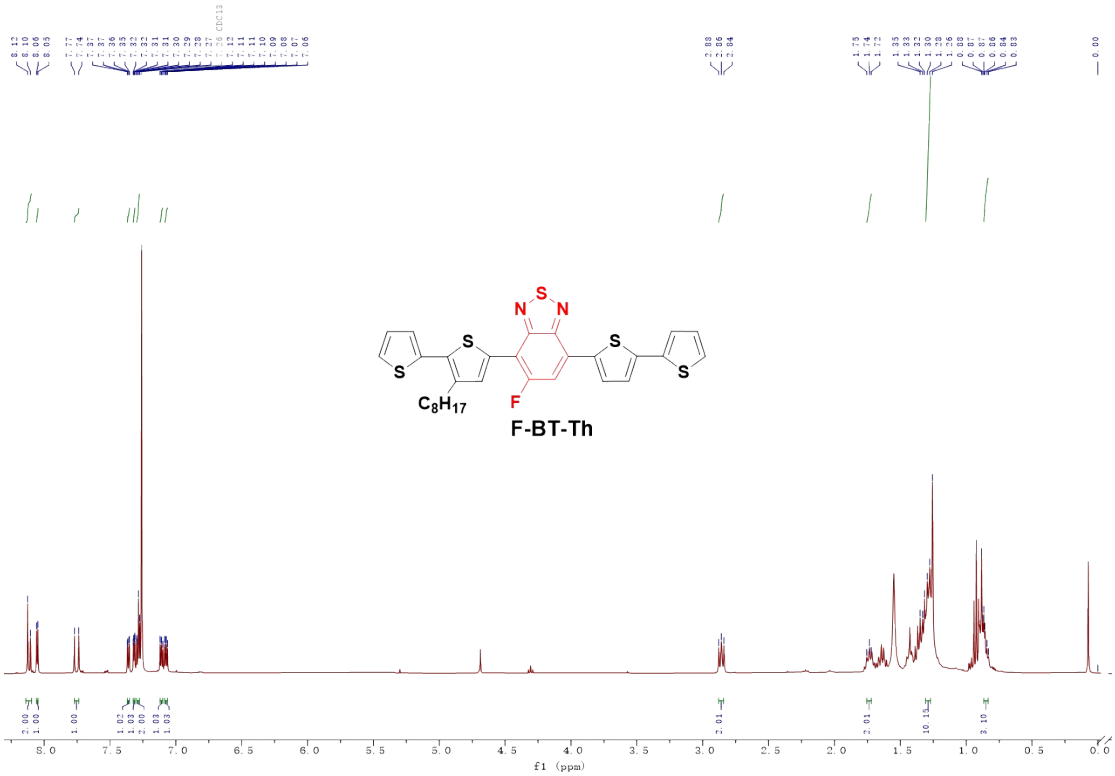

Fig.S2. [1]H NMR spectrum of F-BT-Th in $CDCl_3$.

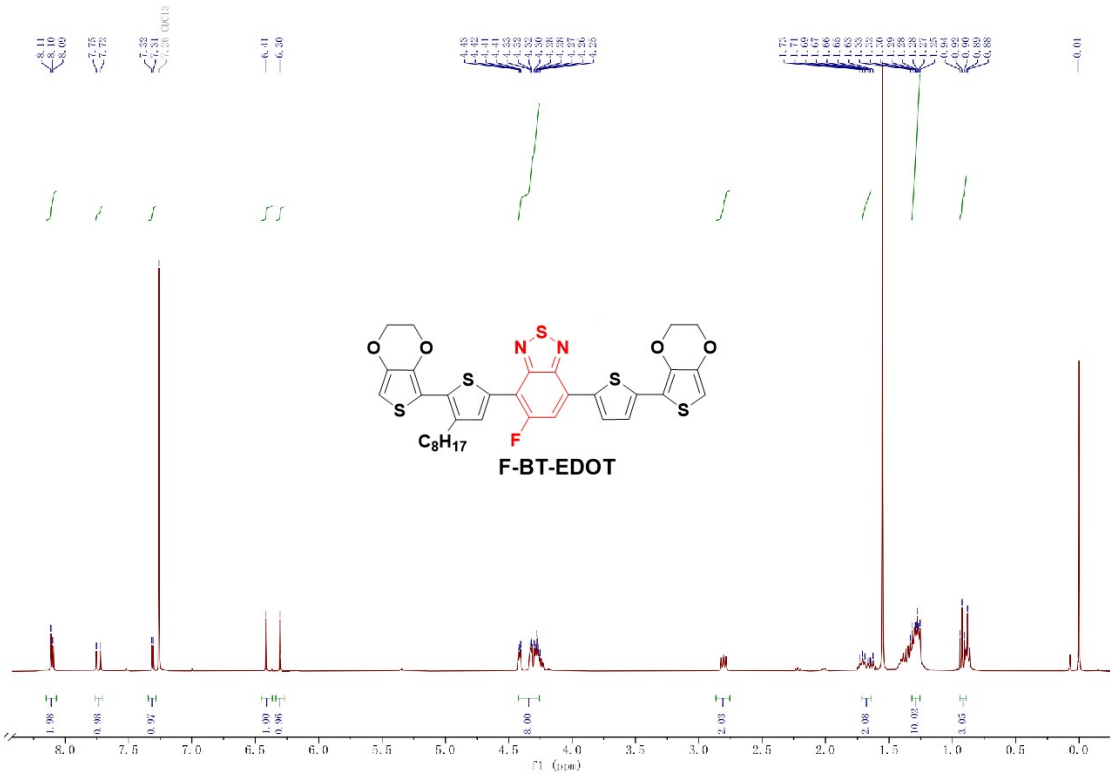

Fig.S3. ^{1}H NMR spectrum of F-BT-EDOT in $CDCl_3$.

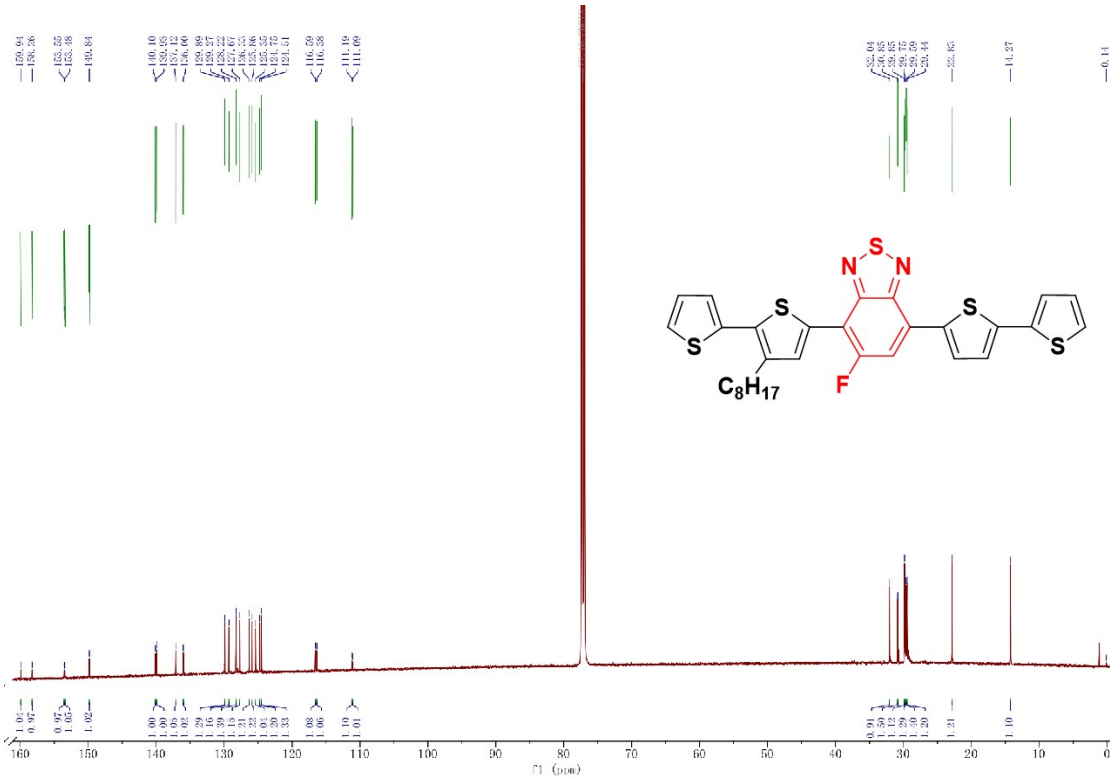

Fig.S4. ^{13}C NMR spectrum of F-BT-Th in $CDCl_3$.

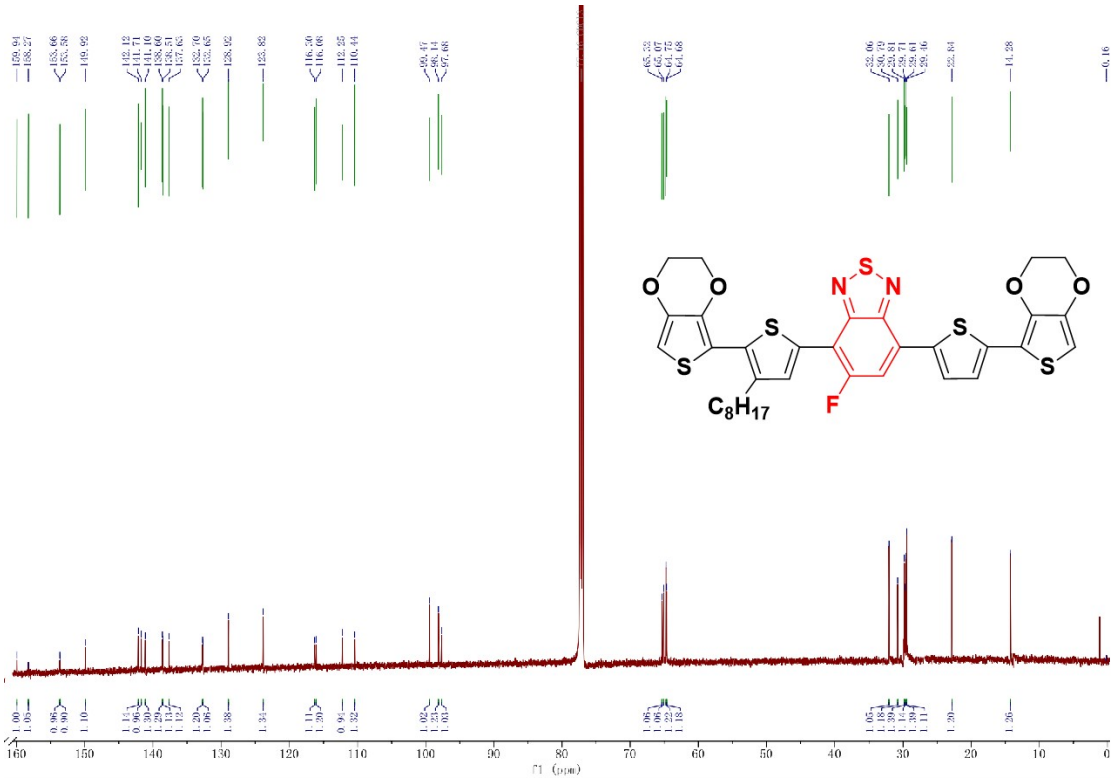

Fig.S5. ^{13}C NMR spectrum of F-BT-EDOT in $CDCl_3$.

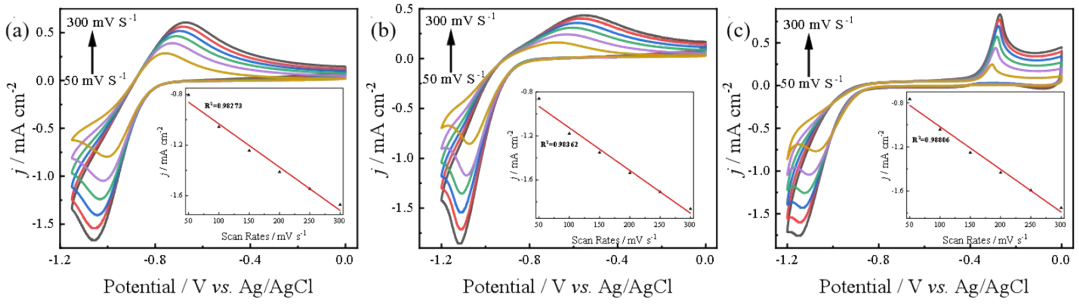

Fig.S6. CV curves of the P(F-BT) (a), P(F-BT-Th) (b) and P(F-EDOT) (c) at different scan rates between 50 and 300 mV s^{-1} in 0.1 M Bu_4NPF_6/ACN solution, respectively. Inset:the linear relationship between peak current density and scanning rate.

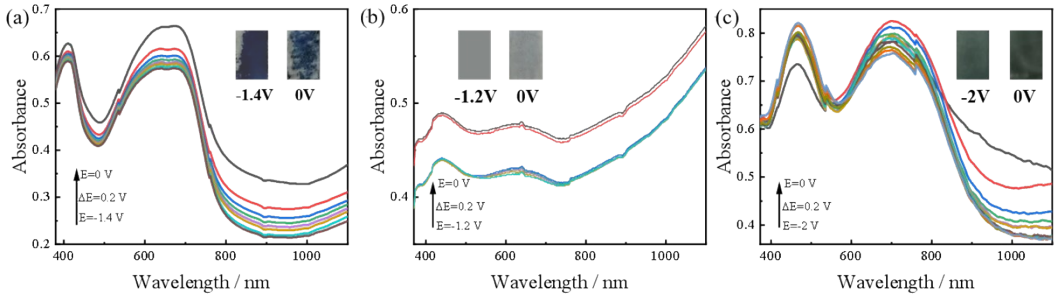

Fig.S7. *n*-Doping behavior of P(F-BT) (a), P(F-BT-Th) (b), and P(F-BT-EDOT) (c) in

spectroelectrochemistry.

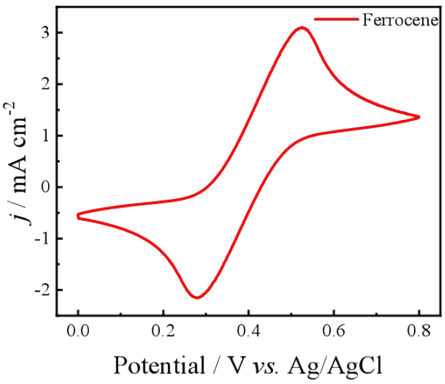

Fig.S8. CV curves of 0.01 mol L^{-1} ferrocene in DCM-Bu_4NPF_6 (0.1 mol L^{-1}) solution at scan rates of 100 m V s^{-1}.

Table S1 L*a*b* parameters and colors of P(F-BT-EDOT) at different voltages.

Compound	Voltages	L*	a*	b*	color
P(F-BT-EDOT)	-0.2V	46.55	-3.16	4.99	
	0V	47.35	-3.28	3.65	
	0.2V	48.50	-2.93	1.80	
	0.4V	49.57	-2.13	-0.16	
	0.6V	50.56	-1.34	-1.80	
	0.8V	51.25	-1.36	-1.68	
	1V	51.98	-1.39	-0.96	
	1.2V	52.34	-1.94	-0.01	

Table S2 Electrochemical and optical performance of polymers.

Polymer	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{cv} (eV)	ΔT/%	Response time / s		CE/C^{-1} cm^2	Ref
					Reduction	Oxidation		
PEDOT	--	--	--	54%	--	--	137	[1-2]
Poly(BT-Th-EDOT)	--	--	--	46 (467 nm)	0.5	0.5	232	[3]
				31 (720nm)	0.5	0.4	271	
				14.6 (615 nm)	1.1	1.52	68.5	
				28.5 (1100 nm)	1.2	1.42	131.3	
P(EDOT-Th-NO_2-BT)	-4.49	-2.60	1.89	8 (399 nm)	0.2	0.6	59.1	[4]
				7.2 (692 nm)	0.2	0.6	54.4	
				21 (1100 nm)	0.2	0.6	126.8	
P(EDOT-Th-$2NO_2$-BT)	-4.89	-3.03	1.86	13 (460 nm)	0.6	0.74	84.4	[4]
				7 (710 nm)	0.5	0.74	54.7	
				23.3 (1100 nm)	0.4	1	129	
P(F-BT)	-5.65	-3.96	1.69	10.7 (1100 nm)	0.1	0.32	150.7	this work
				6 (624 nm)	0.09	0.12	97	
				3.5 (395 nm)	0.1	0.32	66.6	
P(F-BT-Th)	-5.45	-3.86	1.56	5.5 (1100 nm)	0.2	0.2	367.8	this work
				7.2 (817 nm)	0.2	0.2	218	
				1.3 (588 nm)	0.1	0.1	154	
P(F-BT-EDOT)	-5.13	-3.79	1.34	3 (428 nm)	0.1	0.2	504	this work
				33 (1100 nm)	0.9	1.32	196.3	
				16 (723 nm)	0.7	1.14	109.5	
				19 (471 nm)	1.1	1.6	124.7	

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