Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic supplementary information

Chalcogenodiazolo[3,4-*c*]pyridine based Donor-Acceptor-Donor Polymers for Green and Near-Infrared Electrochromics

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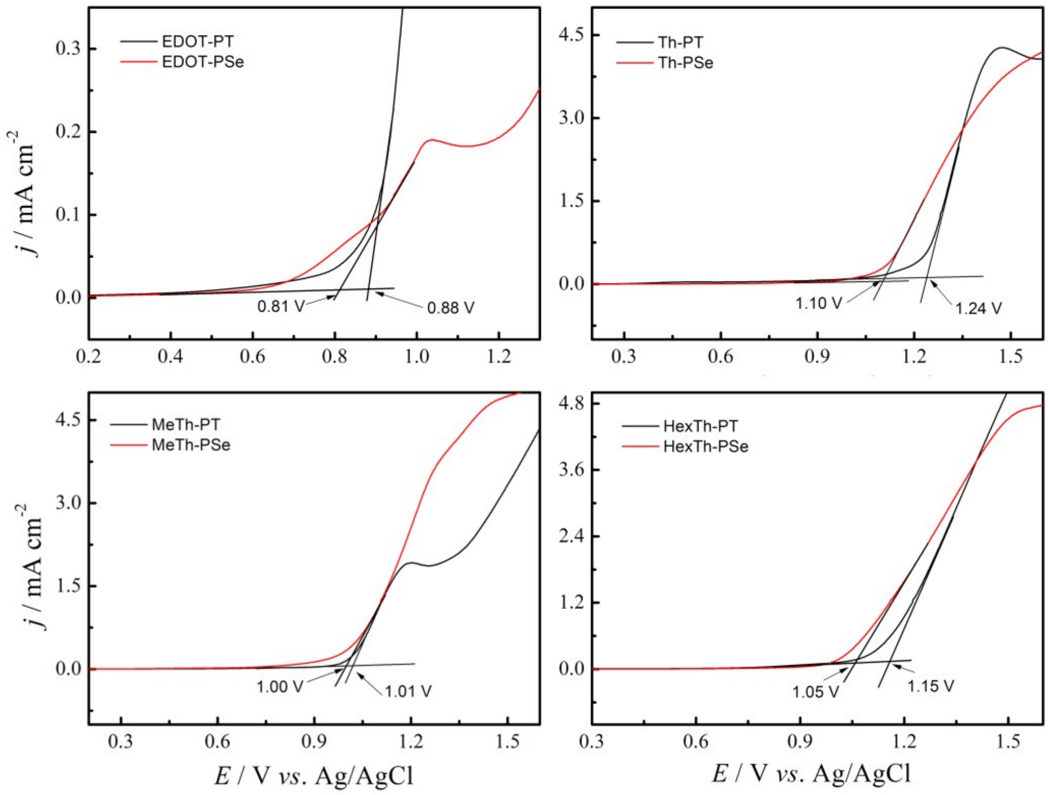

Fig. S1 Anodic polarization curves of 5 mmol L^{-1} these monomers in CH_2Cl_2-Bu_4NPF_6 (0.1 mol L^{-1}) as indicated. Potential scan rate: 50 mV s^{-1}.

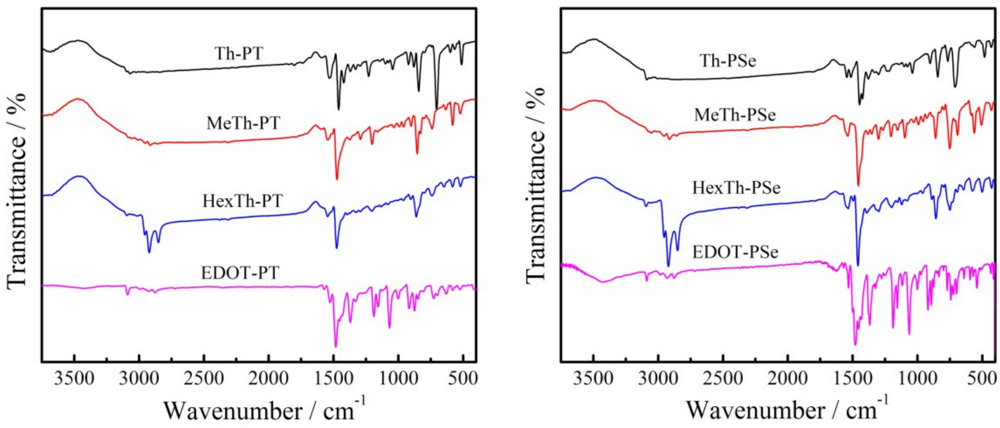

Fig. S2 FT-IR spectra of these D-A-D monomers as indicated.

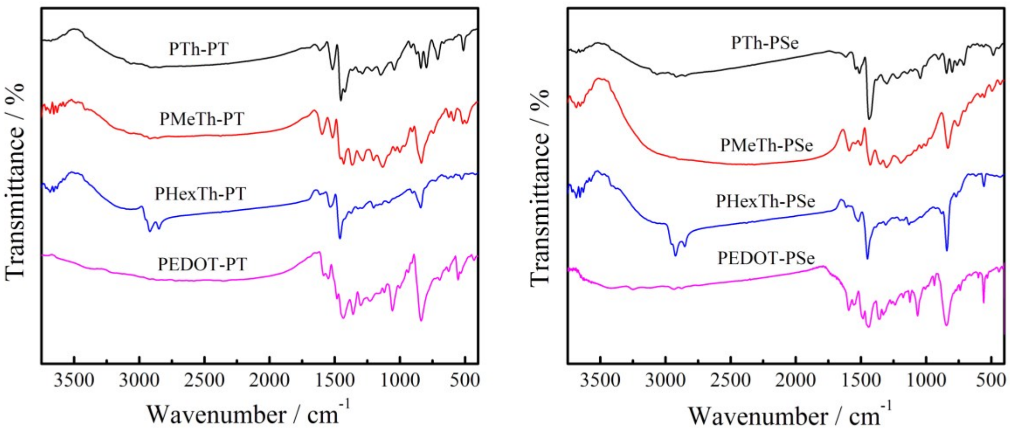

Fig. S3 FT-IR spectra of these D-A-D polymers as indicated.

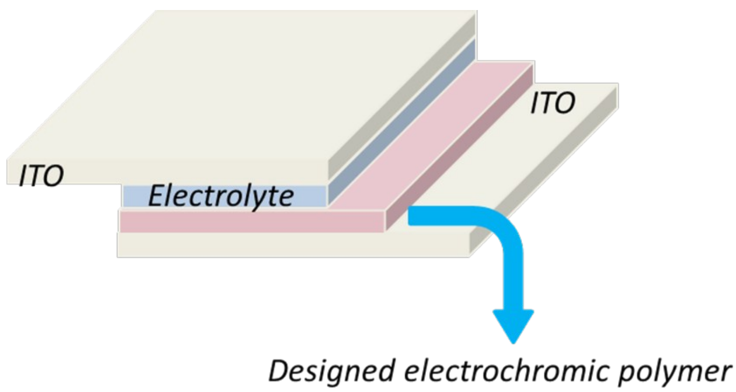

Fig. S4 The schematic representation of a polymer electrochromic device.

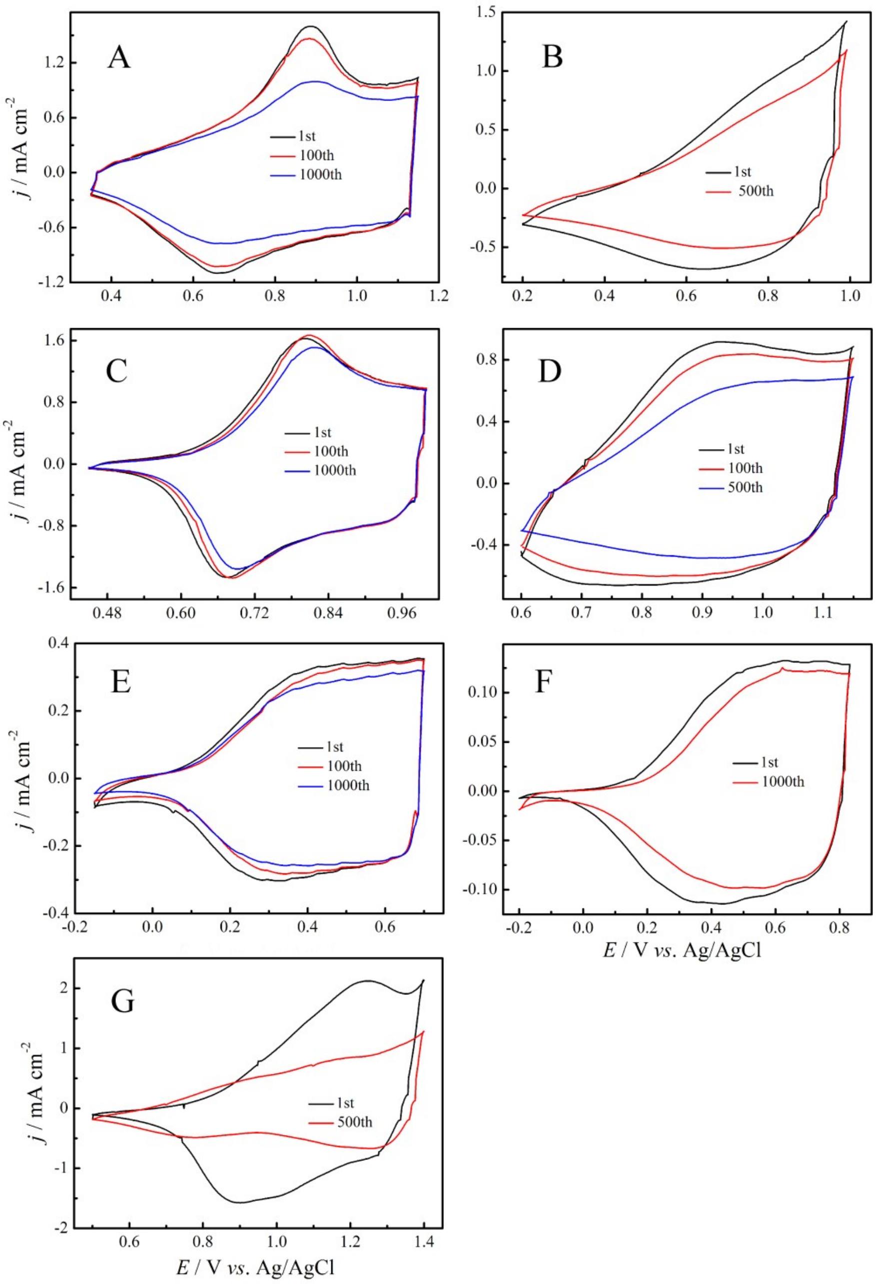

Fig. S5 Long-term CVs of the ECDs in monomer-free CH_2Cl_2-Bu_4NPF_6 (0.10 mol L^{-1}). Potential scan rate: 150 mV s^{-1}. PMeTh-PT (A), PMeTh-PSe (B), PHexTh-PT (C), PHexTh-PSe (D), PEDOT-PT (E), PEDOT-PSe (F), and PTh-PT (G).

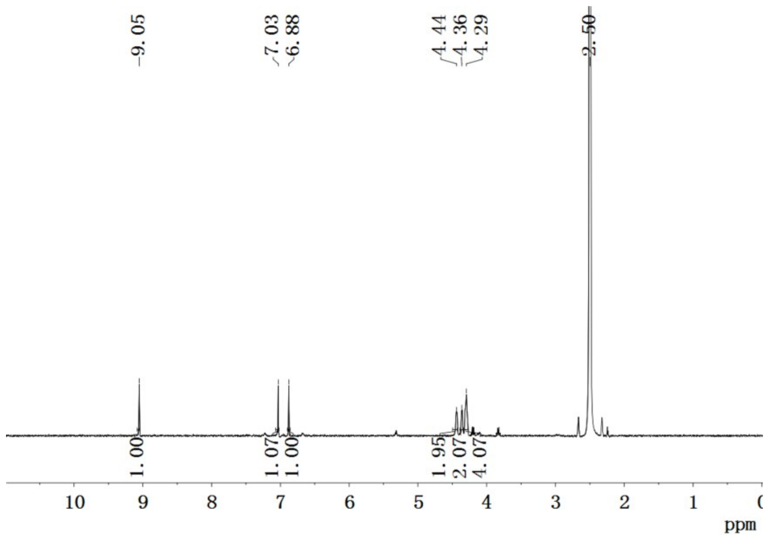

Fig. S6 ^{1}H NMR spectrum of EDOT-PSe in DMSO-d_6.

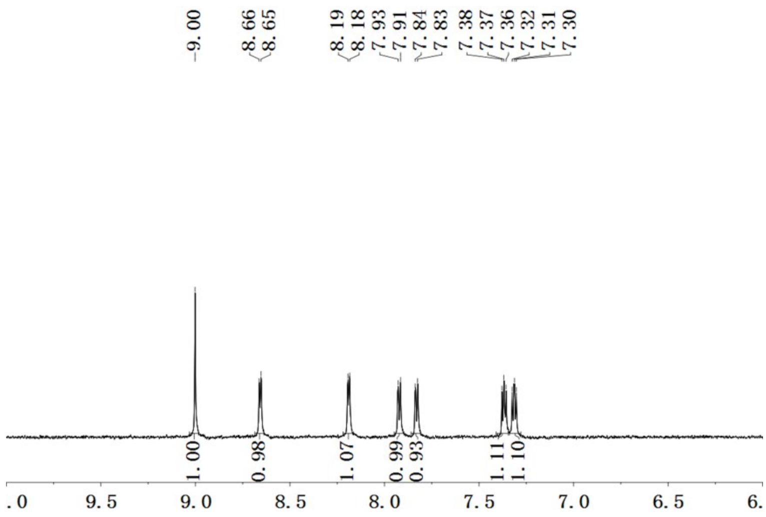

Fig. S7 ^{1}H NMR spectrum of Th-PT in DMSO-d_6.

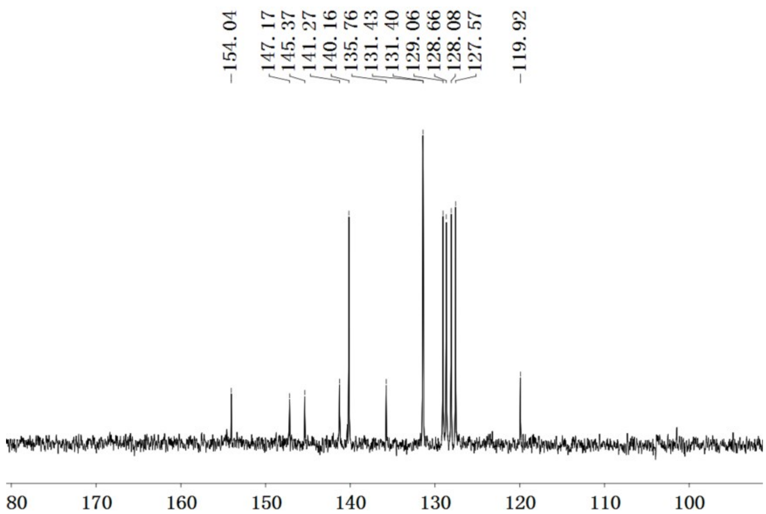

Fig. S8 ^{13}C NMR spectrum of Th-PT in DMSO-d_6.

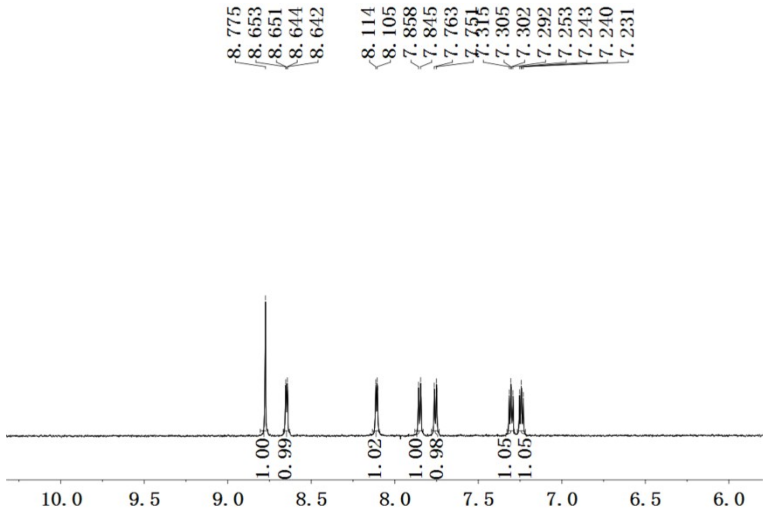

Fig. S9 ^{1}H NMR spectrum of Th-PSe in DMSO-d_6.

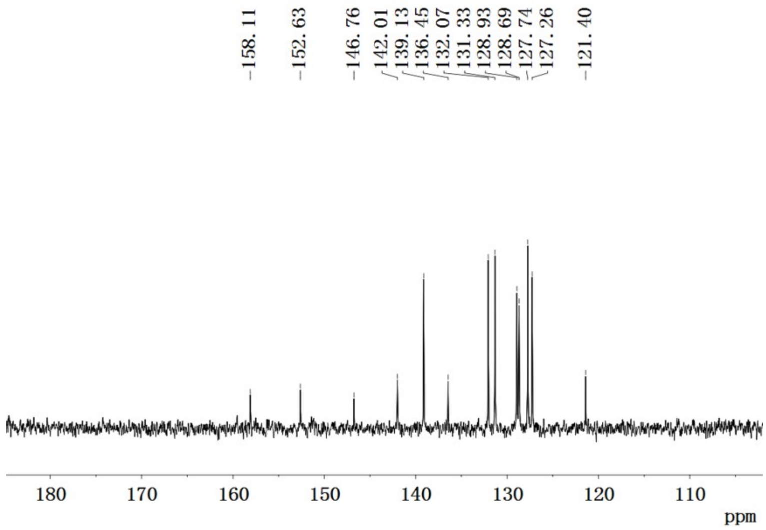

Fig. S10 ^{13}C NMR spectrum of Th-PSe in DMSO-d_6.

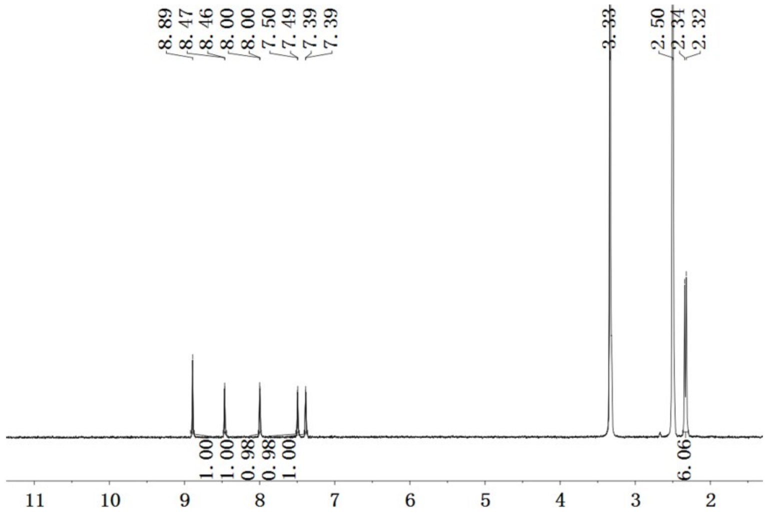

Fig. S11 ^{1}H NMR spectrum of MeTh-PT in DMSO-d_6.

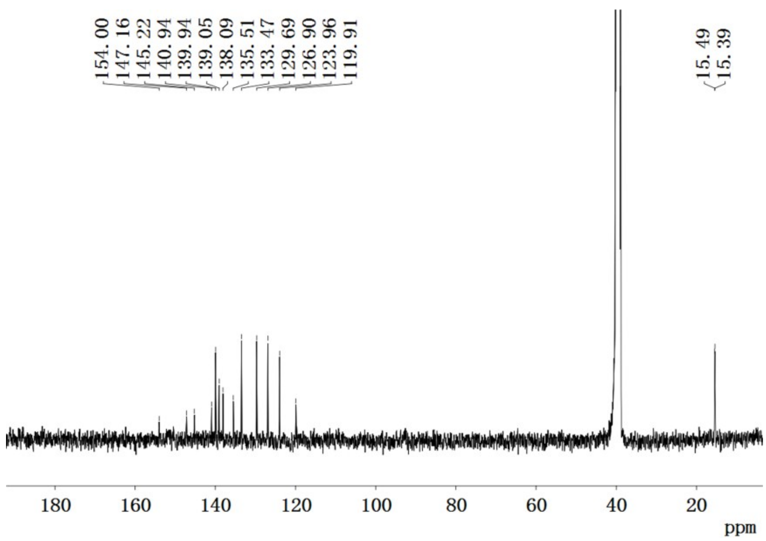

Fig. S12 ^{13}C NMR spectrum of MeTh-PT in DMSO-d_6.

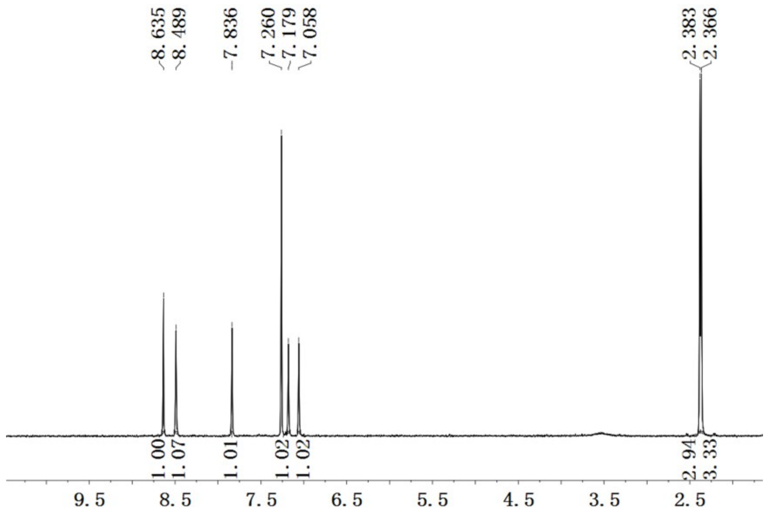

Fig. S13 ^{1}H NMR spectrum of MeTh-PSe in $CDCl_3$.

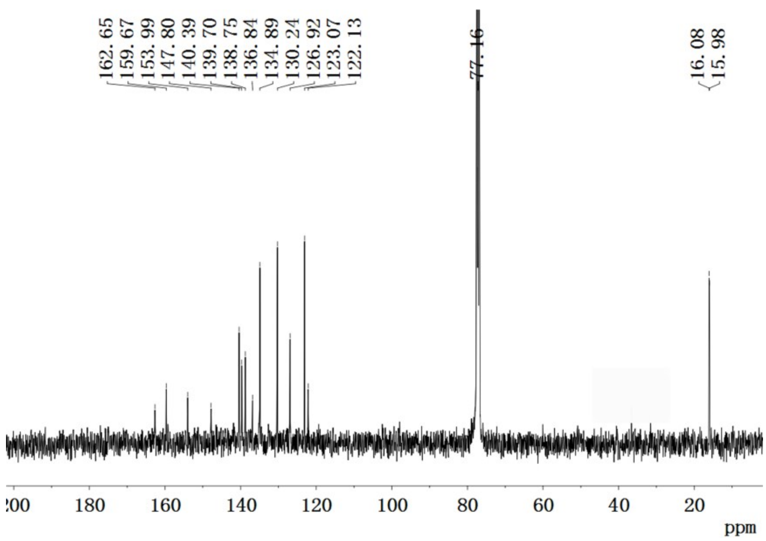

Fig. S14 ^{13}C NMR spectrum of MeTh-PSe in $CDCl_3$.

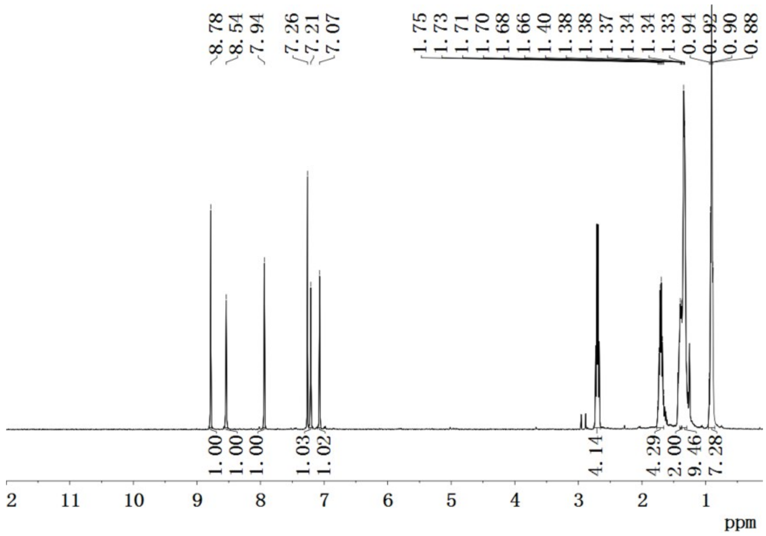

Fig S15 ^{1}H NMR spectrum of HexTh-PT in $CDCl_3$.

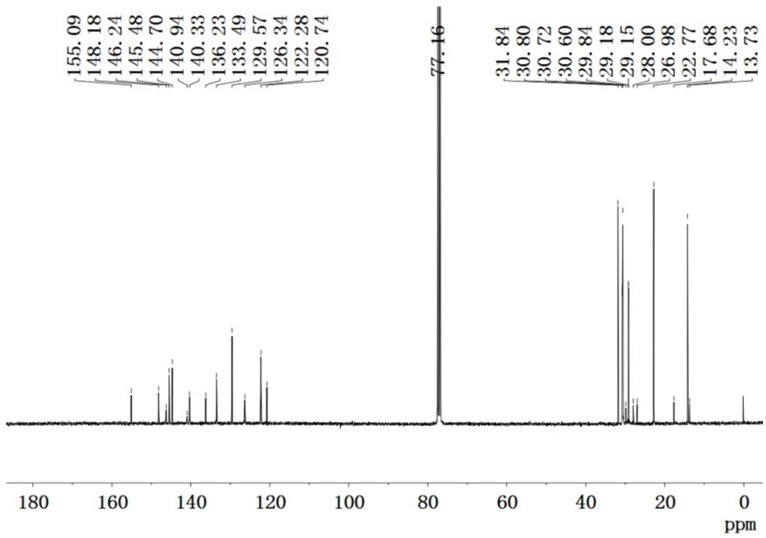

Fig. S16 ^{13}C NMR spectrum of HexTh-PT in $CDCl_3$.

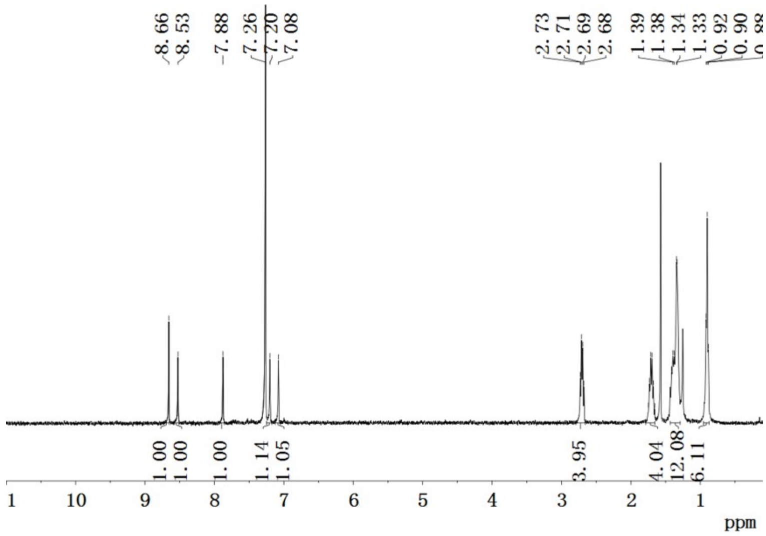

Fig. S17 ^{1}H NMR spectrum of HexTh-PSe in $CDCl_3$.

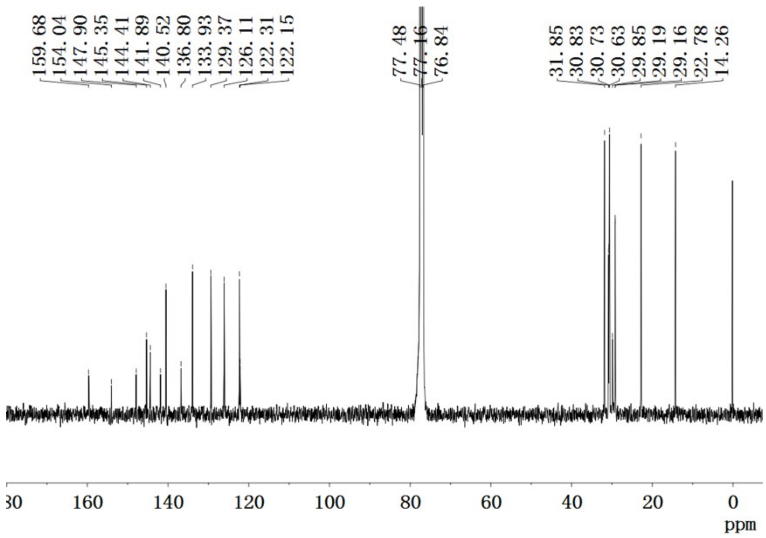

Fig. S18 ^{13}C NMR spectrum of HexTh-PSe in $CDCl_3$.

Table S1 Comparison between observed peaks of EDOT-PT/PSe monomers and corresponding polymers.

Peak (cm^{-1})		Assignment
EDOT-PT/EDOT-PSe	PEDOT-PT/PEDOT-PSe	
3088/3088	--	=C–H vibration of thiophene
2924/2935	2927/2941	=C–H vibration of pyridine
1573, 1526/1570, 1533	1587, 1551/1591, 1553	ring vibration of substituted pyridine
1481, 1454, 1431/1479, 1455, 1433	1485, 1433/1485, 1443	ring vibration of substituted thiophene
1371/1368	1358/1360	C–C stretching
1067/1064	1066/1066	C–O stretching
1188/1188	--	=C–H in-plane of thiophene
916/920	933/937	=C–H out-of-plane of pyridine
874/894	--	=C–H out-of-plane of thiophene
--	840	PF_6^-

Table S2 Comparison between observed peaks of Th-PT/PSe monomers and corresponding polymers.

Peak (cm^{-1})		Assignment
Th-PT/Th-PSe	PTh-PT/PTh-PSe	
3097, 3070/3090	--	=C–H vibration of thiophene
1530/1544, 1516	1518/1539, 1510	ring vibration of substituted pyridine
1462, 1422/1449, 1422	1452, 1422/1441	ring vibration of substituted thiophene
1188/1037	--	=C–H in-plane of thiophene
924/903	914/903	=C–H out-of-plane of pyridine
843/877, 844	overlap/873,839 (weak)	=C–H out-of-plane of thiophene
--	840	PF_6^-

Table S3 Comparison between observed peaks of MeTh-PT/PSe monomers and corresponding polymers.

Peak (cm^{-1})		Assignment
MeTh-PT/MeTh-PSe	PMeTh-PT/PMeTh-PSe	
3084/3076	--	=C–H vibration of thiophene
2918/2914	2918/2914	$–CH_3$ vibration
1549/1539	1600, 1516/1589, 1539	ring vibration of substituted pyridine
1481, 1454, 1431/1479, 1455, 1433	1485, 1433/1485, 1443	ring vibration of substituted thiophene
1292/1296	1283/1303	C–C stretching
1200/1203	--	=C–H in-plane of thiophene
901/--	905/--	=C–H out-of-plane of pyridine
854,827/860	--	=C–H out-of-plane of thiophene
--	840	PF_6^-

Table S4 Comparison between observed peaks of HexTh-PT/PSe monomers and corresponding polymers.

Peak (cm^{-1})		Assignment
HexTh-PT/HexTh-PSe	PHexTh-PT/PHexTh-PSe	
3093/3094	--	=C–H vibration of thiophene
2955, 2922, 2851/2957, 2922, 2853	2953, 2920, 2849/2957, 2924, 2853	$–C_6H_{13}$ vibration
1545/1519	1539/1522	ring vibration of substituted pyridine
1476/1496, 1458	1485, 1433/1485, 1443	ring vibration of substituted thiophene
1292/1298	1319/1311	C–C stretching
1203/1197	--	=C–H in-plane of thiophene
960/962	weak	=C–H out-of-plane of pyridine
862/889, 860	--	=C–H out-of-plane of thiophene
--	840	PF_6^-

Table S5 Electrochromic parameters for PEDOT-PSe

polymer	wavelength	T_{red}	T_{ox}	ΔT	response time (s)		*CE* (cm²/C)
					oxidation	reduction	
PEDOT-PSe	433 nm	59%	71%	12%	0.50	0.45	60
	1200 nm	73%	51%	22%	0.30	0.60	174

Table S6 Electrochromic parameters for PTh-PT

polymer	wavelength	T_{red}	T_{ox}	ΔT	response time (s)		*CE* (cm²/C)
					oxidation	reduction	
PTh-PT	375 nm	50%	56%	6%	4.0	0.8	30
	575 nm	51%	55%	4%	3.8	0.4	28
	1000 nm	88%	61%	27%	4.0	2.0	91

Table S7 Electrochromic parameters for PTh-PSe

polymer	wavelength	T_{red}	T_{ox}	ΔT	response time (s)		*CE* (cm²/C)
					oxidation	reduction	
PTh-PSe	1000 nm	60%	52%	8%	3.8	4.0	33

Table S8 Electrochromic parameters for PMeTh-PT

polymer	wavelength	T_{red}	T_{ox}	ΔT	response time (s)		*CE* (cm²/C)
					oxidation	reduction	
PMeTh-PT	380 nm	14 %	28 %	14 %	3.8	2.0	66
	619 nm	16%	21%	6%	2.4	3.8	28
	1000 nm	88%	51%	37%	3.8	3.4	55

Table S9 Electrochromic parameters for PMeTh-PSe

polymer	wavelength	T_{red}	T_{ox}	ΔT	response time (s)		*CE*
					oxidation	reduction	(cm^2/C)
PMeTh-PSe	1000 nm	60%	46%	14%	3.4	3.2	17

Table S10 Electrochromic parameters for PHexTh-PT

polymer	wavelength	T_{red}	T_{ox}	ΔT	response time (s)		*CE*
					oxidation	reduction	(cm^2/C)
PHexTh-PT	1000 nm	94%	89%	5%	3.4	0.8	37

Table S11 Electrochromic parameters for PHexTh-PSe

polymer	wavelength	T_{red}	T_{ox}	ΔT	response time (s)		*CE*
					oxidation	reduction	(cm^2/C)
PHexTh-PSe	600 nm	10 %	11 %	1 %	--	--	--
	1000 nm	57 %	39 %	18 %	3.6	3.6	66