

Electronic Supplementary Information for *Polymer Chemistry*:

Molecular design of DBT/DBF hybrid thiophenes π -conjugated systems and comparative study on their electropolymerization and optoelectronic properties: from comonomers to electrochromic polymers

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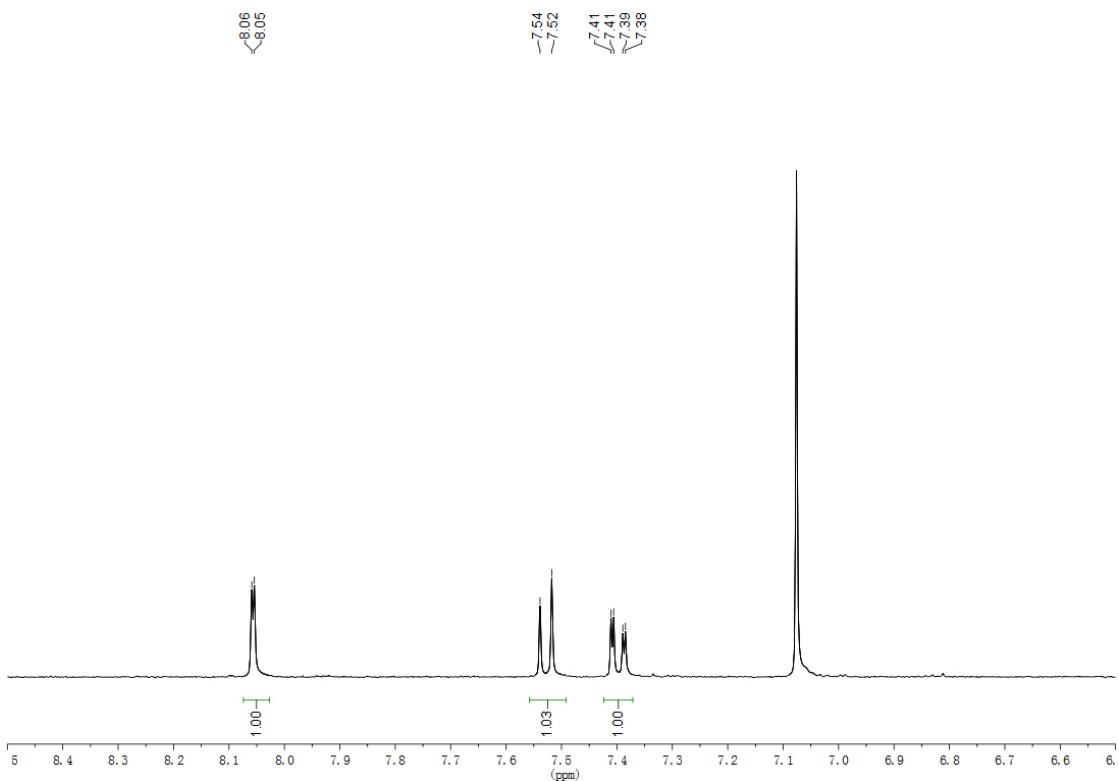


Fig. S1 ^1H NMR spectrum of 2,8-dibromodibenzothiophene.

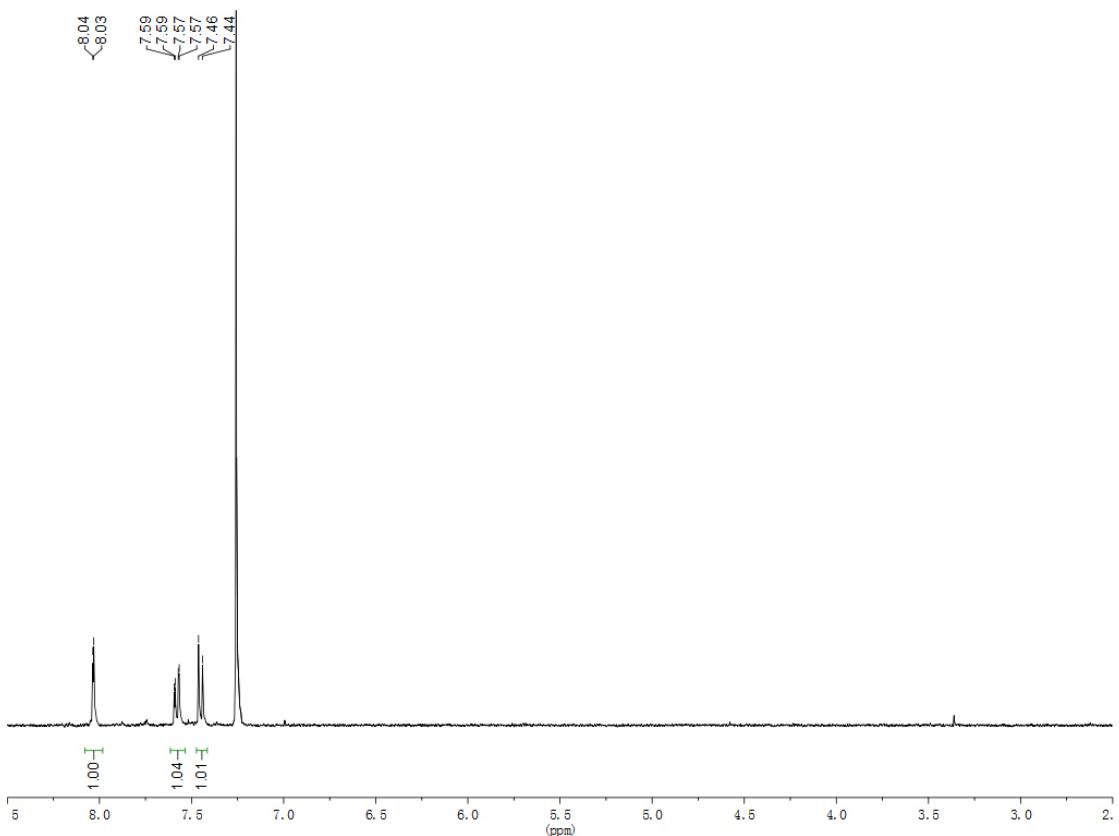
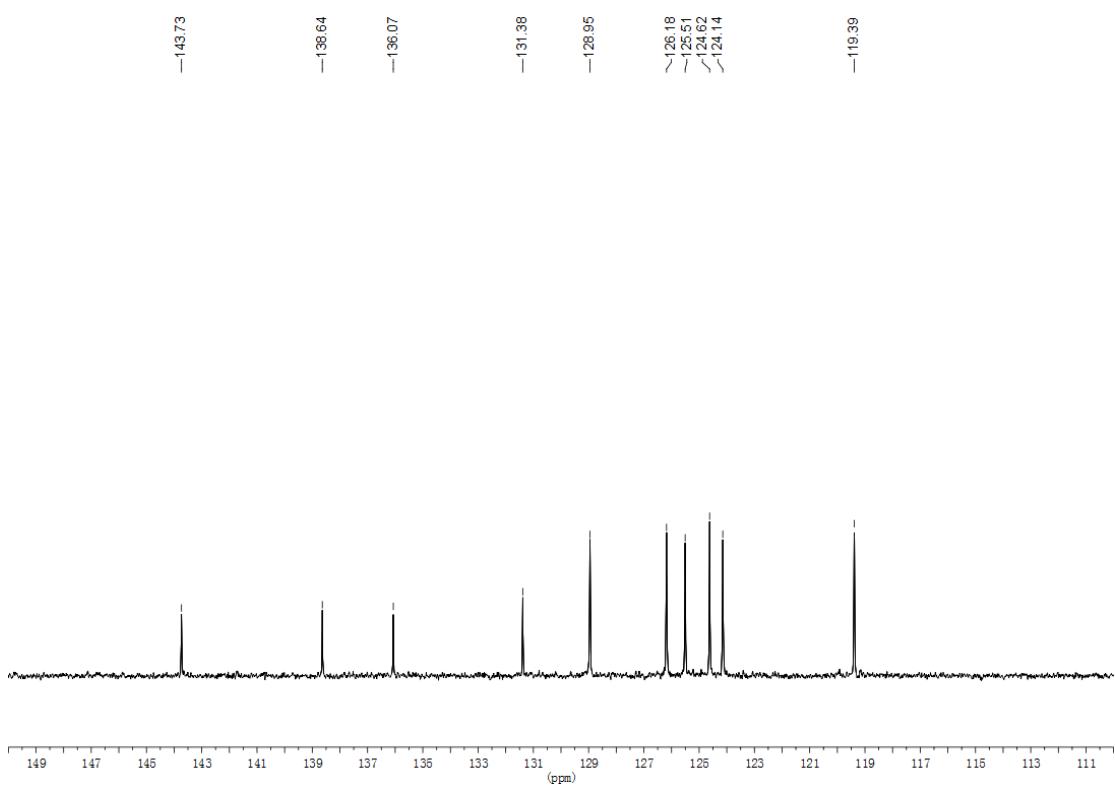
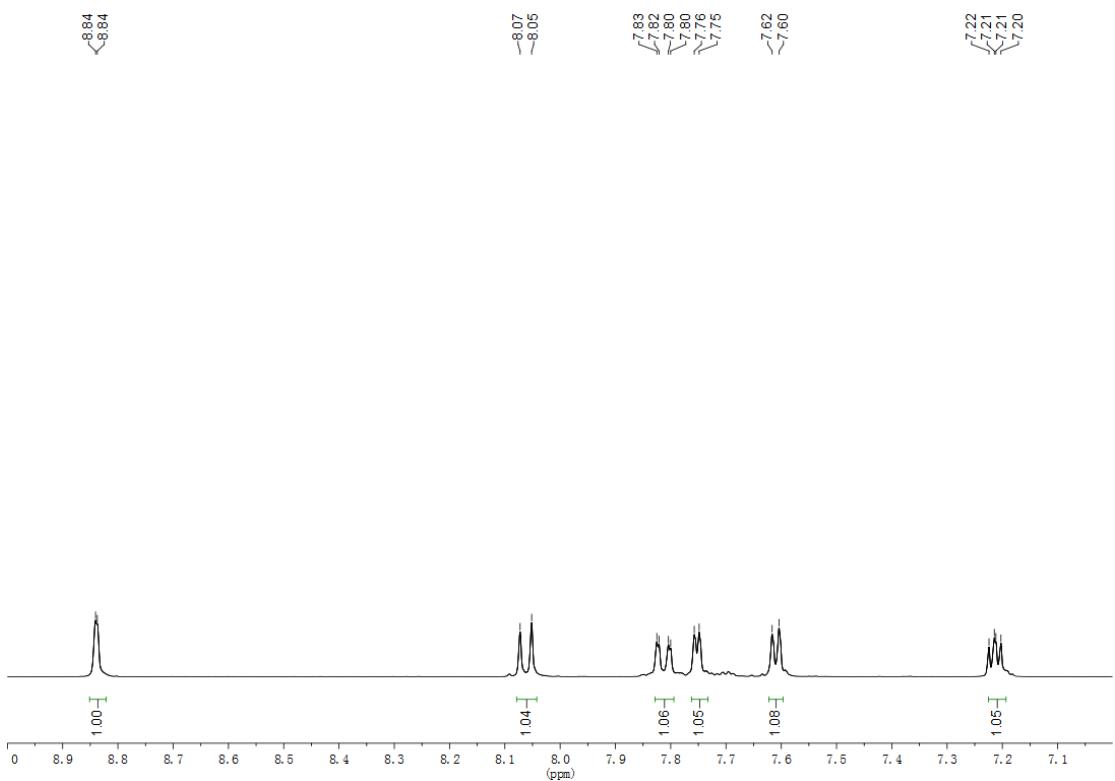


Fig. S2 ^1H NMR spectrum of 2,8-dibromodibenzofuran.



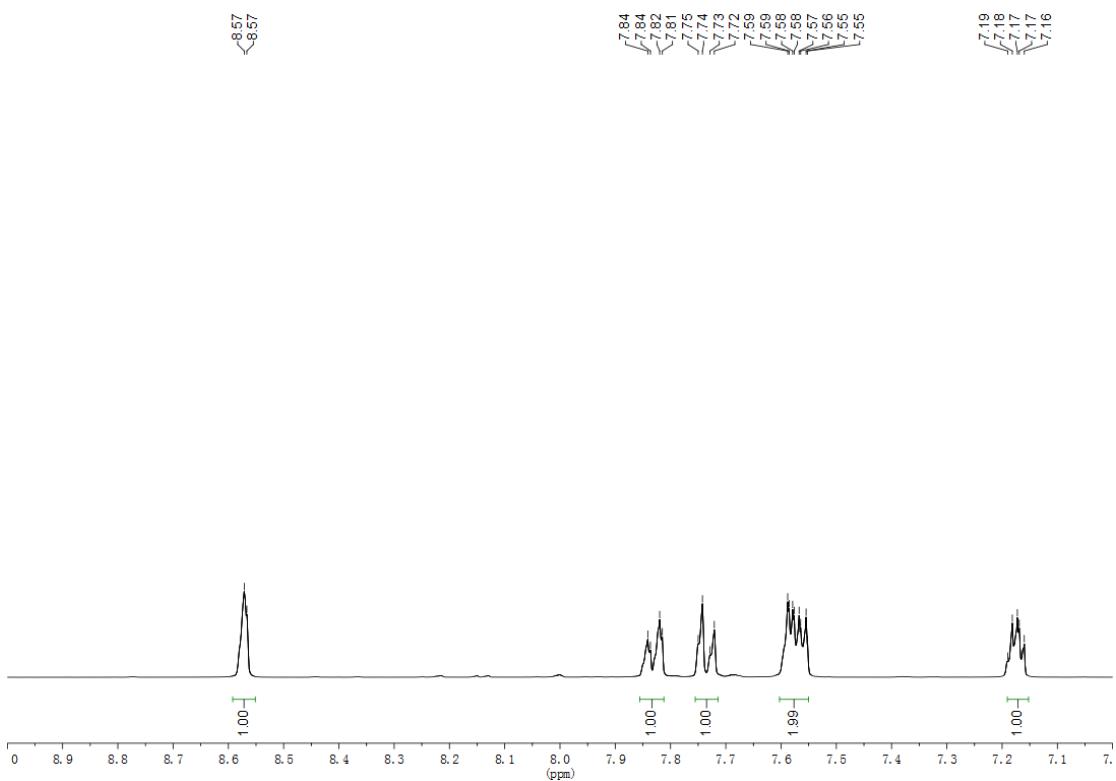


Fig. S5 ^1H NMR spectrum of DBF-Th.

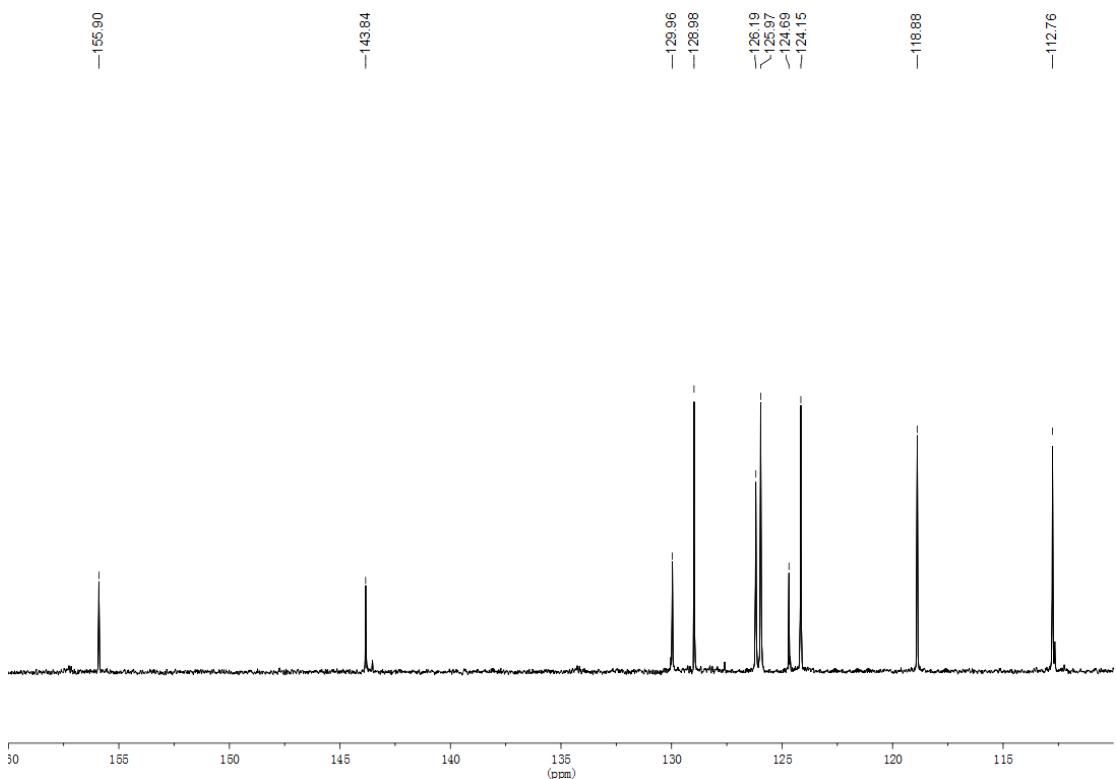
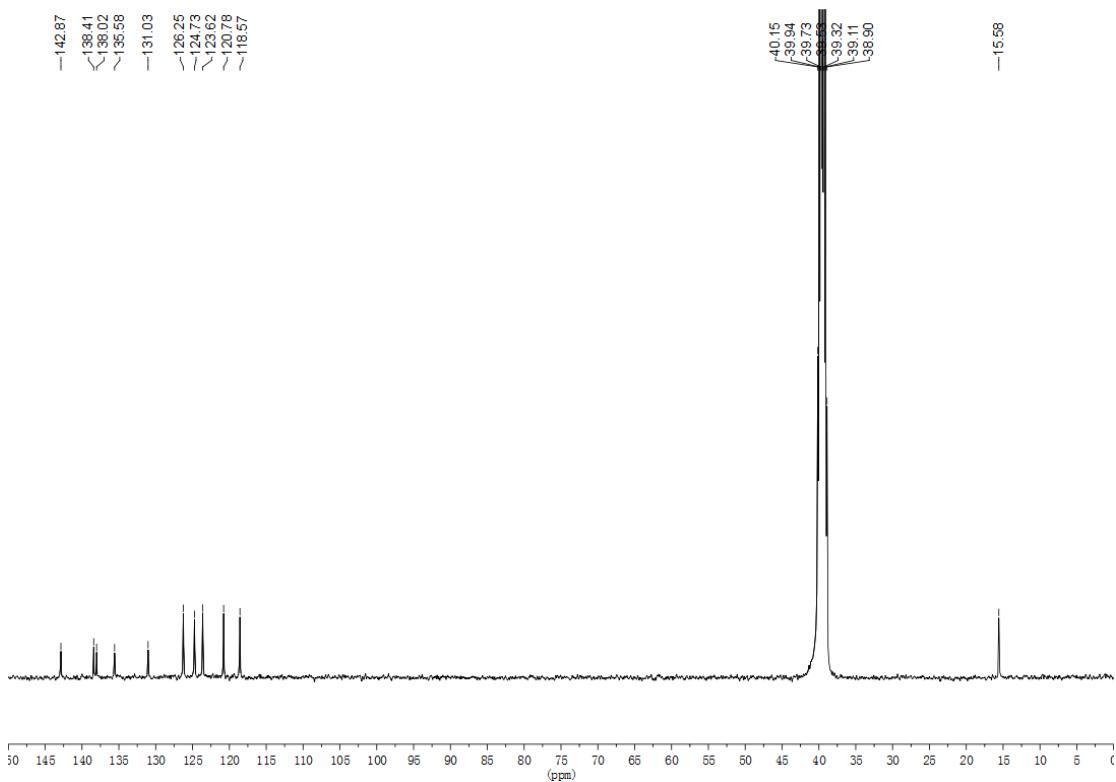
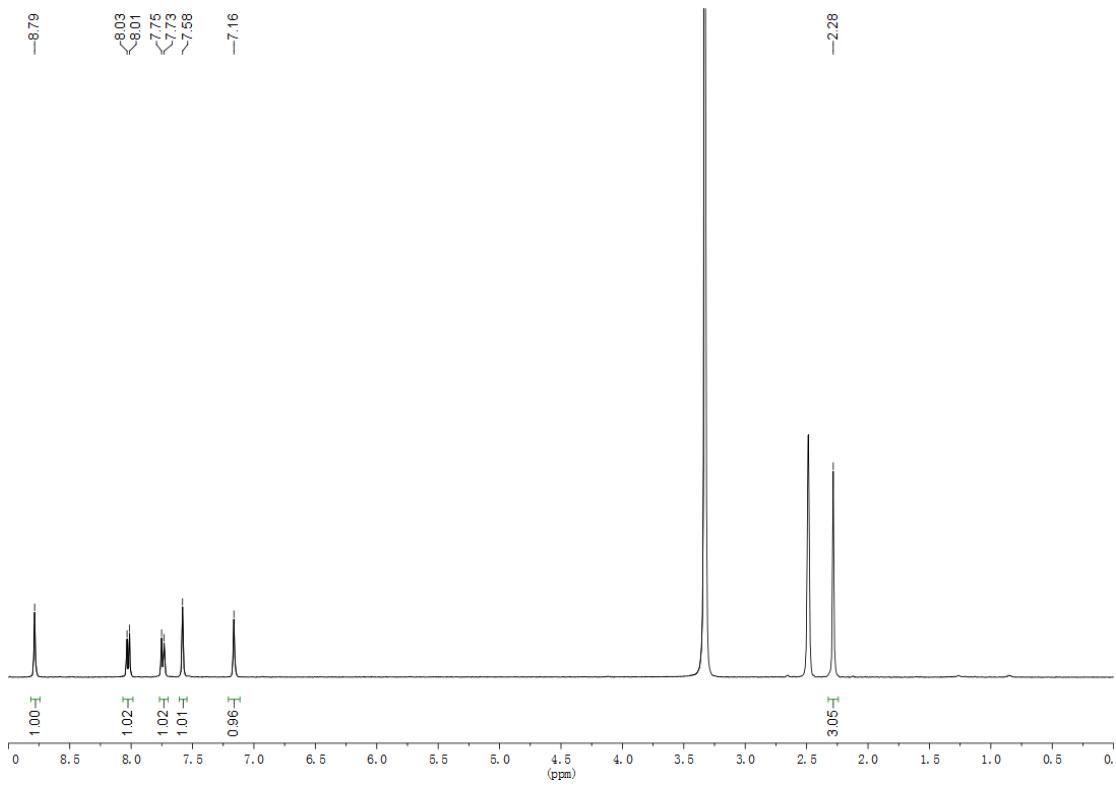
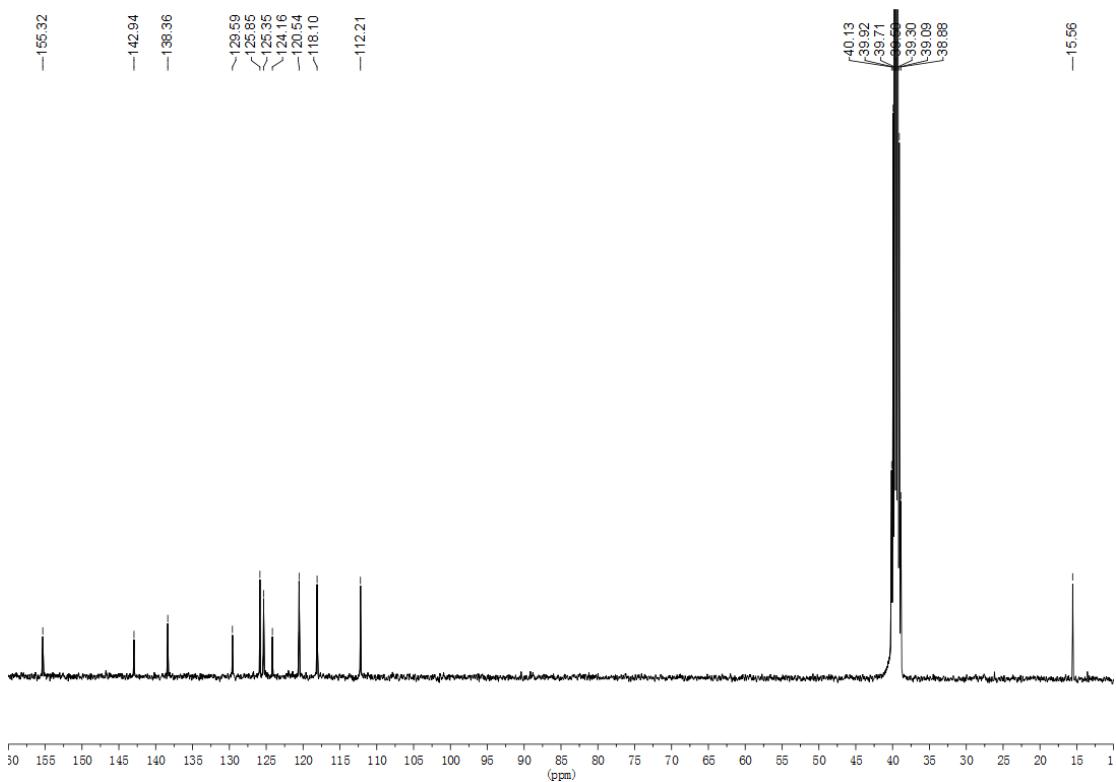
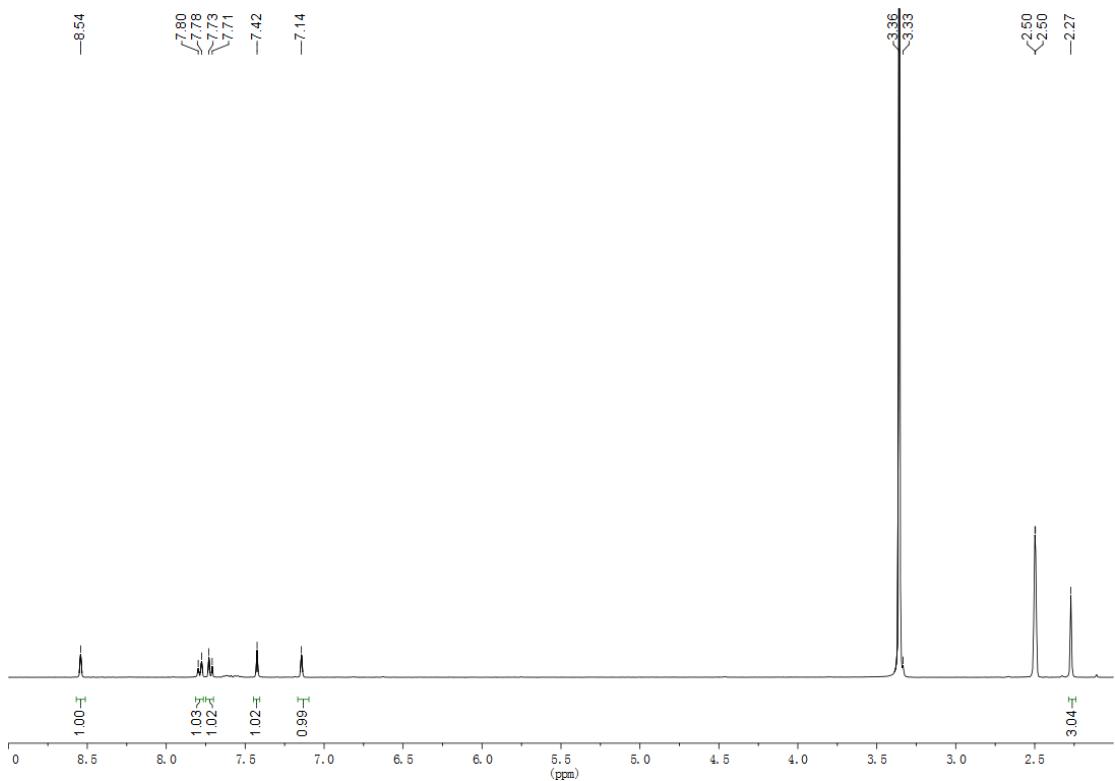


Fig. S6 ^{13}C NMR spectrum of DBF-Th.





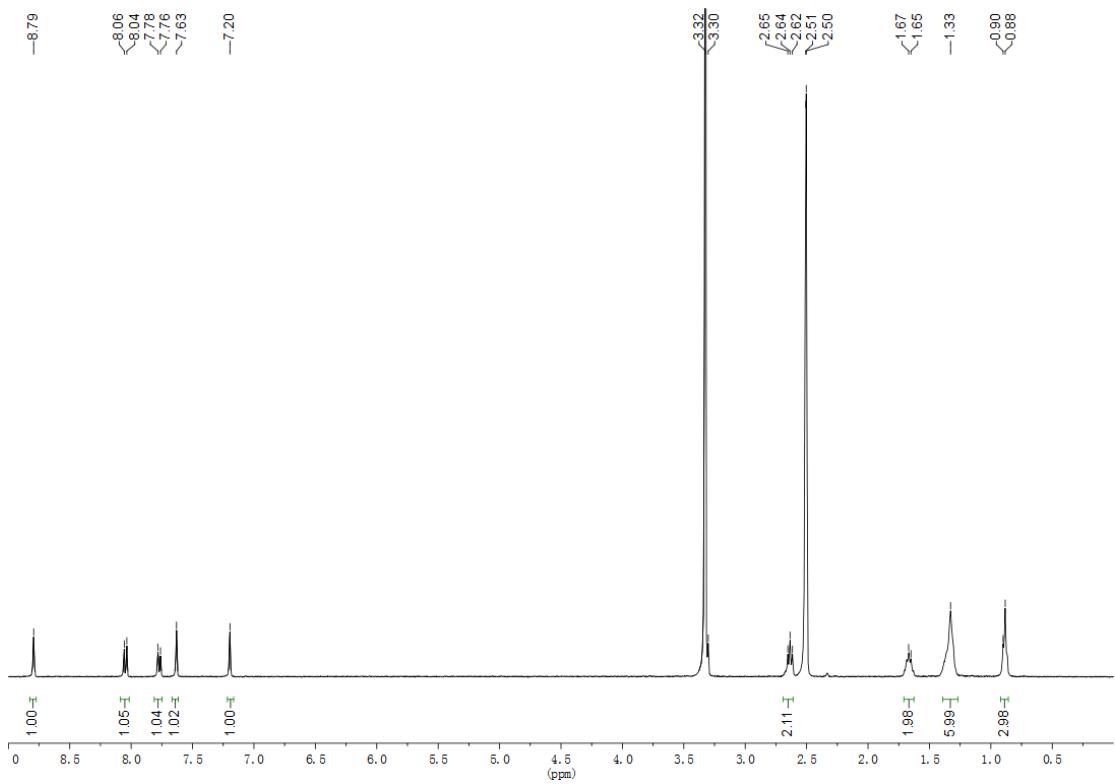


Fig.S11 ^1H NMR spectrum of DBT-3HexTh.

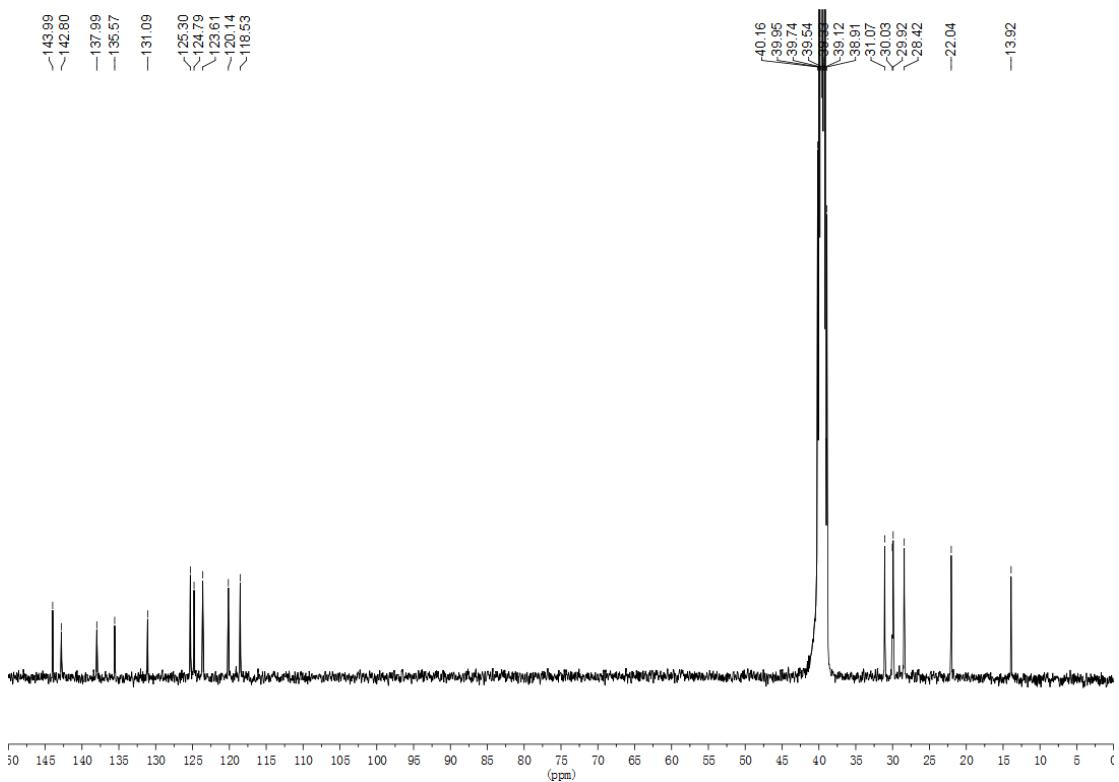
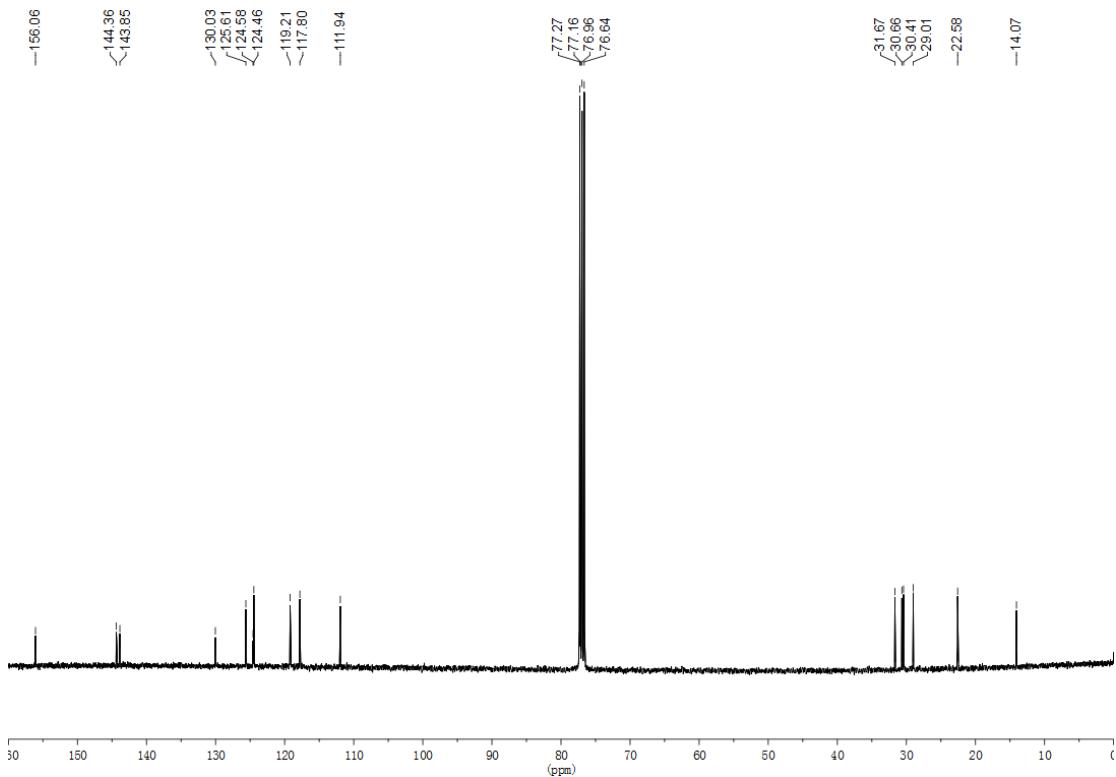
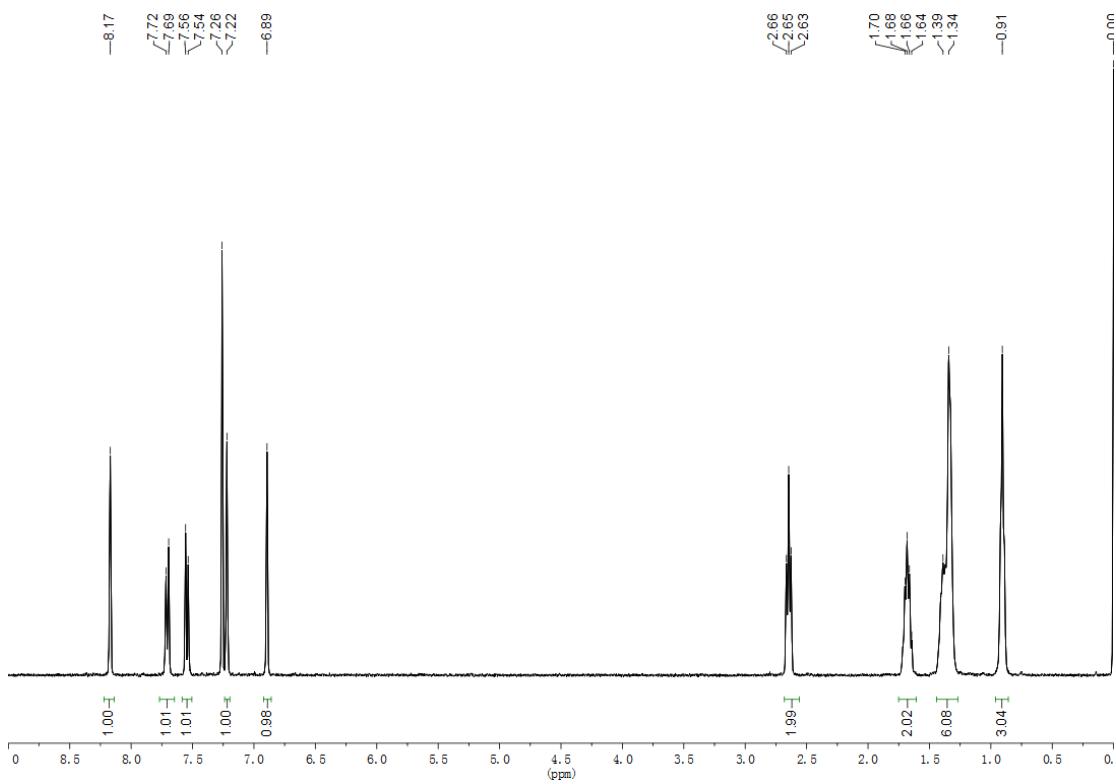


Fig.S12 ^{13}C NMR spectrum of DBT-3HexTh.



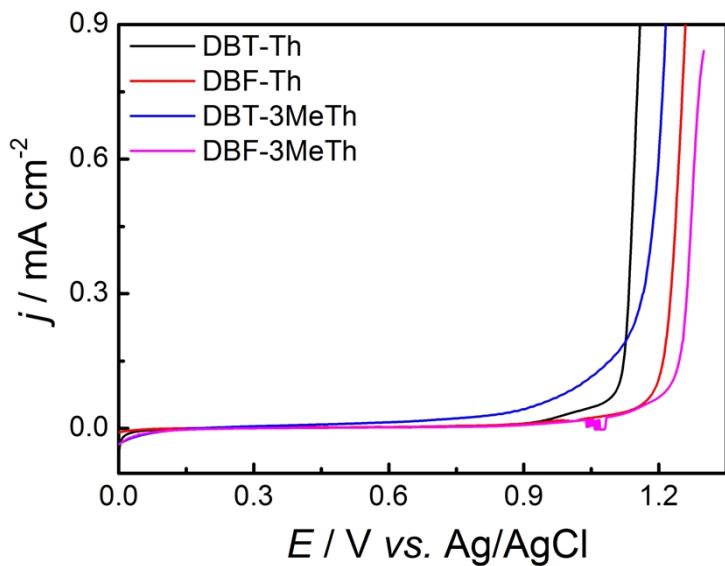


Fig. S15 Anodic polarization curves of 0.01 mol L $^{-1}$ DBT-Th, DBF-Th, DBT-3MeTh, DBF-3MeTh DBT-3HexTh, and DBF-3HexTh in DCM/MeCN-Bu₄NPF₆ (0.1 mol L $^{-1}$). Potential scan rate: 50 mV s $^{-1}$.

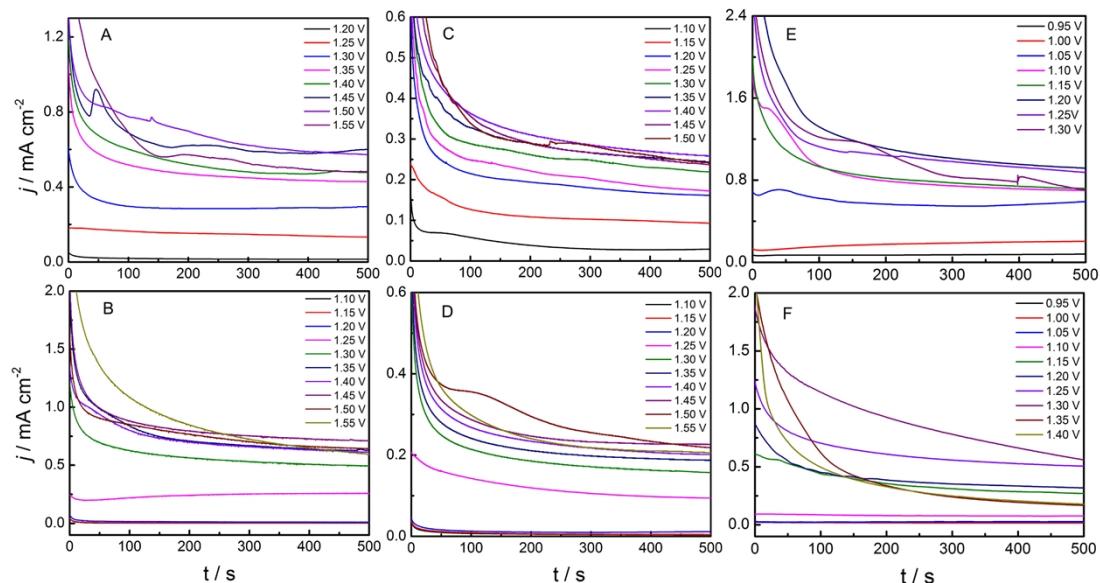


Fig. S16 Chronoamperograms of 0.01 mol L $^{-1}$ DBT-Th (A), DBF-Th (B), DBT-3MeTh (C), DBF-3MeTh (D) DBT-3HexTh (E), and DBF-3HexTh (F) in DCM/MeCN-Bu₄NPF₆ (0.1 mol L $^{-1}$) on Pt electrode at different applied potentials for 500 s.

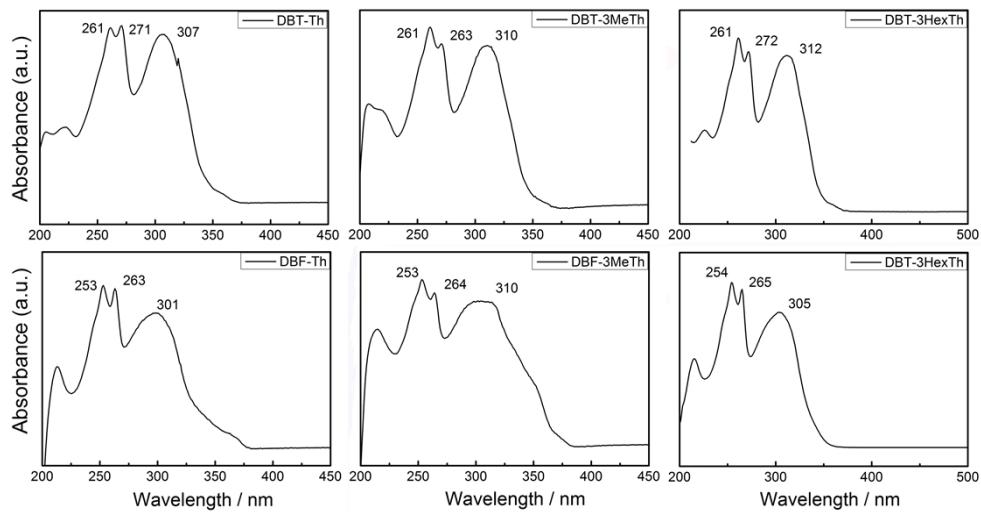


Fig. S17 UV-vis spectra of DBT-Th, DBF-Th, DBT-3MeTh, DBF-3MeTh, DBT-3HexTh, and DBF-3HexTh.

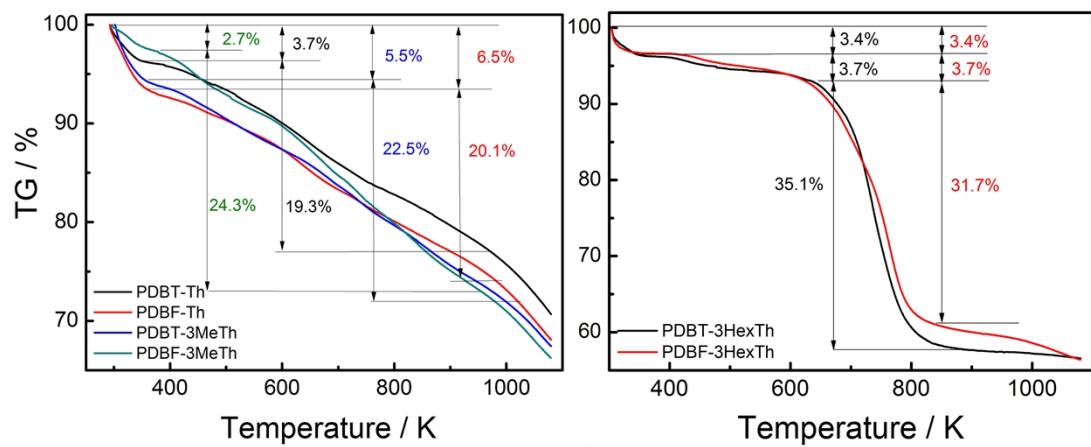


Fig. S18 TG curves of dedoped PDBT-Th, PDBF-Th, PDBT-3MeTh, PDBF-3MeTh, PDBT-3HexTh, and PDBF-3HexTh.

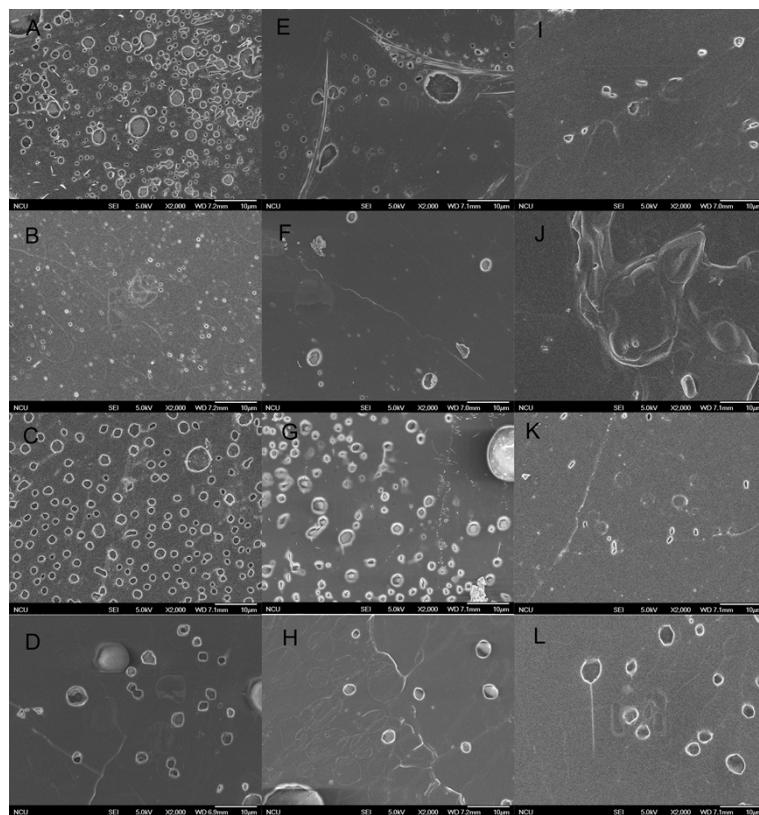


Fig. S19 SEM images of the polymer films deposited electrochemically on the ITO electrode. Magnification: 2000 \times . A, C, E, G, I, K: doped PDBT-Th, PDBF-Th, PDBT-3MeTh, PDBF-3MeTh PDBT-3HexTh, and PDBF-3HexTh, respectively; B, D, F, H, J, L: dedoped PDBT-Th, PDBF-Th, PDBT-3MeTh, PDBF-3MeTh PDBT-3HexTh, and PDBF-3HexTh, respectively.

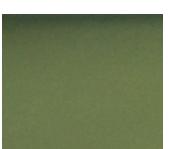
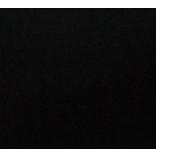
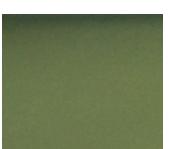
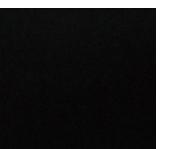
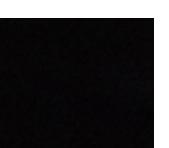
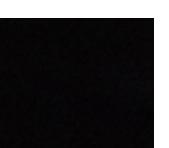
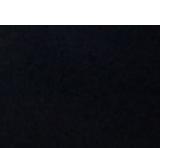
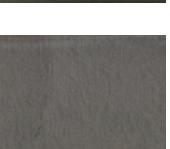
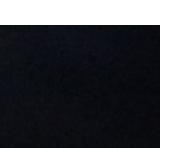
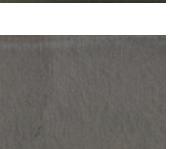
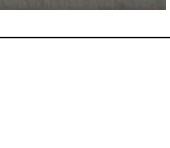
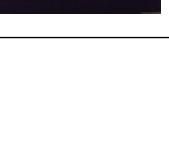
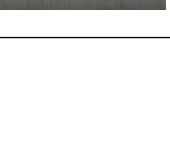
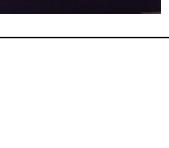
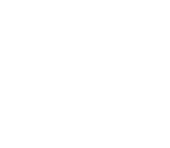
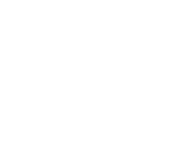
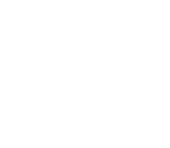
Table S1 Electrochromic parameters of dibenzo-five-membered ring end-capped with heterocycles-based polymers

Samples	λ / nm	$\Delta T / \%$	RT / s	$E_{\text{ox,ons}} / \text{V}$	$E_{\text{g,opt}} / \text{eV}$	Color / (neut.;ox.)	$CE / (\text{cm}^2/\text{C})$	Ref.
1	380	13.5	2.6	1.11	2.49	Yellow; Dark blue	101.6	1
2	470	25	1.0	1.1	1.96	Brown; Blue	415	2
3	336	58	4.0	1.37/ 1.47	1.25	Transparent; Dark green	328	3
6	468	--	--	1.34	2.27	--	6.71(394nm) 46.8(697nm) 9.32(1050nm)	4
7	350	14.2	1.6	1.36	2.32	Orange; Green	20.3	1
8	466	16.63	1.4	1.1	1.68	p-doping Brown;Blue n-doping Brown;Yellow	250(466nm); 242(697nm); 217(1050nm)	5
9	441	28.8	1.94	1.05	1.79	Orange; Dark Blue	144(441nm); 422(684nm); 93(1050nm)	6
14	424	45.17	1.18	--	1.68	Green; Blue	130.27	7
20	401	52.87	0.92	--	2.52	Yellow; Blue	225.1	7
21	420	35	2.7	1.08	2.12	Yellow; Black-gray	212.52	8
22	410	36	1.6	1.00	2.42	Yellow-green; Purple	178.09	8
25	445	62.56	1.24	--	2.13	Orange; Light Blue	177.68	7
26	422	55	0.8	1.25	2.06	Yellow; Dark Gray	126	9
27	418	57	1.3	1.46	2.18	Orange; Dark Blue	264	9
29	424	--	--	0.95	2.58	Yellow; Purple	--	10
30	418	--	--	0.91	2.46	Yellow; Purple	--	10
31	370	--	--	1.6	2.4	Yellow	--	11
32	357	--	--	1.2	2.66	Yellow; Purple	--	12

Table S2. Assignments of FT-IR spectra for all comonomers and polymers

Band (cm ⁻¹)							Assignment
DBT-Th	PDBT-Th	DBT-3MeTh	PDBT-3MeTh	DBT-3HexTh	PDBT-3HexTh		
3104	---	3108	---	3094	---	C _α -H stretching of Th	
3066	3061	3060	3055	3053	3050	C _β -H stretching of Th/C-H stretching of benzene	
2921	2965	2925	2964	2920	2929	C-H stretching of CH ₂ /CH ₃	
2841	2876	2852	2866	2849	2852		
1639	1629	1656	1651	1655	1638	C=C ring stretching of benzene/C-H stretching	
1550	1546	1548	1544	1548	1546	of Th	
1473	1467	1457	1448	1457	1452	C-C inter ring stretching	
1290	1281	1290	1322	1291	1288		
1024	1016	1020	1022	1020	1021	C-H in plane deformation of Th	
870	874	870	870	866	870	C-H out of plane deformation of Th	
---	839	---	840	---	836	characteristic peak of PF ₆ ⁻	
810	788	798	800	802	804	1,2,4-disubstituted benzene rings of DBT/DBF	
692	630	727	628	729	632	C-S stretching of Th	
Band (cm ⁻¹)							Assignment
DBF-Th	PDBF-Th	DBF-3MeTh	PDBF-3MeTh	DBF-3HexTh	PDBF-3HexTh		
3101	---	3101	---	3094	---	C _α -H stretching of Th	
3068	3058	3055	3062	3051	3050	C _β -H stretching of Th/ C-H stretching of benzene	
2916	2965	2917	2964	2922	2922	C-H stretching of CH ₂ /CH ₃	
2850	2876	2856	2872	2850	2852		
1627	1629	1628	1636	1656	1630	C=C ring stretching of benzene/C-H stretching	
1525	1532	1552	1555	1547	1545	of Th	
1477	1475	1492	1461	1465	1452	C-C inter ring stretching	
1282	1277	1282	1275	1289	1289		
1022	1022	1022	1020	1019	1021	C-H in plane deformation of Th	
861	876	861	868	868	868	C-H out of plane deformation of Th	
---	840	---	838	---	837	characteristic peak of PF ₆ ⁻	
804	804	804	806	801	802	1,2,4-disubstituted benzene rings of DBT/DBF	
683	636	721	636	732	631	C-S stretching of Th	

Table S3 Colorimetric data for polymers

Polymers	CIE color coordinates			Colors of polymers	
	Neutral	Oxidized	Neutral	Oxidized	
PDBT-Th	L*	99.32	39.90		
	a*	0.01	5.00		
	b*	1.28	-4.09		
PDBF-Th	L*	84.73	55.88		
	a*	2.39	5.95		
	b*	24.29	-7.48		
PDBT-3MeTh	L*	92.59	66.30		
	a*	1.01	6.45		
	b*	22.74	-1.10		
PDBF-3MeTh	L*	87.96	62.60		
	a*	8.64	2.04		
	b*	30.77	-1.15		
PDBT-3HexTh	L*	92.28	88.89		
	a*	1.60	0.50		
	b*	8.35	-1.64		
PDBF-3HexTh	L*	97.20	81.52		
	a*	0.14	10.04		
	b*	0.28	-10.72		

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