## Electronic Supplementary Information for Polymer Chemistry:

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

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Fig. S1 <sup>1</sup>H NMR spectrum of 2,8-dibromodibenzothiophene.



Fig. S2 <sup>1</sup>H NMR spectrum of 2,8-dibromodibenzofuran.



~8.05 ~8.05 7.83 7.82 7.780 7.75 ~7.60

7.21 7.21 7.21

Fig. S4 <sup>13</sup>C NMR spectrum of DBT-Th.

<sup>8.84</sup>
 <sup>8.84</sup>
 <sup>8.84</sup>



7.19 7.17 7.17 7.17 7.17

Fig. S6 <sup>13</sup>C NMR spectrum of DBF-Th.

8.57
8.57





50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ( (ppm)



Fig.S10 <sup>13</sup>C NMR spectrum of DBF-3MeTh.



50 145 140 135 130 125 120 115 110 105 100 96 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 (ppm)

Fig.S12 <sup>13</sup>C NMR spectrum of DBT-3HexTh.







Fig.S14 <sup>13</sup>C NMR spectrum of DBF-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-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 mol  $L^{-1}$ 

<sup>1</sup>). Potential scan rate: 50 mV s<sup>-1</sup>.



Fig. S16 Chronoamperograms of 0.01 mol L<sup>-1</sup> DBT-Th (A), DBF-Th (B), DBT-

3MeTh (C), DBF-3MeTh (D) DBT-3HexTh (E), and DBF-3HexTh (F) in DCM/MeCN-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 mol L<sup>-1</sup>) on Pt electrode at different applied potentials for



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×. 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.

Samples	λ / nm	ΔT / %	RT/s	E <sub>ox,ons</sub> <sub>et</sub> / V	E <sub>g,opt</sub> / eV	Color / (neut.;ox.)	CE (cm <sup>2</sup> /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 S1 Electrochromic parameters of dibenzo-five-membered ring end-capped with heterocycles-based polymers

Band (cm <sup>-1</sup> )								
DBT-	PDBT	DBT-	PDBT-	DBT-	PDBT-	Assignment		
Th	-Th	3MeTh	3MeTh	3HexTh	3HexTh			
3104		3108		3094		$C_{\alpha}$ -H stretching of Th		
3066	3061	3060	3055	3053	3050	$C_{\beta}$ -H stretching of Th/C-H stretching of benzene		
2921 2841	2965 2876	2925 2852	2964 2866	2920 2849	2929 2852	C-H stretching of CH <sub>2</sub> /CH <sub>3</sub>		
1639	1629	1656	1651	1655	1638	C=C ring stretching of		
1550	1546	1548	1544	1548	1546	benzene/C-H stretching		
1473	1467	1457	1448	1457	1452	of Th		
1290	1281	1290	1322	1291	1288	C-C inter ring stretching		
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 <sub>6</sub> -		
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 <sup>-1</sup> )								
		Ban	$d(cm^{-1})$					
DBF-	PDBF	Ban DBF-	d (cm $^{-1}$ ) PDBF-	DBF-	PDBF-	Assignment		
DBF- Th	PDBF -Th	Ban DBF- 3MeTh	d (cm <sup>-1</sup> ) PDBF- 3MeTh	DBF- 3HexTh	PDBF- 3HexTh	Assignment		
DBF- Th 3101	PDBF -Th	Ban DBF- <u>3MeTh</u> 3101	d (cm <sup>-1</sup> ) PDBF- 3MeTh	DBF- 3HexTh 3094	PDBF- 3HexTh	Assignment $C_{\alpha}$ -H stretching of Th		
DBF- Th 3101 3068	PDBF -Th  3058	Ban DBF- <u>3MeTh</u> 3101 3055	d (cm <sup>-1</sup> ) PDBF- <u>3MeTh</u>  3062	DBF- 3HexTh 3094 3051	PDBF- 3HexTh  3050	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$		
DBF- Th 3101 3068 2916	PDBF -Th  3058 2965	Ban DBF- <u>3MeTh</u> 3101 3055 2917	d (cm <sup>-1</sup> ) PDBF- <u>3MeTh</u>  3062 2964	DBF- 3HexTh 3094 3051 2922	PDBF- 3HexTh  3050 2922	Assignment $C_{\alpha}$ -H stretching of Th $C_{\beta}$ -H stretching of Th/ C-H stretching of benzene		
DBF- Th 3101 3068 2916 2850	PDBF -Th  3058 2965 2876	Ban DBF- 3MeTh 3101 3055 2917 2856	d (cm <sup>-1</sup> ) PDBF- <u>3MeTh</u>  3062 2964 2872	DBF-           3HexTh           3094           3051           2922           2850	PDBF- 3HexTh  3050 2922 2852	Assignment $C_{\alpha}$ -H stretching of Th $C_{\beta}$ -H stretching of Th/ C-Hstretching of benzeneC-H stretching of CH2/CH3		
DBF- Th 3101 3068 2916 2850 1627	PDBF -Th 3058 2965 2876 1629	Ban DBF- 3MeTh 3101 3055 2917 2856 1628	d (cm <sup>-1</sup> ) PDBF- <u>3MeTh</u>  3062 2964 2872 1636	DBF- 3HexTh 3094 3051 2922 2850 1656	PDBF- 3HexTh 3050 2922 2852 1630	Assignment $C_{\alpha}$ -H stretching of Th $C_{\beta}$ -H stretching of Th/ C-Hstretching of benzeneC-H stretching of CH2/CH3C=C ring stretching of		
DBF- Th 3101 3068 2916 2850 1627 1525	PDBF -Th 3058 2965 2876 1629 1532	Ban DBF- 3MeTh 3101 3055 2917 2856 1628 1552	d (cm <sup>-1</sup> ) PDBF- <u>3MeTh</u>  3062 2964 2872 1636 1555	DBF- 3HexTh 3094 3051 2922 2850 1656 1547	PDBF- 3HexTh  3050 2922 2852 1630 1545	Assignment $C_{\alpha}$ -H stretching of Th $C_{\beta}$ -H stretching of Th/ C-Hstretching of benzeneC-H stretching of CH2/CH3C=C ring stretching ofbenzene/C-H stretching		
DBF- Th 3101 3068 2916 2850 1627 1525 1477	PDBF -Th 3058 2965 2876 1629 1532 1475	Ban DBF- 3MeTh 3101 3055 2917 2856 1628 1552 1492	d (cm <sup>-1</sup> ) PDBF- 3MeTh  3062 2964 2872 1636 1555 1461	DBF- 3HexTh 3094 3051 2922 2850 1656 1547 1465	PDBF- 3HexTh  3050 2922 2852 1630 1545 1452	Assignment $C_{\alpha}$ -H stretching of Th $C_{\beta}$ -H stretching of Th/ C-Hstretching of benzeneC-H stretching of CH2/CH3C=C ring stretching ofbenzene/C-H stretchingof Th		
DBF- Th 3101 3068 2916 2850 1627 1525 1477 1282	PDBF -Th 3058 2965 2876 1629 1532 1475 1277	Ban DBF- 3MeTh 3101 3055 2917 2856 1628 1552 1492 1282	d (cm <sup>-1</sup> ) PDBF- 3MeTh  3062 2964 2872 1636 1555 1461 1275	DBF- 3HexTh 3094 3051 2922 2850 1656 1547 1465 1289	PDBF- 3HexTh  3050 2922 2852 1630 1545 1452 1289	Assignment $C_{\alpha}$ -H stretching of Th $C_{\beta}$ -H stretching of Th/ C-Hstretching of benzeneC-H stretching of CH2/CH3C=C ring stretching ofbenzene/C-H stretchingof ThC-C inter ring stretching		
DBF- Th 3101 3068 2916 2850 1627 1525 1477 1282 1022	PDBF -Th 3058 2965 2876 1629 1532 1475 1277 1022	Ban DBF- 3MeTh 3101 3055 2917 2856 1628 1552 1492 1282 1022	d (cm <sup>-1</sup> ) PDBF- 3MeTh  3062 2964 2872 1636 1555 1461 1275 1020	DBF- 3HexTh 3094 3051 2922 2850 1656 1547 1465 1289 1019	PDBF- 3HexTh  3050 2922 2852 1630 1545 1452 1289 1021	Assignment C <sub>α</sub> -H stretching of Th/ C <sub>β</sub> -H stretching of Th/ C-H stretching of benzene C-H stretching of CH <sub>2</sub> /CH <sub>3</sub> C=C ring stretching of benzene/C-H stretching of Th C-C inter ring stretching ABDA ADDA ADDA ADDA ADDA ADDA ADDA ADDA		
DBF- Th 3101 3068 2916 2850 1627 1525 1477 1282 1022 861	PDBF -Th 3058 2965 2876 1629 1532 1475 1277 1022 876	Ban DBF- 3MeTh 3101 3055 2917 2856 1628 1552 1492 1282 1022 861	d (cm <sup>-1</sup> ) PDBF- 3MeTh  3062 2964 2872 1636 1555 1461 1275 1020 868	DBF- 3HexTh 3094 3051 2922 2850 1656 1547 1465 1289 1019 868	PDBF- 3HexTh 3050 2922 2852 1630 1545 1452 1289 1021 868	AssignmentC <sub>α</sub> -H stretching of ThC <sub>β</sub> -H stretching of Th/C-Hstretching of benzeneC-H stretching of CH2/CH3C=C ring stretching ofbenzene/C-H stretchingof ThC-C inter ring stretchingOf ThC-H out of planedeformation of Th		
DBF- Th 3101 3068 2916 2850 1627 1525 1477 1282 1022 861	PDBF -Th 3058 2965 2876 1629 1532 1475 1277 1022 876 840	Ban DBF- 3MeTh 3101 3055 2917 2856 1628 1552 1492 1282 1022 861	d (cm <sup>-1</sup> ) PDBF- 3MeTh  3062 2964 2872 1636 1555 1461 1275 1020 868 838	DBF- 3HexTh 3094 3051 2922 2850 1656 1547 1465 1289 1019 868	PDBF- 3HexTh  3050 2922 2852 1630 1545 1452 1289 1021 868 837	Assignment $C_{\alpha}$ -H stretching of Th $C_{\beta}$ -H stretching of Th/ C-Hstretching of benzene <b>C</b> -H stretching of CH2/CH3C=C ring stretching ofbenzene/C-H stretchingof ThC-C inter ring stretchingC-H in plane deformationof ThC-H out of planedeformation of Thcharacteristic peak of PF6		
DBF- Th 3101 3068 2916 2850 1627 1525 1477 1282 1022 861  804	PDBF -Th 3058 2965 2876 1629 1532 1475 1277 1022 876 840 840	Ban DBF- 3MeTh 3101 3055 2917 2856 1628 1628 1552 1492 1282 1022 861  804	d (cm <sup>-1</sup> ) PDBF- <u>3MeTh</u>  3062 2964 2872 1636 1555 1461 1275 1020 868 838 838	DBF- 3HexTh 3094 3051 2922 2850 1656 1547 1465 1289 1019 868  801	PDBF- 3HexTh 3050 2922 2852 1630 1545 1452 1289 1021 868 837 802	AssignmentC <sub>α</sub> -H stretching of ThC <sub>β</sub> -H stretching of Th/C-Hstretching of benzeneC-H stretching of CH2/CH3C=C ring stretching ofbenzene/C-H stretchingof ThC-C inter ring stretchingC-H out of planeof ThC-H out of planedeformation of Thcharacteristic peak of PF61,2,4-disubstituted benzenerings of DBT/DBF		

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

Dalymara	(	CIE color coor	dinates	Colors of polymers		
Polymers		Neutral	Oxidized	Neutral	Oxidized	
	L*	99.32	39.90	Construction of the local		
PDBT-Th	a*	0.01	5.00			
	b*	1.28	-4.09			
	L*	84.73	55.88			
PDBF-Th	a*	2.39	5.95	5		
	b*	24.29	-7.48	10.0-07		
	L*	92.59	66.30			
PDBT-3MeTh	a*	1.01	6.45			
	b*	22.74	-1.10			
	L*	87.96	62.60			
PDBF-3MeTh	a*	8.64	2.04			
	b*	30.77	-1.15	and the second second second		
	L*	92.28	88.89			
PDBT-3HexTh	a*	1.60	0.50			
	b*	8.35	-1.64			
	L*	97.20	81.52			
PDBF-3HexTh	a*	0.14	10.04			
	b*	0.28	-10.72			

 Table S3 Colorimetric data for polymers

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