Supplementary Information

Conjugated Donor-Acceptor Terpolymers Entailing Pechmann Dye and Dithienyl-Diketopyrrolopyrrole as Co-Electron Acceptors: Tuning HOMO/LUMO Energies and Photovoltaic Performances

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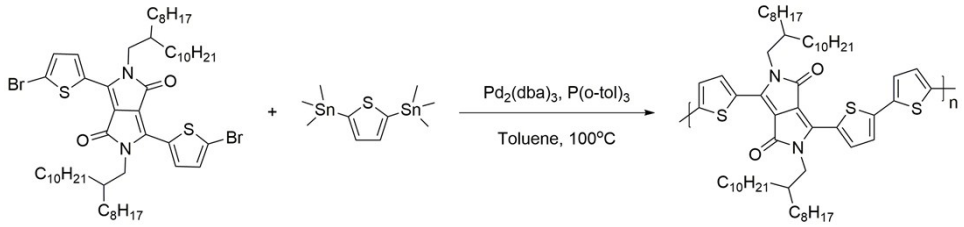
1. Synthesis and Characterization of PDPP3T



3 **4** **PDPP3T**

Synthesis of PDPP3T Compound **3** (200 mg, 0.196 mmol), 2,5-bis(trimethylstannyl)thiophene (**4**) (80 mg, 0.196 mmol) and P(*o*-tol)$_3$ (4.8 mg, 0.0158 mmol) were dissolved in toluene (10 mL). The solution was purged with N_2 for 30 min, followed by addition of $Pd_2(dba)_3$ (1.8 mg, 0.00196 mmol). The reaction mixture was stirred at 100 ^{o}C for 48 hrs. The resulting mixture was poured into methanol and stirred for 30 mins. The dark precipitate was filtered off and subjected to Soxhlet extraction for two days successively with methanol, hexane and acetone to remove oligomers and the remaining catalyst. The resulting polymer was extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and dried under vacuum at 50 ^{o}C for 48 hrs. The purified polymer was collected to give deep blue solid (170 mg, 92.0% yield). ^{1}H NMR (500 MHz; 1,1,2,2-tetrachloroethane-d2; 100 ^{o}C): δ = 8.8(m, br, 2H), 7.35-7.01 (m, br, 4H), 4.05(m, br, 4H), 1.99 (m, br, 2H), 1.42-1.26 (m, br, 64H), 0.87 (m, br, 12H); M_w/M_n (GPC) = 70/30 kg/mol. Anal. calcd. for $(C_{58}H_{88}N_2O_2S_3)_n$: C, 73.99; H, 9.42; N, 2.98; S, 10.22; Found: C, 74.11; H, 9.57; N, 2.82; S, 10.42.

2. TGA and DSC Analysis

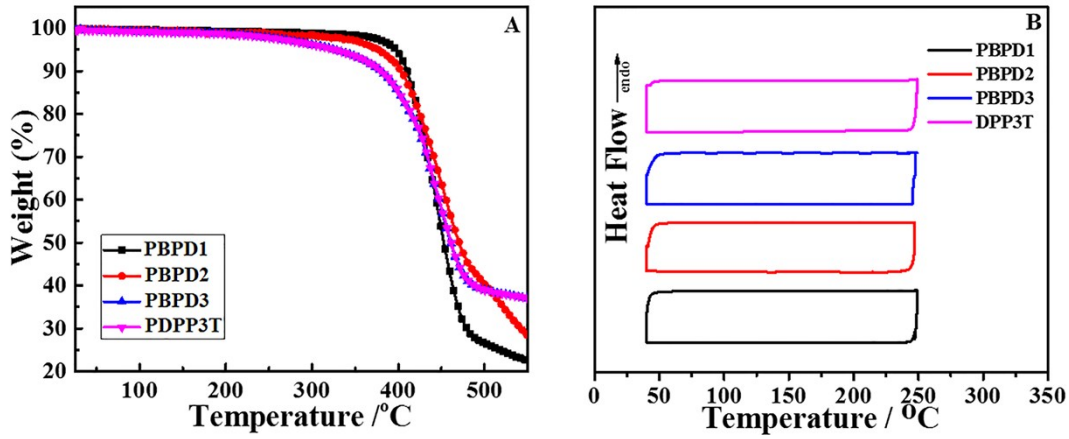


Fig. S1 (A) TGA curves of **PBPD1**, **PBPD2**, **PBPD3** and **PDPP3T**: heating rate: 10 °C/min. from 25 °C to 550 °C under nitrogen atmosphere. (B) DSC curves (endo up) of **PBPD1**, **PBPD2**, **PBPD3** and **PDPP3T** recorded at a heating and cooling rate of 10 °C/min under nitrogen.

3. The Cyclic Voltammograms of Dibromo-BBPD and Dibromo-TBPD and Their Absorption Spectra in Solutions.

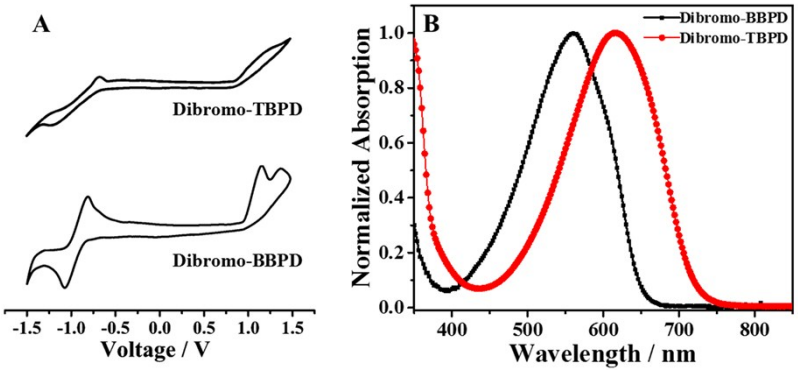


Fig. S2 The cyclic voltammogram(A) of dibromo-BBPD and dibromo-TBPD (1.0×10^{-3} M) in $CHCl_3$ at a scan rate of 100 mV s^{-1}, with Pt as the working and counter electrode and an Ag/AgCl electrode (saturated KCl) as the reference electrode,

and n-Bu_4NPF_6 (0.1 M) as supporting electrolyte, and their absorption spectrum(B) in $CHCl_3$ (1.0×10^{-5} M).

4. Cyclic Voltammograms of Polymers

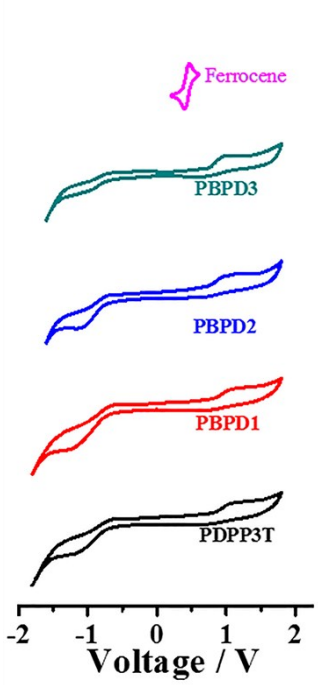


Fig. S3 Cyclic voltammograms of **PBPD1**, **PBPD2**, **PBPD3** and **PDPP3T** (1.0×10^{-3} M) in CH_2Cl_2 at a scan rate of 100 mV s^{-1}, with Pt as the working and counter electrodes and an Ag/AgCl electrode (saturated KCl) as the reference electrode, and *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte.

5. Density Functional Theory Calculations

Geometries optimization and frequency analysis were performed at the level of B3LYP /6-31G(d) by using Gaussian09 (revision A.02)[S1]. Table S1 and Table S2 listed the coordinates and energies at the optimized geometries for molecular **M1**, **M2** and **M3**, and there were no any imaginary frequencies. Then the molecular orbitals were analyzed, the energy gaps between HOMO and LUMO were obtained.

Table S1 Coordinates and energy **M1**

		X	Y	Z
1	S	14.10592	2.129267	-0.0457
2	C	15.31618	0.900527	-0.21874
3	C	14.76533	-0.35188	-0.26111
4	C	13.34832	-0.33661	-0.14735
5	C	12.819	0.932008	-0.01858
6	S	2.330867	-0.50133	-0.04178
7	C	1.048041	-1.68924	-0.03744
8	C	1.567702	-2.97531	-0.04615
9	C	2.971732	-3.01305	-0.06582
10	S	10.15005	0.178134	-0.14888
11	C	11.43561	1.327996	0.121204
12	C	10.92464	2.567815	0.467933
13	C	9.519608	2.601551	0.517344
14	C	6.498595	3.372229	0.440843
15	C	5.983728	-3.7235	-0.46738
16	O	4.124048	1.863003	0.312123
17	O	8.359162	-2.21892	-0.31482
18	C	8.912574	1.386326	0.211951
19	C	3.57342	-1.75648	-0.07148
20	C	7.522545	1.02591	0.169152
21	N	6.463877	1.928047	0.312682
22	S	-13.2521	0.838575	0.270256
23	C	-14.4483	2.04502	-0.02064
24	C	-13.9062	3.23128	-0.4458
25	C	-12.4943	3.181967	-0.52977
26	S	-5.47729	-0.28699	0.060765
27	C	-4.2617	-1.54311	0.028174
28	C	-4.85113	-2.79868	0.017213
29	C	-6.2551	-2.75959	0.044679
30	C	-9.29387	-3.30644	0.498414
31	C	-9.44141	3.806782	-0.39841
32	O	-11.5867	-1.67664	0.368656
33	O	-7.14619	2.175779	-0.29242
34	C	-6.78638	-1.47233	0.075973
35	C	-11.9552	1.952726	-0.16919
36	C	-8.1537	-1.03202	0.103766
37	N	-9.25785	-1.87841	0.24841
38	C	-2.86078	-1.21009	0.010111
39	C	-2.26637	0.040321	0.003343
40	C	-0.85707	0.001511	-0.01333
41	C	-0.33233	-1.27986	-0.01983
42	S	-1.63014	-2.46479	-0.00394
43	C	5.192538	1.265858	0.23454

44	N	6.021514	-2.29466	-0.22278
45	C	7.292315	-1.62713	-0.18822
46	C	6.949042	-0.23431	-0.00634
47	C	5.535634	-0.1254	0.040086
48	C	4.962507	-1.39123	-0.08501
49	C	-10.4919	-1.14356	0.228833
50	N	-9.48005	2.361185	-0.28442
51	C	-8.24328	1.633647	-0.21102
52	C	-8.65778	0.26309	-0.01149
53	C	-10.076	0.229789	0.04623
54	C	-10.5815	1.515685	-0.13088
55	H	16.35982	1.17809	-0.28048
56	H	15.35082	-1.2587	-0.36509
57	H	12.73604	-1.2323	-0.14596
58	H	0.949769	-3.86699	-0.03614
59	H	3.522515	-3.94161	-0.06174
60	H	11.54916	3.42452	0.697814
61	H	8.97533	3.492502	0.792647
62	H	5.460942	3.705877	0.379674
63	H	6.910308	3.684419	1.407097
64	H	7.075953	3.829357	-0.36881
65	H	5.372209	-3.96149	-1.34346
66	H	7.016254	-4.02527	-0.65387
67	H	5.609645	-4.27527	0.4023
68	H	-14.4928	4.109014	-0.69354
69	H	-11.9039	4.021895	-0.86469
70	H	-4.28283	-3.72225	-0.014
71	H	-6.85604	-3.65642	0.025506
72	H	-10.3375	-3.55048	0.706348
73	H	-8.96856	-3.88109	-0.37609
74	H	-8.67869	-3.57466	1.36305
75	H	-10.0218	4.282276	0.397926
76	H	-8.39137	4.090397	-0.30448
77	H	-9.80824	4.147947	-1.37301
78	H	-2.83764	0.962547	0.008652
79	H	-0.23621	0.891102	-0.02063
80	H	-15.4939	1.808641	0.129143

Total energy: = -4448.93493469 Hartrees

Table S2 Coordinates and energy of **M2**

		X	**Y**	**Z**
1	C	-12.2603	0.373927	0.361631
2	C	-11.3779	-0.67636	0.120177
3	C	-10.0453	-0.18629	0.106109

4	C	-10.0811	1.234058	0.371928
5	N	-11.4811	1.523405	0.515241
6	C	-11.3438	-2.09517	-0.15868
7	N	-9.94787	-2.37641	-0.34875
8	C	-9.16624	-1.22774	-0.18998
9	C	-13.7002	0.349127	0.437895
10	C	-7.73617	-1.18777	-0.32709
11	O	-9.20946	2.088777	0.491888
12	O	-12.212	-2.95793	-0.22446
13	C	-11.8889	2.867028	0.878716
14	C	-9.53234	-3.74554	-0.58467
15	C	-6.84183	-2.17144	-0.74176
16	C	-5.49969	-1.75396	-0.76032
17	C	-5.32448	-0.43879	-0.3591
18	S	-6.85577	0.296205	0.050131
19	C	-14.6123	1.396106	0.498789
20	C	-15.9617	0.97342	0.55561
21	C	-16.0848	-0.39273	0.540013
22	S	-14.561	-1.19236	0.440598
23	C	-4.09935	0.3163	-0.26428
24	C	-3.93189	1.673309	-0.05759
25	C	-2.57889	2.079595	-0.02625
26	C	-1.67725	1.048791	-0.20854
27	S	-2.53592	-0.46895	-0.4068
28	C	2.62412	1.286551	-0.31812
29	C	4.084207	1.315146	-0.34432
30	C	4.923868	0.228184	-0.25838
31	C	6.271981	0.691015	-0.28511
32	C	6.205176	2.180067	-0.42961
33	N	4.842055	2.500075	-0.42872
34	C	7.453933	-0.00745	-0.18849
35	C	7.522189	-1.49682	-0.03979
36	N	8.882517	-1.80268	0.089268
37	C	9.639065	-0.61957	-0.01932
38	C	8.800571	0.458951	-0.18588
39	C	11.09674	-0.57623	0.073176
40	O	6.621158	-2.32503	-0.05239
41	O	7.110386	2.994194	-0.55728
42	C	9.343929	-3.17886	0.023409
43	C	4.39421	3.836532	-0.78048
44	C	11.80656	0.392074	-0.666
45	C	13.18633	0.495017	-0.57716
46	C	13.92918	-0.35613	0.265554
47	C	13.21943	-1.31825	1.00733

48	C	11.83837	-1.43153	0.910011
49	C	1.9435	0.188758	-0.88243
50	C	0.559863	0.105345	-0.84766
51	C	-0.21834	1.112167	-0.24189
52	C	0.463639	2.201348	0.336673
53	C	1.847528	2.291005	0.293416
54	C	15.38509	-0.22631	0.35705
55	C	16.16592	0.87737	0.089643
56	C	17.55853	0.655892	0.284548
57	C	17.83986	-0.61728	0.69911
58	S	16.4007	-1.57014	0.853366
59	H	-10.9685	3.420249	1.07515
60	H	-12.4267	3.363914	0.063406
61	H	-12.5116	2.86194	1.778376
62	H	-9.11239	-3.87555	-1.58833
63	H	-8.80451	-4.07563	0.16325
64	H	-10.4358	-4.35305	-0.50335
65	H	-7.13949	-3.16365	-1.0462
66	H	-4.68178	-2.3928	-1.07606
67	H	-14.3322	2.438976	0.484732
68	H	-16.8036	1.655244	0.602865
69	H	-4.76577	2.359775	0.045143
70	H	-2.27481	3.113472	0.092668
71	H	4.620872	-0.79807	-0.12011
72	H	9.101115	1.494019	-0.23392
73	H	10.18279	-3.27247	-0.67154
74	H	9.649529	-3.55989	1.004477
75	H	8.503446	-3.78078	-0.32876
76	H	4.040898	4.397259	0.092425
77	H	5.25634	4.362477	-1.19624
78	H	3.593475	3.793791	-1.5239
79	H	11.26234	1.045974	-1.34039
80	H	13.70408	1.22562	-1.19102
81	H	13.7543	-1.97014	1.692511
82	H	11.32797	-2.16306	1.526657
83	H	2.514556	-0.58895	-1.37968
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86	H	2.333114	3.128546	0.781655
87	H	15.74985	1.832997	-0.20995
88	H	18.31714	1.415519	0.129936
89	H	18.80414	-1.05496	0.919889
90	H	-16.9948	-0.97792	0.572354

Total energy: -3884.83328278 Hartrees

Table S3 Coordinates and energy of **M3**

		X	Y	Z
1	C	-15.9404	-0.05278	0.619626
2	C	-14.5162	-0.33846	0.42632
3	C	-13.515	0.585887	0.245596
4	C	-12.2737	-0.10652	0.124171
5	C	-12.5936	-1.56763	0.217939
6	N	-13.9754	-1.63887	0.430334
7	C	-10.9973	0.379386	-0.03912
8	C	-10.676	1.839258	-0.13855
9	N	-9.28149	1.913869	-0.24082
10	C	-8.74373	0.611325	-0.25752
11	C	-9.75501	-0.31362	-0.13773
12	C	-7.31487	0.321595	-0.35176
13	O	-11.428	2.804601	-0.16354
14	O	-11.8552	-2.53789	0.109152
15	C	-8.62891	3.165257	-0.58541
16	C	-14.6773	-2.9084	0.352428
17	C	-6.32364	1.1435	0.217965
18	C	-4.97998	0.798946	0.149681
19	C	-4.55717	-0.37646	-0.49921
20	C	-5.55012	-1.19519	-1.07591
21	C	-6.89204	-0.85799	-0.99934
22	C	-16.7479	-0.79345	1.503234
23	C	-18.0875	-0.45921	1.690536
24	C	-18.6492	0.617002	1.000947
25	C	-17.858	1.363003	0.123805
26	C	-16.5194	1.032629	-0.0664
27	C	-3.14702	-0.75393	-0.577
28	C	-2.60323	-2.0058	-0.78134
29	C	-1.18772	-2.02145	-0.79349
30	C	-0.61291	-0.78191	-0.59881
31	S	-1.86524	0.431784	-0.413
32	C	3.580945	0.200379	-0.44217
33	C	5.01697	0.457555	-0.36856
34	C	6.008609	-0.49019	-0.25813
35	C	7.266519	0.174518	-0.17163
36	C	6.977742	1.640883	-0.26949
37	N	5.584295	1.747219	-0.3589
38	C	8.532796	-0.34022	-0.0108
39	C	8.819669	-1.80737	0.088877
40	N	10.21234	-1.91534	0.183193
41	C	10.78119	-0.62652	0.193018

42	C	9.791279	0.322648	0.077796
43	C	12.21791	-0.37349	0.276634
44	O	8.045071	-2.75474	0.117958
45	O	7.751006	2.58935	-0.30058
46	C	10.83717	-3.18144	0.526331
47	C	4.957017	3.012348	-0.70067
48	C	13.18179	-1.2206	-0.30253
49	C	14.53516	-0.91372	-0.24167
50	C	14.99429	0.245894	0.409529
51	C	14.02904	1.090464	0.993922
52	C	12.6769	0.792074	0.923942
53	C	2.617419	1.045595	0.140976
54	C	1.265535	0.731158	0.094653
55	C	0.806281	-0.43565	-0.54494
56	C	1.771418	-1.27737	-1.13575
57	C	3.121633	-0.97045	-1.08075
58	C	16.4181	0.581072	0.482834
59	C	17.00044	1.818659	0.65196
60	C	18.42337	1.784742	0.676415
61	C	18.92612	0.521011	0.527553
62	S	17.66204	-0.65229	0.359706
63	H	-13.632	1.658316	0.258645
64	H	-9.63169	-1.38253	-0.05934
65	H	-8.11425	3.61337	0.272278
66	H	-7.90839	3.016267	-1.39429
67	H	-9.41166	3.854077	-0.91037
68	H	-14.9722	-3.27883	1.340915
69	H	-15.5694	-2.81818	-0.2731
70	H	-13.9865	-3.62941	-0.08995
71	H	-6.6074	2.038541	0.760013
72	H	-4.24755	1.438719	0.634139
73	H	-5.25929	-2.09078	-1.61606
74	H	-7.63232	-1.49525	-1.47283
75	H	-16.3184	-1.6115	2.071458
76	H	-18.692	-1.03739	2.384082
77	H	-18.287	2.20005	-0.42015
78	H	-15.9118	1.601013	-0.76377
79	H	-3.20722	-2.90094	-0.88053
80	H	-0.60554	-2.92976	-0.90278
81	H	5.861308	-1.5553	-0.16984
82	H	9.940738	1.387514	-0.00993
83	H	11.32835	-3.6472	-0.33569
84	H	11.57253	-3.04588	1.323959
85	H	10.042	-3.84839	0.866399

86	H	4.465594	3.476854	0.161953
87	H	5.75089	3.680915	-1.04065
88	H	4.221449	2.876393	-1.49816
89	H	12.86941	-2.1055	-0.8456
90	H	15.24698	-1.57181	-0.73228
91	H	14.34969	1.975336	1.534992
92	H	11.95746	1.448627	1.403329
93	H	2.929899	1.934875	0.676683
94	H	0.555441	1.387974	0.589452
95	H	1.452059	-2.16728	-1.66914
96	H	3.840088	-1.62527	-1.56384
97	H	16.42409	2.734319	0.726145
98	H	19.04537	2.66576	0.791943
99	H	19.96106	0.20685	0.509776
100	H	-19.6951	0.872903	1.146206

Total energy: -3320.73397771 Hartrees

(S1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

6. 1-D GIXRD Patterns

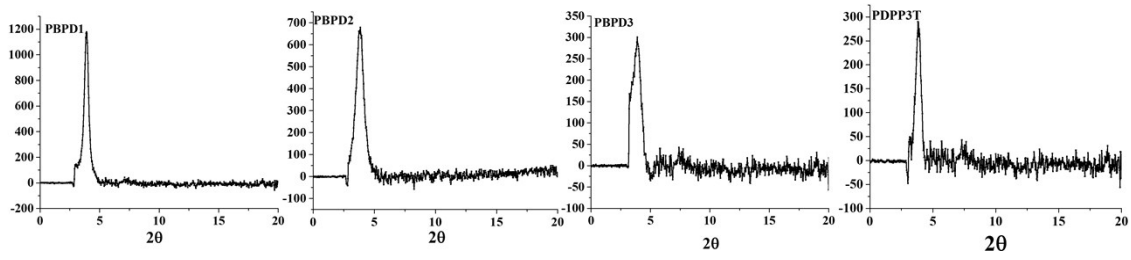


Fig. S4. 1-D GIXRD patterns in the out-of-plane direction of the thin blend films of **PBPD1**, **PBPD2**, **PBPD3** and **PDPP3T** with $PC_{71}BM$.

7. TEM Images of OSC Devices.

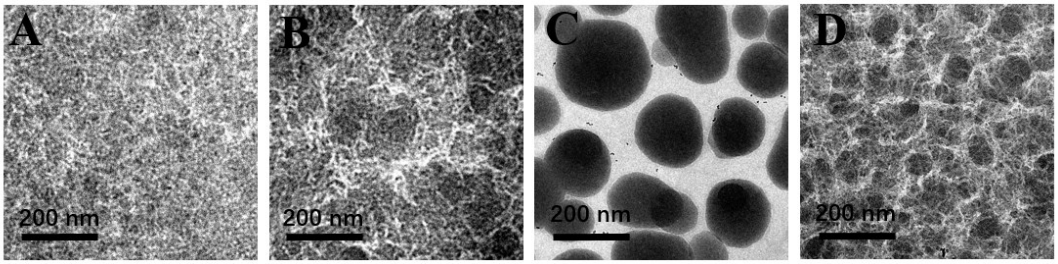
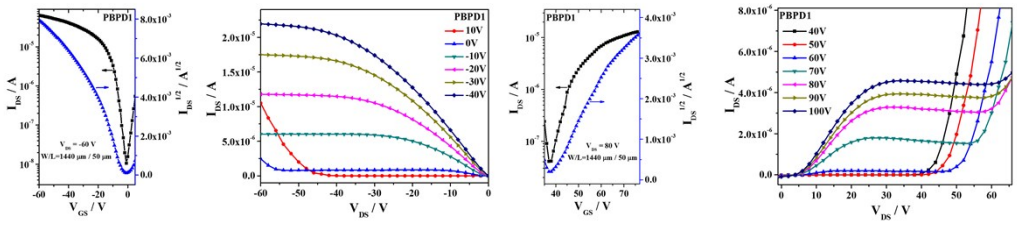


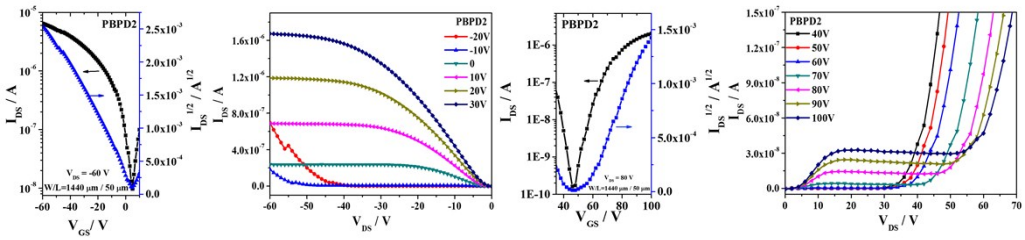
Fig. S5. TEM images of **PBPD1**:$PC_{71}BM$ (1:2, w/w) (A), **PBPD2**:$PC_{71}BM$ (1:2, w/w) (B), **PBPD3**:$PC_{71}BM$ (1:2, w/w) (C) and **PDPP3T**:$PC_{71}BM$ (1:2, w/w) (D) blend thin films.

8. Transfer and Output Curves with Thin films of PBPD1, PBPD2, PBPD3 and PDPP3T.

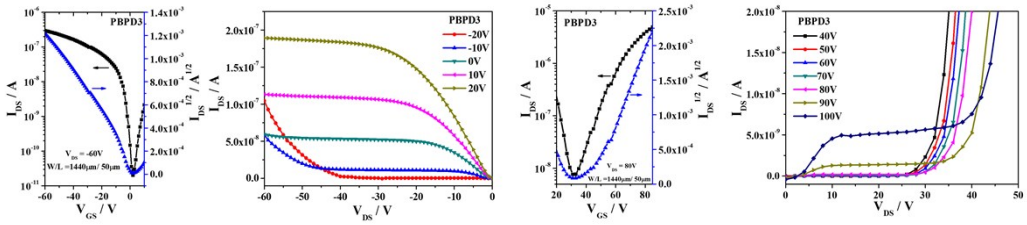
PBPD1



PBPD2



PBPD3



PDPP3T

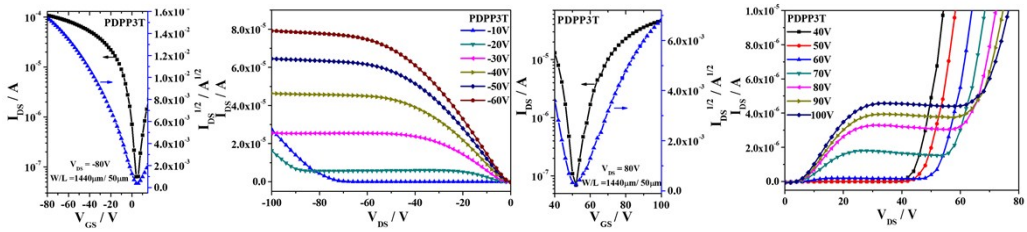


Fig. S6 The transfer and output characteristics of BGBC OFET devices based on **PBPD1, PBPD2**, **PBPD3** and **PDPP3T** annealed at 120 °C (V_{DS} for transfer characteristics are -60 V and 80 V, respectively). The channel width (*W*) and length (*L*) were 1400 μm and 50 μm, respectively.

9. **AFM Images of OFET Devices.**

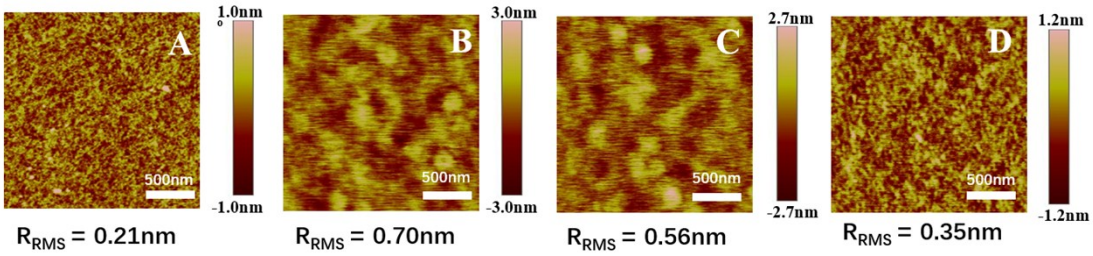
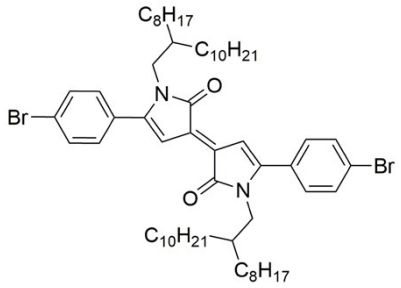


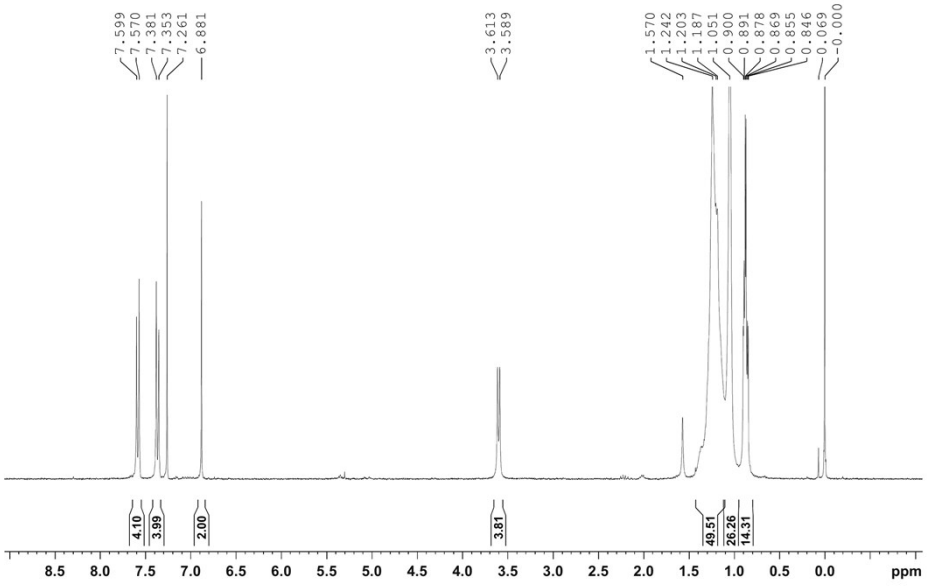
Fig. S7. AFM height images of thin films of **PBPD1**(A), **PBPD2** (B), **PBPD3** (C) and **PDPP3T** (D) deposited on OTS-modified SiO_2/Si substrates after thermal annealing at 120 °C.

10. ^{1}H-NMR and ^{13}C-NMR spectra

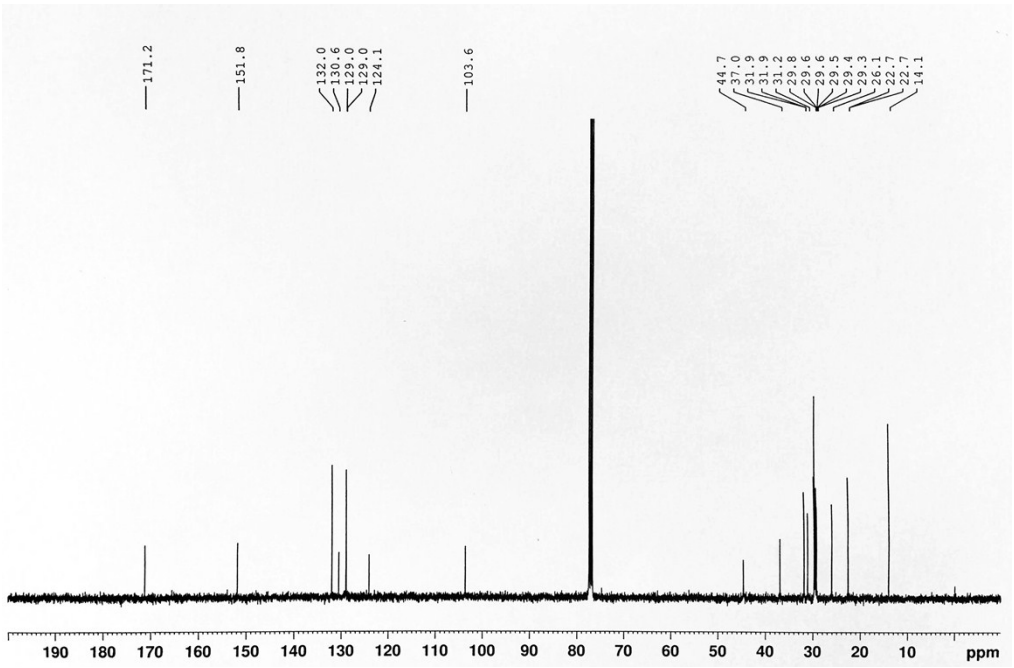


dibromo-BBPD

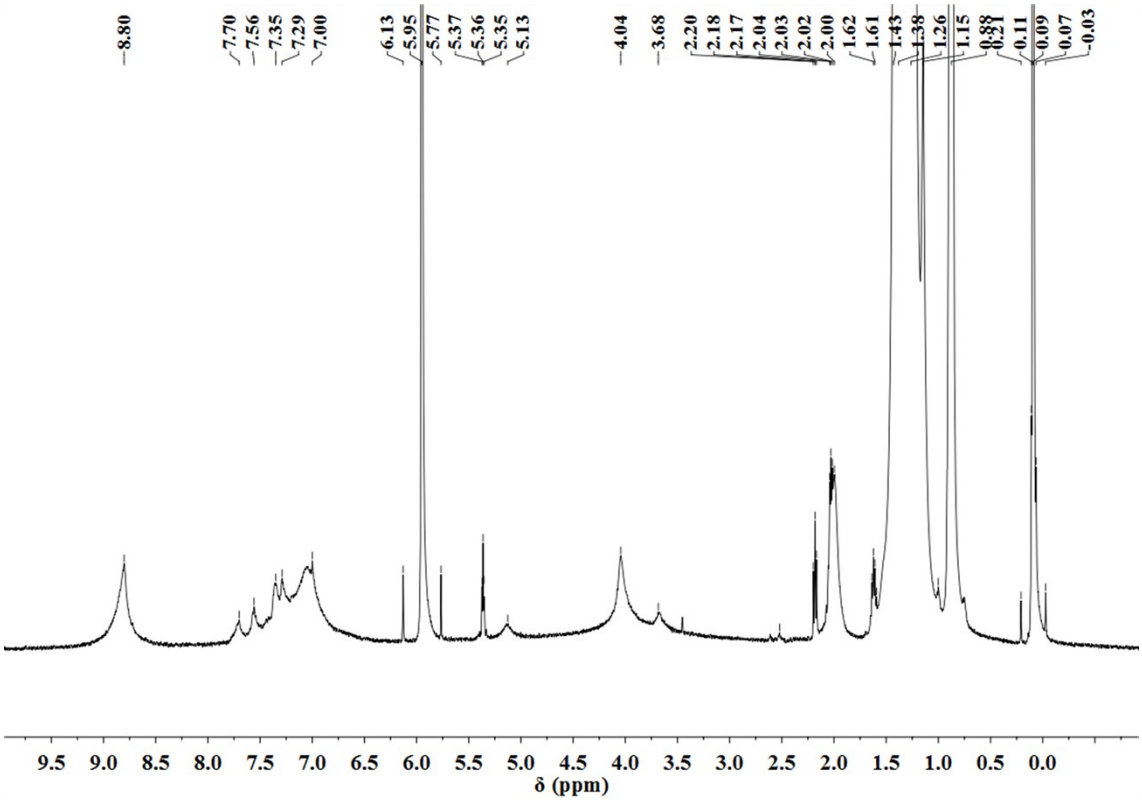
^{1}H NMR



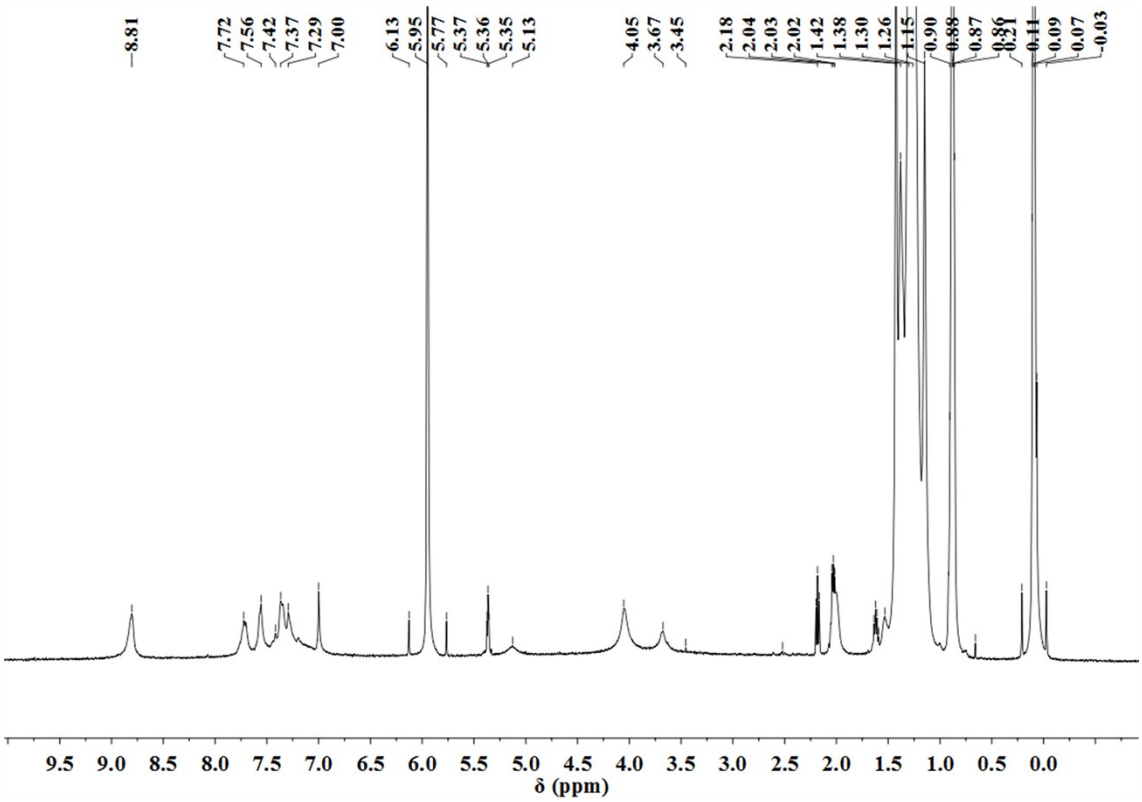
^{13}C NMR



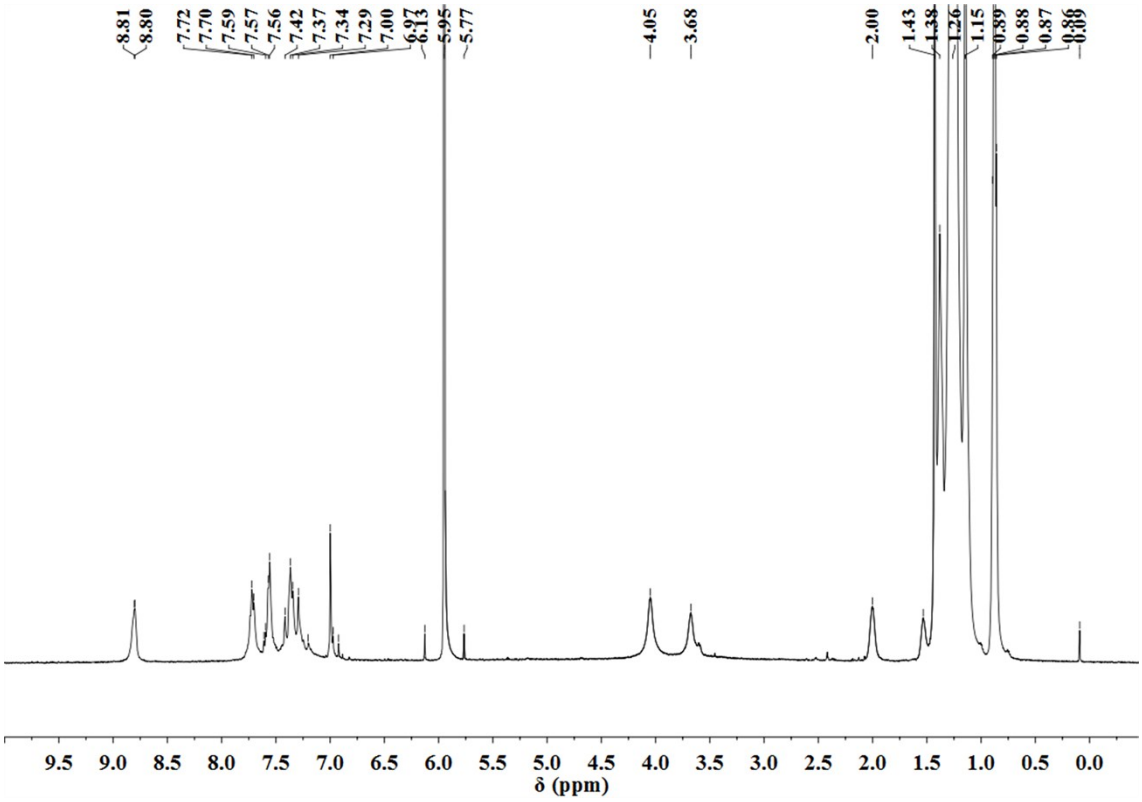
^{1}H NMR of **PBPD1**



^{1}H NMR of **PBPD2**



^{1}H NMR of **PBPD3**



^{1}H NMR of **PDPP3T**