Supporting Information

Alternating Conjugated Electron Donor-Acceptor Polymers Entailing Pechmann Dye Framework as the Electron Acceptor Moieties for High Performance Organic Semiconductors with Tunable Characteristics

Zhengxu Cai, Hewei Luo, Penglin Qi, Jianguo Wang, Guanxin Zhang, Zitong Liu*, Deqing Zhang*

Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
E-mail: dqzhang@iccas.ac.cn, drzitong@gmail.com

Table of Contents

1. Characterization techniques

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker ADVANCE III 300 MHz spectrometer, Bruker ADVANCE III 400 MHz spectrometer and Bruker AVANCE III 600 MHz spectrometer. MALDI-TOF MS spectra were recorded with BEFLEX III spectrometer. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. Solution and thin films absorption spectra were measured with JASCO V-570 UV-Vis spectrophtometer. TGA (SHIMADZU DTG-60) measurements were performed under nitrogen atmosphere at a heating rate of 10 °C/min.

Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt wires of 2.0 mm diameter as working and counter electrodes, and an Ag/AgCl reference electrode on a computer-controlled CHI660C instruments at room temperature; *n*-Bu_4NPF_6 was used as the conducting electrolyte. Ultraviolet photoelectron spectroscopy was measured by AXIS ULTRA DLD with the illuminant of He I.

The GIXRD data were measured at 1W1A, Beijing Synchrotron Radiation Facility. The thin-films were imaged in air using a Digital Instruments Nanoscope V atomic force microscope (AFM) operated in tapping mode with a Nanoscope V instrument.

2. TGA analysis

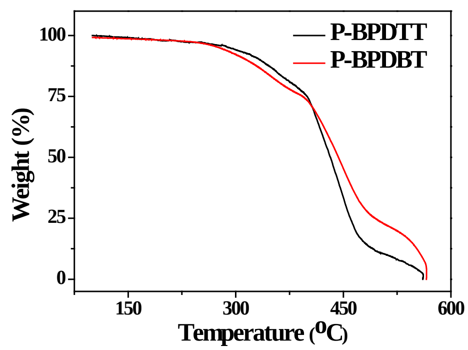


Figure S1. TGA curves of **P-BPDTT** and **P-BPDBT**: heating rate: 10 K/min. from 100 °C to 500 °C under nitrogen atmosphere.

3. Cyclic voltammetry and ultraviolet photoelectron spectroscopy

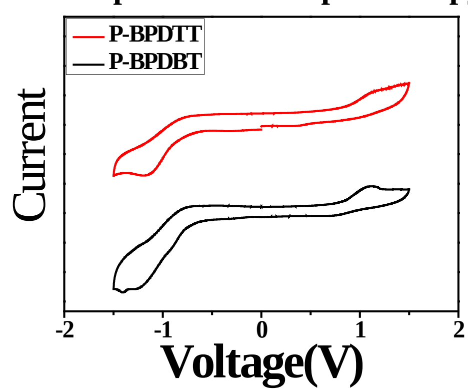


Figure S2. Cyclic voltammograms of **P-BPDTT** and **P-BPDBT** (in the form of thin films) at a scan rate of 50 mV s^{-1}, with Pt as the working and counter electrodes and an Ag/AgCl electrode (saturated KCl) as the reference electrode, and *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte.

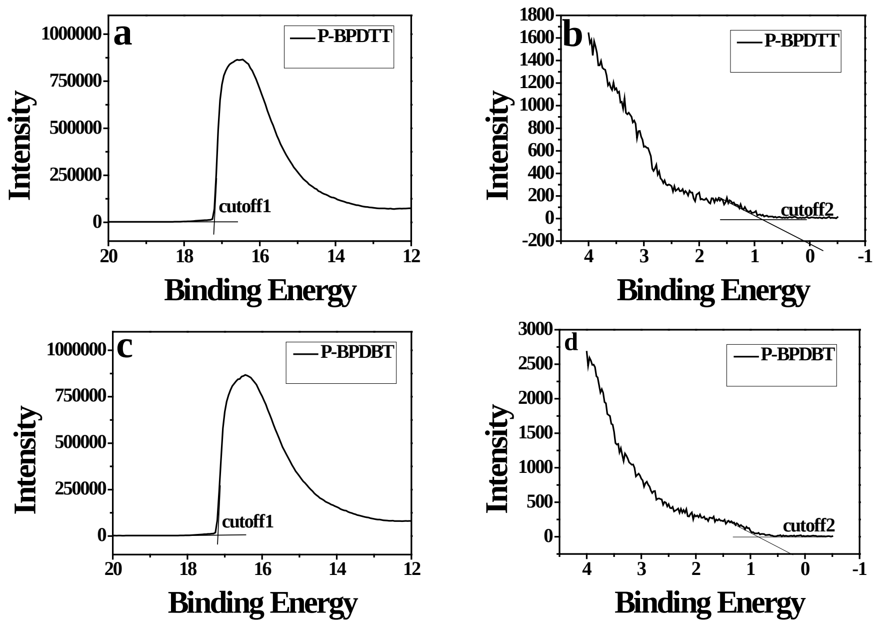


Figure S3. Ultraviolet photoelectron spectra (UPS) of **P-BPDTT** (a and b) and **P-BPDBT** (c and d) and $E_{IP}^{UPS} = h\nu - (E_{cutoff1} - E_{cutoff2})$, incident photon energy ($h\nu$ = 21.22 eV) for He I.

4. Density Funtional Theory calculations

Geometries optimization and frequency analysis were performed at the level of B3LYP /6-31G* by using Gaussian09 (revision A.02)[S1]. Table S1 and Table S2 listed the coordinates and energies at the optimized geometries for two repeated units of **P-BPDTT** and **P-BPDBT**, 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 of two repeated units of **P-BPDTT**

		X	Y	Z
1	C	-7.48135	1.627749	0.590757
2	C	-7.68625	0.247701	0.053775
3	C	-9.08698	0.048948	-0.03112
4	C	-9.72399	1.200345	0.397813
5	N	-8.7647	2.163377	0.760734
6	C	-6.64562	-0.59726	-0.28339
7	C	-5.24459	-0.39892	-0.19732
8	C	-4.60785	-1.55147	-0.62328
9	N	-5.56775	-2.51431	-0.98617
10	C	-6.85085	-1.97727	-0.81911
11	O	-7.88979	-2.56454	-1.09222
12	O	-6.44257	2.215693	0.862507
13	C	-3.18952	-1.77443	-0.68984
14	C	-11.1429	1.420968	0.469825
15	C	-2.45136	-2.94891	-0.72145
16	C	-1.05651	-2.74578	-0.71731

17	C	-0.68497	-1.41172	-0.69073
18	S	-2.10702	-0.38628	-0.69143
19	C	-11.8835	2.592932	0.508368
20	C	-13.279	2.385846	0.507062
21	C	-13.6458	1.051833	0.475554
22	S	-12.2224	0.030369	0.470219
23	C	-8.95728	3.447025	1.407257
24	C	-5.37544	-3.79784	-1.63297
25	C	0.639129	-0.8464	-0.67575
26	C	1.030551	0.432121	-1.03211
27	C	2.422148	0.621506	-0.88261
28	C	3.111235	-0.49696	-0.41039
29	S	2.019739	-1.83246	-0.15276
30	S	3.514051	1.956467	-1.14172
31	C	4.88974	0.979984	-0.58895
32	C	4.499646	-0.30113	-0.2409
33	C	-14.9703	0.479728	0.462024
34	C	-15.3539	-0.78257	0.055572
35	C	-16.7508	-0.98116	0.186027
36	C	-17.4451	0.118397	0.685667
37	S	-16.3556	1.436841	1.023743
38	S	-17.8456	-2.29837	-0.14967
39	C	-19.2039	-1.33681	0.391624
40	C	-18.8492	-0.08183	0.804469
41	C	12.37425	2.151802	-0.49316
42	C	12.16265	0.756121	0.000483
43	C	10.75947	0.548724	0.042562
44	C	10.1293	1.708456	-0.36963
45	N	11.09319	2.686143	-0.68062
46	C	13.19671	-0.09154	0.343531
47	C	14.60133	0.114946	0.303962
48	C	15.22748	-1.04351	0.719242
49	N	14.26434	-2.02067	1.028957
50	C	12.98355	-1.48696	0.837402
51	O	11.94061	-2.08634	1.064997
52	O	13.41659	2.750901	-0.72265
53	C	16.64971	-1.26765	0.829269
54	C	8.711508	1.92705	-0.46904
55	C	17.38645	-2.43873	0.798551
56	C	18.78855	-2.22857	0.883395
57	C	19.12255	-0.90404	0.984772
58	S	17.72526	0.114888	0.982561
59	C	7.968319	3.098251	-0.48224
60	C	6.574709	2.88849	-0.52277
61	C	6.210423	1.552608	-0.54999
62	S	7.637771	0.534709	-0.54597

63	C	10.91028	3.984465	-1.30021
64	C	14.44832	-3.3188	1.649034
65	H	-9.56669	-0.83816	-0.41448
66	H	-4.76491	0.488017	0.186592
67	H	-2.8998	-3.9324	-0.70398
68	H	-0.33733	-3.55696	-0.70866
69	H	-11.438	3.57783	0.492689
70	H	-14.0012	3.194264	0.501359
71	H	-9.66637	3.368072	2.235652
72	H	-9.30637	4.212064	0.704887
73	H	-7.98172	3.752725	1.788946
74	H	-4.66404	-3.71959	-2.45948
75	H	-5.02964	-4.56412	-0.93029
76	H	-6.35048	-4.10173	-2.01747
77	H	0.334195	1.191808	-1.36599
78	H	5.189338	-1.04731	0.134681
79	H	-14.658	-1.51463	-0.33617
80	H	-20.1952	-1.7678	0.370876
81	H	-19.5559	0.651927	1.171591
82	H	10.2745	-0.35023	0.390007
83	H	15.08903	1.013315	-0.04088
84	H	16.94165	-3.41765	0.682892
85	H	19.5186	-3.02926	0.864669
86	H	20.10774	-0.46684	1.069109
87	H	8.410836	4.082676	-0.42013
88	H	5.85087	3.695402	-0.50673
89	H	11.89284	4.302204	-1.65309
90	H	10.21957	3.92336	-2.14546
91	H	10.54358	4.731679	-0.58767
92	H	13.46976	-3.63036	2.018113
93	H	15.15362	-3.25895	2.48184
94	H	14.79991	-4.06994	0.93304

Total energy: = -5552.6128138 Hartrees

Table S2. Coordinates and energy of two repeated units of **P-BPDBT**

		X	**Y**	**Z**
1	C	-8.00727	1.769976	0.277327
2	C	-8.10775	0.278979	0.30798
3	C	-9.4891	-0.03545	0.288106
4	C	-10.2118	1.145073	0.261561
5	N	-9.32731	2.239406	0.269909
6	C	-7.00565	-0.55426	0.357382
7	C	-5.6246	-0.23843	0.393437
8	C	-4.90233	-1.41717	0.462554
9	N	-5.78709	-2.51141	0.479409
10	C	-7.10558	-2.04458	0.396011

11	O	-8.09499	-2.76444	0.350622
12	O	-7.01563	2.48733	0.246502
13	C	-3.47189	-1.54486	0.517228
14	C	-11.6428	1.275658	0.236053
15	C	-2.66346	-2.58854	0.945166
16	C	-1.28511	-2.29679	0.901681
17	C	-0.99585	-1.02584	0.433407
18	S	-2.47559	-0.18143	0.019506
19	C	-12.4688	2.337374	0.575705
20	C	-13.8442	2.044483	0.475243
21	C	-14.1128	0.754459	0.049289
22	S	-12.6165	-0.10841	-0.24985
23	C	-9.61542	3.649324	0.092504
24	C	-5.49178	-3.92808	0.390515
25	C	4.200151	0.004226	0.057147
26	S	5.19161	1.45222	-0.03678
27	C	6.676525	0.511607	-0.0409
28	C	6.385668	-0.83777	0.046994
29	C	5.003945	-1.12079	0.101921
30	C	-15.3886	0.119149	-0.16072
31	S	-16.8808	1.047778	-0.10901
32	C	-17.8533	-0.37559	-0.4419
33	C	-17.0429	-1.48583	-0.57589
34	C	-15.6658	-1.21033	-0.41697
35	C	-19.2933	-0.28242	-0.53612
36	C	-20.0866	0.840828	-0.64975
37	C	-21.4771	0.550372	-0.72157
38	C	-21.7443	-0.78993	-0.66393
39	S	-20.2934	-1.72705	-0.50875
40	C	14.06681	2.170912	0.096329
41	C	13.97349	0.6903	-0.09205
42	C	12.59207	0.378532	-0.18075
43	C	11.86708	1.551341	-0.07563
44	N	12.7471	2.639604	0.076559
45	C	15.07729	-0.13485	-0.17043
46	C	16.46049	0.176043	-0.0839
47	C	17.18177	-0.99629	-0.19198
48	N	16.30255	-2.08395	-0.34253
49	C	14.98265	-1.61523	-0.35851
50	O	13.9964	-2.32307	-0.51758
51	O	15.05242	2.878529	0.257772
52	C	18.61861	-1.13585	-0.15573
53	C	10.43588	1.683952	-0.11998
54	C	19.41536	-2.21641	0.180185
55	C	20.80571	-1.92828	0.144264
56	C	21.07171	-0.63588	-0.22316

57	S	19.62352	0.255614	-0.53746
58	C	9.629771	2.774552	-0.41191
59	C	8.251259	2.478997	-0.41742
60	C	7.960821	1.1573	-0.12285
61	S	9.438712	0.26648	0.186637
62	C	12.44285	4.023989	0.382657
63	C	16.60833	-3.46842	-0.64743
64	C	0.287573	-0.39668	0.261872
65	S	1.77513	-1.32314	0.403063
66	C	2.762878	0.094398	0.081194
67	C	1.956757	1.200318	-0.12093
68	C	0.576019	0.92673	-0.01917
69	H	-9.89976	-1.03222	0.331147
70	H	-5.21631	0.760166	0.40764
71	H	-3.05172	-3.52506	1.320432
72	H	-0.51947	-2.99193	1.227193
73	H	-12.0976	3.289623	0.928173
74	H	-14.6236	2.754192	0.728606
75	H	-10.0175	4.104491	1.004388
76	H	-8.66583	4.133744	-0.14096
77	H	-10.3187	3.807013	-0.72958
78	H	-6.42962	-4.42539	0.137409
79	H	-5.13467	-4.33398	1.343493
80	H	-4.75001	-4.12809	-0.38743
81	H	7.152464	-1.60411	0.049771
82	H	4.603537	-2.12688	0.153806
83	H	-17.4325	-2.47384	-0.79296
84	H	-14.8943	-1.96916	-0.48277
85	H	-19.6802	1.844899	-0.69711
86	H	-22.246	1.307934	-0.81871
87	H	-22.7032	-1.28744	-0.70177
88	H	12.1878	-0.60669	-0.35364
89	H	16.86732	1.16055	0.086532
90	H	19.01882	-3.1774	0.478205
91	H	21.57581	-2.65121	0.386681
92	H	22.03429	-0.15673	-0.3359
93	H	10.01996	3.752295	-0.65816
94	H	7.486823	3.210218	-0.65466
95	H	13.37433	4.479988	0.722266
96	H	11.69031	4.095998	1.172408
97	H	12.09414	4.572477	-0.4994
98	H	15.68107	-3.92298	-1.00019
99	H	16.94521	-4.01902	0.237883
100	H	17.37206	-3.53896	-1.42615
101	H	2.354532	2.184177	-0.34228
102	H	-0.19242	1.682007	-0.13879

Total energy: -5707.4494474 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.

5. Characterization of OFETs with different channel widths and lengths

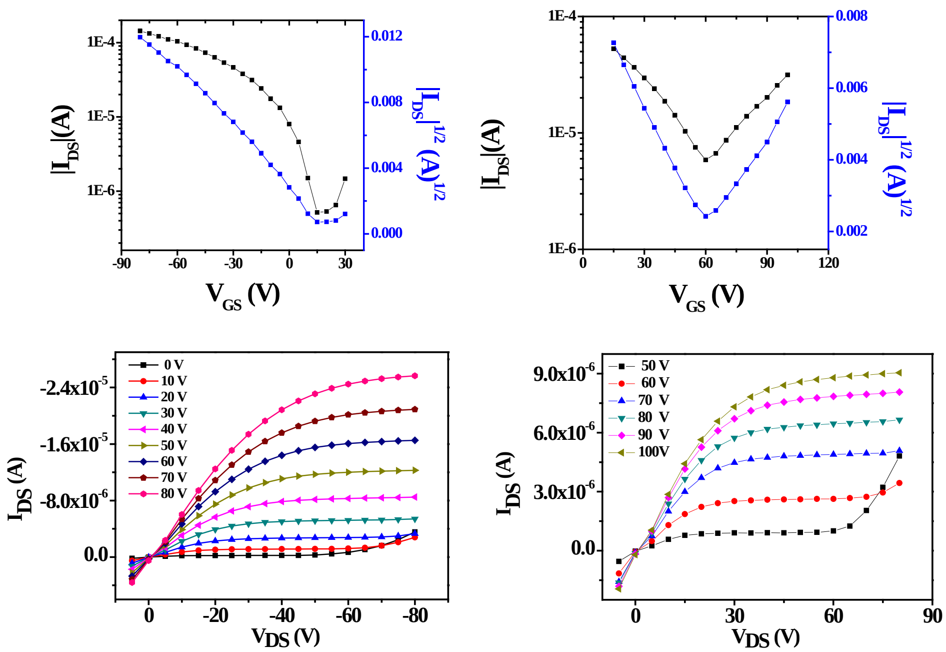


Figure S4. The transfer and output characteristics of OFET devices based on **P-BPDTT** annealed at 200 °C (V_{DS} for transfer characteristics are -100 V and 100 V, respectively). The channel width (*W*) and length (*L*) were 1400 μm and 50 μm, respectively.

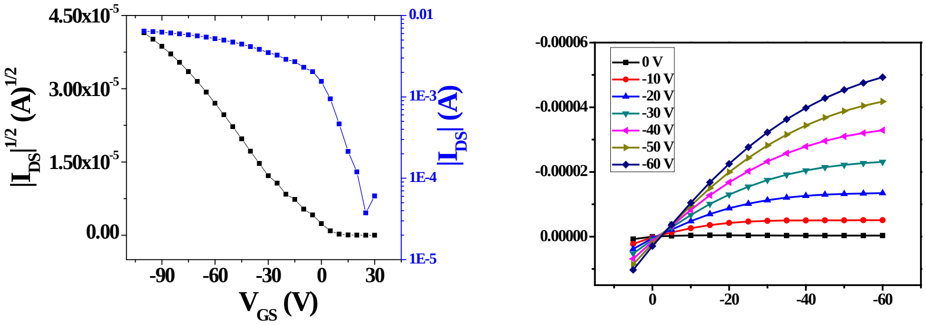


Figure S5. the transfer and output characteristics for OFET with **P-BPDBT** after annealing at 120 °C; the channel width (W) and length (L) were 1400 μm and 50 μm, respectively.

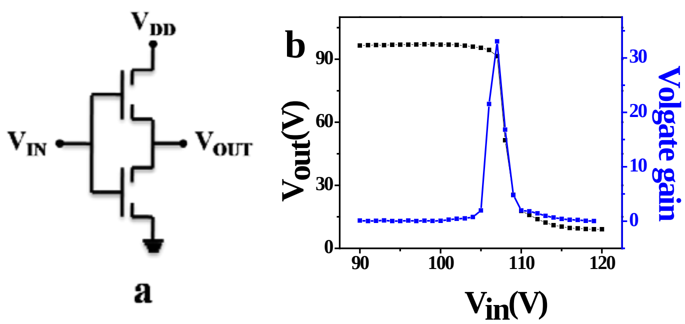
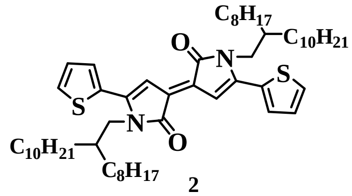
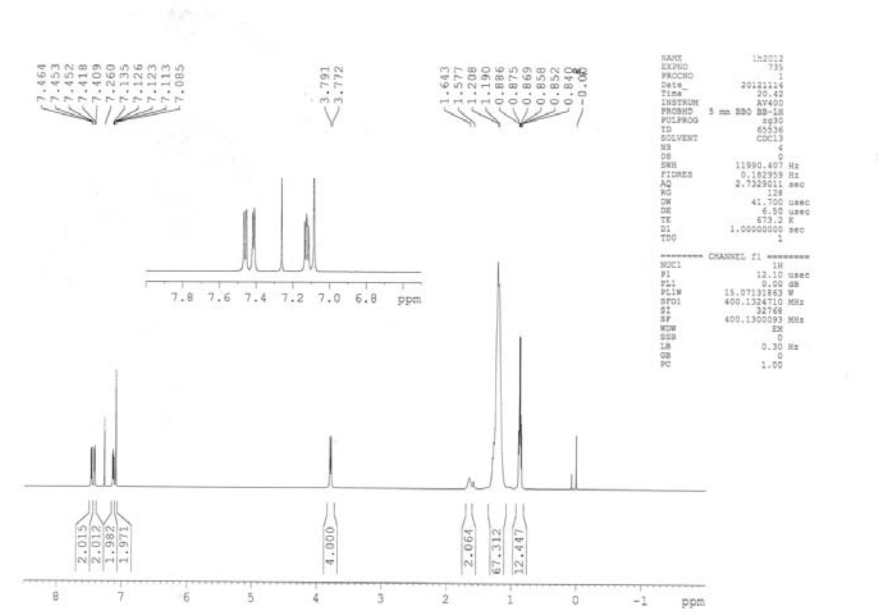


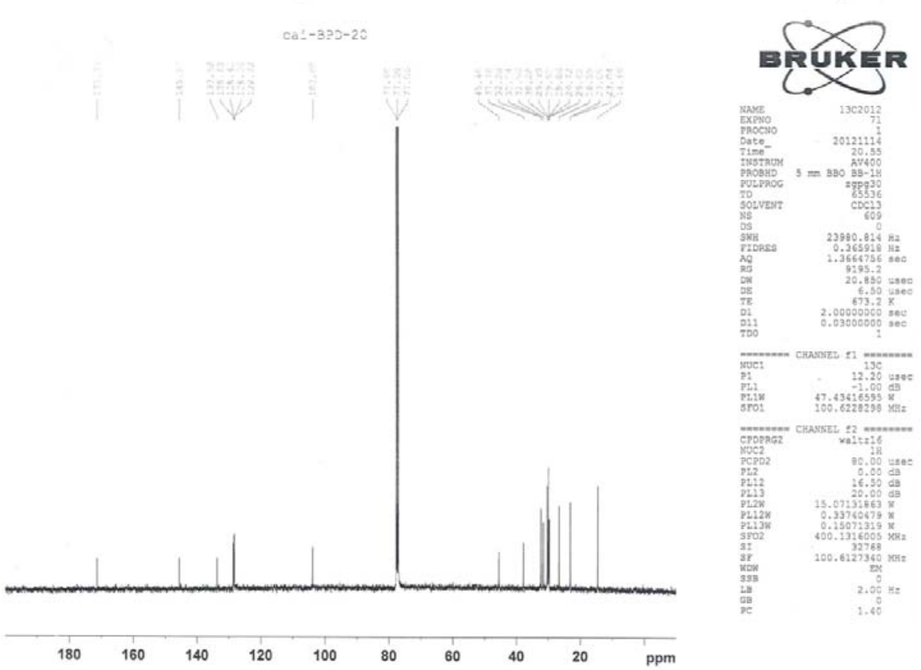
Figure S6. Complementary inverters fabricated with thin-films of **2**: (a) Schematic electrical layout of the inverters; (b) Static switching characteristics and gain data of a spin-coated inverter on OTS-treated Si / SiO_2 substrate annealed at 200 ^{o}C.

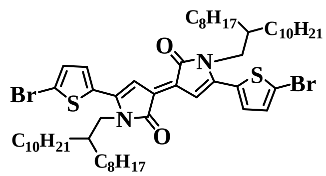
6. ^{1}H-NMR and ^{13}C-NMR spectra



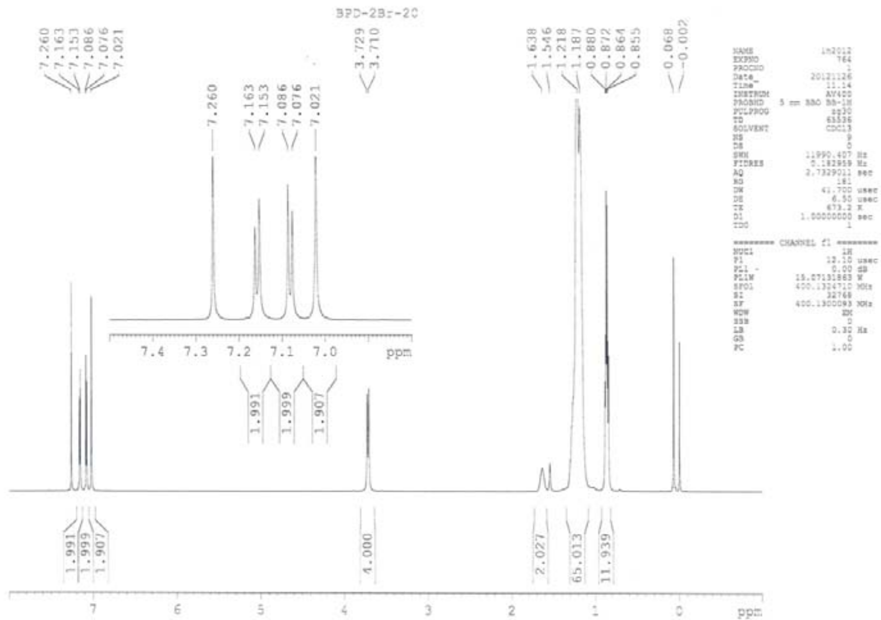
2

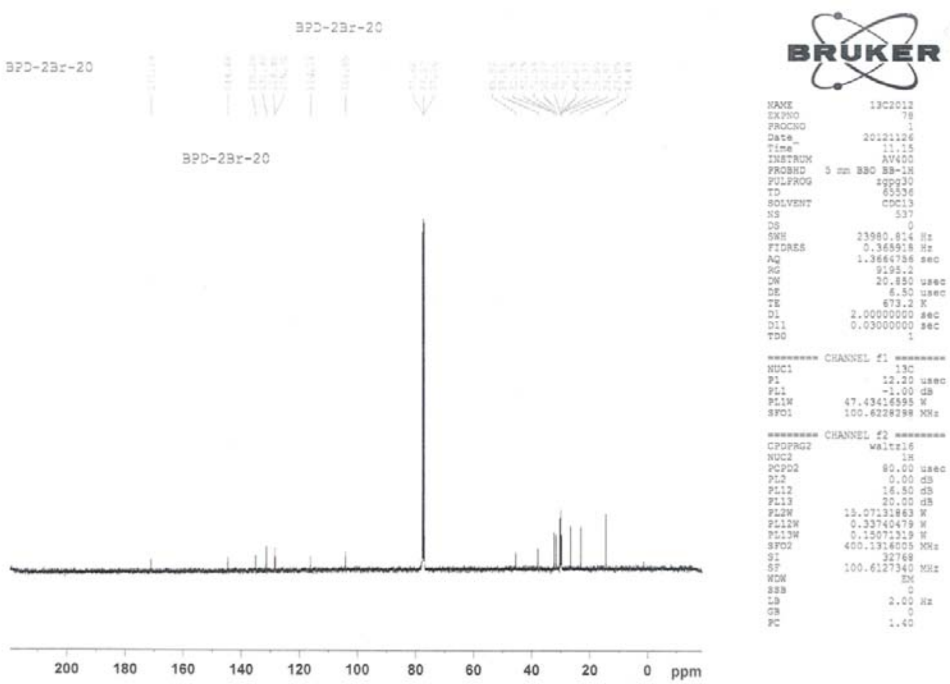


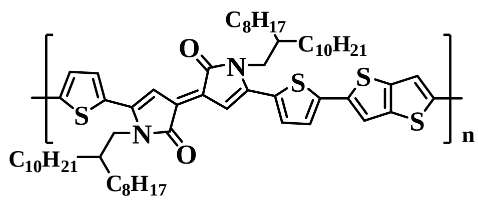



C8H17
C10H21
O
N
S
Br
Br
S
N
O
C10H21
C8H17

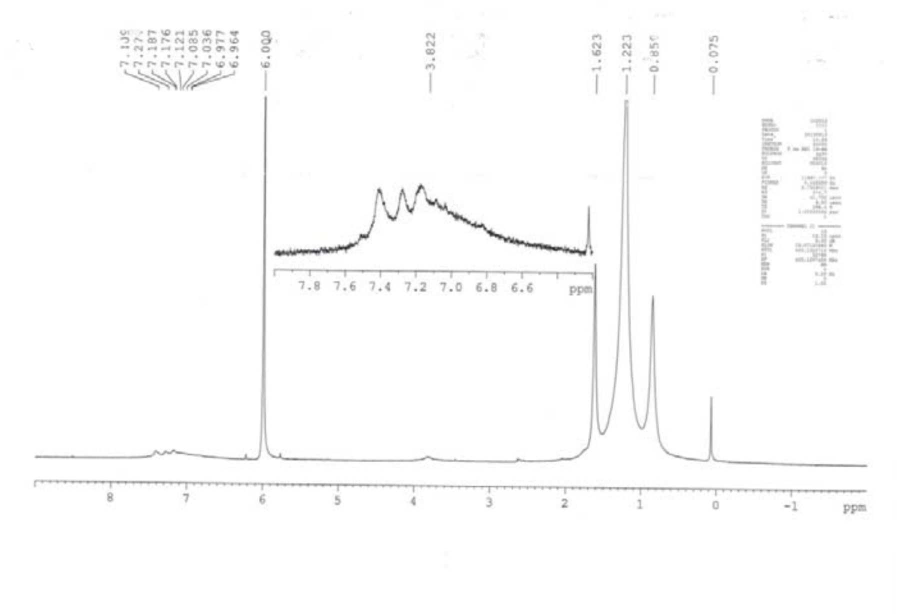
3


BPD-2Br-20
ppm

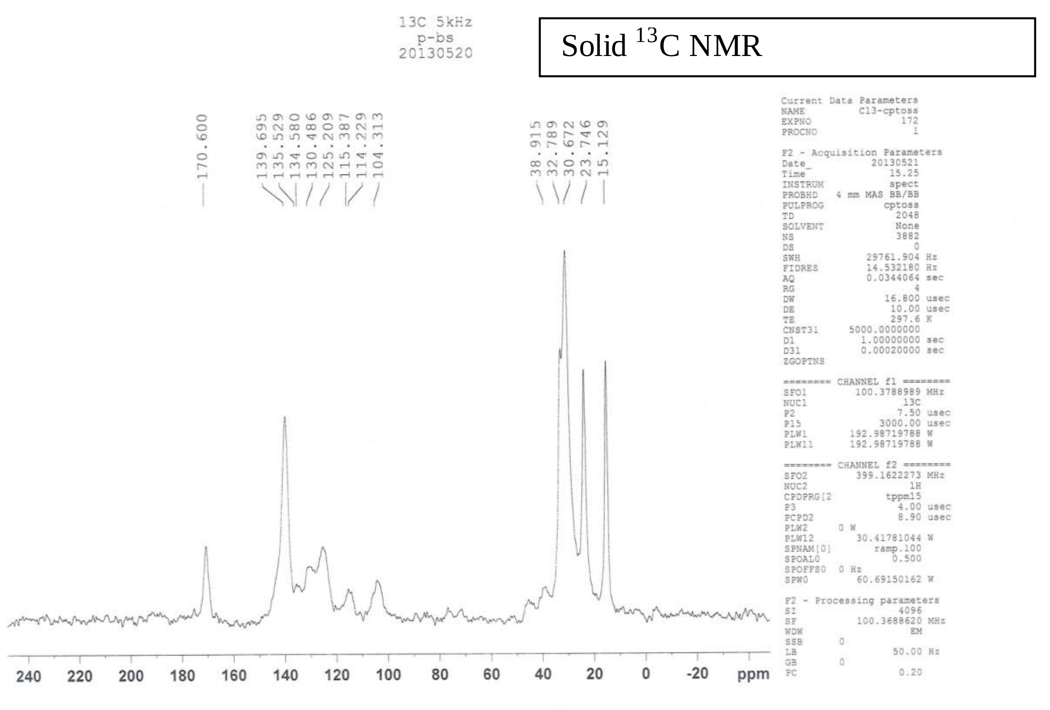

BPD-2Br-20
BRUKER
ppm



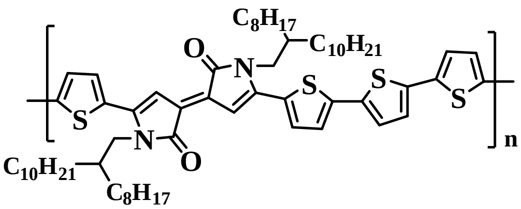
P-BPDTT



6.000
3.822
1.623
1.223
0.075
7.8 7.6 7.4 7.2 7.0 6.8 6.6 ppm
8 7 6 5 4 3 2 1 0 -1 ppm



13C 5kHz
p-bs
20130520
Solid ^{13}C NMR
170.600
139.695
135.529
134.580
130.486
125.209
115.387
114.229
104.313
38.915
32.789
30.672
23.746
15.129
Current Data Parameters
NAME C13-cptoss
EXPNO 172
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130521
Time 15.25
INSTRUM spect
PROBHD 4 mm MAS BB/BB
PULPROG cptoss
TD 2048
SOLVENT None
NS 3882
DS 0
SWH 29761.904 Hz
FIDRES 14.532180 Hz
AQ 0.0344064 sec
RG 4
DW 16.800 usec
DE 10.00 usec
TE 297.6 K
CNST31 5000.0000000
D1 1.00000000 sec
D31 0.00020000 sec
ZGOPTNS
======== CHANNEL f1 ========
SFO1 100.3788989 MHz
NUC1 13C
P2 7.50 usec
P15 3000.00 usec
PLW1 192.98719788 W
PLW11 192.98719788 W
======== CHANNEL f2 ========
SFO2 399.1622273 MHz
NUC2 1H
CPDPRG[2 tppm15
P3 4.00 usec
PCPD2 8.90 usec
PLW2 0 W
PLW12 30.41781044 W
SPNAM[0] ramp.100
SPOAL0 0.500
SPOFFS0 0 Hz
SPW0 60.69150162 W
F2 - Processing parameters
SI 4096
SF 100.3688620 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 ppm



P-BPDBT