Supporting Information

Solution-processed core-extended naphthalene diimides toward organic n-type and ambipolar semiconductors

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Contents

1. Materials and general methods

Materials. The reagents and starting materials were commercially available and used without any further purification if not specified elsewhere. **TBNDI** and sodium *1,1*-dicyanoethylene-*2,2*-dithiolate were synthesized according to the reported procedures.[S1-S2] Compounds **5-6** were also synthesized according to the previous report[S3] and the crude compounds were used without further purification.

General methods. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker DMX-400 NMR Spectrometer using tetramethylsilane as an internal standard. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. MALDI-TOF MS were recorded with BEFLEX III spectrometer. Thin films absorption spectra were measured with JASCO V-570 UV-Vis spectrophotometer. TGA-DTA measurements were carried out on a SHIMADZU DTG-60 instruments under a dry nitrogen flow, heating from room temperature to 500 ^{o}C, with a heating rate of 10 ^{o}C/min. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button as working electrodes of 2 mm diameter, a platinum wire as counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI660C instrument at room tempera-ture. X-ray diffraction (XRD) measurements were carried out in the reflection mode at room temperature using a 2 kW Rigaku X-ray diffraction system. Atomic force microscopy (AFM) images of the thin films were obtained on a Nanoscope IIIa AFM (Digital In struments) operating in tapping mode. The molecular structures of the compounds were optimized using the DFT method at B3LYP/6-31G(d) level. All calculations were performed with the programs Gaussian 03.

S1. X. Gao, W. Qiu, X. Yang, Y. Liu, Y. Wang, H. Zhang, T. Qi, Y. Liu, K. Lu, C. Du, Z. Shuai, G. Yu and D. Zhu, *Org. Lett.*, 2007, **9**, 3917.

S2. C. Rögerr and F. Würthner, J. Org. Chem., 2007, **72**, 8070.

S3. B. Chenard, R. Harlow, A. Johnson and S. Valduchick, *J. Am. Chem. Soc.*, 1985, **107**, 3871.

2. Synthesis of compounds 5 and 6

Compound 5. Under nitrogen atmosphere 1,2-benzenedithiol (500 mg, 3.5 mmol) was dissolved in 10 ml of NaOH (5%, wt%) solution. After 5.0 min, tetra-*n*-butylammonium bromide (1.15 g, 3.57 mmol) in 5 ml of water was added, followed by addition of zinc chloride (365.58 mg, 1.75 mmol) in 5.0 ml of ethanol. The reaction mixture was stirred at room temperature for 2.0 h and then filtered and dried. The collected white solid (1.4 g, 96%) was used in following steps without further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.16 (s, 4H), 6.37 (s, 4H), 3.15 (t, J = 7.48 Hz, 16H), 1.56 (b, 16H), 1.31 (b, 16H), 0.93 (t, J = 7.08, 24H). MS (ESI)

m/z: 172.8 [M-2(*n*-Bu_4N)]$^{2-}$, 242.2[*n*-Bu_4N]$^+$, 586.1 [M- (*n*-Bu_4N)]$^-$.

Compound 6. A portion of 5.4 mL of *n*-butyllithium (1.3 M in hexane, 7.0 mmol) was added dropwise to a solution of 2, 3-dibromonaphthalene (500 mg, 1.75 mmol) and sublimed sulfur (112 mg, 3.5 mmol) in anhydrous THF (10 mL) under argon atmosphere at -78 ^oC. After 30 min, the reaction was quenched by 2.0 ml of NaOH solution (1.0 M). Tetra-*n*-butylammonium bromide (675 mg, 2.1 mmol) in 5.0 ml of water and zinc chloride (182 mg, 0.88 mmol) in 5 ml of ethanol was injected to the reaction mixture in sequence. The mixture was warmed up to room temperature and stirred 2.0 h and then filtered and dried. The collected yellow solid (350 mg, 22%) was used in following steps without further purification. ^1H NMR (400 MHz, DMSO-d_6) δ 7.69 (s, 4H), 7.34 (s, 4H), 6.99 (s, 4H), 3.15 (t, J = 7.36 Hz, 16H), 1.55 (b, 16H), 1.30 (b, 16H), 0.93 (t, J = 7.02, 24H). MS (ESI) m/z: 222.9 [M-2(*n*-Bu_4N)]$^{2-}$, 242.2[*n*-Bu_4N]$^+$, 686.0 [M- (*n*-Bu_4N)]$^-$.

3. TGA and DSC analysis data for1-4

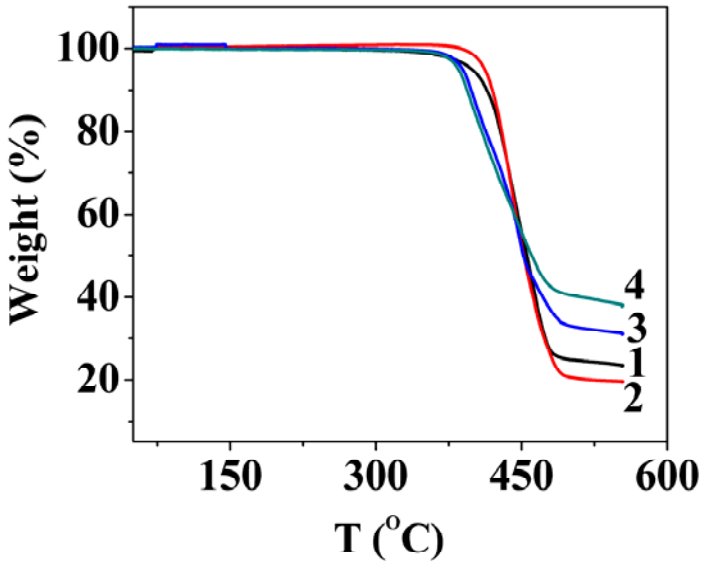


Figure S1. TGA curves of **1-4**

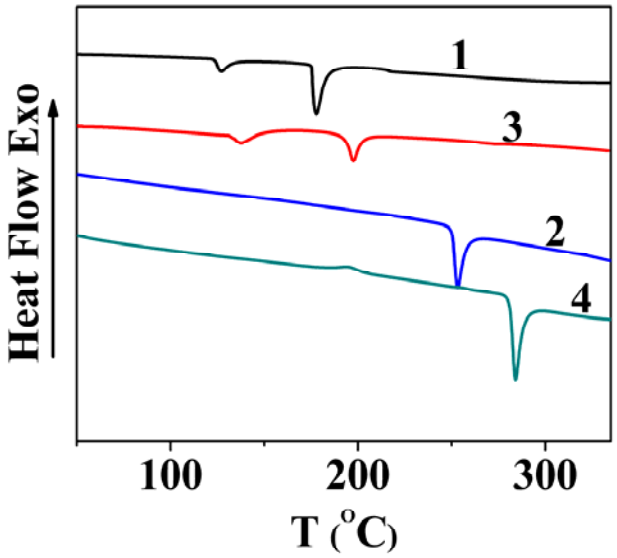


Figure S2. DSC curves of **1-4**

4. **Cyclic voltammograms of *N,N'*-hexyl NDI**

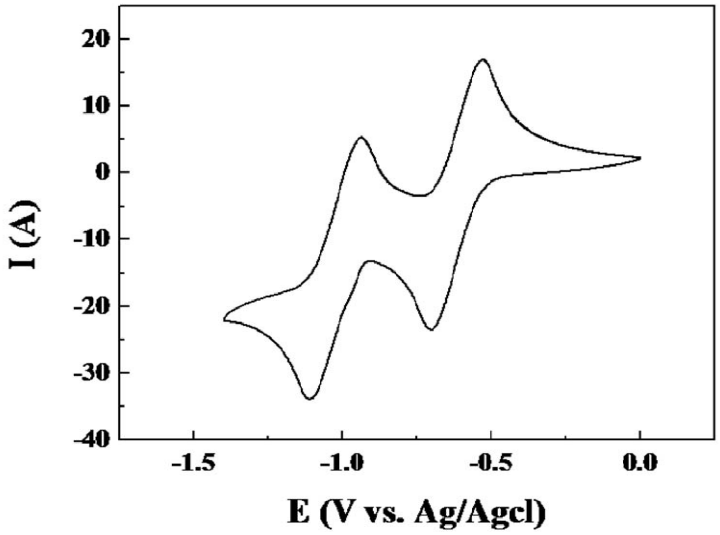
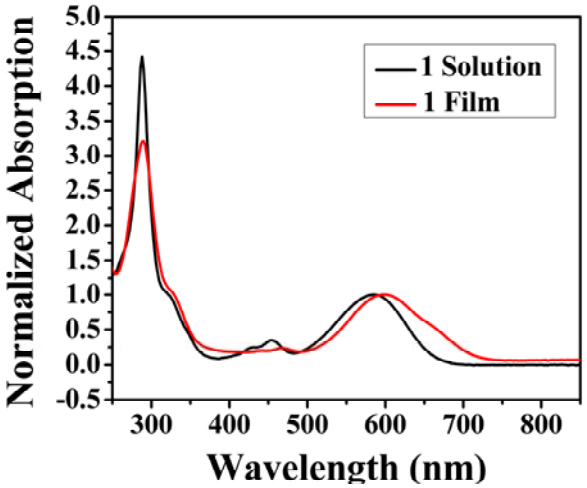
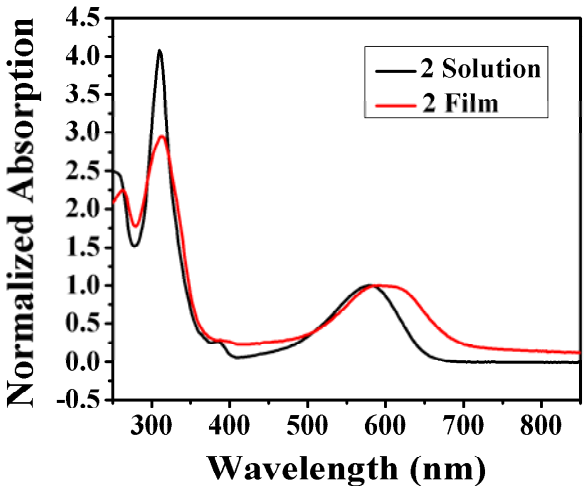
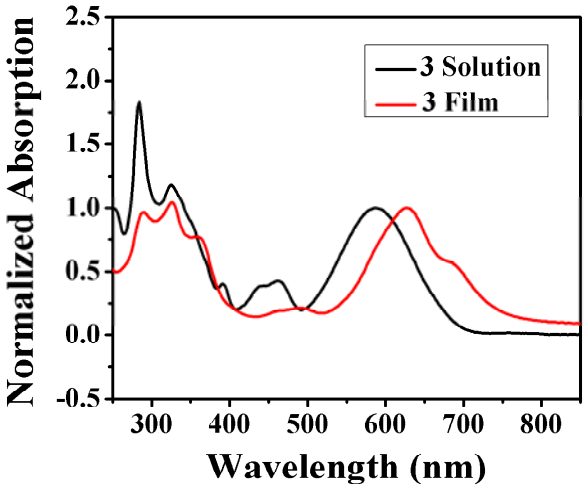


Figure S3. Cyclic voltammogram of *N,N'*-hexyl NDI (1.0 mM) in CH_2Cl_2 at a scan rate of 50 mVs^{-1}, with Pt as the working and counter electrodes and Ag/AgCl electrode (saturated KCl) as the reference electrode, and *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte.

5. Absorption spectra of 1-4 and N, N'-hexyl NDI







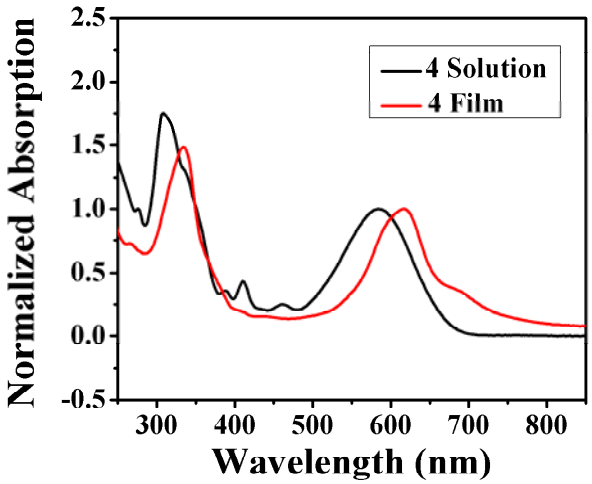


Figure S4. Absorption spectra of solutions of **1-4** (1.0×10^{-5} M) in CH_2Cl_2 and those of their thin-films.

6. DFT calculation data

Table S1. Coordinates and energy of compound **1**

		X	Y	Z
1	C	-2.403781	-0.717818	0.504728
2	C	-2.403767	0.718367	0.504402
3	C	-1.194395	1.403375	0.312368
4	C	0.002793	0.707039	-0.010534
5	C	0.002698	-0.706830	-0.010544
6	C	-1.194538	-1.402961	0.312569
7	C	1.199542	1.404454	-0.332445
8	C	2.409918	0.718056	-0.516735
9	C	2.409827	-0.718268	-0.516707
10	C	1.199309	-1.404473	-0.332509
11	C	1.124201	-2.871503	-0.537940
12	N	0.001381	-3.518244	-0.016161
13	C	-1.115203	-2.869349	0.508347
14	C	-1.115044	2.869773	0.507859
15	N	0.002450	3.518441	-0.015058
16	C	1.124675	2.871516	-0.537794
17	S	-3.880864	-1.658321	0.865692
18	C	-5.150418	-0.696802	0.068813
19	C	-5.150419	0.696798	0.068293
20	S	-3.880941	1.659036	0.864449
21	S	3.892367	1.655736	-0.865801
22	C	5.150005	0.696552	-0.047577

23	C	5.149921	-0.696997	-0.047537
24	S	3.892167	-1.656149	-0.865617
25	C	-6.202415	-1.395569	-0.537216
26	C	-7.268093	-0.698752	-1.103309
27	C	-7.268091	0.697851	-1.103843
28	C	-6.202417	1.395100	-0.538277
29	C	6.191999	1.395265	0.575399
30	C	7.248417	0.698009	1.158199
31	C	7.248342	-0.698617	1.158230
32	C	6.191848	-1.395789	0.575472
33	O	-1.980097	-3.520102	1.081354
34	O	1.995702	-3.503645	-1.120893
35	O	-1.980604	3.520826	1.079550
36	O	1.995950	3.503474	-1.121274
37	C	-0.023797	-4.986572	0.007452
38	C	-0.022463	4.986765	0.009052
39	H	-6.182025	-2.480991	-0.554571
40	H	-8.088615	-1.246272	-1.556438
41	H	-8.088610	1.245027	-1.557393
42	H	-6.182032	2.480509	-0.556458
43	H	6.171416	2.480671	0.592765
44	H	8.061674	1.245239	1.624596
45	H	8.061550	-1.245910	1.624638
46	H	6.171154	-2.481193	0.592898
47	H	0.868279	-5.341102	-0.501830
48	H	-0.045215	-5.337887	1.041070
49	H	-0.922282	-5.346627	-0.496766
50	H	0.877543	5.341242	-0.486102
51	H	-0.060385	5.336653	1.042559
52	H	-0.912463	5.348299	-0.509227

Total energy: -3078.6631212 Hartrees

Table S2. Coordinates and energy of compound **2**

		X	**Y**	**Z**
1	C	-2.350058	-0.861472	0.765796
2	C	-2.338755	0.575000	0.783822
3	C	-1.151096	1.252261	0.468680
4	C	-0.001415	0.550610	0.009463
5	C	-0.002140	-0.864962	0.008273
6	C	-1.170830	-1.553868	0.450178
7	C	1.149471	1.250167	-0.449355
8	C	2.335207	0.572928	-0.769091
9	C	2.345185	-0.863527	-0.753269

10	C	1.165756	-1.554731	-0.435224
11	C	1.086743	-3.025547	-0.599665
12	N	-0.003458	-3.630334	0.007554
13	C	-1.092991	-3.024842	0.615102
14	C	-1.044925	2.718131	0.674187
15	N	0.000674	3.366064	0.013656
16	C	1.041122	2.715423	-0.645984
17	S	-3.788165	-1.797638	1.262679
18	C	-5.130770	-0.823427	0.618537
19	C	-5.118352	0.590254	0.642093
20	S	-3.759253	1.517499	1.320929
21	S	3.751675	1.517942	-1.311343
22	C	5.115926	0.589022	-0.645430
23	C	5.127576	-0.824674	-0.621732
24	S	3.780735	-1.800136	-1.255374
25	C	-6.232684	-1.499690	0.134776
26	C	-7.384515	-0.798175	-0.304487
27	C	-7.372223	0.634213	-0.280598
28	C	-6.208539	1.300741	0.181445
29	C	6.210412	1.298812	-0.193915
30	C	7.377333	0.631706	0.258920
31	C	7.388729	-0.800666	0.283429
32	C	6.232953	-1.501413	-0.146473
33	O	-1.904858	-3.703753	1.227127
34	O	1.898485	-3.705416	-1.210914
35	O	-1.831271	3.347358	1.370005
36	O	1.823605	3.362515	-1.330318
37	C	0.022007	4.834294	-0.014465
38	C	-8.542596	-1.468674	-0.781256
39	C	-9.638213	-0.755893	-1.212442
40	C	-9.626088	0.660668	-1.188798
41	C	-8.518566	1.339864	-0.734415
42	C	8.527809	1.336712	0.703184
43	C	9.638372	0.656871	1.149099
44	C	9.649573	-0.759693	1.173450
45	C	8.550017	-1.471846	0.751360
46	H	-0.003485	-4.644323	0.007958
47	H	-6.225727	-2.585396	0.094581
48	H	-6.183057	2.386923	0.177695
49	H	6.185653	2.385015	-0.190225
50	H	6.225607	-2.587112	-0.105954
51	H	-0.800155	5.189015	0.601291
52	H	-0.085029	5.184081	-1.043244
53	H	0.975674	5.195519	0.374492

54	H	-8.549153	-2.555086	-0.798810
55	H	-10.518637	-1.278506	-1.573979
56	H	-10.497362	1.210016	-1.532451
57	H	-8.506629	2.426228	-0.715776
58	H	8.516570	2.423072	0.684054
59	H	10.512792	1.205712	1.485497
60	H	10.532424	-1.282791	1.528301
61	H	8.555846	-2.558254	0.769464

Total energy: -3346.6450677 Hartrees

Table S3. Coordinates and energy of compound **3**

		X	**Y**	**Z**
1	C	-2.501870	0.721389	-0.437812
2	C	-2.501878	-0.721201	-0.437987
3	C	-1.276642	-1.409370	-0.447832
4	C	-0.047967	-0.708129	-0.315631
5	C	-0.047944	0.708259	-0.315632
6	C	-1.276616	1.409547	-0.447674
7	C	1.177894	-1.407489	-0.171167
8	C	2.375104	-0.709625	-0.009074
9	C	2.375150	0.709624	-0.009172
10	C	1.177967	1.407553	-0.171282
11	C	1.203260	2.880673	-0.172227
12	N	-0.006408	3.527487	-0.387541
13	C	-1.223289	2.879210	-0.639007
14	C	-1.223306	-2.879017	-0.639427
15	N	-0.006565	-3.527371	-0.387494
16	C	1.203086	-2.880603	-0.171916
17	S	-4.009105	1.667214	-0.556142
18	C	-5.170808	0.696218	0.379087
19	C	-5.170842	-0.696289	0.378825
20	S	-4.009145	-1.666954	-0.556763
21	C	-6.144048	1.395416	1.104680
22	C	-7.134378	0.698076	1.793141
23	C	-7.134416	-0.698594	1.792868
24	C	-6.144119	-1.395717	1.104140
25	O	-2.184050	3.541302	-1.007098
26	O	2.249554	3.504131	-0.009620
27	O	-2.183953	-3.540989	-1.008000
28	O	2.249305	-3.504103	-0.008969
29	C	-0.011727	4.993706	-0.498313
30	C	-0.011900	-4.993577	-0.498284
31	S	3.934256	-1.504587	0.209201

32	C	4.840793	-0.000091	0.328575
33	S	3.934387	1.504473	0.208945
34	C	6.206690	-0.000132	0.512611
35	C	6.933686	1.223495	0.610916
36	N	7.509801	2.232822	0.689049
37	C	6.933582	-1.223807	0.611090
38	N	7.509628	-2.233162	0.689372
39	H	-6.122755	2.480821	1.119632
40	H	-7.895318	1.245379	2.340343
41	H	-7.895392	-1.246070	2.339846
42	H	-6.122881	-2.481130	1.118668
43	H	-0.174085	5.290743	-1.536927
44	H	-0.824388	5.394935	0.107411
45	H	0.951321	5.356632	-0.149297
46	H	0.950828	-5.356584	-0.148455
47	H	-0.825090	-5.394735	0.106769
48	H	-0.173349	-5.290627	-1.537039

Total energy: -3109.5050274 Hartrees

Table S4. Coordinates and energy of compound **4**

		X	**Y**	**Z**
1	C	1.705347	-0.721673	-0.858128
2	C	1.705330	0.721727	-0.858107
3	C	0.484432	1.409410	-0.750338
4	C	-0.724213	0.708263	-0.494335
5	C	-0.724199	-0.708240	-0.494341
6	C	0.484446	-1.409374	-0.750354
7	C	-1.929034	1.407678	-0.225403
8	C	-3.103139	0.709733	0.058105
9	C	-3.103137	-0.709734	0.058081
10	C	-1.929024	-1.407665	-0.225427
11	C	-1.954325	-2.880868	-0.224503
12	N	-0.773544	-3.527401	-0.564657
13	C	0.411226	-2.878566	-0.939182
14	C	0.411185	2.878598	-0.939186
15	N	-0.773596	3.527426	-0.564731
16	C	-1.954339	2.880887	-0.224457
17	S	3.193524	-1.665434	-1.126139
18	C	4.439527	-0.706443	-0.293637
19	C	4.439502	0.706491	-0.293560
20	S	3.193523	1.665515	-1.126060
21	C	5.461681	-1.400356	0.322385
22	C	6.547209	-0.716381	0.926582

23	C	6.547177	0.716352	0.926679
24	C	5.461628	1.400360	0.322557
25	O	1.328433	-3.539624	-1.406527
26	O	-2.978341	-3.504409	0.044867
27	O	1.328393	3.539660	-1.406531
28	O	-2.978338	3.504414	0.044997
29	C	-0.780069	-4.993322	-0.678400
30	C	-0.780122	4.993345	-0.678547
31	S	-4.632044	1.504537	0.434410
32	C	-5.522157	-0.000013	0.643335
33	S	-4.632031	-1.504566	0.434344
34	C	-6.863282	-0.000034	0.961019
35	C	-7.577197	-1.223642	1.130064
36	N	-8.143154	-2.232847	1.264085
37	C	-7.577219	1.223556	1.130102
38	N	-8.143217	2.232733	1.264161
39	C	7.625556	-1.404979	1.543678
40	C	8.657022	-0.708481	2.131098
41	C	8.656989	0.708385	2.131197
42	C	7.625490	1.404916	1.543871
43	H	5.442963	-2.486489	0.341942
44	H	5.442872	2.486491	0.342241
45	H	0.090974	-5.395757	-0.161057
46	H	-0.726433	-5.288210	-1.728869
47	H	-1.701776	-5.356973	-0.232076
48	H	-1.701898	5.357001	-0.232374
49	H	-0.726321	5.288159	-1.729026
50	H	0.090827	5.395838	-0.161086
51	H	7.623231	-2.491457	1.542849
52	H	9.477304	-1.244331	2.598834
53	H	9.477245	1.244209	2.599007
54	H	7.623113	2.491394	1.543191

Total energy: -3263.1520747 Hartrees

7. OFETs characteristics of 1 and 2 under ambient conditions

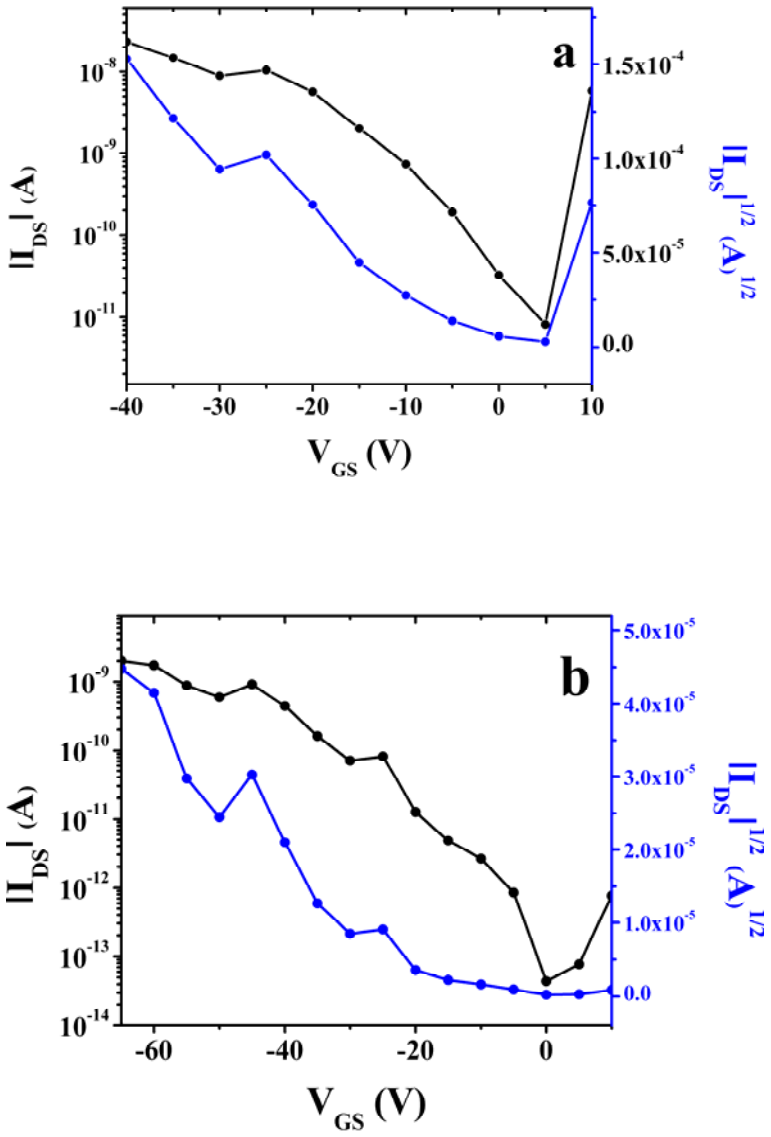


Figure S5 The transfer characteristics of OTFT devices based on **1** (a) annealed at 120 °C (V_{DS} for transfer characteristics is -80 V) and **2** (b) annealed at 140 °C (V_{DS} for transfer characteristics is -80 V) under ambient conditions; the transistor channel width and channel length were 1400 μm and 50 μm, respectively.

8. Complementary inverters of 2

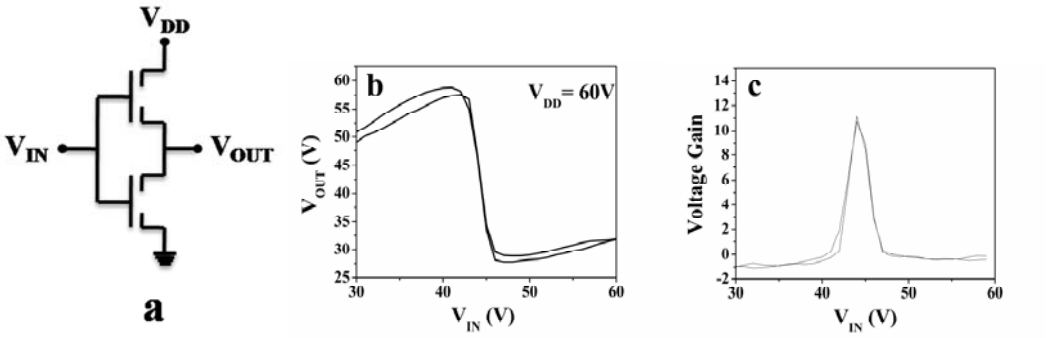


Figure S6. Complementary inverters fabricated from thin-films of **2**: (a) Schematic electrical layout of the inverters; (b) Static switching characteristics of a spin-coated inverter on OTS-treated Si / SiO_2 substrate annealed at 140 ^{o}C; (c) Gain data for the devices.

9. Variation of mobilities and on/off ratios for OFETs of 3 and 4 in air

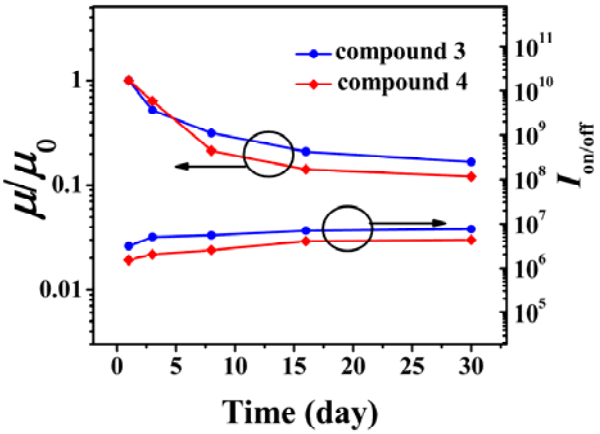


Figure S7. Variation of the electron mobilities and on/off ratios for OFETs of **3** and **4** in air for 30 days.

10. Possible intermolecular packing for molecules 1-4 on the substrate surface

Compounds	1	2	3	4
d-spacing (Å)	23.4	23.9	24.5	21.5

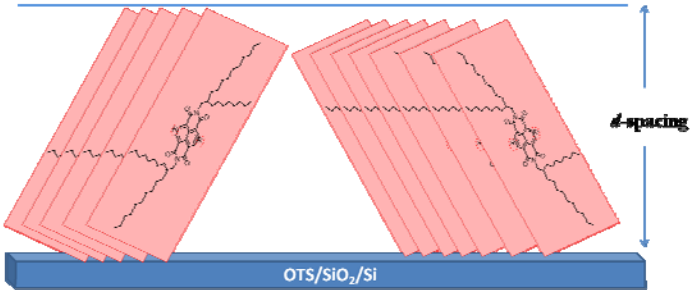
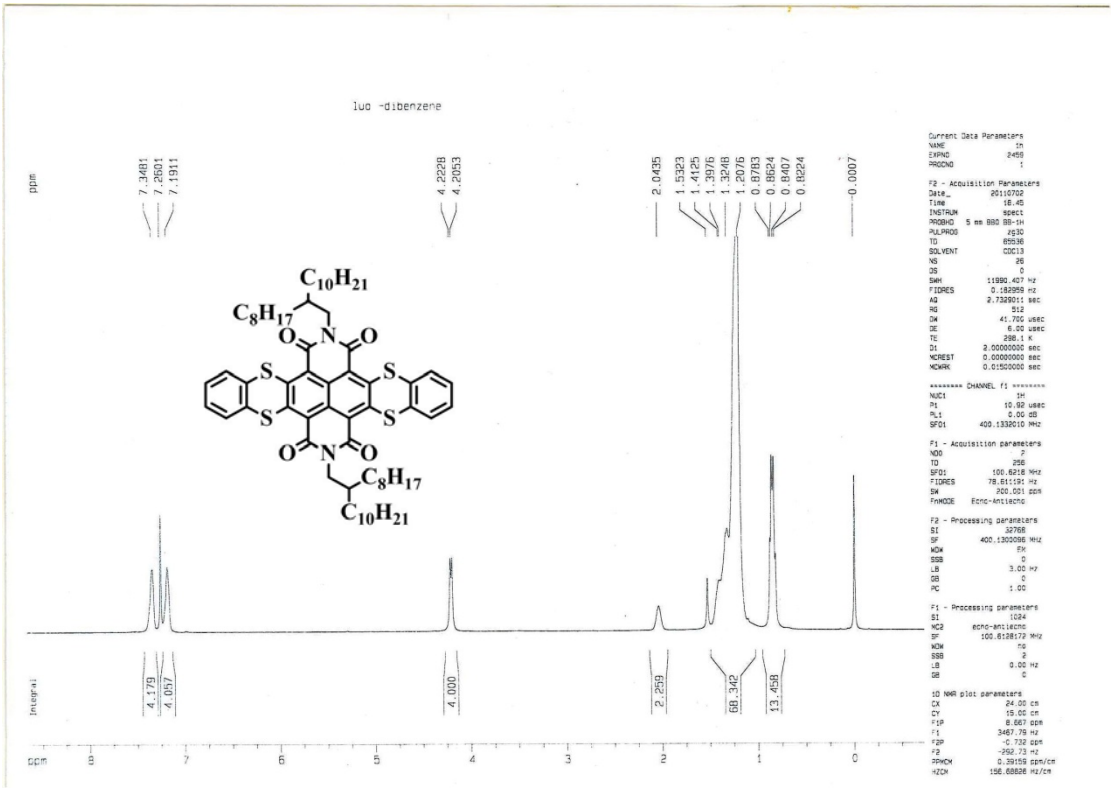
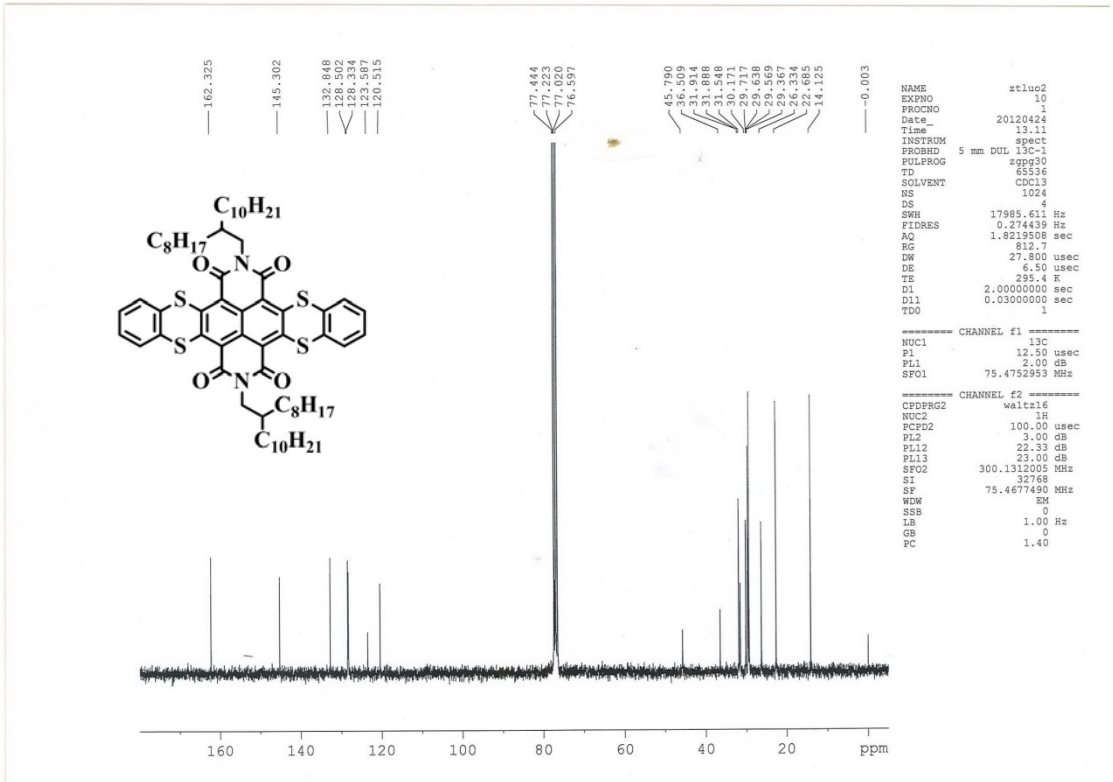


Figure S8. The proposed intermolecular packing on the substrate surface for molecules **1-4**.

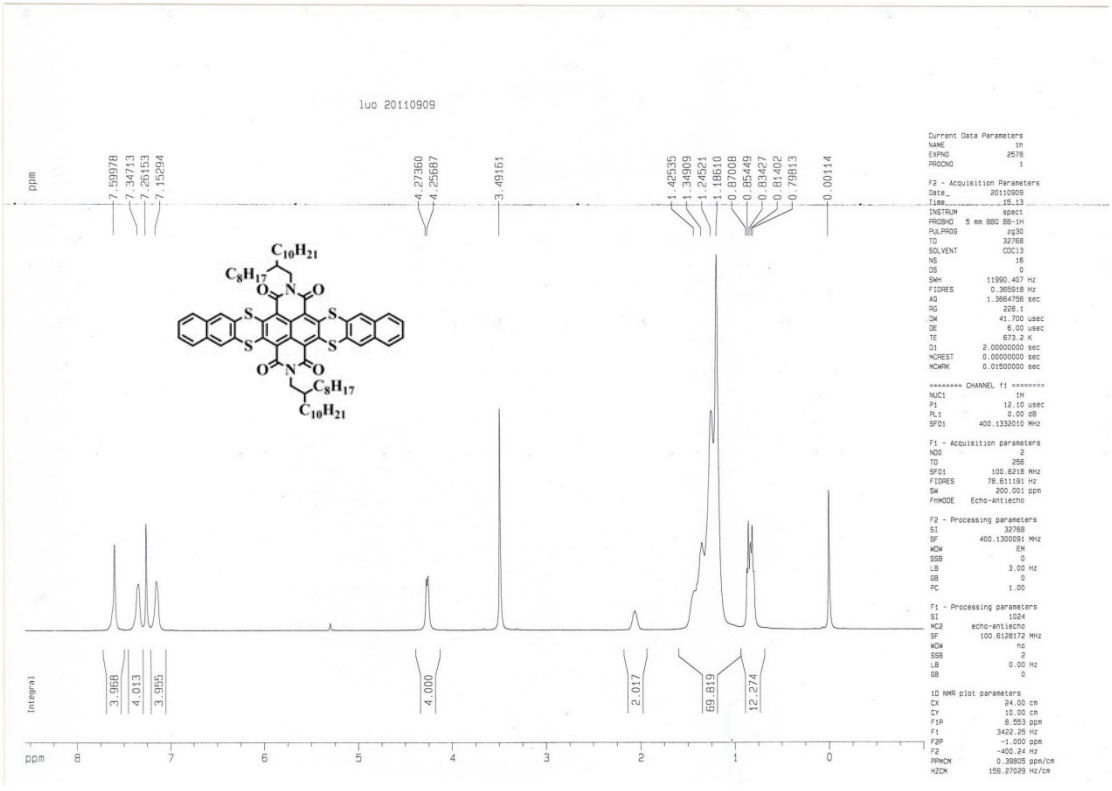
11. ^{1}H- and ^{13}C-NMR spectra of 1-6

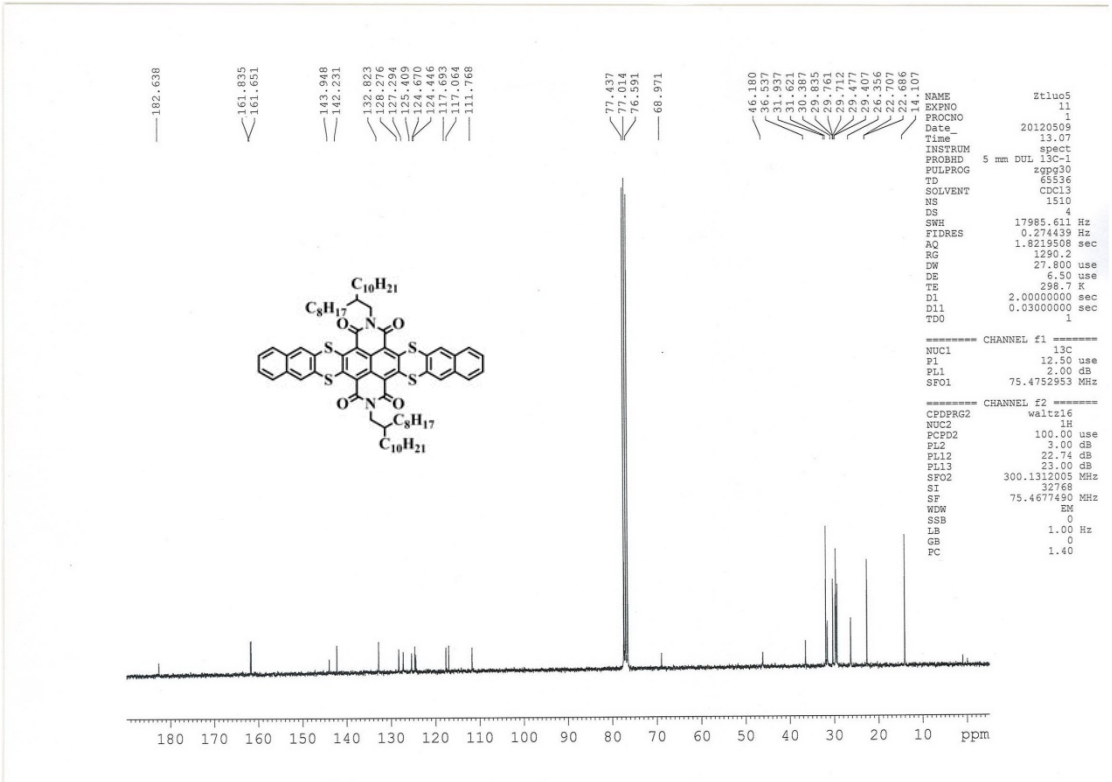
Compound 1



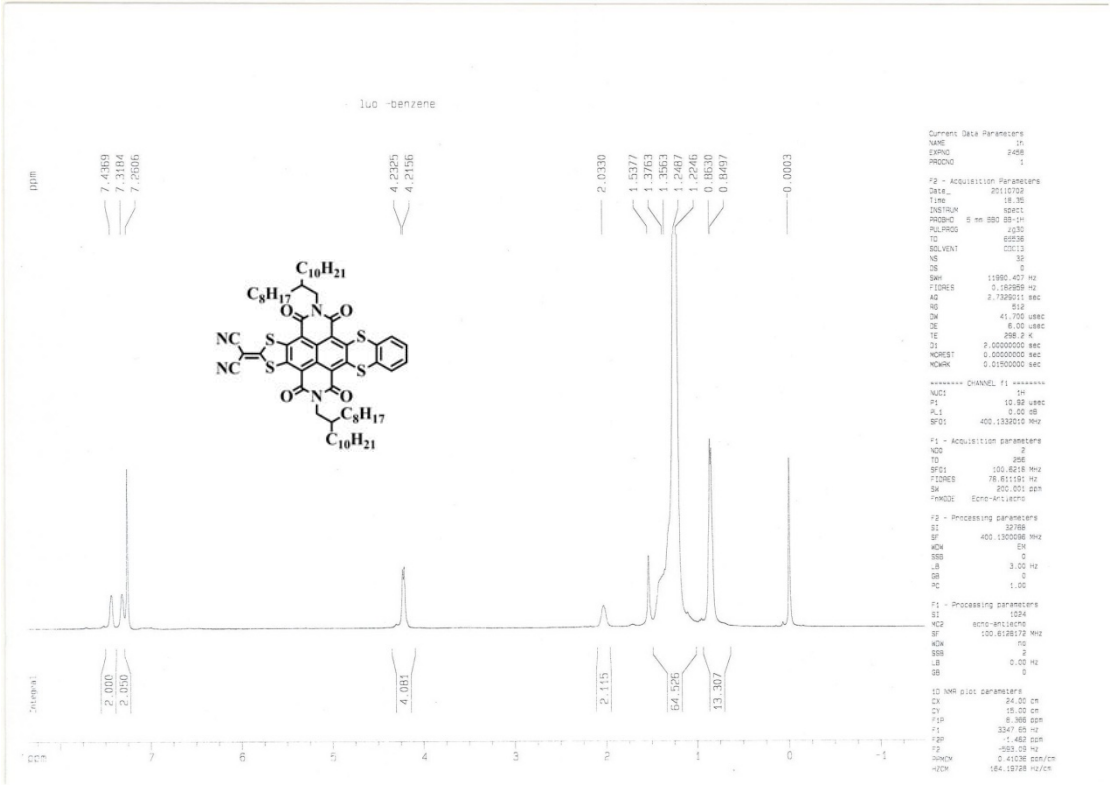


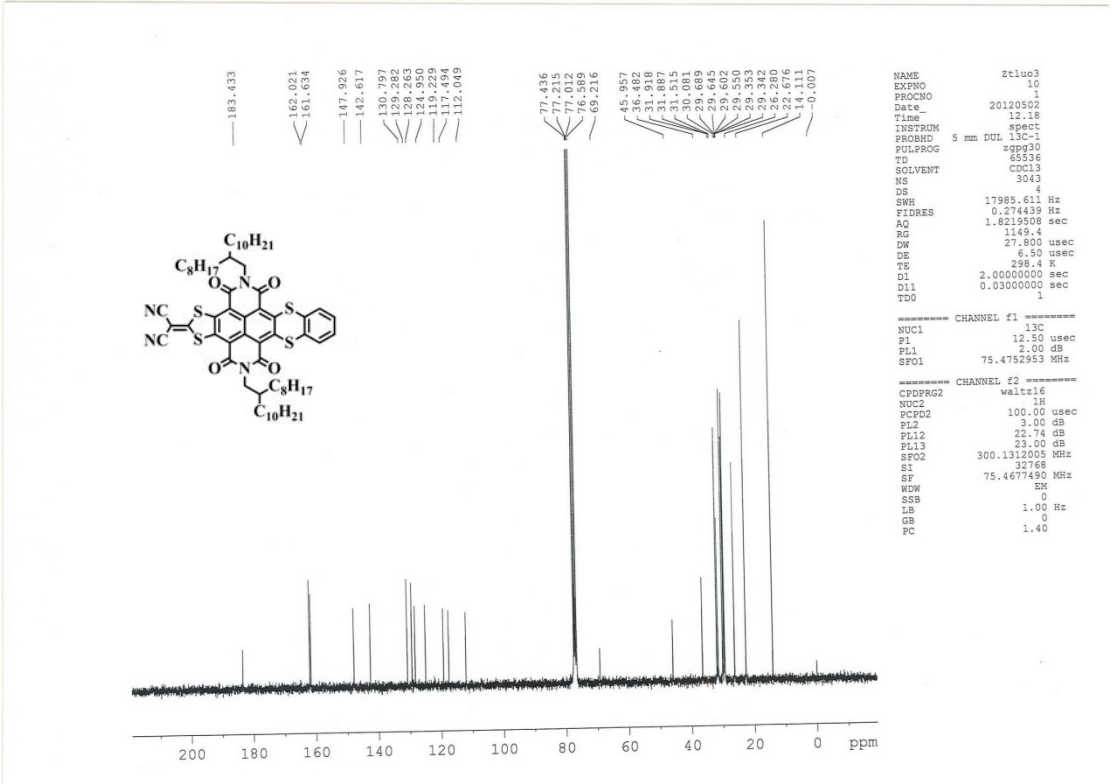
Compound 2


luo 20110909
ppm
7.59978
7.34713
7.26153
7.15294
4.27360
4.25687
3.49161
1.42535
1.34909
1.24521
1.18610
0.87008
0.85449
0.83427
0.81402
0.79813
0.00114
Integral
3.968
4.013
3.995
4.000
2.017
69.819
12.274
ppm 8 7 6 5 4 3 2 1 0

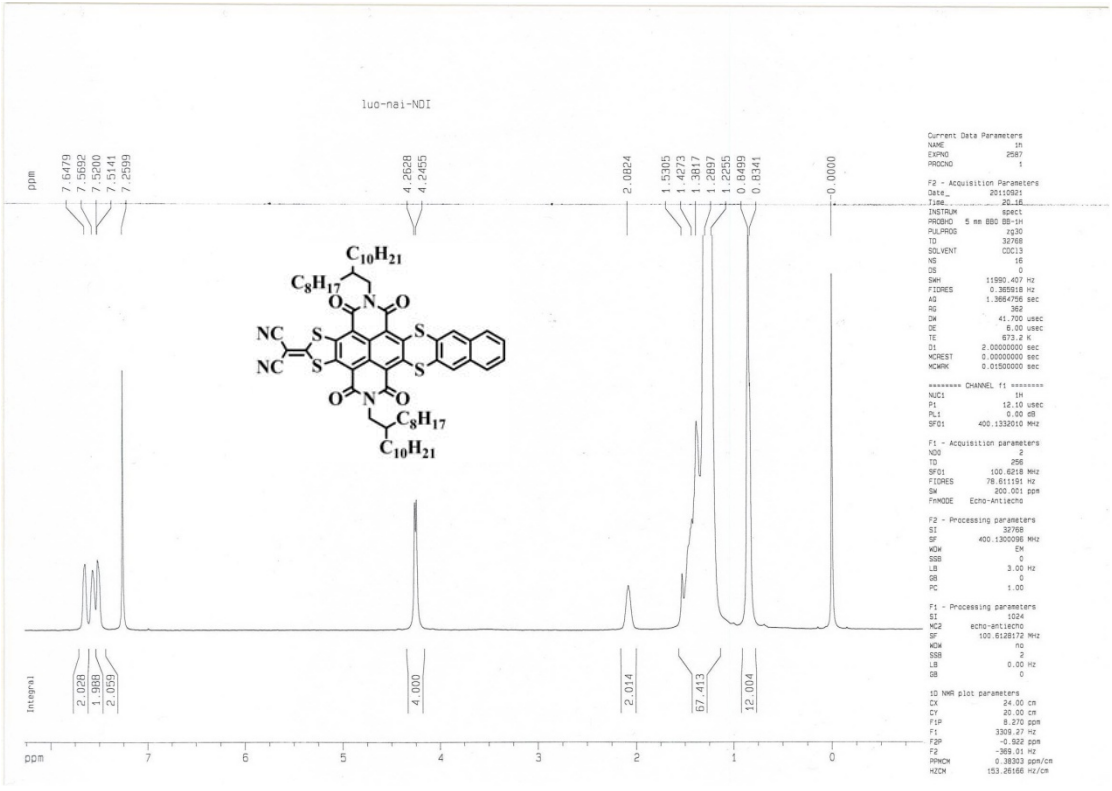

182.638
161.835
161.651
143.948
142.231
132.823
128.276
127.294
127.109
125.470
124.446
117.693
117.064
111.768
77.437
77.014
76.591
68.971
46.180
36.537
31.937
31.621
30.387
29.835
29.761
29.712
29.477
29.407
26.356
22.707
22.686
14.107
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

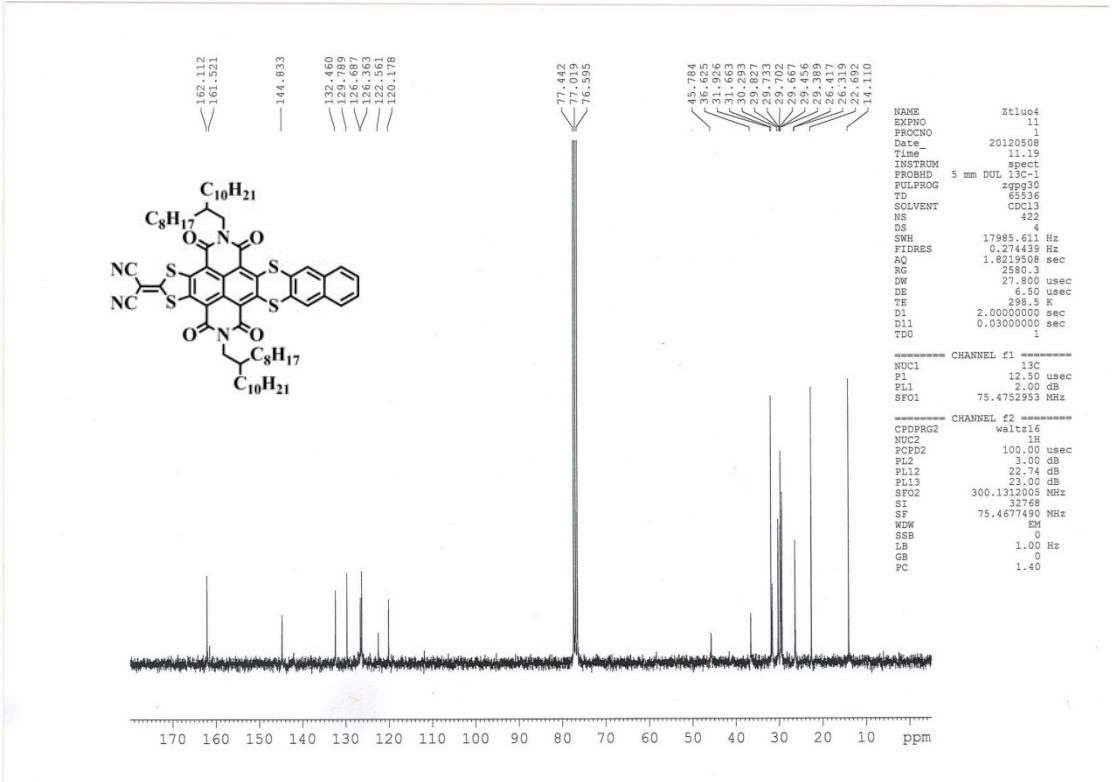
Compound 3


luo -benzene
ppm
7.4369
7.3184
7.2606
4.2325
4.2156
2.0330
1.5377
1.3763
1.3563
1.2487
1.2246
0.8530
0.8497
0.0003
2.000
2.050
4.081
2.115
64.506
13.307

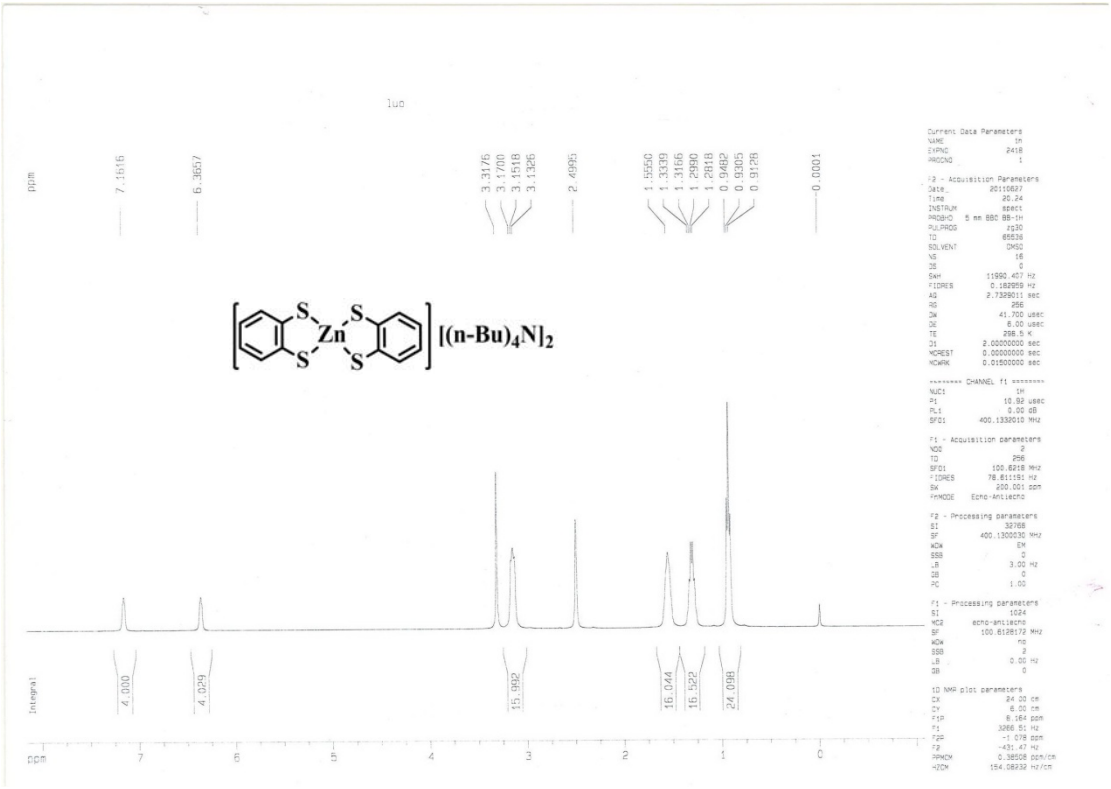

183.433
162.021
161.634
147.926
142.617
130.797
129.282
128.263
124.930
119.229
117.494
112.049
77.436
77.215
77.012
76.589
69.216
45.957
36.482
31.918
31.887
31.515
30.081
29.689
29.645
29.602
29.550
29.353
29.342
26.280
22.676
14.111
-0.007
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 4


luo-nai-NDI
ppm
7.6479
7.5692
7.5200
7.5141
7.2999
4.2628
4.2455
2.0824
1.5305
1.4273
1.3817
1.2897
1.2295
0.8499
0.8341
0.0000
Integral
2.028
1.988
2.059
4.000
2.014
67.413
12.004
ppm
7
6
5
4
3
2
1
0


162.112
161.521
144.833
132.460
129.789
126.687
126.363
122.561
120.178
77.442
77.019
76.595
45.784
36.625
31.926
31.663
30.293
30.227
29.733
29.702
29.667
29.456
29.389
26.417
26.319
22.692
14.110
NAME Ztluo4
EXPNO 11
PROCNO 1
Date_ 20120508
Time 11.19
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 422
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2580.3
DW 27.800 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Compound 5



Compound 6