Supporting Information

New Core-expanded Naphthalene Diimides with Different Functional groups for Air-stable Solution-processed Organic *n*-type Semiconductors

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Contents:

1. TGA-DTA analysis

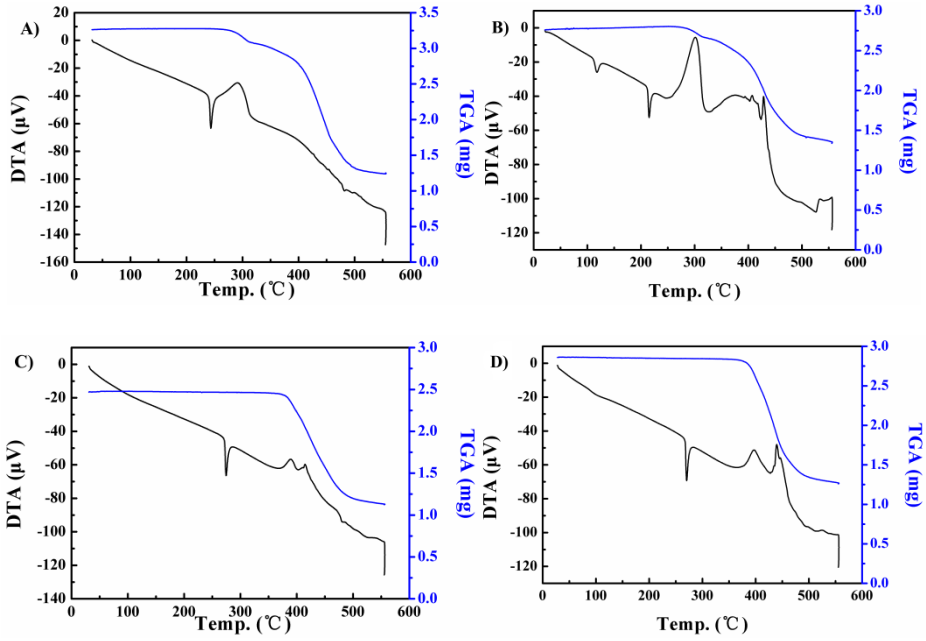


Figure S1. TGA-DTA curves of **1**–**4** (A–D), heating rate: 10 °C/min. from 25 °C to 550 °C under nitrogen atmosphere.

2. Cyclic voltammograms of 2 and 4

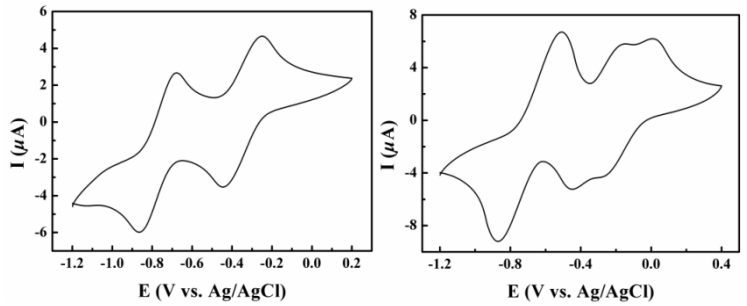


Figure S2. Cyclic voltammograms of **2** (*left*) and **4** (*right*) in CH_2Cl_2 (1.0×10^{-3} M) at a scan rate of 100 $mV \cdot s^{-1}$, with Pt as the working and counter electrodes and Ag/AgCl electrode (saturated KCl) as the reference electrode, and *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte.

3. UV-Vis absorption spectra of 2 and 4

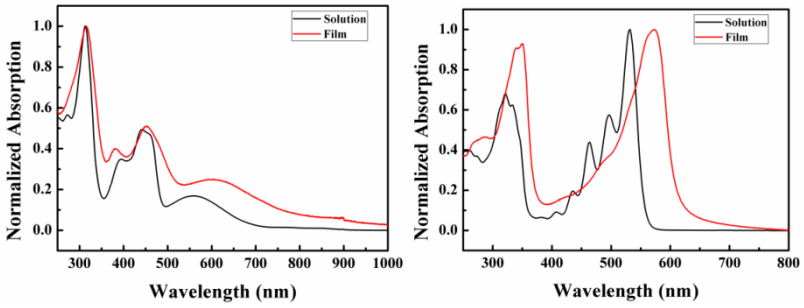


Figure S3. Normalized absorption spectra of **2** (*left*) and **4** (*right*) in CH_2Cl_2 and thin films.

4. DFT calculation data of 2 and 4

Calculation method: B3LYP/6-31G (d, p) with Gaussian 09

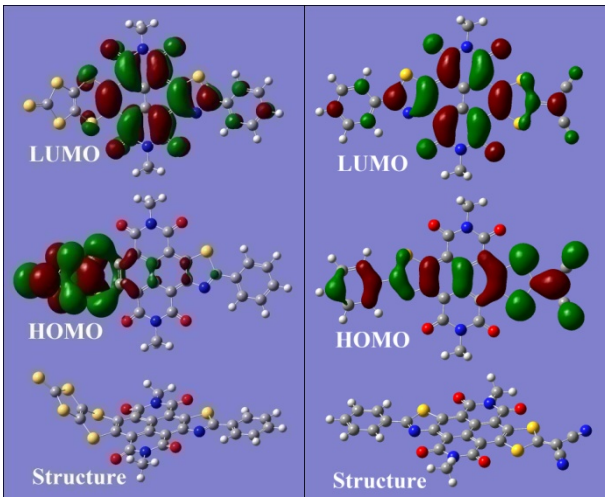


Figure S4. LUMO, HOMO orbitals and structures of compounds **2** (*left*) and **4** (*right*) obtained by DFT calculations; the alkyl chains were replaced by methyl groups in the calculations.

Data for compound **1**:

		Coordinates		
		X	Y	Z
1	C	-2.037588	0.753648	-0.821000
2	C	-1.936049	-0.676555	-0.884539
3	C	-0.676501	-1.283583	-0.817182
4	C	0.495699	-0.526870	-0.536989
5	C	0.389792	0.892672	-0.493482
6	C	-0.868513	1.516547	-0.704092
7	C	1.741584	-1.171059	-0.301637
8	C	2.873830	-0.385604	-0.029517
9	C	2.746578	1.046161	0.003865
10	C	1.537357	1.680960	-0.226819
11	C	1.464676	3.152363	-0.179922
12	N	0.228034	3.720493	-0.480875
13	C	-0.905880	2.993458	-0.853644
14	C	-0.520386	-2.730272	-1.110914

15	N	0.675247	-3.333812	-0.752685
16	C	1.833986	-2.655394	-0.318503
17	O	-1.882173	3.587734	-1.293753
18	O	2.831357	-3.280436	-0.008391
19	C	0.123078	5.184248	-0.556695
20	C	0.754119	-4.787776	-0.948119
21	O	2.443349	3.842102	0.087136
22	O	-1.403952	-3.386219	-1.653419
23	N	4.141150	-0.849936	0.213526
24	C	4.975614	0.127875	0.432030
25	S	4.284152	1.780797	0.369099
26	S	-3.609334	1.610711	-1.002811
27	S	-3.377790	-1.721545	-1.167396
28	C	6.372589	-0.078685	0.707386
29	C	-4.674428	0.491711	-0.141108
30	C	-4.580522	-0.848029	-0.207091
31	S	-5.899986	1.153666	0.943526
32	C	-6.586546	-0.393674	1.462247
33	S	-5.696720	-1.773520	0.799930
34	S	-7.878304	-0.532468	2.468595
35	C	7.362804	0.857117	0.946090
36	C	8.631375	0.271945	1.179445
37	C	8.593459	-1.100113	1.115963
38	S	7.014984	-1.706354	0.771559
39	H	0.029786	5.501593	-1.597968
40	H	1.023466	5.603097	-0.115042
41	H	-0.766045	5.508629	-0.015548
42	H	0.732325	-5.025148	-2.014518
43	H	1.684969	-5.129040	-0.503618

44	H	-0.104209	-5.262986	-0.471801
45	H	7.181286	1.926112	0.952151
46	H	9.531487	0.838513	1.384855
47	H	9.414471	-1.790565	1.254465

total energy: -4172.52218358 Hartrees

Data for compound **2**:

		Coordinates		
		X	Y	Z
1	C	-2.016819	0.744195	-0.821597
2	C	-1.937180	-0.688409	-0.876884
3	C	-0.686576	-1.313182	-0.812659
4	C	0.498221	-0.572182	-0.542494
5	C	0.414405	0.849460	-0.505762
6	C	-0.836413	1.490093	-0.715231
7	C	1.734977	-1.233412	-0.309171
8	C	2.877975	-0.462174	-0.043683
9	C	2.774810	0.970568	-0.016269
10	C	1.573611	1.622696	-0.247008
11	C	1.520955	3.095950	-0.207702
12	N	0.290989	3.679390	-0.509962
13	C	-0.853526	2.966428	-0.874515
14	C	-0.553262	-2.763608	-1.098222
15	N	0.635898	-3.382987	-0.743616
16	C	1.807242	-2.719545	-0.322174
17	O	-1.823282	3.570714	-1.315807
18	O	2.798582	-3.358401	-0.019239
19	C	0.206550	5.143983	-0.595118
20	C	0.691427	-4.839041	-0.931775
21	O	2.508206	3.774526	0.053684

22	O	-1.449274	-3.410134	-1.631263
23	N	4.137980	-0.946030	0.199285
24	C	4.993202	0.010959	0.412773
25	S	4.326346	1.674660	0.342416
26	S	-3.576390	1.623442	-1.002269
27	S	-3.395463	-1.713162	-1.146817
28	C	-4.654530	0.525616	-0.129532
29	C	-4.581161	-0.815747	-0.187418
30	S	-5.865414	1.212845	0.955761
31	C	-6.573030	-0.320696	1.487221
32	S	-5.706986	-1.718065	0.829873
33	S	-7.862259	-0.433676	2.499884
34	C	6.408320	-0.235846	0.693268
35	C	7.321188	0.813137	0.895629
36	C	8.659578	0.537161	1.159816
37	C	9.101658	-0.786041	1.225152
38	C	8.199418	-1.835140	1.025076
39	C	6.861117	-1.567563	0.760625
40	H	0.113042	5.455579	-1.638102
41	H	-0.675336	5.484727	-0.052152
42	H	1.114861	5.552723	-0.160312
43	H	1.617567	-5.192932	-0.487410
44	H	-0.173501	-5.297833	-0.451455
45	H	0.663874	-5.081673	-1.996871
46	H	6.990191	1.846475	0.846238
47	H	9.357492	1.353982	1.314440
48	H	10.146255	-0.999039	1.431543
49	H	8.541953	-2.864069	1.076085
50	H	6.145408	-2.366876	0.603382

total energy: -3851.76970673 Hartrees

Data for compound **3**:

		Coordinates		
		X	Y	Z
1	C	2.630353	0.643494	0.000115
2	C	2.509731	-0.775460	0.000022
3	C	1.252319	-1.375264	0.000073
4	C	0.071779	-0.583500	0.000143
5	C	0.201192	0.837336	0.000112
6	C	1.486024	1.438164	0.000132
7	C	-1.209355	-1.196671	0.000187
8	C	-2.353329	-0.379879	0.000063
9	C	-2.199668	1.051681	0.000045
10	C	-0.953029	1.656333	0.000082
11	C	-0.838520	3.125883	0.000126
12	N	0.449665	3.665371	0.000039
13	C	1.622647	2.909282	0.000266
14	C	1.161251	-2.849047	0.000046
15	N	-0.107251	-3.404228	0.000333
16	C	-1.320537	-2.678967	0.000471
17	O	2.727553	3.445001	0.000466
18	O	-2.371545	-3.292557	0.000805
19	C	0.548866	5.132152	0.000093
20	C	-0.237716	-4.868213	0.000535
21	O	-1.820024	3.860323	0.000222
22	O	2.177104	-3.543413	-0.000210
23	N	-3.653934	-0.811253	-0.000057
24	C	-4.491562	0.188765	-0.000137
25	S	-3.759587	1.826317	-0.000057
26	C	-5.919330	0.018493	-0.000265

27	S	4.264191	1.303079	0.000185
28	C	5.050242	-0.272020	-0.000062
29	S	4.015305	-1.696668	-0.000126
30	C	6.423753	-0.384040	-0.000201
31	C	-6.913267	0.981058	-0.000437
32	C	-8.217037	0.428512	-0.000533
33	C	-8.202029	-0.945692	-0.000440
34	S	-6.603088	-1.593684	-0.000167
35	C	7.255006	0.775593	-0.000169
36	N	7.917183	1.733852	-0.000511
37	C	7.056533	-1.662874	-0.000378
38	N	7.557543	-2.714367	-0.000862
39	H	1.603084	5.395419	-0.003723
40	H	0.055483	5.531974	0.887779
41	H	0.048581	5.532126	-0.883578
42	H	0.762206	-5.293430	0.002211
43	H	-0.790933	-5.186160	-0.884879
44	H	-0.793828	-5.185492	0.884334
45	H	-6.709816	2.046140	-0.000514
46	H	-9.125335	1.018689	-0.000682
47	H	-9.051620	-1.615150	-0.000488

total energy: -3125.55871234 Hartrees

Data for compound **4**:

		Coordinates		
		X	Y	Z
1	C	2.606577	0.656162	-0.000009
2	C	2.512637	-0.764987	0.000004
3	C	1.267141	-1.386610	0.000089
4	C	0.071129	-0.619122	0.000145

5	C	0.172975	0.804387	0.000103
6	C	1.447588	1.428660	0.000067
7	C	-1.196780	-1.258755	0.000205
8	C	-2.354795	-0.461688	0.000114
9	C	-2.231076	0.972058	0.000044
10	C	-0.995737	1.601707	0.000086
11	C	-0.907326	3.073963	0.000081
12	N	0.371721	3.636305	0.000351
13	C	1.557705	2.901941	0.000070
14	C	1.198495	-2.859382	0.000088
15	N	-0.054346	-3.444166	0.000275
16	C	-1.286490	-2.745245	0.000443
17	O	2.653268	3.456813	-0.000091
18	O	-2.335063	-3.362918	0.000765
19	C	0.444496	5.104709	0.000442
20	C	-0.085547	-4.913858	0.000349
21	O	-1.900434	3.791665	-0.000060
22	O	2.217779	-3.548567	-0.000049
23	N	-3.646726	-0.918161	0.000067
24	C	-4.509010	0.056840	-0.000036
25	S	-3.807878	1.708369	-0.000113
26	S	4.228336	1.344711	-0.000134
27	C	5.042680	-0.216620	-0.000135
28	S	4.033621	-1.659830	-0.000110
29	C	6.417863	-0.303897	-0.000175
30	C	-5.955549	-0.161133	-0.000150
31	C	-6.869986	0.906100	0.000241
32	C	-8.239092	0.656085	0.000099
33	C	-8.710465	-0.658679	-0.000430

34	C	-7.806983	-1.725662	-0.000798
35	C	-6.438059	-1.484189	-0.000656
36	C	7.073290	-1.571314	-0.000196
37	N	7.592177	-2.614091	-0.000244
38	C	7.228138	0.870545	-0.000208
39	N	7.872724	1.840703	-0.000317
40	H	1.493824	5.386813	0.000648
41	H	-0.059351	5.495641	-0.885278
42	H	-0.059673	5.495493	0.886044
43	H	-1.127414	-5.221113	-0.000121
44	H	0.429493	-5.291997	-0.884754
45	H	0.428569	-5.291945	0.886024
46	H	-6.516026	1.933017	0.000697
47	H	-8.938156	1.486395	0.000412
48	H	-9.779132	-0.851092	-0.000547
49	H	-8.172583	-2.747834	-0.001197
50	H	-5.720978	-2.297535	-0.000911

total energy: -2804.80618111 Hartrees

5. Transfer, output characteristics and stability studies for OFET of 1-4

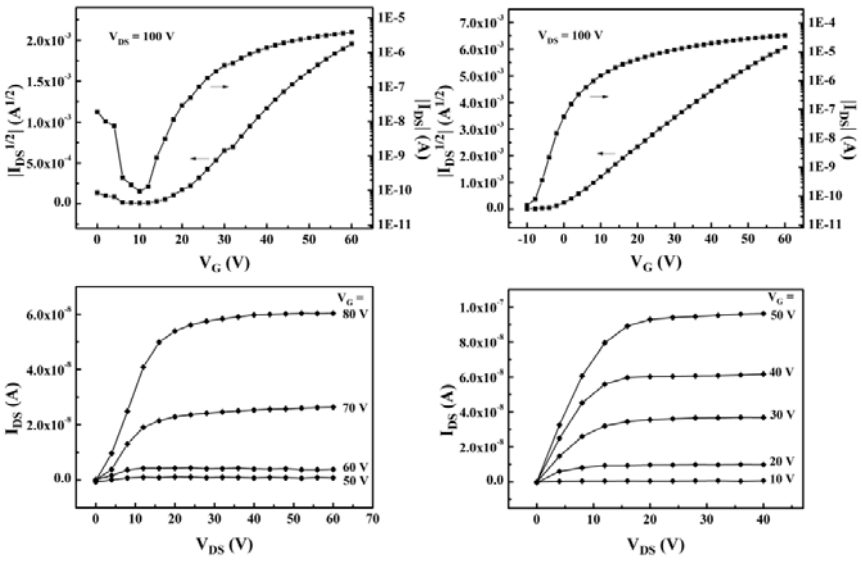


Figure S5. Transfer and output characteristics for OFET of **2** (*left*) and **4** (*right*) after annealing at 180 °C; the channel width (*W*) and length (*L*) were 1440 μm and 50 μm, respectively.

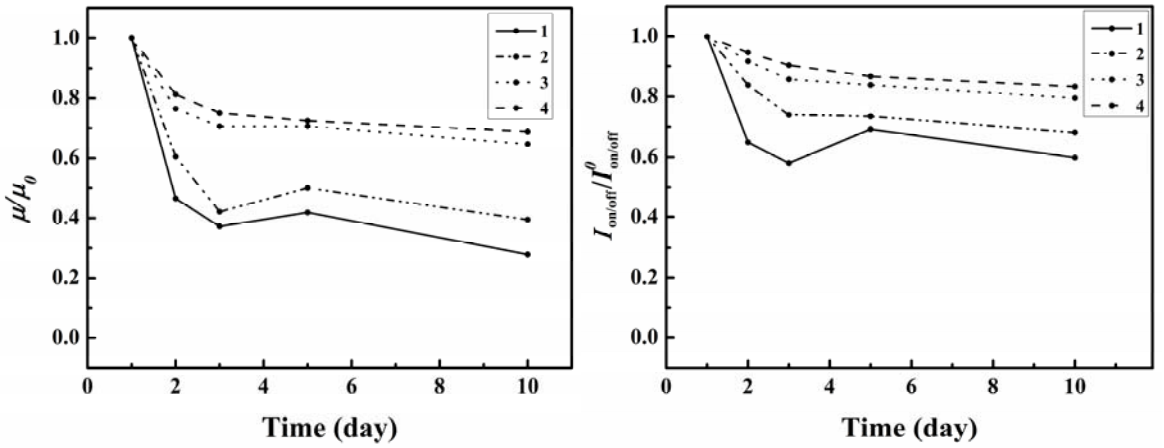


Figure S6. Variation of electron mobilities (*left*) and on/off ratio (*right*) for OFET devices of **1**-**4** left in air for 10 days.

6. XRD patterns and AFM images of thin films of 1-4

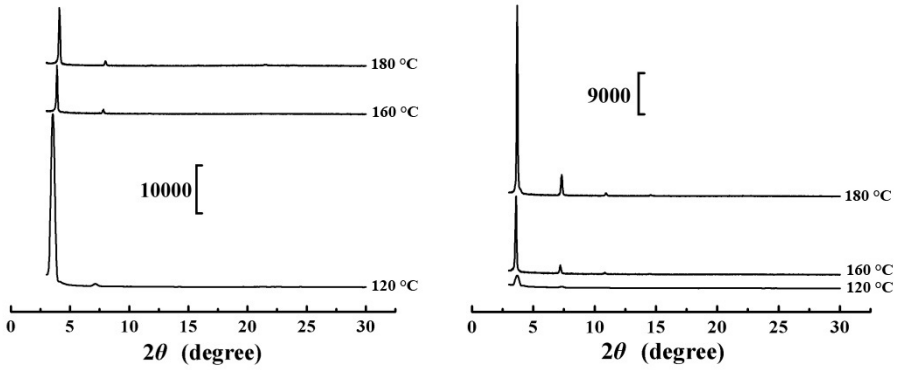


Figure S7. XRD patterns of thin films of **2** (*left*) and **4** (*right*) after annealing at 120 °C, 160 °C and 180 °C, respectively.

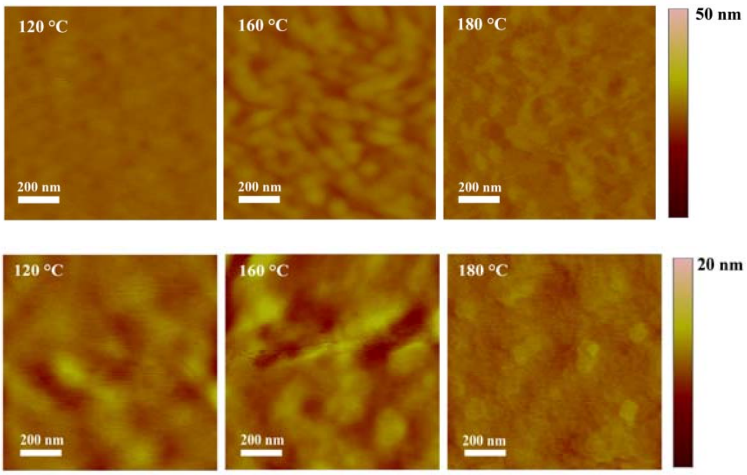


Figure S8. AFM images of thin films of **2** (*above*) and **4** (*below*) after annealing at 120 °C, 160 °C and 180 °C, respectively.

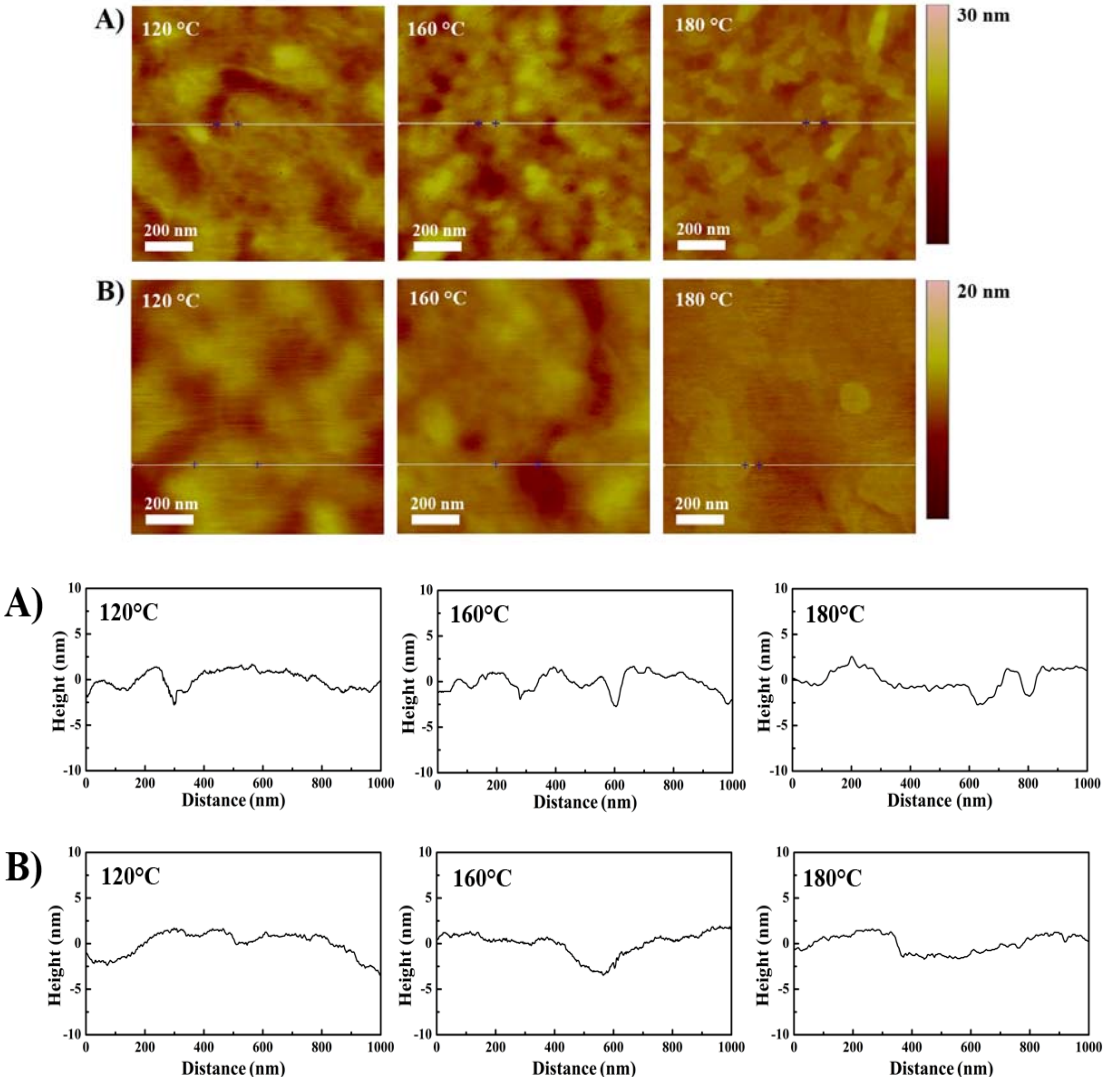


Figure S9. AFM images of thin films of **1** (A) and **3** (B) (upper) and the respective cross-section analysis of the line marked in upper AFM images for thin films of **1** (A) and **3** (B) (lower).

7. ^{1}H NMR and ^{13}C NMR spectra of 1–6

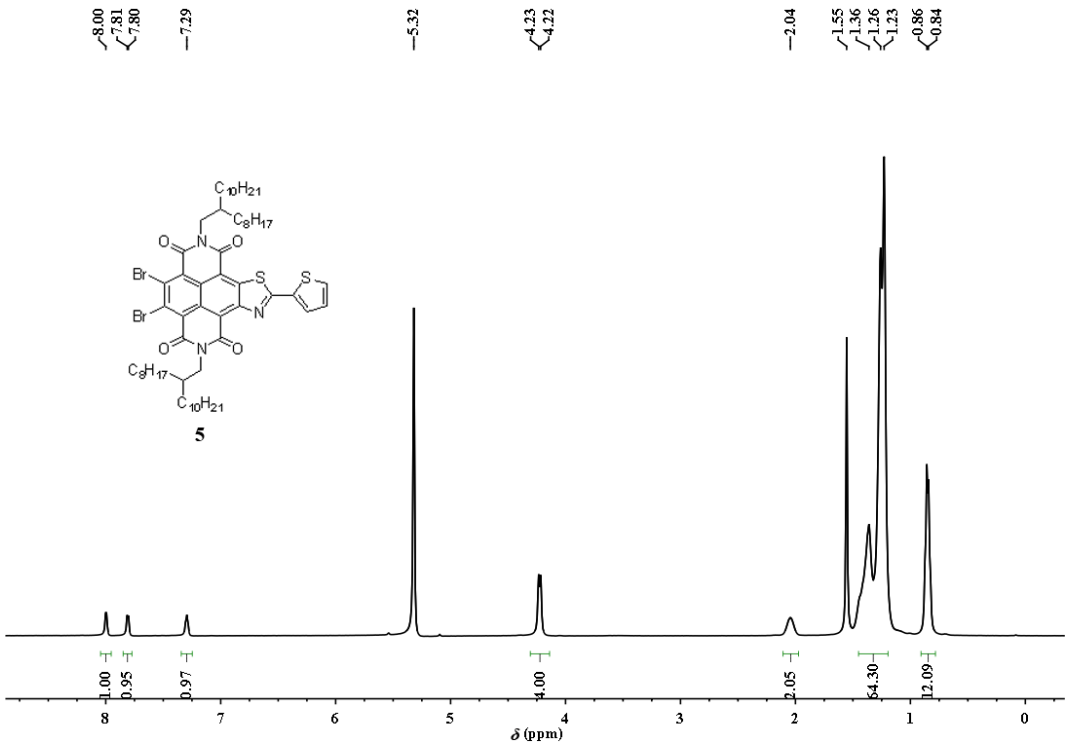


Figure S10. ^{1}H NMR spectra of **5**

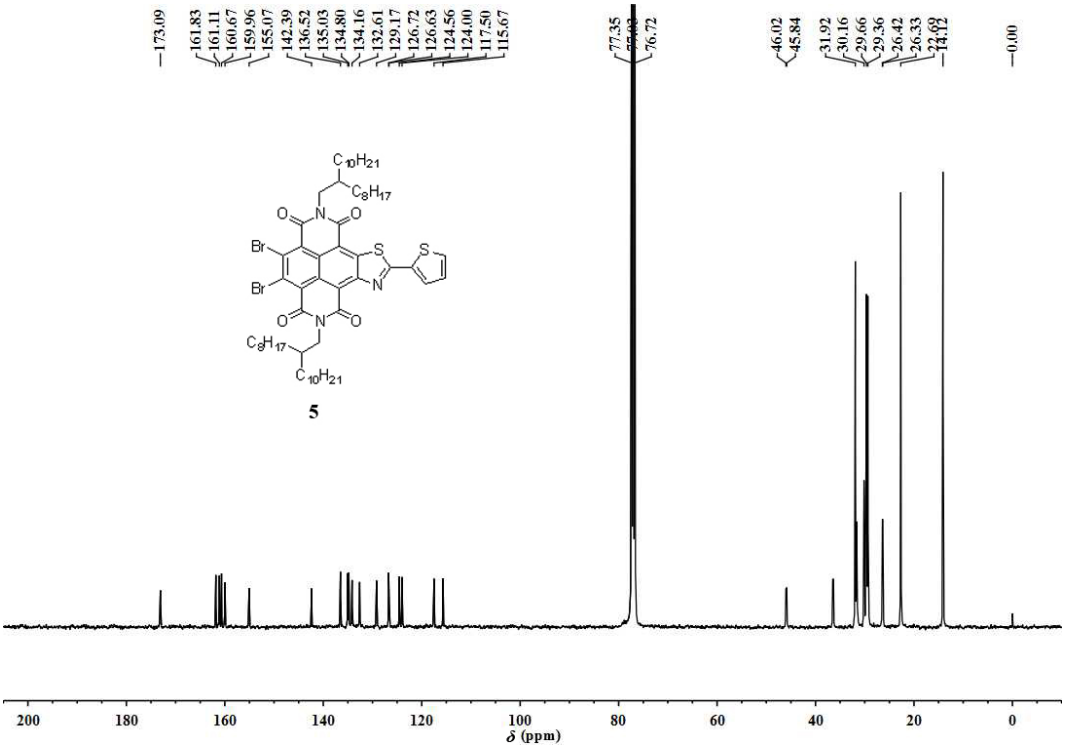


Figure S11. ^{13}C NMR spectra of **5**

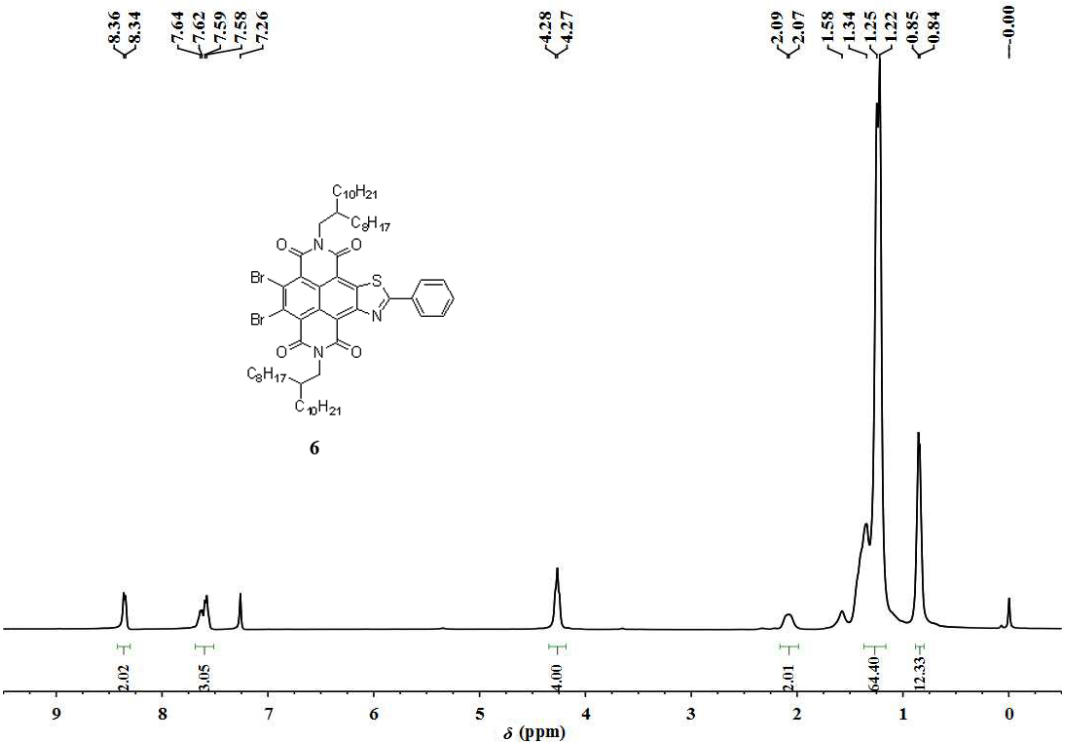


Figure S12. ^{1}H NMR spectra of **6**

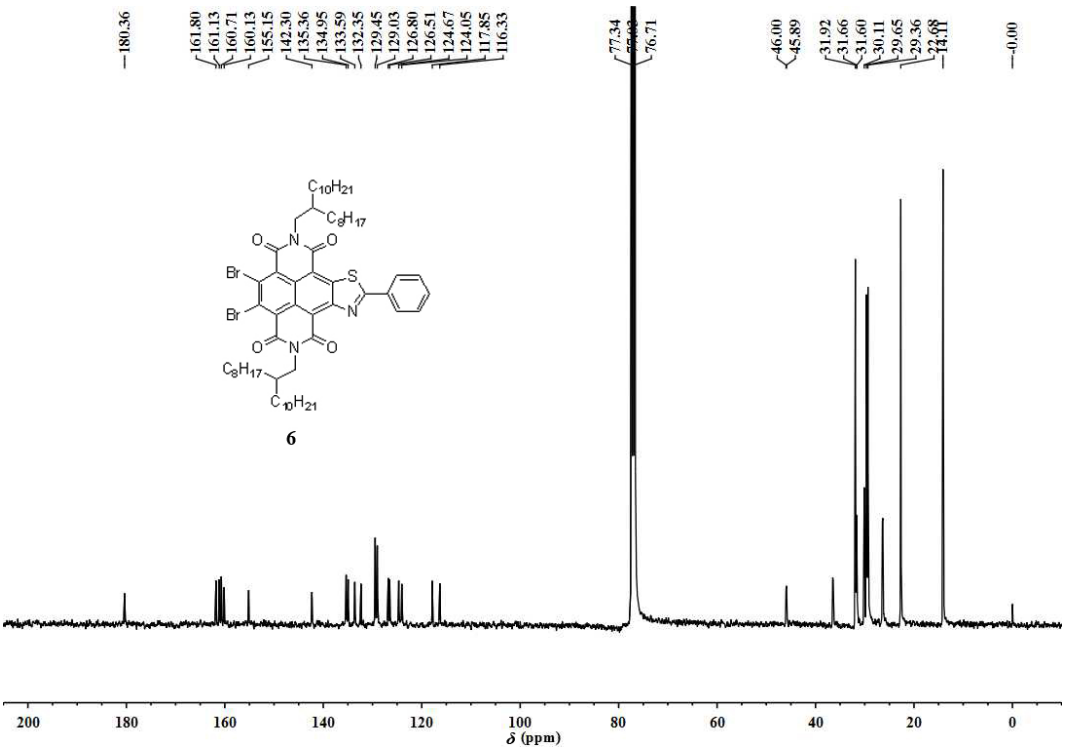
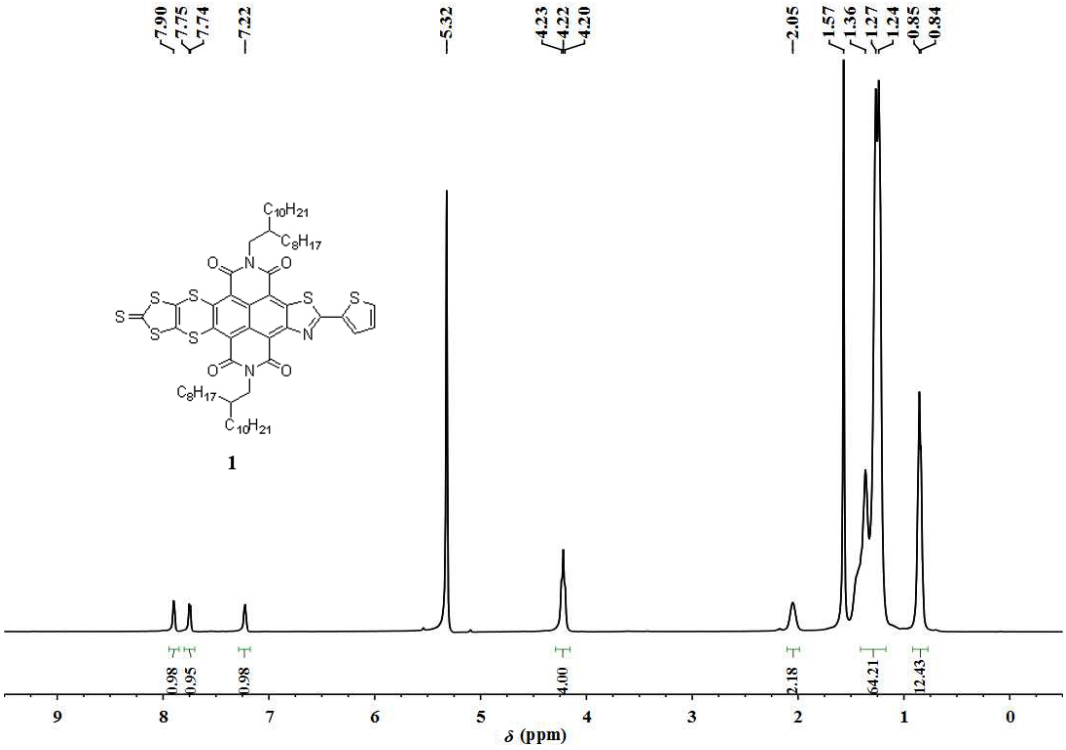
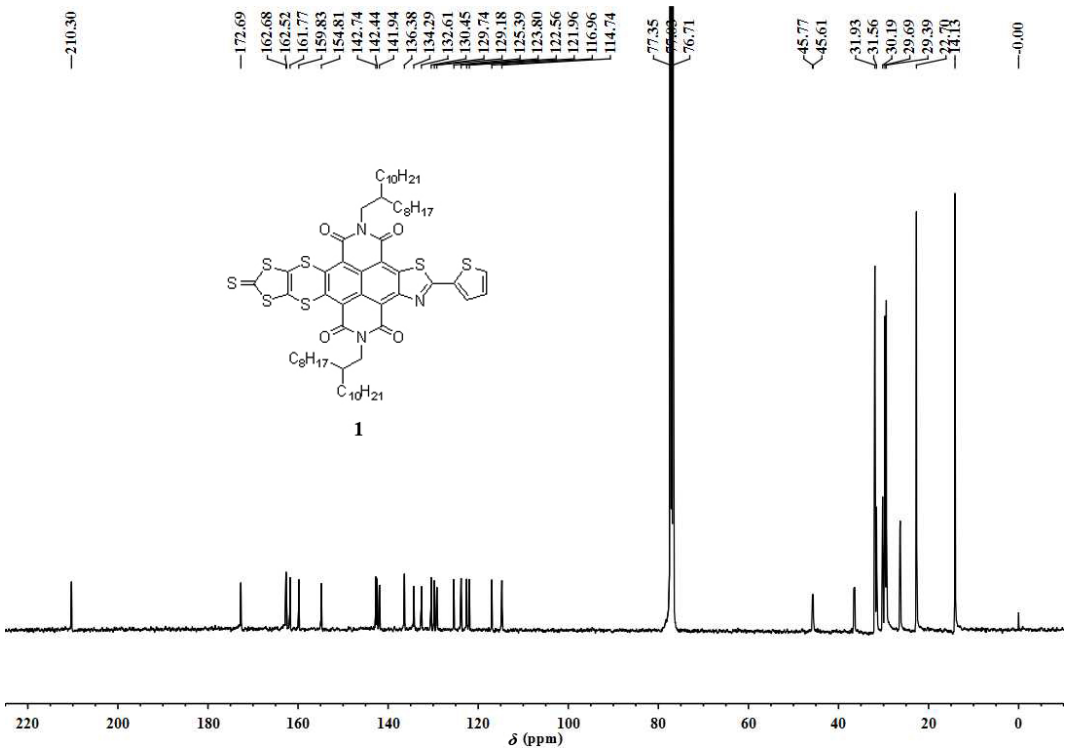


Figure S13. ^{13}C NMR spectra of **6**



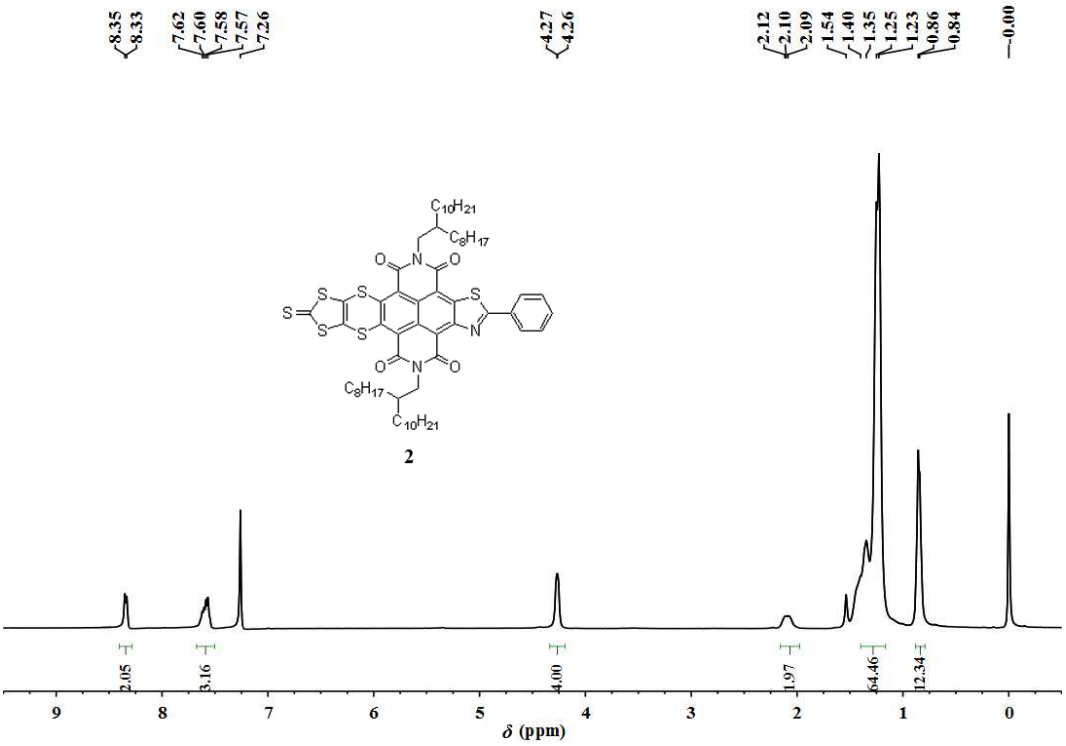
1

Figure S14. ^{1}H NMR spectra of **1**



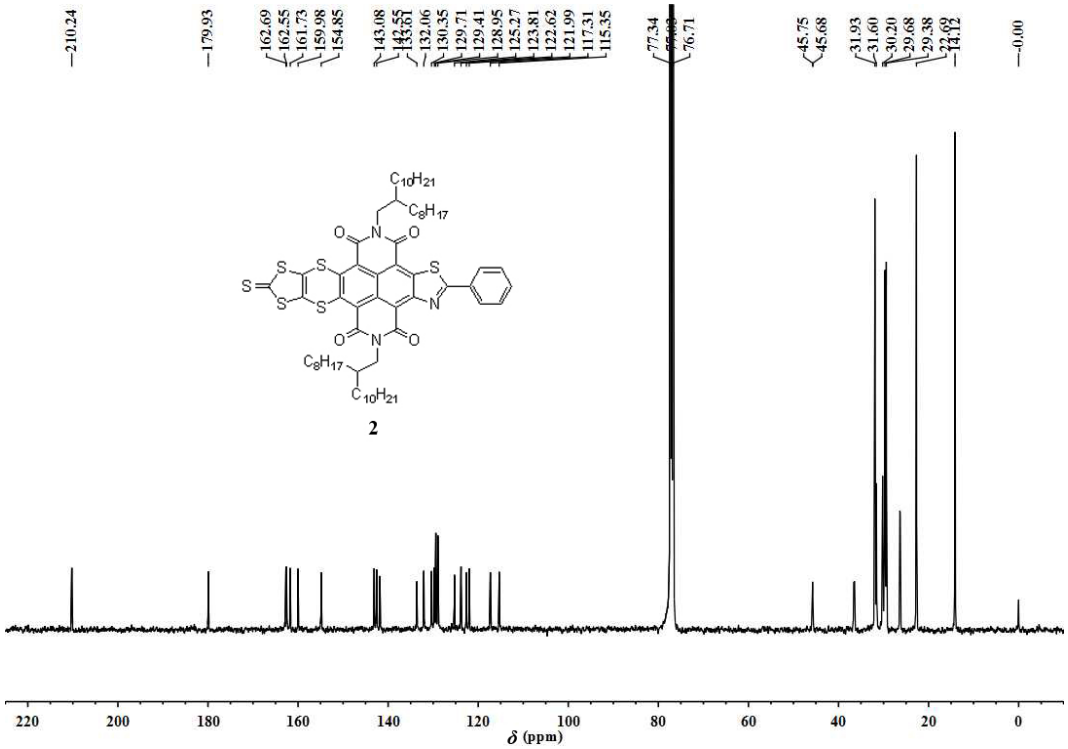
1

Figure S15. ^{13}C NMR spectra of **1**



2

Figure S16. ^{1}H NMR spectra of **2**



2

Figure S17. ^{13}C NMR spectra of **2**

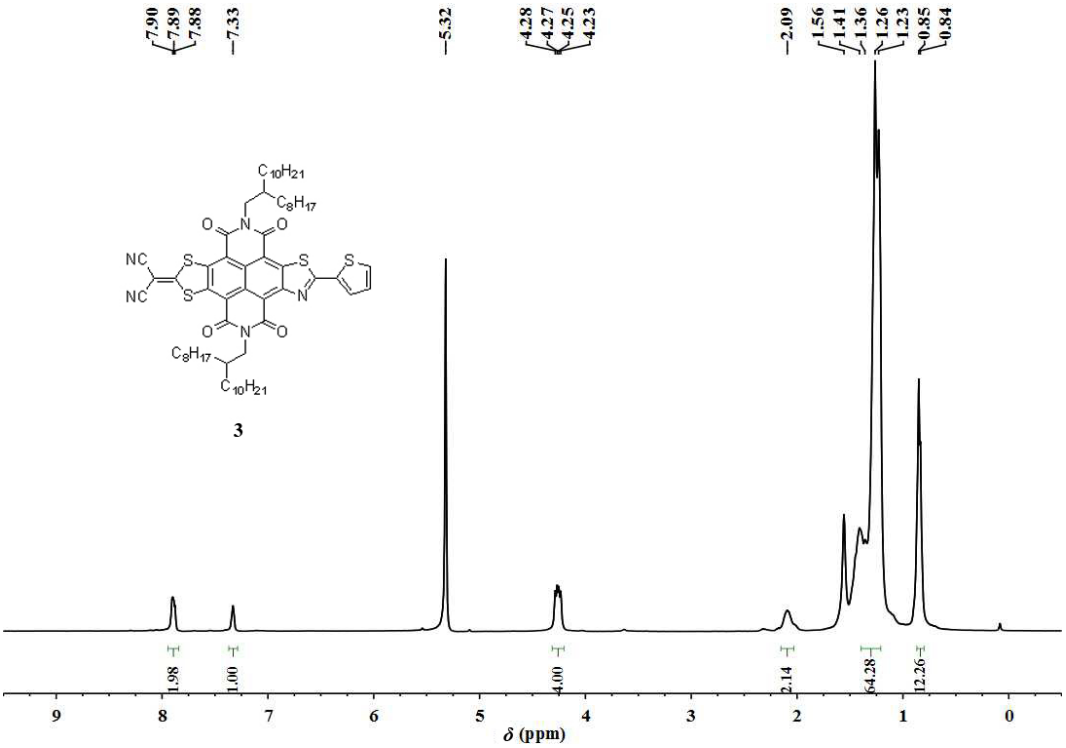


Figure S18. ^{1}H NMR spectra of **3**

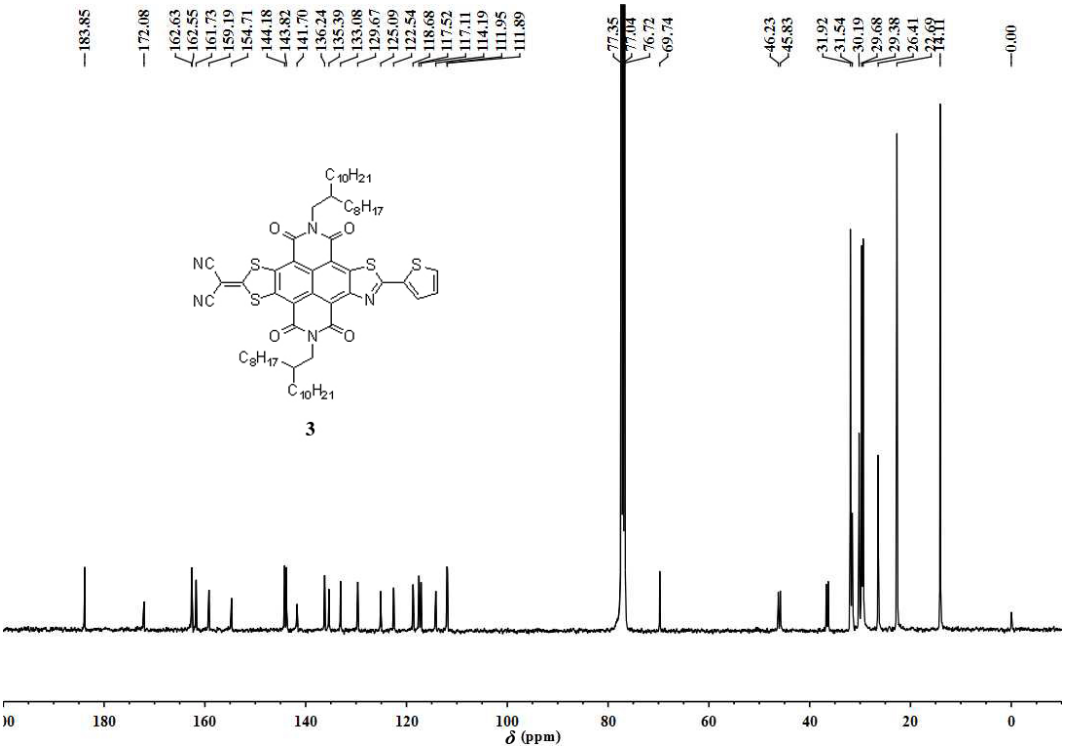


Figure S19. ^{13}C NMR spectra of **3**

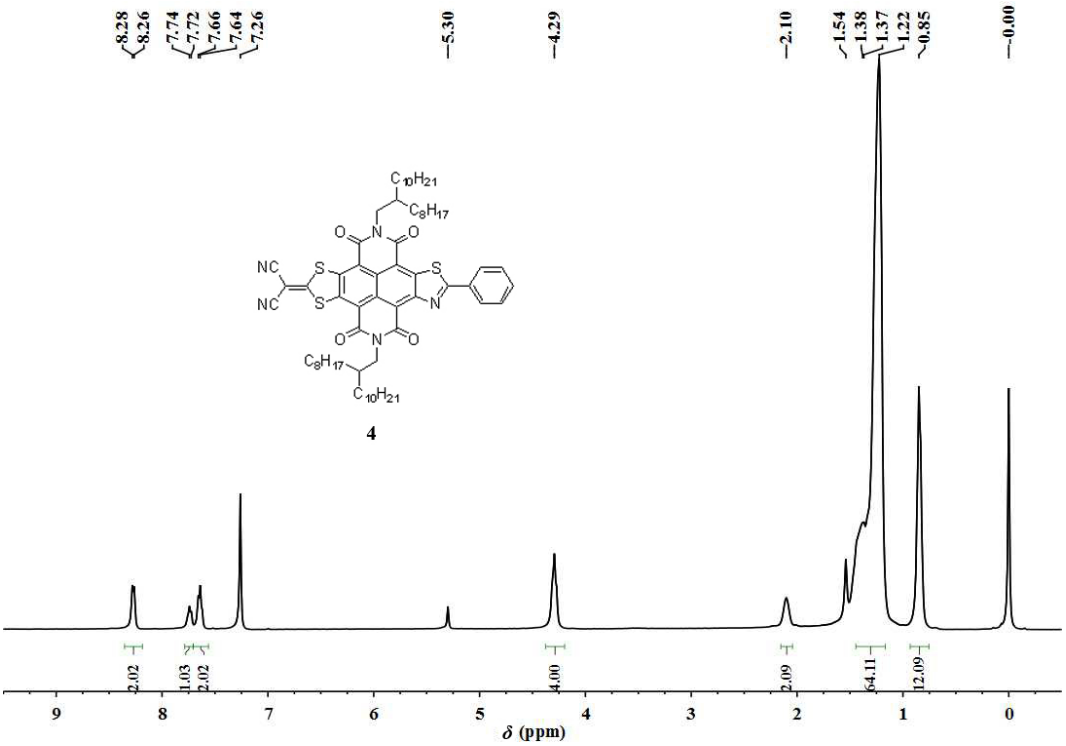


Figure S20. ^{1}H NMR spectra of **4**

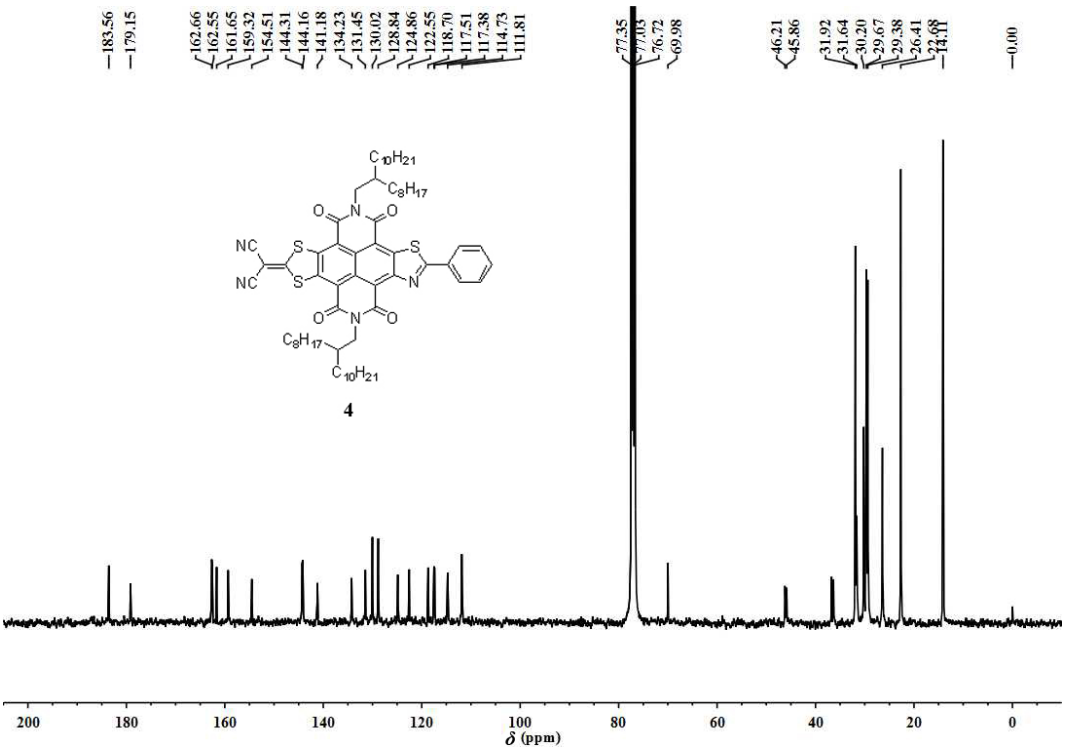


Figure S21. ^{13}C NMR spectra of **4**