Thieno[3,2-*b*]thiophene fused BODIPYs: synthesis, near-infrared luminescence and photosensitive properties

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Electronic Supplementary Information

I. Experimental Section

I. Experimental Section

I.1 Materials and instrumentations

All reactions and manipulations of air-sensitive compounds were carried out under a dry argon atmosphere by using Schlenk techniques and/or vacuum line techniques. All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air- and moisture-sensitive reactions were carried out under a nitrogen atmosphere. Glassware was dried in an oven at 100°C and cooled under a stream of inert gas before use. Dichloromethane and triethylamine were distilled over calcium hydride. ^{1}H NMR, ^{19}F NMR, ^{11}B NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of the solvent. HR-MS were recorded on a Bruker Daltonics microTOF-Q II spectrometer. All the solvents employed for the spectroscopic measurements were of spectroscopic grade.

I.2 Spectroscopic measurements

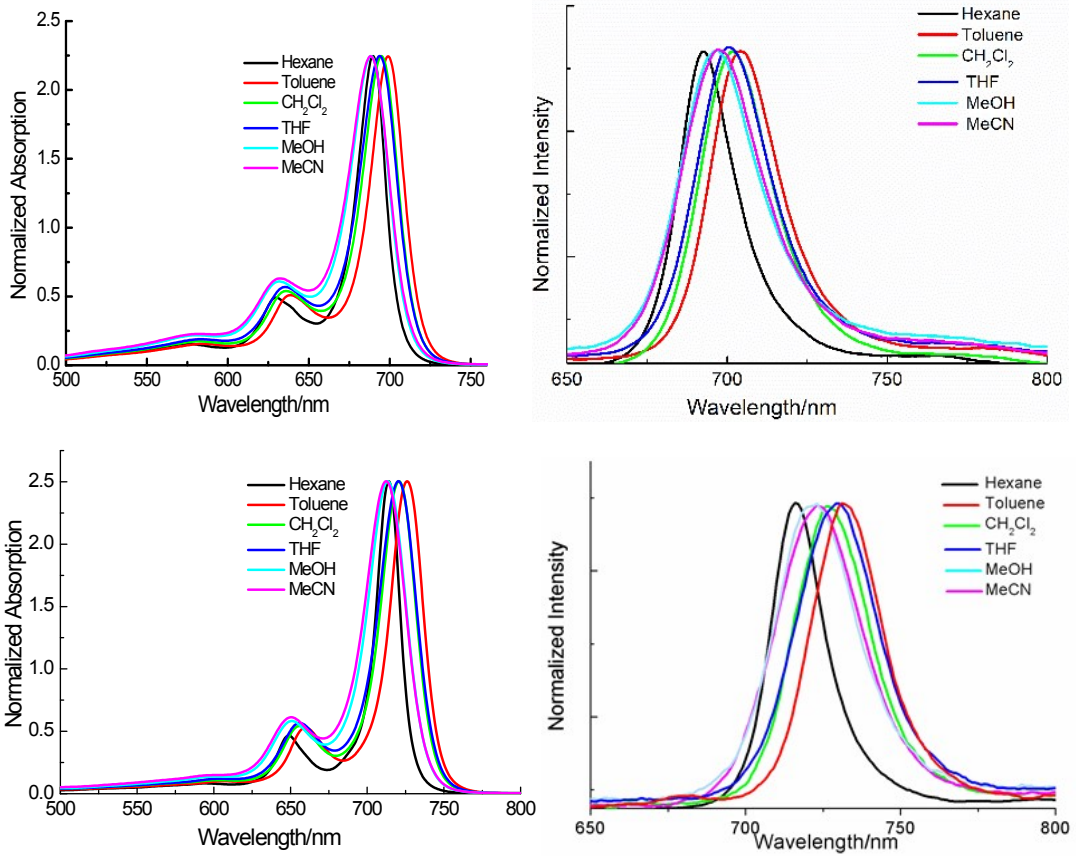


Fig S1. The absorption and emission spectra of **1**-**2** in hexane, toluene, DCM, THF, MeOH, CH_3CN (Top for **1**; bottom for **2**. left: absorption spectra, right: emission)

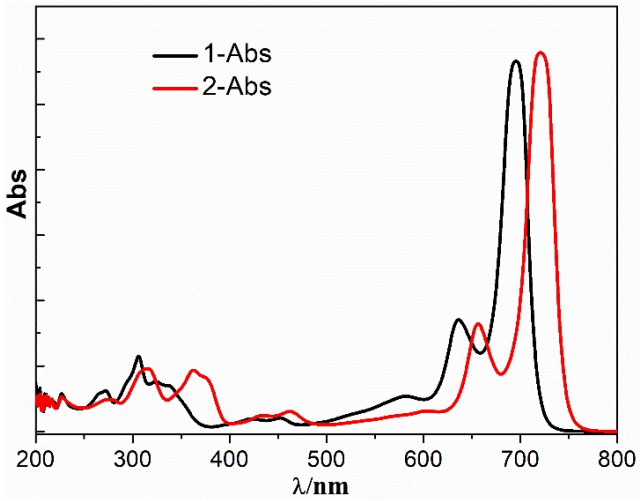


Fig S2. The absorption of full spectra of **1** and **2** in DCM.

I.3 The quantum yield of singlet oxygen

Singlet oxygen quantum yields of the photosensitizers were calculated by monitoring the photooxidation of 1,3-diphenyl isobenzofuran (DPBF), a known singlet oxygen scavenger, using MB as the standard (Φ_{Δ}= 0.57 in dichloromethane).[S2] The mixture of photosensitizer and DPBF was irradiated with a 690 nm laser beam at a power of 100 mW cm^{-2} at 30 s intervals. The absorbance was measured after each irradiation and a decrease in the absorption band intensity for DPBF at 410 nm was observed. The following equation was used to calculate the singlet oxygen quantum yield of sensitizer:

$$\Phi_{\Delta(x)} = \Phi_{\Delta(\mathrm{std})}\left(\frac{S_x}{S_{\mathrm{std}}}\right)\left(\frac{F_{\mathrm{std}}}{F_x}\right)$$

where $\Phi_{\Delta(x)}$ is the single oxygen quantum yield of sample, the 'χ' and 'std' subscripts denote the sample and MB standard, respectively, *S* denotes the slope of a plot of the change in absorbance for DPBF at 410 nm *vs* the irradiation time, and F is the absorption correction factor, which is given by $F = 1-10^{-OD}$ (where OD represents the optical density of sample and MB at the irradiation wavelength).

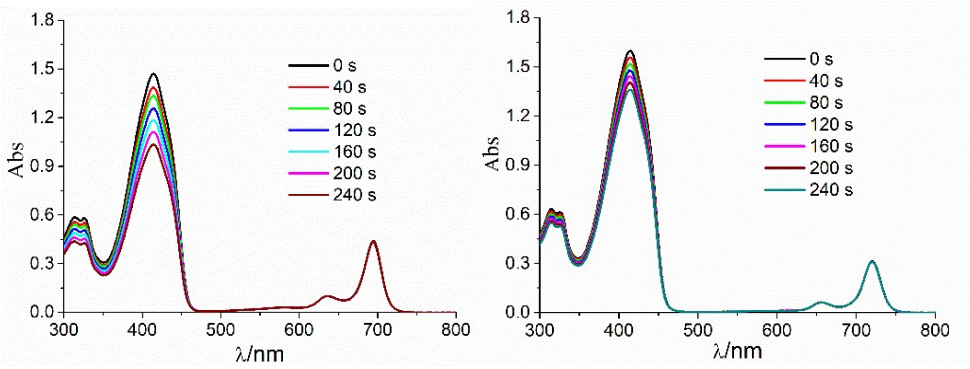
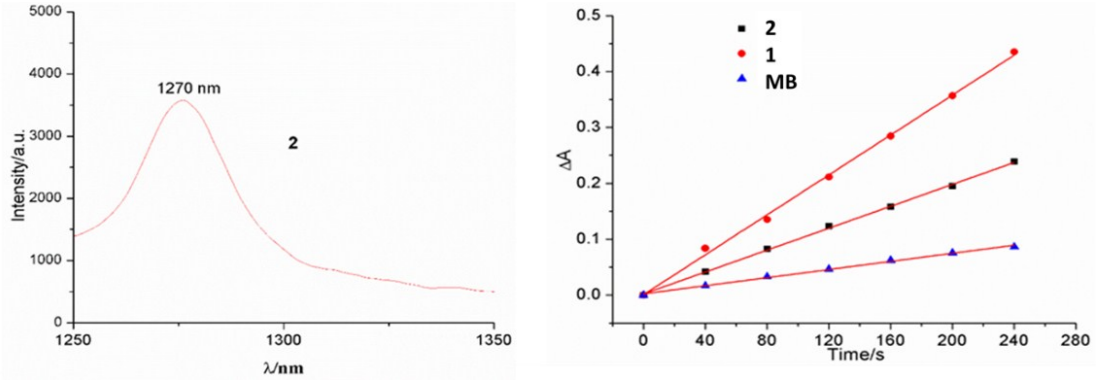


Fig. S3 Changes in the absorption spectra of DPBF upon irradiation (λ_{irr}=690 nm) in the presence of **1** (left) and **2** (right) with 40s interval in CH_2Cl_2.



	1	2	MB
Slope	1.79×10^{-3}	9.80×10^{-4}	3.62×10^{-4}
R2 values	0.9979	0.9990	0.9952

Fig. S4 The slope of the graph obtained by plotting the changes in optical density against time is used to calculate the quantum yield of singlet oxygen.

I.4 NICS value calculations

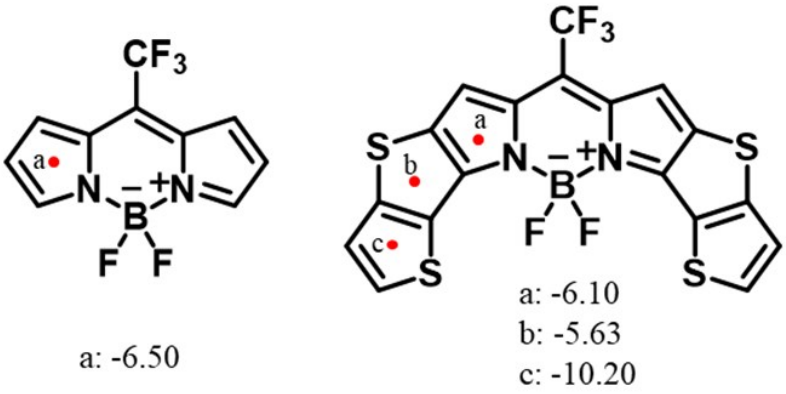


Fig. S5 Nuclear Independent Chemical Shift (NICS (0)) values were calculated using the DFT-GIAO method with the 6-31g(d, p)[S1] for the optimized structures of parent BODIPY and **1**

I.5 DFT optimized geometry of compound **BDP-1b, BDP-3b, 1, 2**

Table S1. DFT optimized geometry of compound **BDP-1b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.815139	0.914249	0.014117
2	7	0	0.441887	1.537840	-0.000103
3	5	0	1.785894	0.831451	0.072108
4	7	0	1.510389	-0.673055	0.003408
5	6	0	0.251321	-1.332110	0.013261
6	6	0	-0.911000	-0.498738	0.030280
7	6	0	2.498354	-1.569852	-0.039999
8	6	0	1.965297	-2.865712	-0.063834
9	6	0	0.584824	-2.760682	-0.031914
10	6	0	-1.791311	1.982101	-0.031151
11	6	0	-1.090443	3.178877	-0.070891
12	6	0	0.281783	2.866679	-0.048328
13	6	0	-2.347554	-0.987817	0.025692
14	9	0	2.608150	1.225009	-1.012621
15	9	0	2.445260	1.150006	1.287943
16	9	0	-2.563526	-2.314220	0.213398
17	9	0	-3.086597	-0.393324	1.023896
18	9	0	-2.971104	-0.684092	-1.169081
19	1	0	2.543428	-3.776113	-0.102031
20	1	0	-1.504546	4.174574	-0.111760
21	6	0	-0.292463	-4.014163	-0.052069
22	1	0	-0.857223	-4.082576	0.856794
23	1	0	-0.957639	-3.985553	-0.893125
24	1	0	0.344302	-4.878028	-0.135993
25	6	0	-3.320013	1.888789	-0.040448
26	1	0	-3.643969	1.255414	-0.844131
27	1	0	-3.667583	1.489028	0.891507
28	1	0	-3.730349	2.873937	-0.177344
29	6	0	1.485333	3.808123	-0.071267
30	1	0	2.095843	3.629559	0.796322
31	1	0	2.065800	3.626227	-0.958439
32	1	0	1.143824	4.828068	-0.067370

33	6	0	3.962267	-1.131806	-0.057630
34	1	0	4.153208	-0.556057	-0.945892
35	1	0	4.165083	-0.527306	0.808777
36	1	0	4.597249	-1.999953	-0.047722

---------- Electronic energies of optimized geometries of **BDP-1b**: -1175.21783360 a.u.

Table S2. DFT optimized geometry of compound **BDP-3b**. :

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	5.091137	-0.625102	-0.211581
2	16	0	-5.134494	-0.535961	-0.210112
3	9	0	-0.055285	-2.869405	-0.653226
4	9	0	-0.045274	-2.315889	1.595345
5	9	0	0.545806	3.178790	-1.167538
6	9	0	-1.122782	3.344154	0.297163
7	7	0	-1.252367	-0.873435	0.055809
8	7	0	1.204687	-0.911313	0.054244
9	6	0	-3.267960	-2.485600	-0.099030
10	6	0	4.578588	-2.363341	-0.190246
11	6	0	2.566385	0.956795	-0.022728
12	6	0	-2.592263	1.012603	-0.025497
13	6	0	-0.001866	1.200734	0.082595
14	6	0	-2.541428	-1.268650	-0.039622
15	6	0	2.489692	-1.323503	-0.041455
16	6	0	3.349886	-0.178690	-0.090066
17	6	0	-3.387280	-0.112903	-0.090195
18	6	0	0.083144	2.703730	0.062708
19	5	0	-0.035240	-1.777161	0.267469
20	6	0	3.200087	-2.549709	-0.103316
21	6	0	1.208727	0.495845	0.063732
22	6	0	-1.234881	0.538867	0.062696
23	6	0	-4.644248	-2.280642	-0.185255
24	9	0	0.970435	3.191374	1.020936
25	1	0	-5.349854	-3.083621	-0.232644
26	1	0	-2.810733	-3.452799	-0.079808
27	1	0	2.730009	-3.510750	-0.085255
28	1	0	5.273483	-3.175462	-0.240032
29	6	0	-3.024803	2.490399	-0.050529
30	1	0	-2.758489	2.955712	0.875462
31	1	0	-2.532135	2.992622	-0.856724
32	1	0	-4.084317	2.549643	-0.187719

33	6	0	3.011105	2.431060	-0.041939
34	1	0	2.492394	2.949953	-0.820777
35	1	0	2.784861	2.884159	0.900618
36	1	0	4.065054	2.483393	-0.219006

Electronic energies of optimized geometries of **BDP-3b**: -2045.31138242 a.u.

Table S3. DFT optimized geometry of compound **1**. :

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.859332	-3.042546	0.018206
2	16	0	2.821802	-3.072322	0.012610
3	16	0	5.048615	0.531748	-0.307298
4	16	0	-5.057382	0.578423	-0.311936
5	9	0	-0.020896	-1.796613	-0.197085
6	9	0	-0.013886	-0.866038	1.893631
7	9	0	0.215835	4.244069	-1.273688
8	9	0	-1.082104	4.448774	0.458503
9	7	0	-1.233025	0.270632	0.144378
10	7	0	1.221365	0.252576	0.144369
11	6	0	5.328930	-2.377592	-0.272272
12	1	0	6.403960	-2.438923	-0.392957
13	6	0	-3.231130	-1.344029	-0.045847
14	6	0	4.582105	-1.175110	-0.208446
15	6	0	2.569632	2.114044	-0.055501
16	1	0	2.872888	3.146209	-0.130396
17	6	0	-2.567705	2.141781	-0.062251
18	1	0	-2.865474	3.174098	-0.144197
19	6	0	0.005404	2.349201	0.122307
20	6	0	-4.547297	-3.429084	-0.156257
21	1	0	-4.852175	-4.467572	-0.172042
22	6	0	-2.511827	-0.127830	0.008706
23	6	0	2.497766	-0.155329	0.009202
24	6	0	4.506871	-3.472346	-0.161902
25	1	0	4.803216	-4.513250	-0.179961
26	6	0	3.355643	0.981692	-0.120200
27	6	0	-3.361104	1.015219	-0.124079
28	6	0	-5.360559	-2.328026	-0.269957
29	1	0	-6.435962	-2.380874	-0.391277
30	6	0	0.045434	3.859892	0.009724
31	5	0	-0.011406	-0.612490	0.535002
32	6	0	3.207573	-1.376841	-0.047150

33	6	0	1.222775	1.649321	0.100768
34	6	0	-1.222487	1.669224	0.097198
35	6	0	-4.603990	-1.131684	-0.208646
36	9	0	1.062912	4.389859	0.722739

Electronic energies of optimized geometries of **1**: -2915.44102221 a.u.

Table S4. DFT optimized geometry of compound **2**. :

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.849454	-1.468785	0.105133
2	16	0	2.831712	-1.492324	0.102495
3	16	0	5.054665	2.106525	-0.293885
4	16	0	-5.051374	2.141794	-0.303645
5	9	0	-0.012308	-0.224595	-0.135726
6	9	0	-0.007232	0.750702	1.934511
7	9	0	0.218191	5.791817	-1.341801
8	9	0	-1.080722	6.032249	0.385061
9	7	0	-1.226875	1.848155	0.160738
10	7	0	1.227533	1.832846	0.162117
11	6	0	5.338191	-0.801075	-0.196229
12	1	0	6.413340	-0.863785	-0.315131
13	6	0	-3.223107	0.227547	0.004442
14	6	0	4.590005	0.401665	-0.158565
15	6	0	2.573822	3.691095	-0.077161
16	1	0	2.875965	4.721751	-0.174097
17	6	0	-2.563540	3.712939	-0.086600
18	1	0	-2.862417	4.742923	-0.190833
19	6	0	0.009258	3.927152	0.094507
20	6	0	-4.536913	-1.860869	-0.061670
21	6	0	-2.505177	1.445441	0.033139
22	6	0	2.504444	1.423558	0.036267
23	6	0	4.517299	-1.894123	-0.062694
24	6	0	3.361115	2.558493	-0.117190
25	6	0	-3.355663	2.584422	-0.124526
26	6	0	-5.351347	-0.763418	-0.199337
27	1	0	-6.426639	-0.820063	-0.319932
28	6	0	0.047662	5.435119	-0.050499
29	5	0	-0.004447	0.974997	0.570748
30	6	0	3.215629	0.201910	0.006468

31	6	0	1.227413	3.228332	0.088510
32	6	0	-1.217867	3.245421	0.083516
33	6	0	-4.596131	0.434810	-0.163443
34	9	0	1.064244	5.981423	0.651376
35	53	0	-5.055445	-3.634596	-0.050723
36	53	0	5.025228	-3.670933	-0.055120

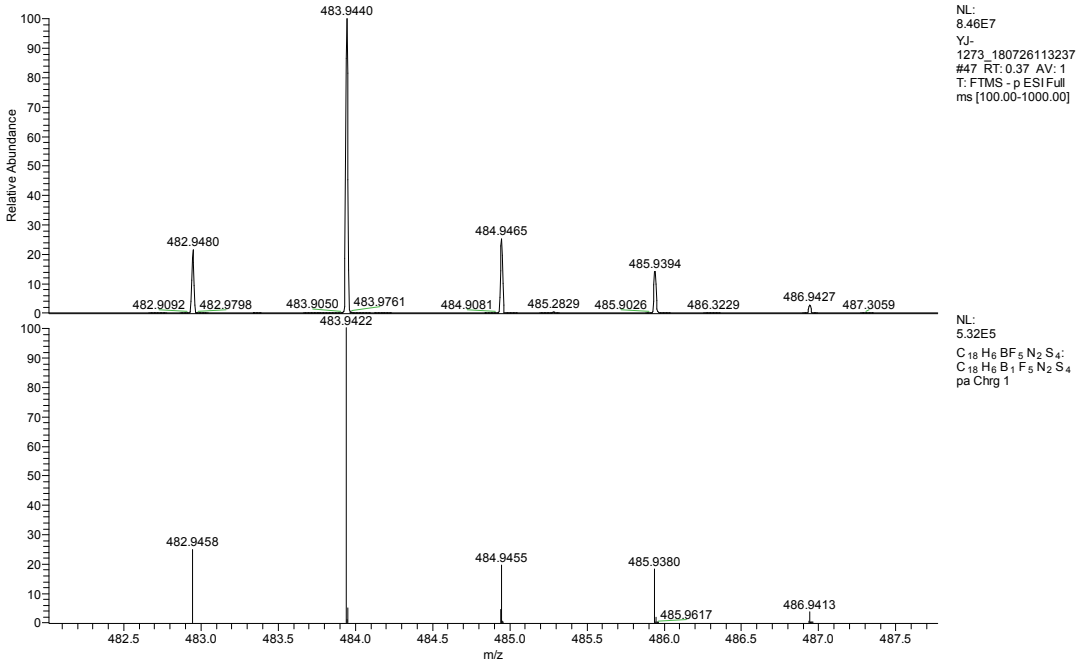
Electronic energies of optimized geometries of **2**: -2936.90870422 a.u.

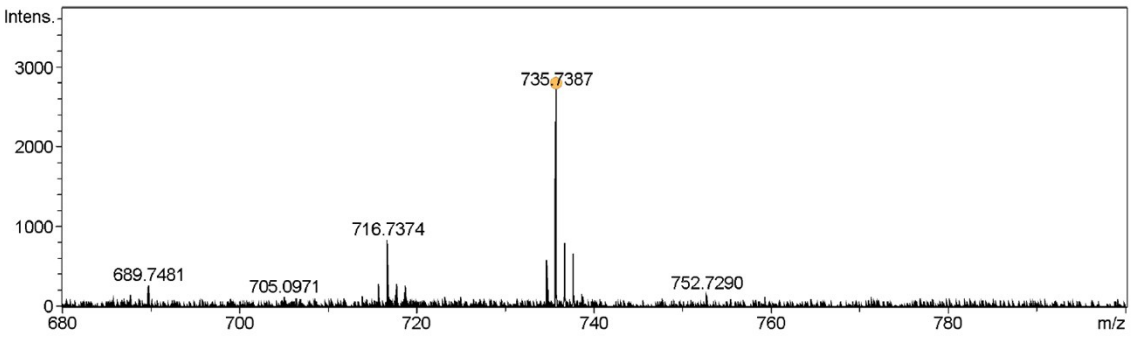
II. References

S1 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

S2 Y. C. Yang, Q. L. Guo, H. C. Chen, Z. K. Zhou, Z. J. Guo and Z. Shen, C*hem. Commun.,* **2013**, *49*, 3940.

III. HRMS-ESI and ^{1}H NMR spectra





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
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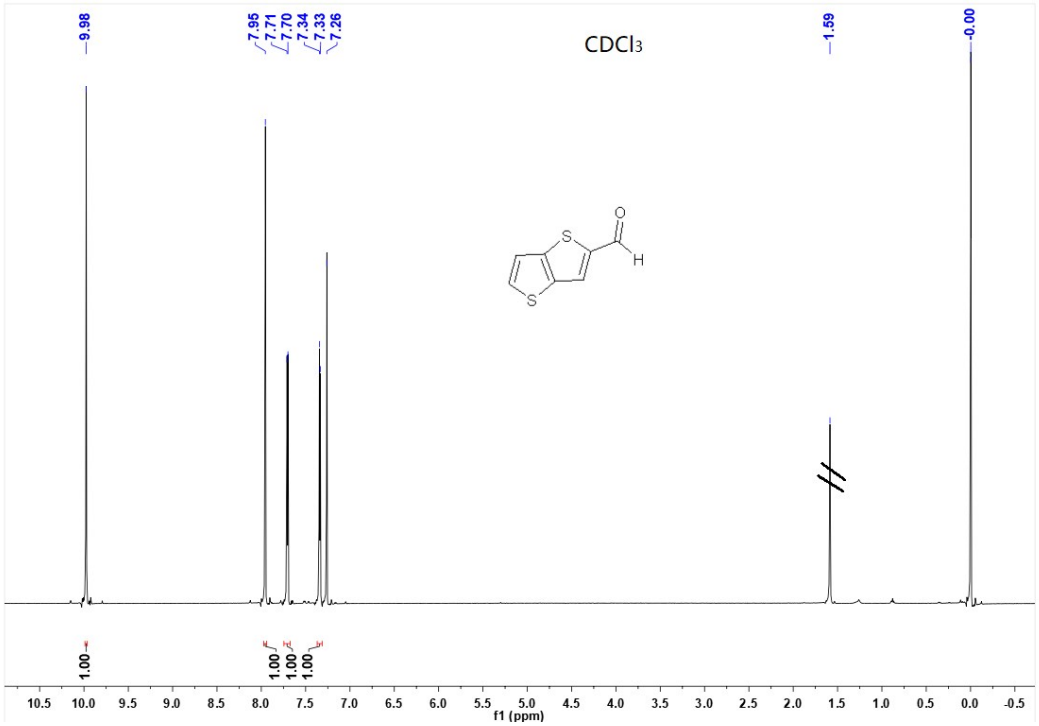
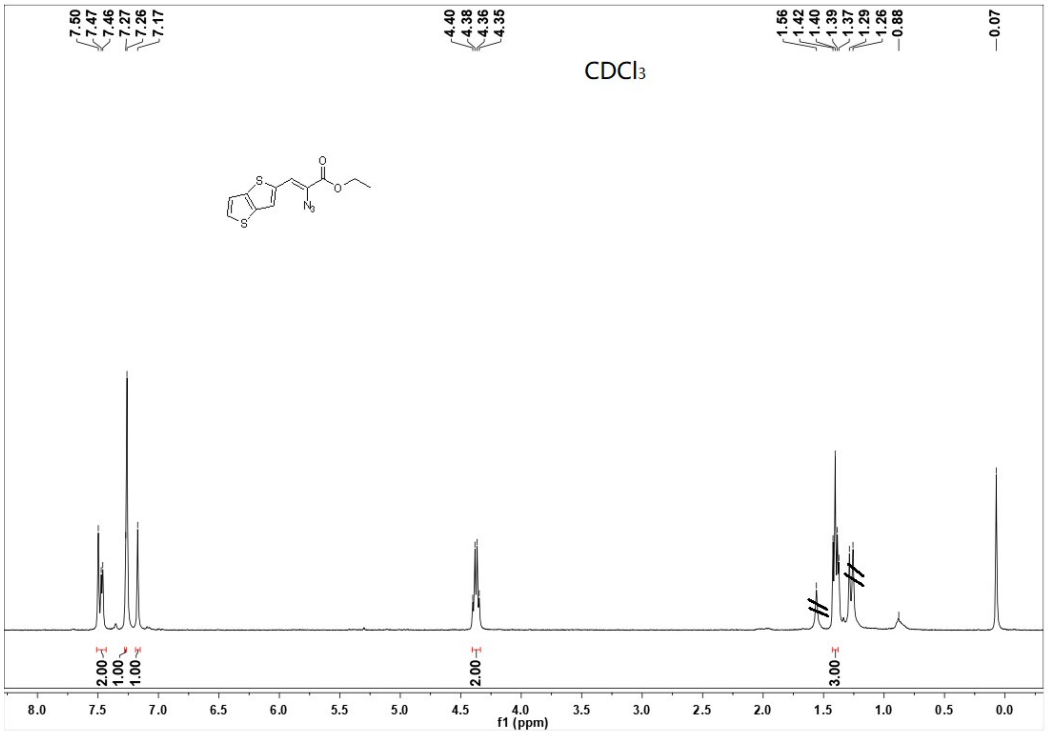
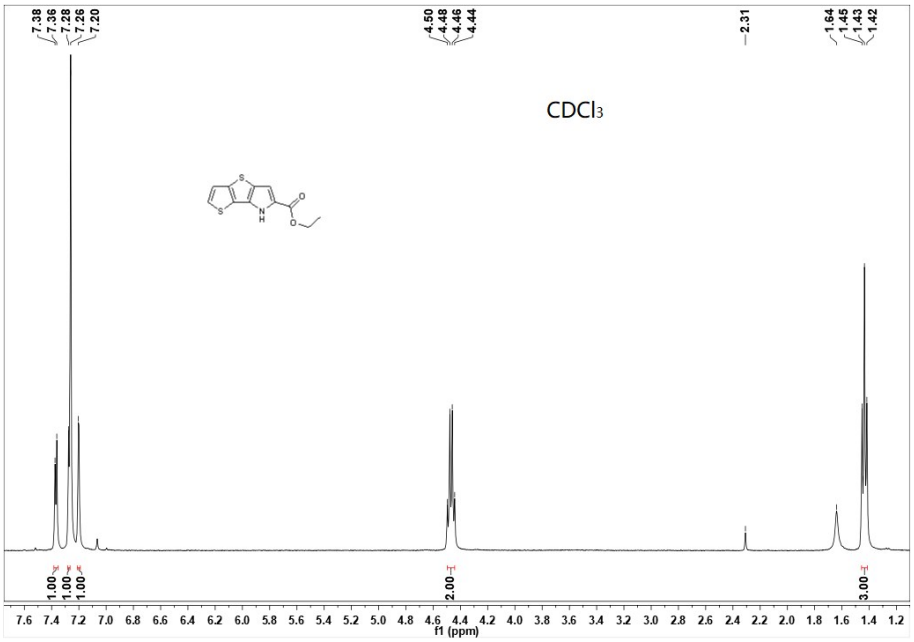


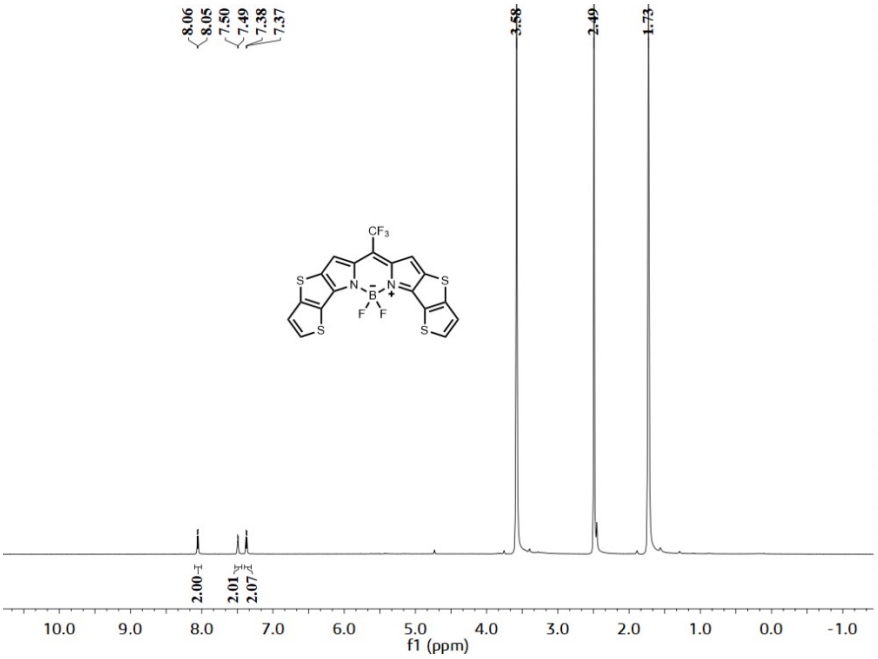
^{1}H NMR spectra of compound 6



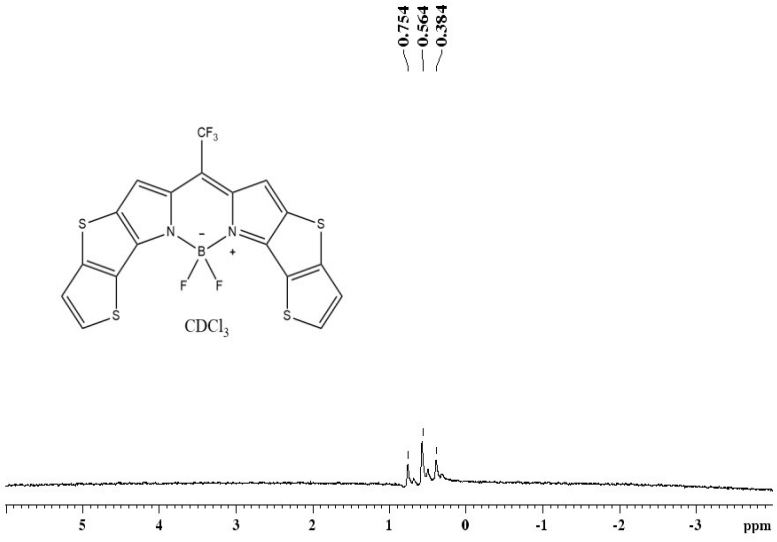
^{1}H NMR spectra of compound 5



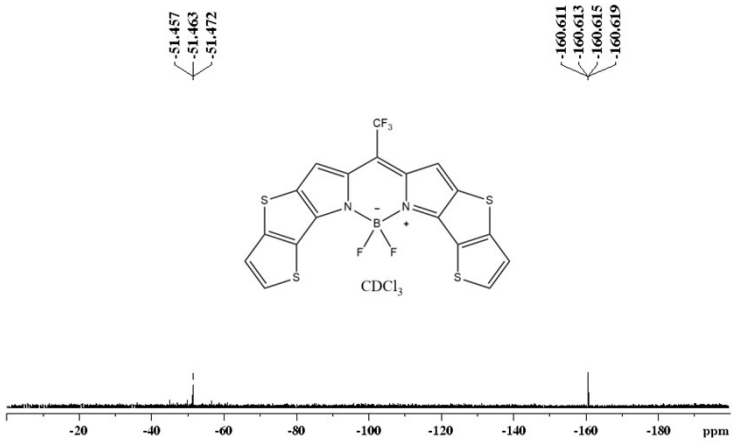
^{1}H NMR spectra of compound 4



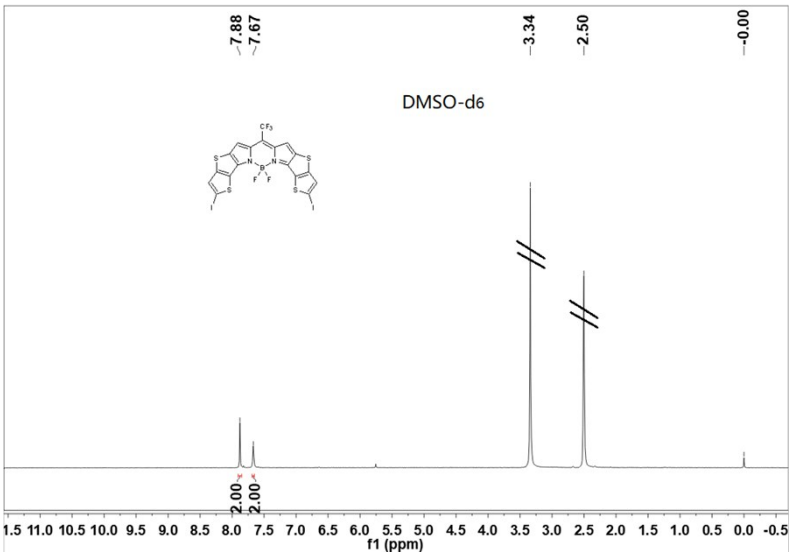
^{1}H NMR spectra of compound 2



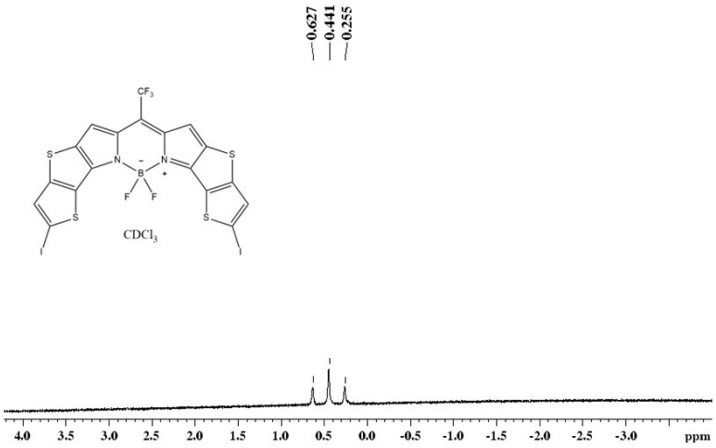
^{11}B NMR spectra of compound 1



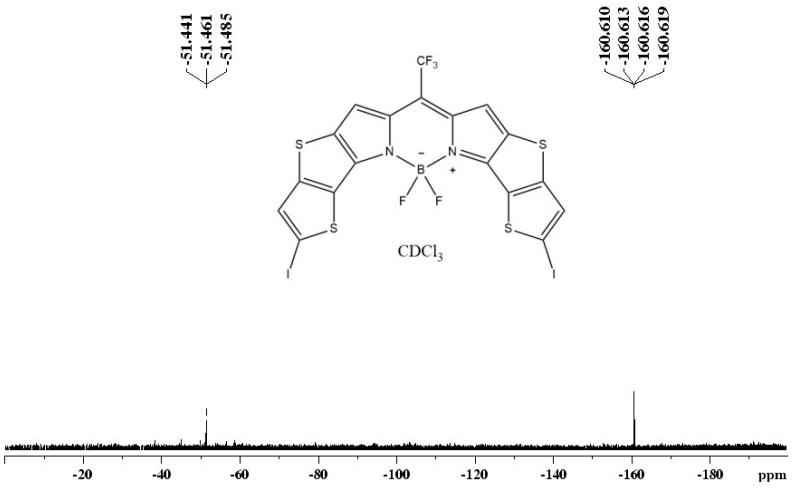
^{19}F NMR spectra of compound 1



^{1}H NMR spectra of compound 2



^{11}B NMR spectra of compound 2



^{19}F NMR spectra of compound 2