Supporting Information

Double anchor indolo[3,2-*b*]indole derived metal-free dyes with extra electron donors as efficient sensitizers for dye-sensitized solar cells

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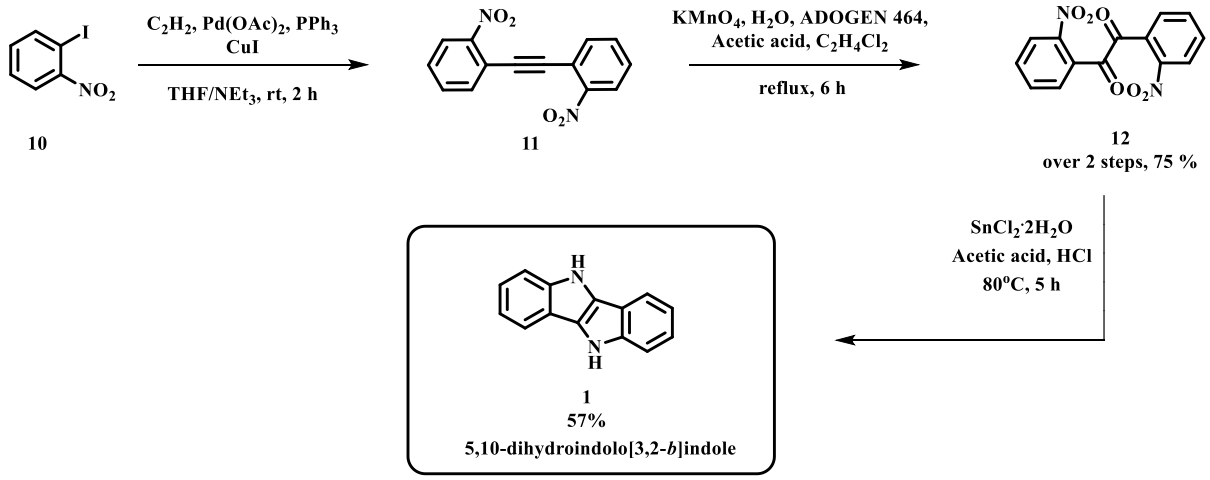
Contents

1. General methods

All reagents and anhydrous solvents were purchased from Sigma Aldrich or TCI. Other solvents were distilled and dried before use according to standard procedures if required. The products were purified by Column chromatography (Silica Flash P60, 230–400 mesh). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) were recorded on a Varian AMX400 (400 MHz) or a Varian Inova (500 MHz) spectrometer. The chemical shifts were calibrated in δ values (ppm) relative to its corresponding solvent, for example, Acetone-d_6 (1H: δ = 2.05 and 13C: δ = 206.68, 29.92) and DMSO-d_6 (1H: δ = 2.50 and 13C: δ = 39.52), where the splitting parameters for ^{1}H-NMR were nominated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). UV-Visible absorption spectra were recorded on a Cary 60 UV/Vis (Agilent Technologies) spectrophotometer in a spectrograde solvent. High-resolution mass spectrum (HRMS) spectra were performed on a mass spectrometer (Bruker micrOTOF with ESI and/or APCI ionization sources and Bruker Autoflex Speed with HRMS MALDI-TOF mass analysis). Cyclic voltammogram (CV) were measured on an Autolab PGSTA101.

2. Synthesis of indolo[3,2-*b*]indole

The synthesis of indolo[3,2-*b*]indole (**1**) was started from Sonogashira cross-coupling reaction of 1-iodo-2-nitrobenzene (**10**) with acetylene gas to provide compound **11**. Then, without further purification, the crude compound **11** was oxidized by $KMnO_4$ to give diketone **12**. Finally, the reduction and cyclization reaction of compound **12** was performed in acidic condition using $SnCl_2$ as a reducing agent providing the core donor **1** in good yield, (Scheme **S1**). [1]



Scheme S1. The synthesis of 5,10-dihydroindolo[3,2-*b*]indole (**1**).

3. Cyclic voltammetry of dyes 1 and 2

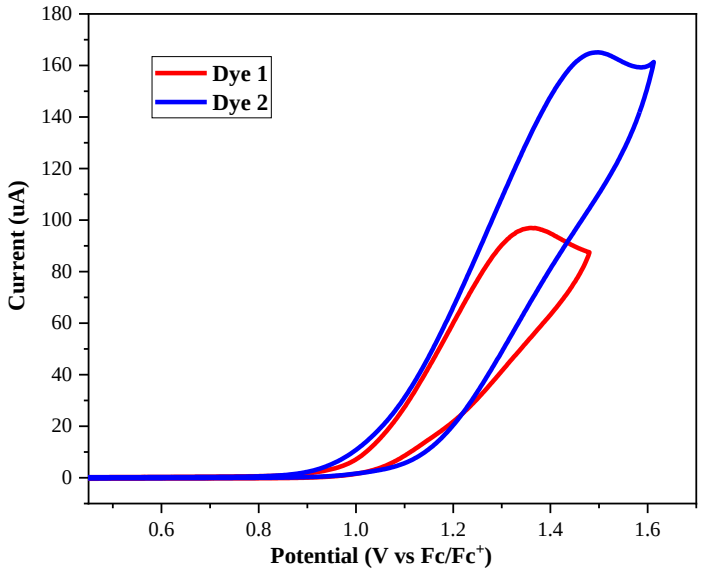


Fig. S1. Cyclic voltammogram of dyes **1** and **2** in DMSO.

4. Bode phase plot and electron recombination lifetime

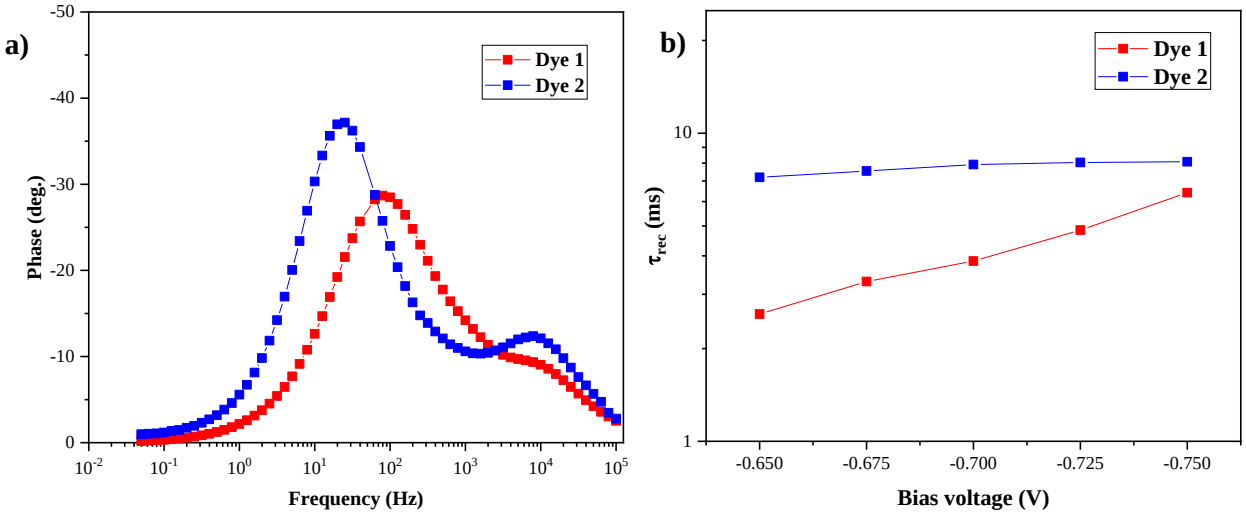


Fig. S2. Plots of a) Bode-phase measured at 0.7 V bias voltage, b) Electron recombination lifetime (τ_{rec}) as a function of bias voltages of the DSSCs in the dark.

5. FTIR spectra

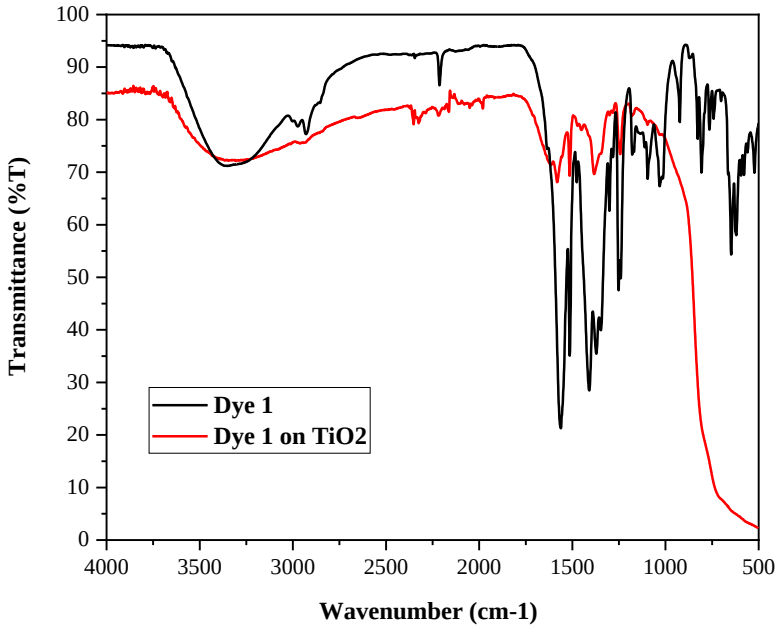


Fig. S3. FTIR spectrum of dye **1** in DMSO (black) and on TiO_2 (red)

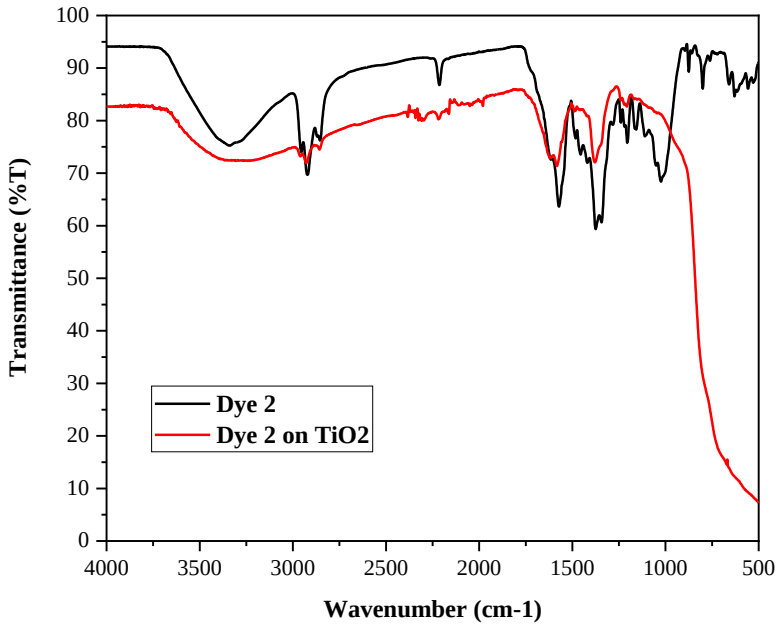


Fig. S4. FTIR spectrum of dye **2** in DMSO (black) and on TiO_2 (red)

6. Long-term stability of the devices of dye 1, 2, and N719

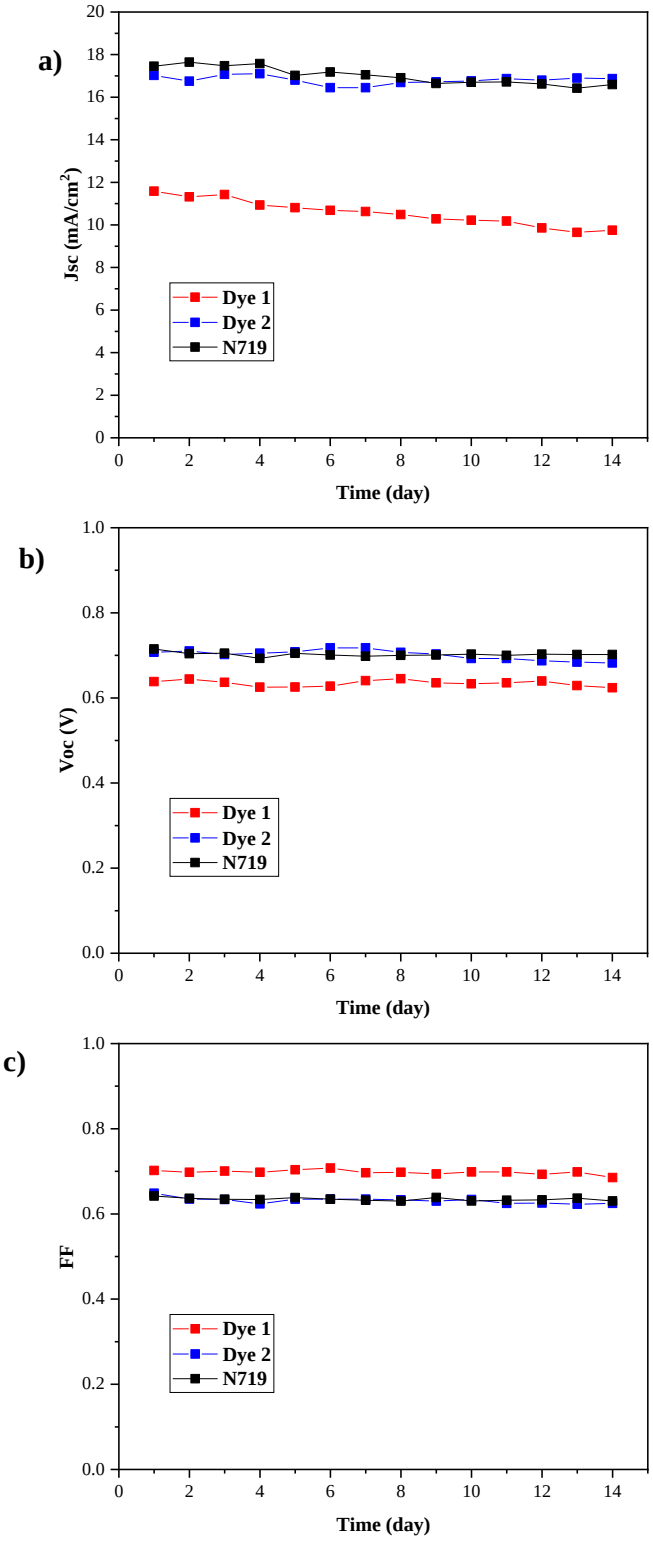


Fig. S5. Comparing photovoltaic metrics of the devices of dyes **1**, **2**, and **N719**: a) J_{sc}, b) V_{oc}, c) *FF*

7. Parameters of electronic transitions from Gaussian

Table S1. Calculated TD-DFT excitation energies (E) and characters, oscillator strengths (*f*), MO compositions and the experimental maximum absorptions for all of dyes.

dye	n[a]	*E* (eV, nm)	*f*	composition	character	experiment (eV, nm)
1	1	2.52 (493)	0.11	98% HOMO →LUMO	CT	2.69 (463)
	3	3.12 (397)	0.34	89% HOMO -1 →LUMO	$\pi \rightarrow \pi^*$	3.13 (396)
2	1	2.50 (496)	0.10	98% HOMO →LUMO	CT	2.57 (483)
	3	3.10 (400)	0.33	90% HOMO -1 →LUMO	$\pi \rightarrow \pi^*$	3.04 (408)

[a] Sequence of calculated transitions in order of energy

Table S2. Energies (Ha) and atom coordinates (Å)

Dye **1** Energy = -2056.625784 Hartree

C	2.371500	-3.622752	-0.069723
C	3.321412	-2.556823	-0.038279
C	2.861341	-1.223764	-0.059332
C	1.491596	-0.971804	-0.093958
C	0.559566	-2.072996	-0.089531
C	1.008088	-3.400405	-0.092576
N	-0.736799	-1.594140	-0.106830
C	-0.663839	-0.201756	-0.139017
C	0.661383	0.193942	-0.139426
N	0.735055	1.585709	-0.113983
C	-0.562326	2.064694	-0.100277
C	-1.494177	0.964357	-0.099850
C	-2.864991	1.215886	-0.065828
C	-3.324695	2.548703	-0.051989
C	-2.374374	3.613774	-0.090530
C	-1.010712	3.391827	-0.111095

C	-1.926637	-2.386302	-0.148483
C	1.925639	2.376259	-0.151098
C	-2.770733	-2.324995	-1.266299
C	-3.924790	-3.094563	-1.307586
C	-4.246846	-3.949001	-0.239222
C	-3.399489	-4.015655	0.875127
C	-2.248334	-3.226857	0.917419
C	2.239065	3.224341	0.911440
C	3.392606	4.009955	0.874719
C	4.251185	3.932486	-0.230280
C	3.937538	3.070809	-1.295334
C	2.780860	2.304665	-1.259890
C	4.709226	-2.942185	0.004836
C	5.869590	-2.224624	0.125436
C	7.161004	-2.985853	0.125060
C	5.951355	-0.811988	0.272375
N	6.116702	0.336143	0.403201
O	7.221215	-4.194433	0.022850
O	8.300705	-2.270224	0.245410
C	-4.713263	2.938861	-0.009277
C	-5.876951	2.230962	0.129012
C	-7.150121	3.000619	0.123455
C	-5.960717	0.818572	0.299196
N	-6.043837	-0.334594	0.446450
O	-7.232198	4.208846	-0.002507
O	-8.228872	2.203639	0.275844
O	-5.391732	-4.667184	-0.383014
O	5.399870	4.646148	-0.367496
C	5.781732	5.526456	0.687958

C	-5.784828	-5.536867	0.677095
H	2.740030	-4.644336	-0.069668
H	3.558338	-0.394943	-0.059965
H	0.306420	-4.227055	-0.110964
H	-3.562931	0.388268	-0.059883
H	-2.742386	4.635591	-0.097056
H	-0.309340	4.218664	-0.133971
H	-2.514867	-1.679647	-2.101194
H	-4.590333	-3.056421	-2.163803
H	-3.628037	-4.661297	1.714410
H	-1.602490	-3.262654	1.789331
H	1.584827	3.268366	1.776682
H	3.614199	4.661601	1.711235
H	4.611132	3.024814	-2.144859
H	2.531454	1.654259	-2.092835
H	4.890108	-4.012970	-0.064120
H	8.121765	-1.314523	0.315929
H	-4.885946	4.009899	-0.094257
H	-9.015273	2.781770	0.261286
H	5.030963	6.310218	0.844550
H	6.720404	5.981397	0.369480
H	5.940335	4.979208	1.624635
H	-5.954458	-4.980003	1.606090
H	-5.035325	-6.318394	0.850188
H	-6.719509	-5.995833	0.352711

Dye **2** Energy = -2449.774003 Hartree

C	-0.001384	4.327019	-0.278263
C	-1.380110	3.955490	-0.251519

C	-1.724826	2.587974	-0.268232
C	-0.716421	1.627104	-0.296250
C	0.666584	2.038094	-0.291775
C	1.017828	3.394506	-0.297431
N	1.488956	0.927393	-0.305953
C	0.665347	-0.197712	-0.336917
C	-0.659872	0.196854	-0.337360
N	-1.483951	-0.927128	-0.310268
C	-0.660853	-2.038594	-0.298276
C	0.721675	-1.628307	-0.299529
C	1.731263	-2.589385	-0.271621
C	1.386347	-3.956529	-0.259688
C	0.007627	-4.326983	-0.291484
C	-1.012006	-3.394705	-0.309251
C	2.917885	0.936127	-0.357810
C	-2.912482	-0.932242	-0.359681
C	3.579614	0.407409	-1.475000
C	4.965996	0.413381	-1.527553
C	5.715445	0.960513	-0.471540
C	5.053124	1.496761	0.641671
C	3.658023	1.472864	0.695901
C	-3.652773	-1.486407	0.685021
C	-5.048174	-1.502717	0.634038
C	-5.711114	-0.940561	-0.465915
C	-4.961753	-0.375511	-1.512511
C	-3.575094	-0.378273	-1.464175
C	-2.330009	5.038310	-0.216654
C	-3.696216	5.075391	-0.125805
C	-4.355359	6.421902	-0.122045

C	-4.546384	3.939670	-0.019638
N	-5.322679	3.073007	0.075497
O	-3.738365	7.465184	-0.197089
O	-5.703003	6.450639	-0.029366
C	2.333862	-5.044158	-0.225250
C	3.698368	-5.091739	-0.122516
C	4.336618	-6.435795	-0.123620
C	4.552140	-3.957346	0.000051
N	5.264964	-3.041337	0.106251
O	3.736017	-7.491065	-0.213884
O	5.679915	-6.363428	-0.011588
O	7.064133	0.924100	-0.626317
O	-7.060185	-0.893813	-0.615782
C	-7.895821	-1.438449	0.415784
C	7.899986	1.449801	0.414817
C	9.347362	1.252600	-0.011693
C	10.341154	1.793513	1.024480
C	11.804581	1.589031	0.611961
C	12.808984	2.134100	1.635204
C	14.267969	1.920904	1.218693
C	-9.343312	-1.228829	-0.004418
C	-10.337184	-1.784523	1.023828
C	-11.800564	-1.570682	0.615876
C	-12.805197	-2.128421	1.632042
C	-14.264080	-1.907311	1.219307
H	0.249837	5.383572	-0.279927
H	-2.761978	2.276293	-0.270088
H	2.057545	3.702228	-0.314806
H	2.768630	-2.279276	-0.268673

H	-0.244256	-5.383427	-0.297742
H	-2.051558	-3.702860	-0.330071
H	3.003825	-0.000678	-2.300213
H	5.493347	0.004065	-2.383006
H	5.606722	1.919342	1.471279
H	3.145899	1.867821	1.567945
H	-3.140632	-1.900418	1.548140
H	-5.601424	-1.939433	1.456548
H	-5.489268	0.053186	-2.358333
H	-2.999722	0.042576	-2.283245
H	-1.892389	6.033375	-0.266449
H	-6.080781	5.553430	0.022364
H	1.888019	-6.034979	-0.286337
H	6.016650	-7.279573	-0.020347
H	-7.686033	-0.929996	1.366599
H	-7.674236	-2.507089	0.543223
H	7.693019	0.921543	1.355332
H	7.675750	2.515072	0.564207
H	9.502100	1.752962	-0.976445
H	9.522212	0.181744	-0.176842
H	10.165541	1.302481	1.992665
H	10.155651	2.865485	1.185263
H	11.978845	2.072878	-0.360474
H	11.990810	0.516129	0.456812
H	12.631570	1.653409	2.607815
H	12.624486	3.207119	1.787111
H	14.960570	2.321563	1.967831
H	14.483815	2.418054	0.264783
H	14.491975	0.854220	1.093729

H	-9.501463	-1.711418	-0.977618
H	-9.514954	-0.154611	-0.150291
H	-10.159718	-1.309510	1.999635
H	-10.153603	-2.859281	1.167142
H	-11.976804	-2.039862	-0.363346
H	-11.984613	-0.495216	0.476610
H	-12.626509	-1.661583	2.611141
H	-12.622213	-3.203719	1.768878
H	-14.481106	-2.390996	0.258779
H	-14.486618	-0.838688	1.109154
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8. NMR spectra of new compounds

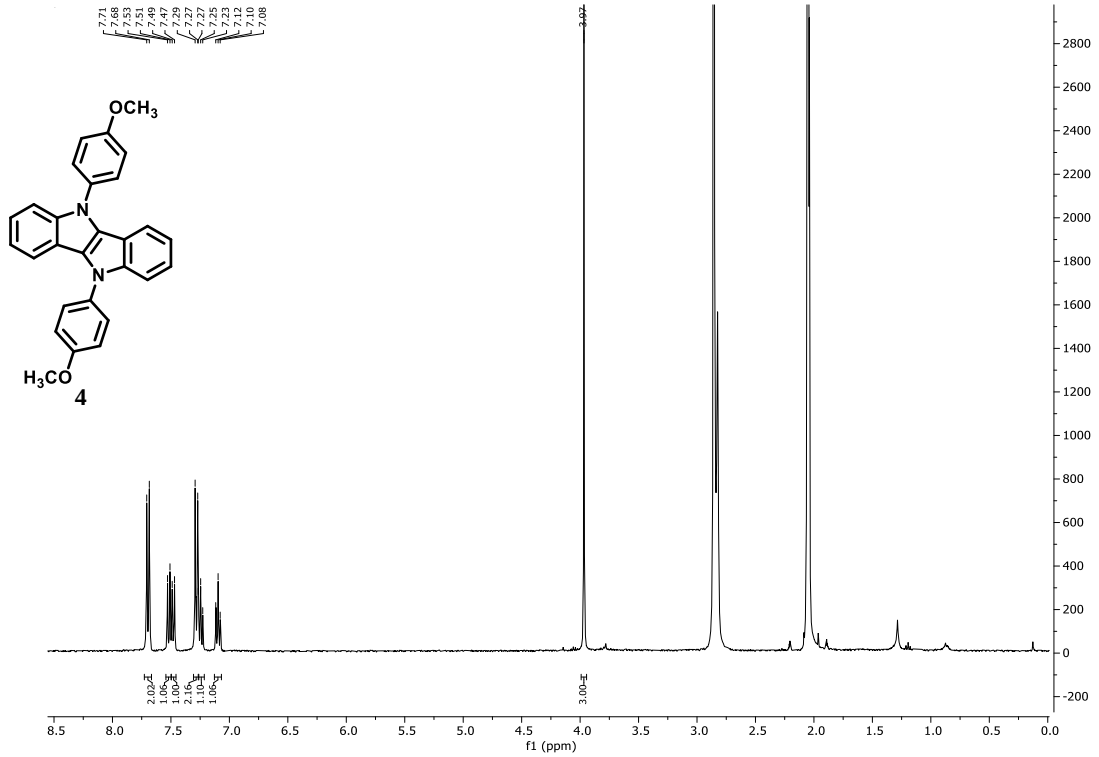

Fig. S6. ^{1}H NMR spectrum of compound **4** in acetone-d_6.

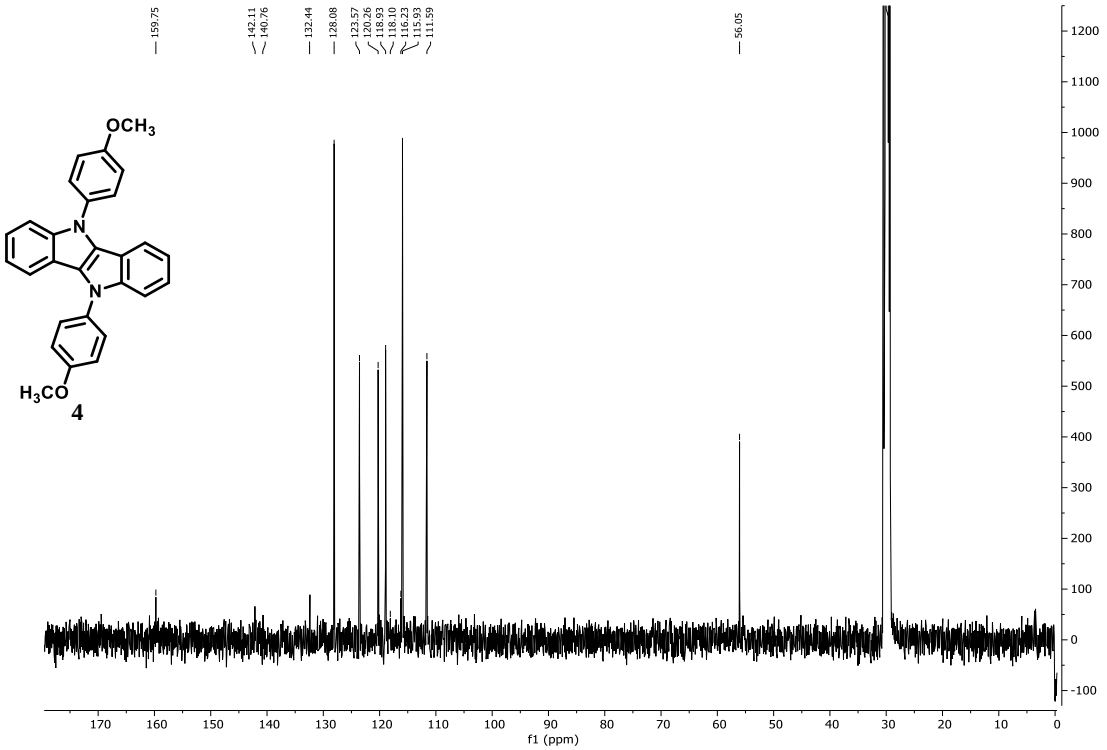

Fig. S7. ^{13}C NMR spectrum of compound **4** in acetone-d_6.

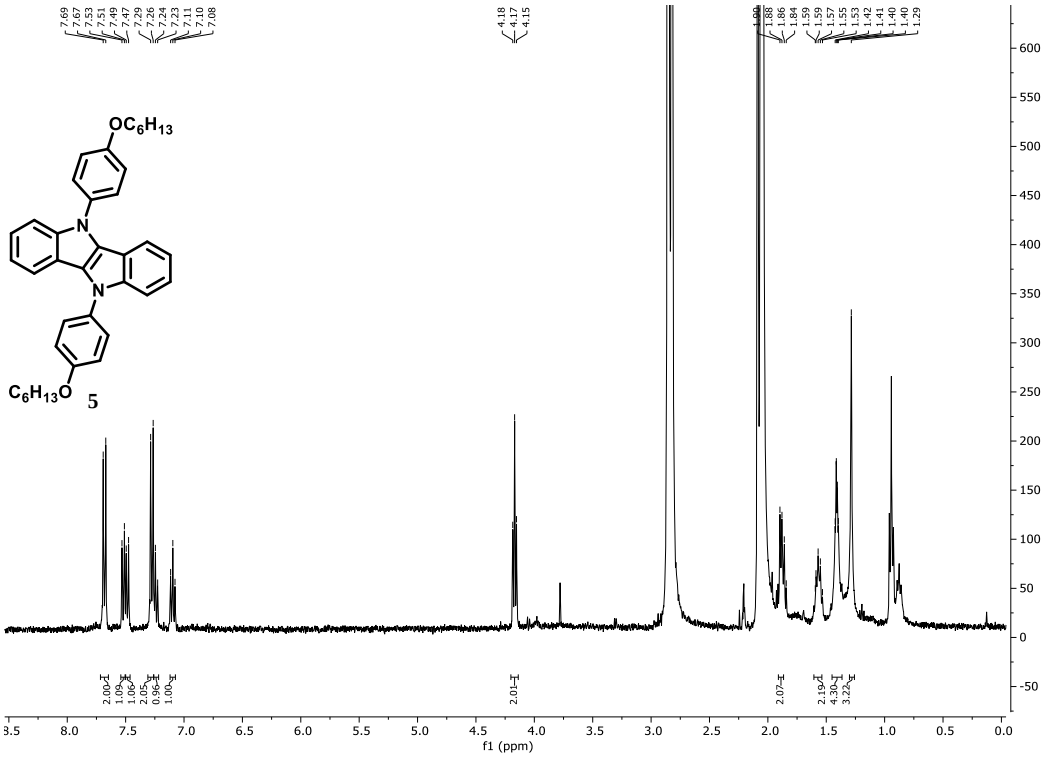

Fig. S8. ^{1}H NMR spectrum of compound **5** in acetone-d_6.

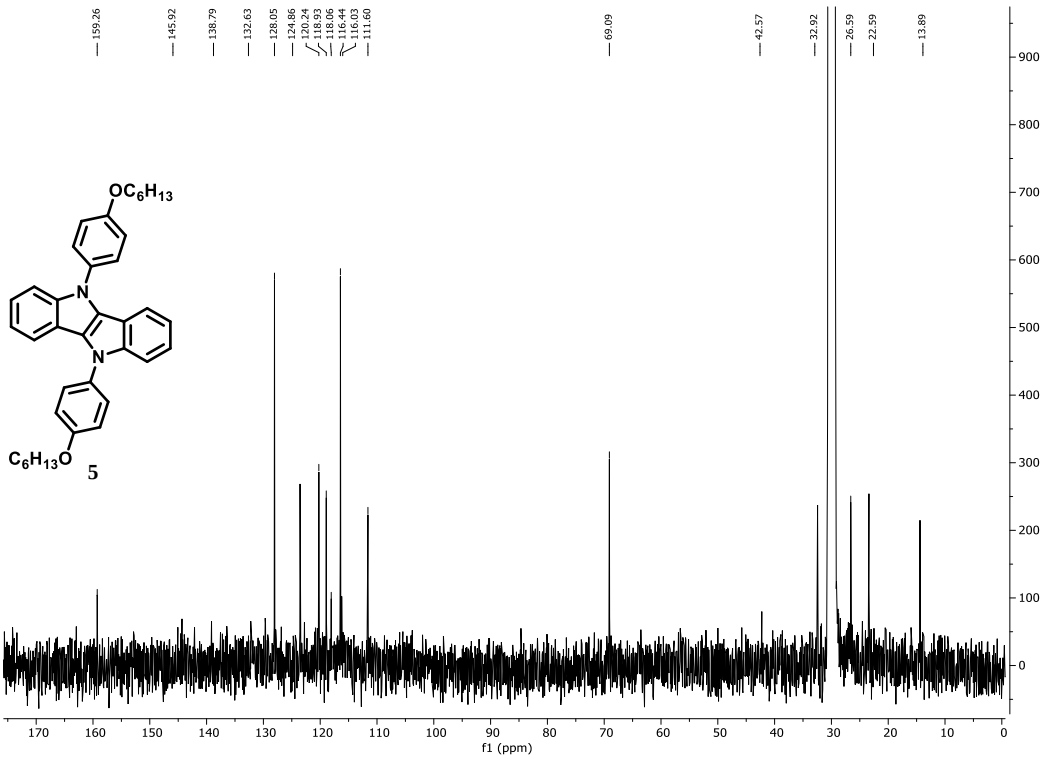

Fig. S9. ^{13}C NMR spectrum of compound **5** in acetone-d_6.

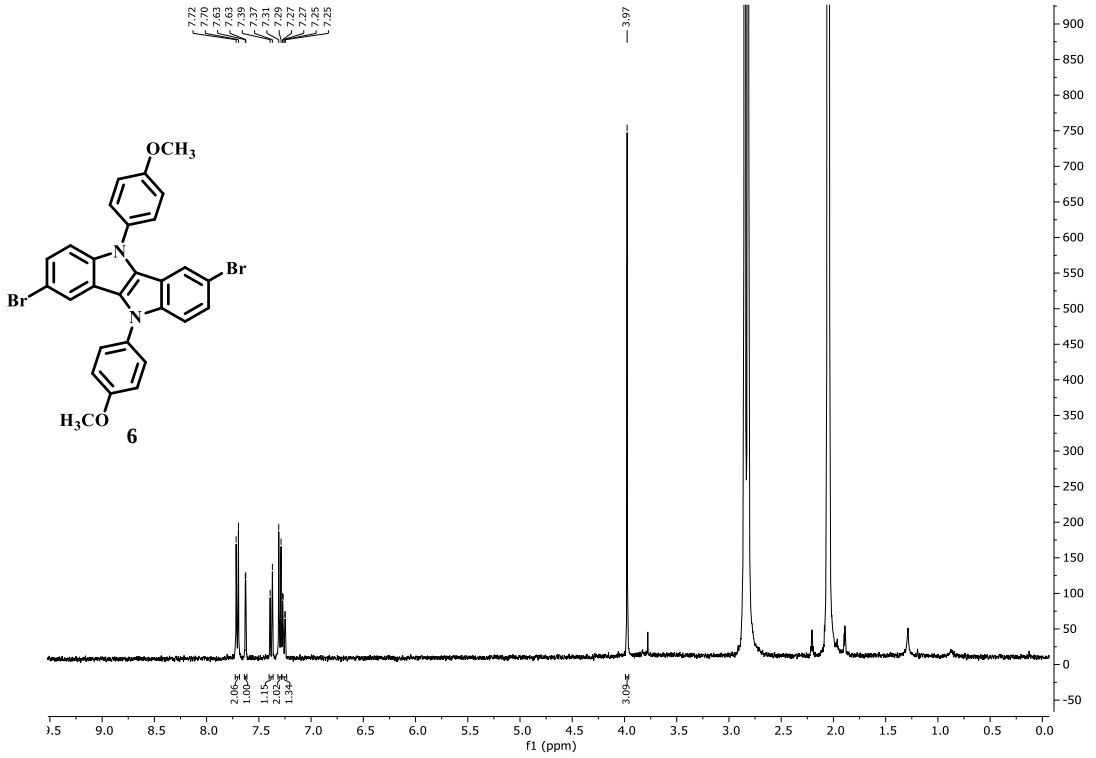

Fig. S10. ^{1}H NMR spectrum of compound **6** in acetone-d_6.

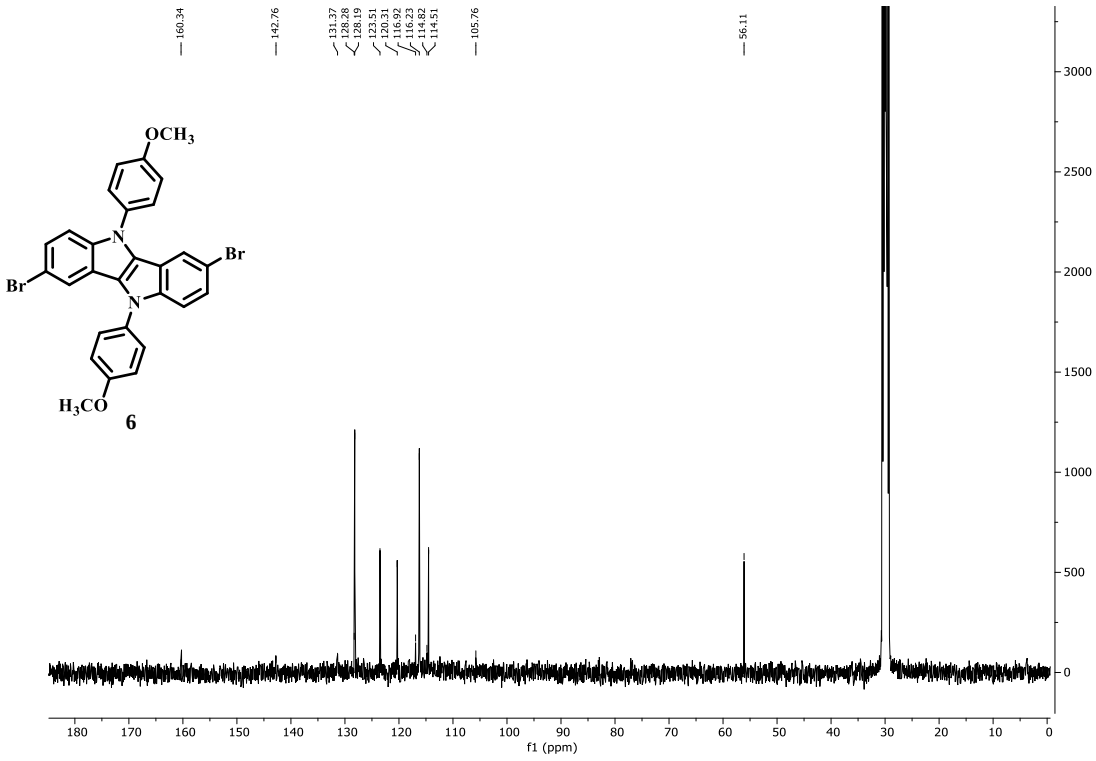

Fig. S11. ^{13}C NMR spectrum of compound **6** in acetone-d_6.

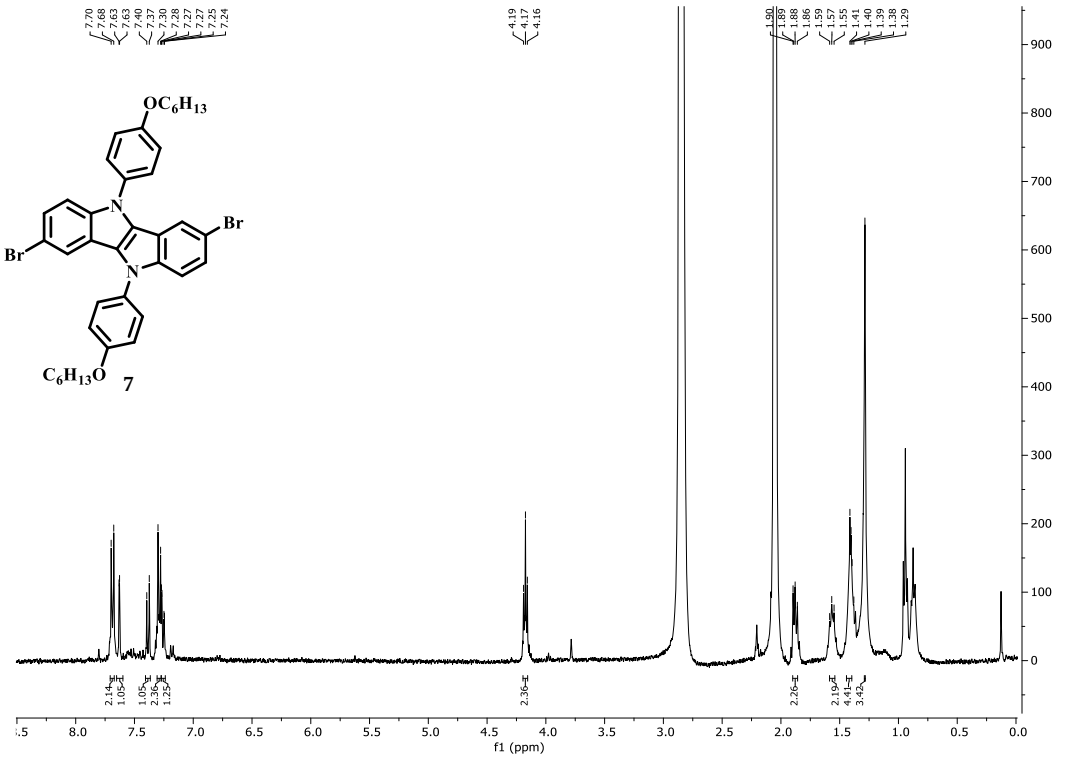

Fig. S12. ^{1}H NMR spectrum of compound **7** in acetone-d_6.

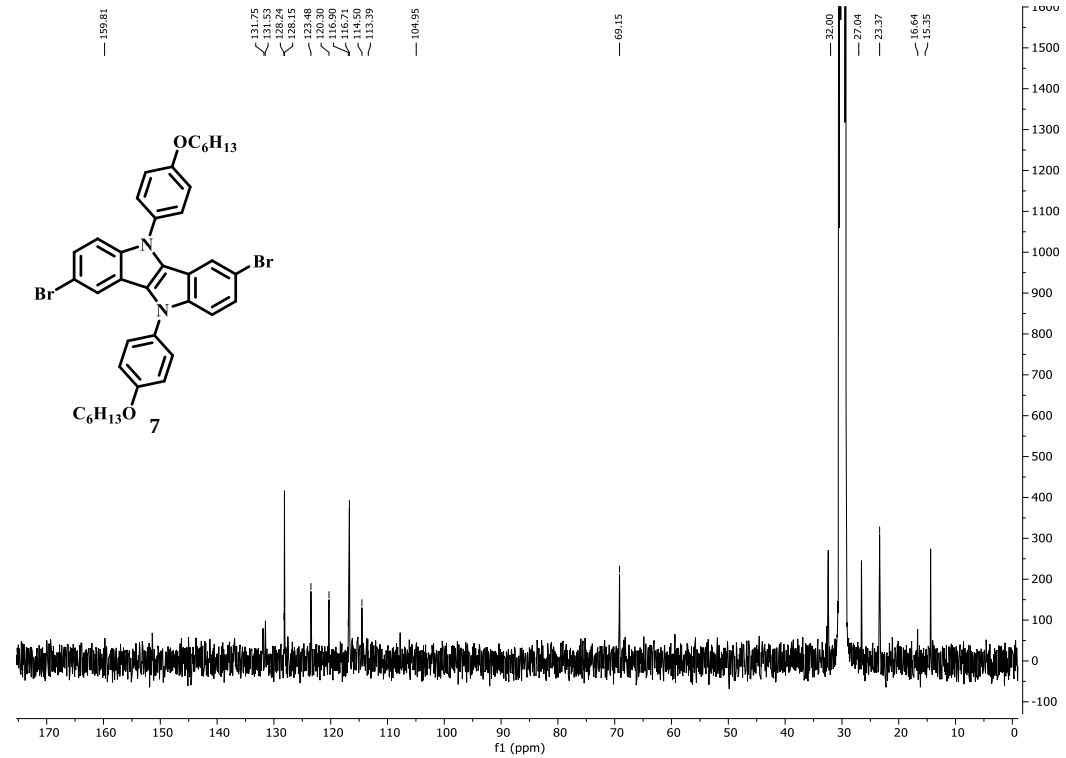

Fig. S13. ^{13}C NMR spectrum of compound **7** in acetone-d_6.

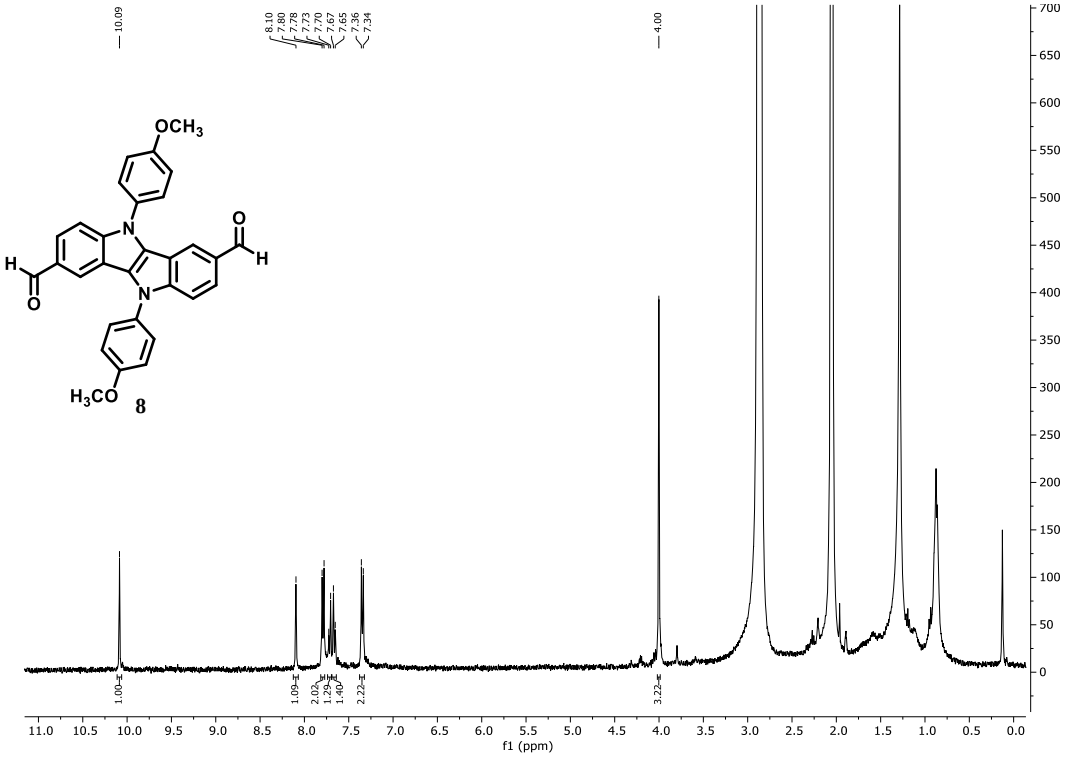

Fig. S14. [1]H NMR spectrum of compound **8** in acetone-d_6.

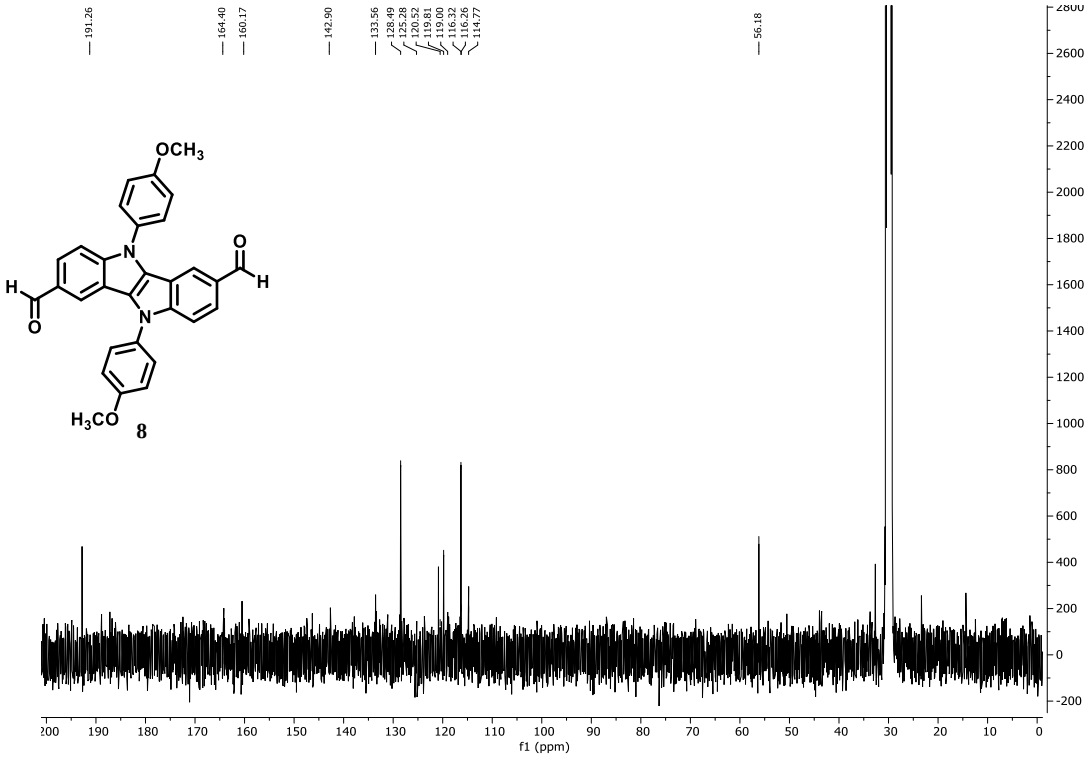

Fig. S15. [13]C NMR spectrum of compound **8** in acetone-d_6.

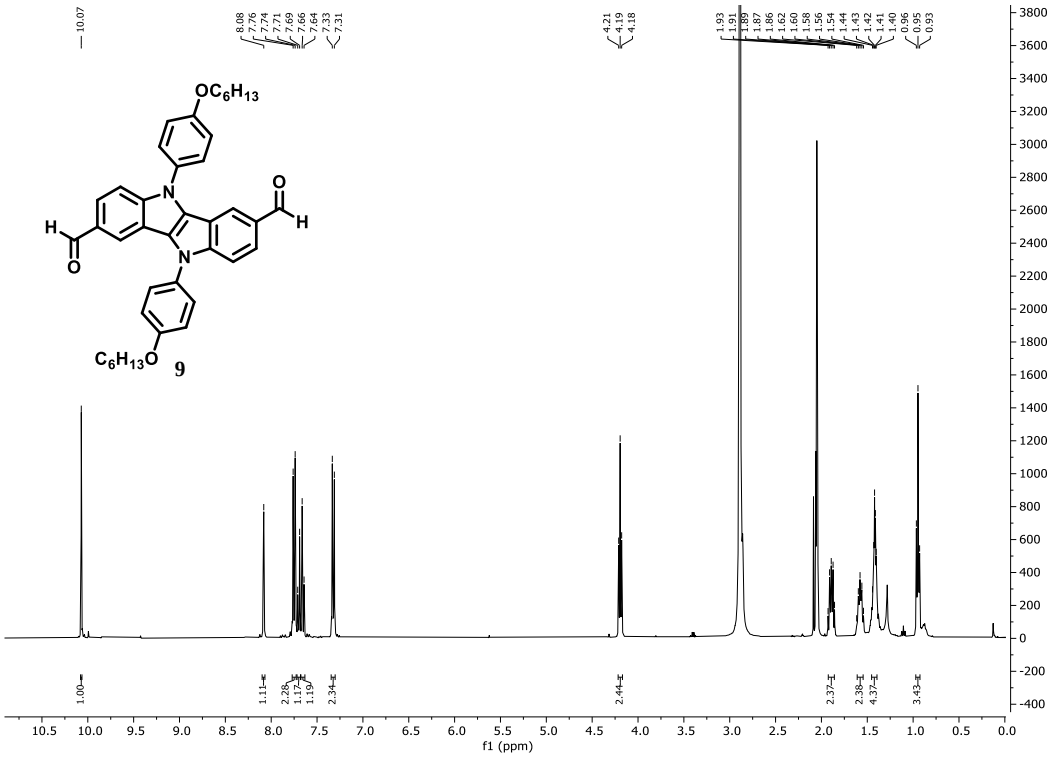

Fig. S16. ^{1}H NMR spectrum of compound **9** in acetone-d_6.

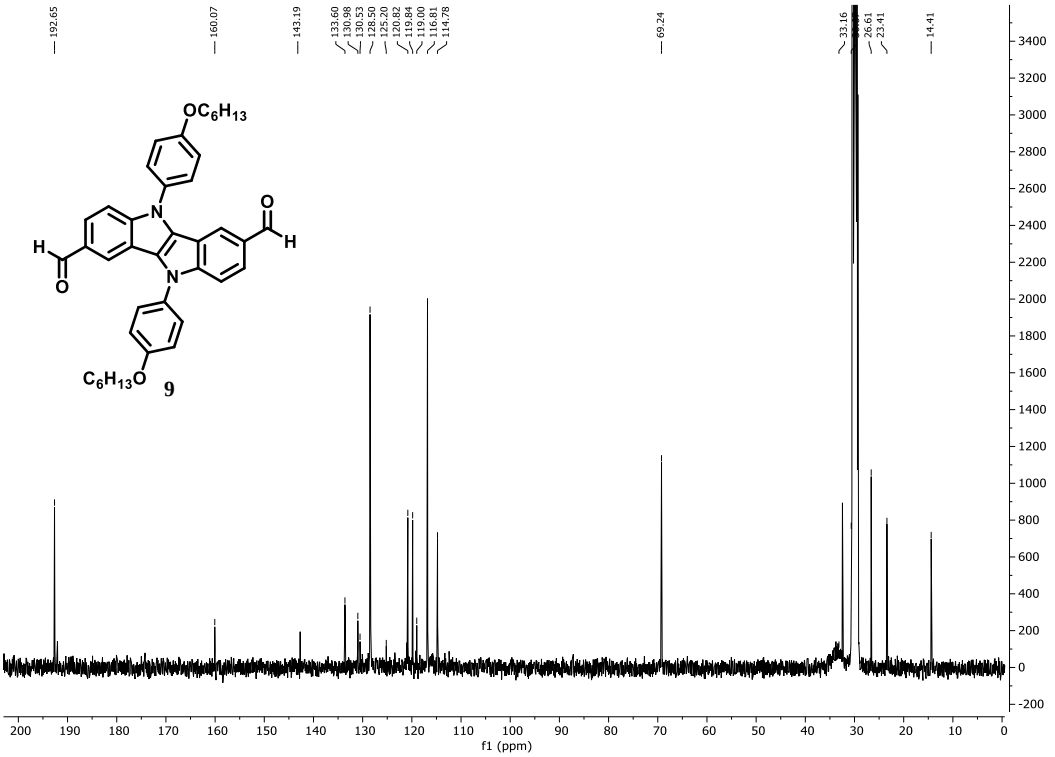

Fig. S17. ^{13}C NMR spectrum of compound **9** in acetone-d_6.

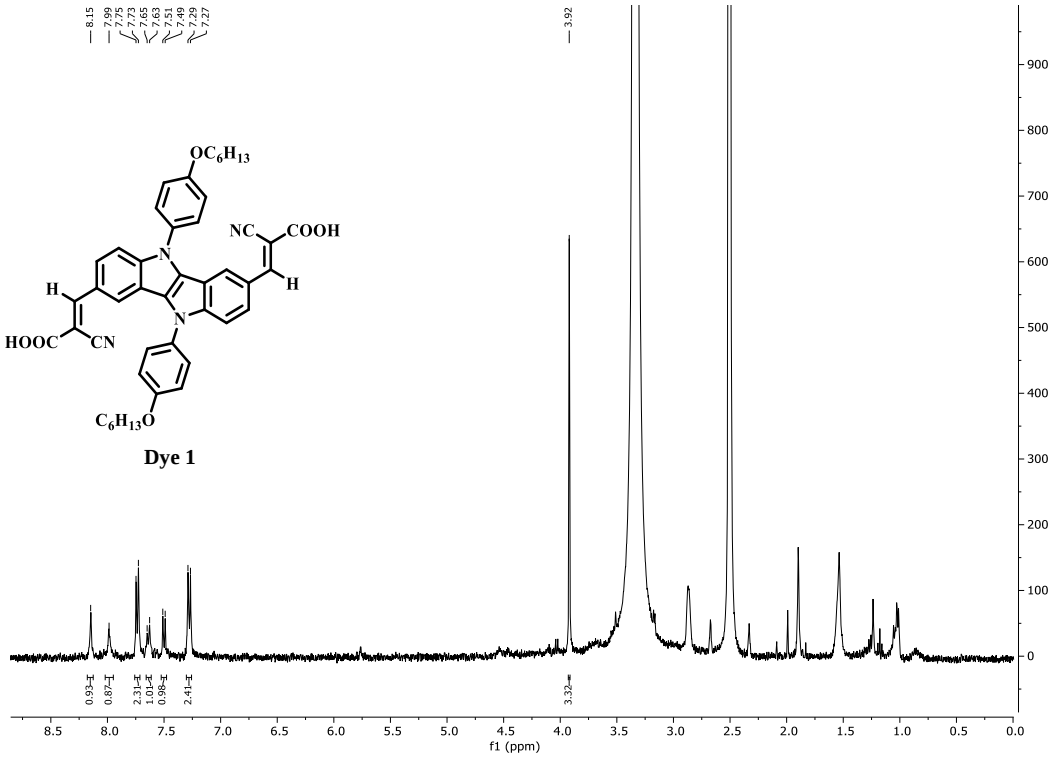

Fig. S18. ^{1}H NMR spectrum of dye **1** in DMSO-d_6.

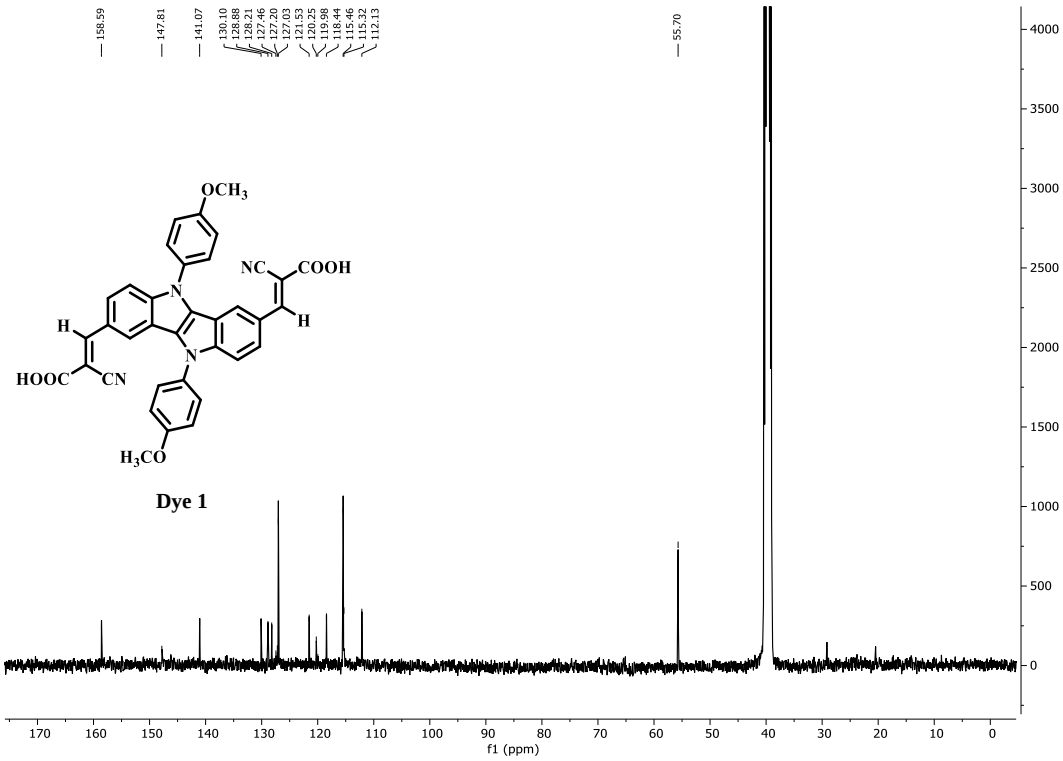

Fig. S19. ^{13}C NMR spectrum of dye **1** in DMSO-d_6.

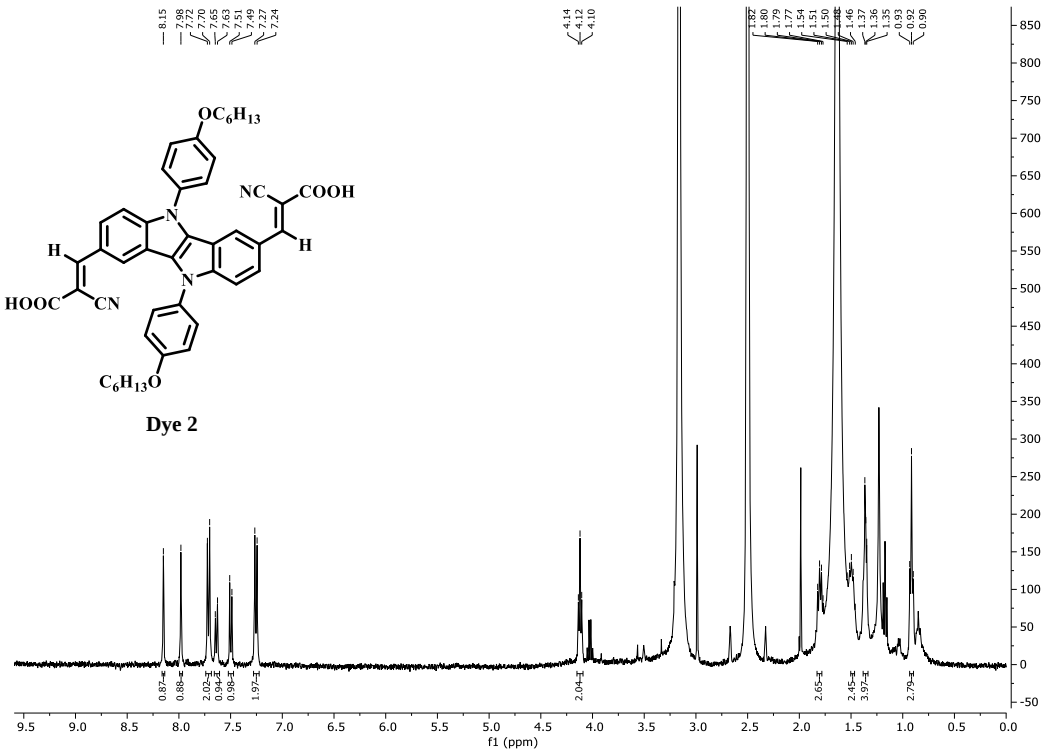

Fig. S20. ^{1}H NMR spectrum of dye **2** in DMSO-d_6.

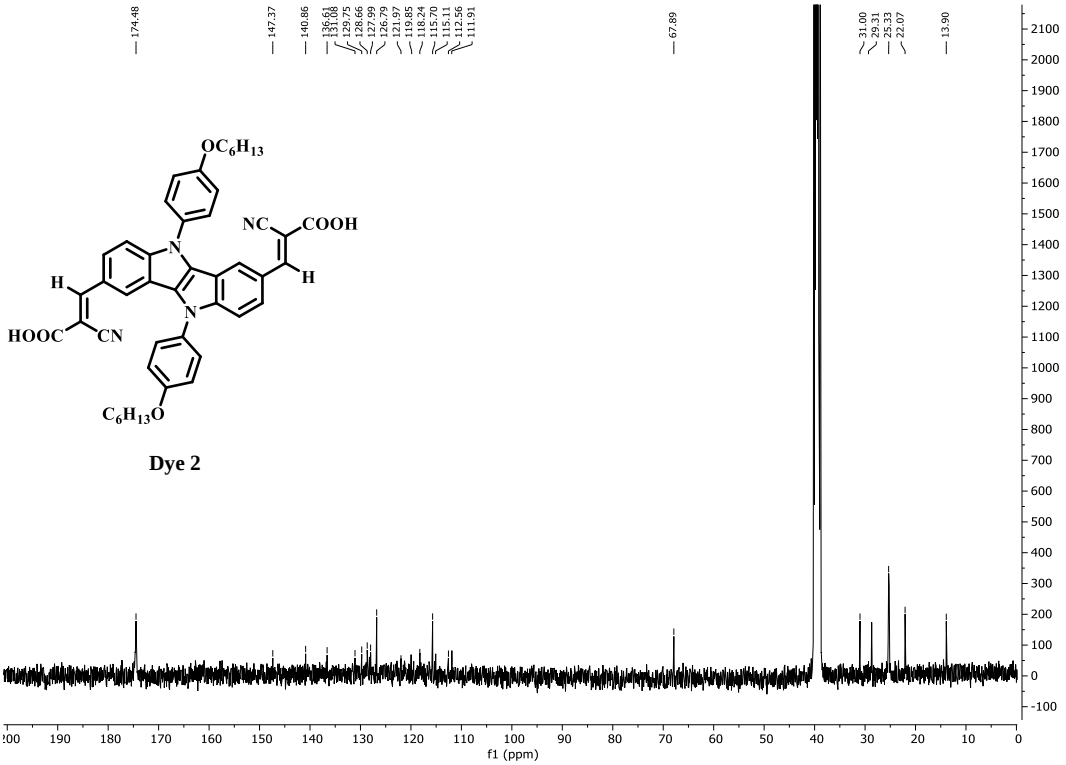

Fig. S21. ^{13}C NMR spectrum of dye **2** in DMSO-d_6.

8. References

[1] Jin Y, Kim K, Song S, Kim J, Kim J, Sung HP, et al. New conjugated polymer based on dihydroindoloindole for LEDs. Bull Korean Chem Soc 2006;27:1043–7. https://doi.org/10.5012/bkcs.2006.27.7.1043.