

Variation of Donor and Acceptor in D-A- π -A based Cyanopyridine Dyes and its effect on Dye Sensitized Solar Cells

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General Methods. All chemicals and reagents were purchased from the commercial sources. The solvents were distilled before use. ¹H-NMR and ¹³C-NMR spectra were recorded by using deuterated solvents (CDCl₃ or DMSO-*d*₆) on a Jeol AV-III400 (L) spectrometer operating at 400 MHz and 100 MHz, respectively, with TMS as reference. Absorption and photoluminescence spectra were recorded with Shimadzu UV-1800 and Shimadzu RF-5301PC, respectively. Mass spectra were collected by Turbo Ion spray (ESI), SynaptG2, Waters instrument. ATR-IR spectra were recorded by using Bruker ALPHA eco-ATRIR on ZnSe crystal. Cyclic voltammetry (CV) measurements for the dyes were collected using an Ag/AgNO₃ as reference electrode, glassy carbon as working electrode and Pt wire as counter electrode in tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte solution (0.1 M) in acetonitrile with CHI660D potentiostat CH instrument. Theoretical calculations were done with Gaussian 09 program using B3LYP (Becke's 43 three parameters hybrid functional and Lee, Yang, and Parr's) correlational functional and 6-31G(d, p) basis set.

Solar Cell Fabrication and Characterization

The working electrodes (FTO, TEC 15 Ω /Sq cm, GreatCell Solar) were cleaned subsequently with detergent, deionized water, acetone and isopropyl alcohol, with an ultrasonic bath. Then, the cleaned working electrodes were heated to 500 °C, and UV-Ozone treated for 15 min. Later, the

substrates were immersed into 40 mM TiCl_4 and then kept at 70 °C for 30 min, then washed with deionized water and ethanol subsequently. The doctor-blading technique was used to get TiO_2 (GreatCell Solar) layer the substrates were then placed for a ramp heating (325 °C for 15 min, 375 °C for 15 min, 450 °C for 15 min and 500 °C for 30 min). Then it was allowed to cool down to room temperature. The coated TiO_2 electrodes were soaked for 15 hours in respective dye solutions (0.3 mM) in acetonitrile. Pt paste (GreatCell Solar) over counter electrodes was coated and annealed at 380 °C for 20 min. 25 μm thick surlyn spacer was used to assemble the electrodes and standard I^-/I_3^- electrolyte was filled through drilled holes and then holes were sealed using cover glass.

The current density versus voltage (J - V) curve of the fabricated DSSCs were measured under AM 1.5 irradiation (100 mWcm^{-2}) using Newport class AAA simulator (Oriel Sol3A- 94023A) at room temperature. The incident-photon-to-current conversion efficiency (IPCE) spectra was measured in DC mode (Newport, 350W Xenon lamp). Electrochemical impedance spectroscopy, charge extraction (CE) and intensity modulated photo-current spectroscopy (IMPS) measurements were carried out using electrochemical workstation (Autolab PGSTAT302N) with reference to reported methods.¹⁻⁶ The photo-current response was measured in warm-white LED, from 0.1 Hz to 10 kHz frequency range using a 10% DC light perturbation.

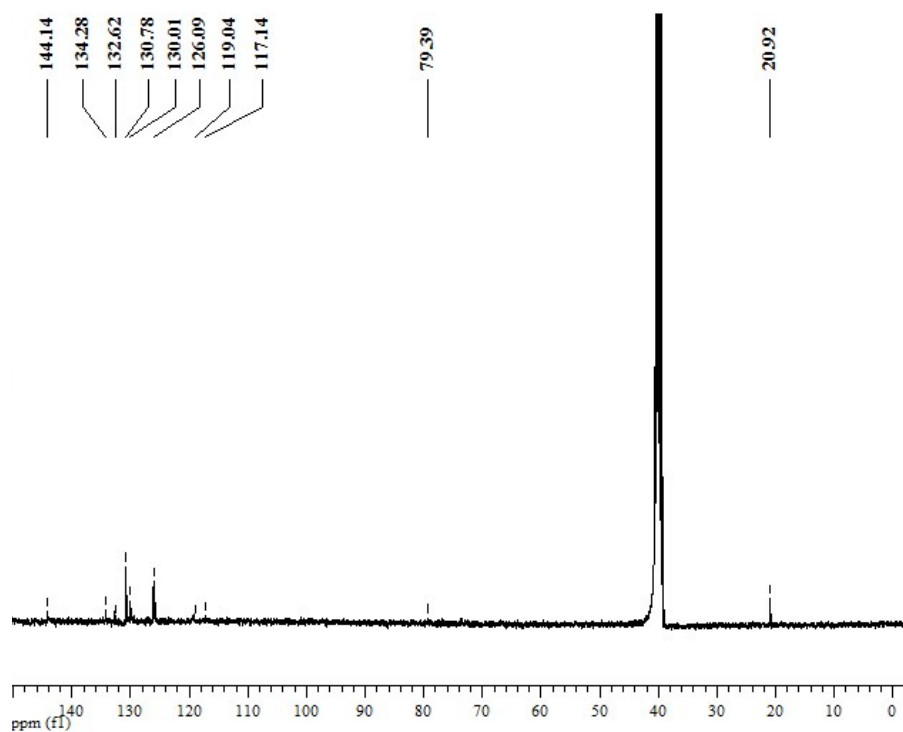
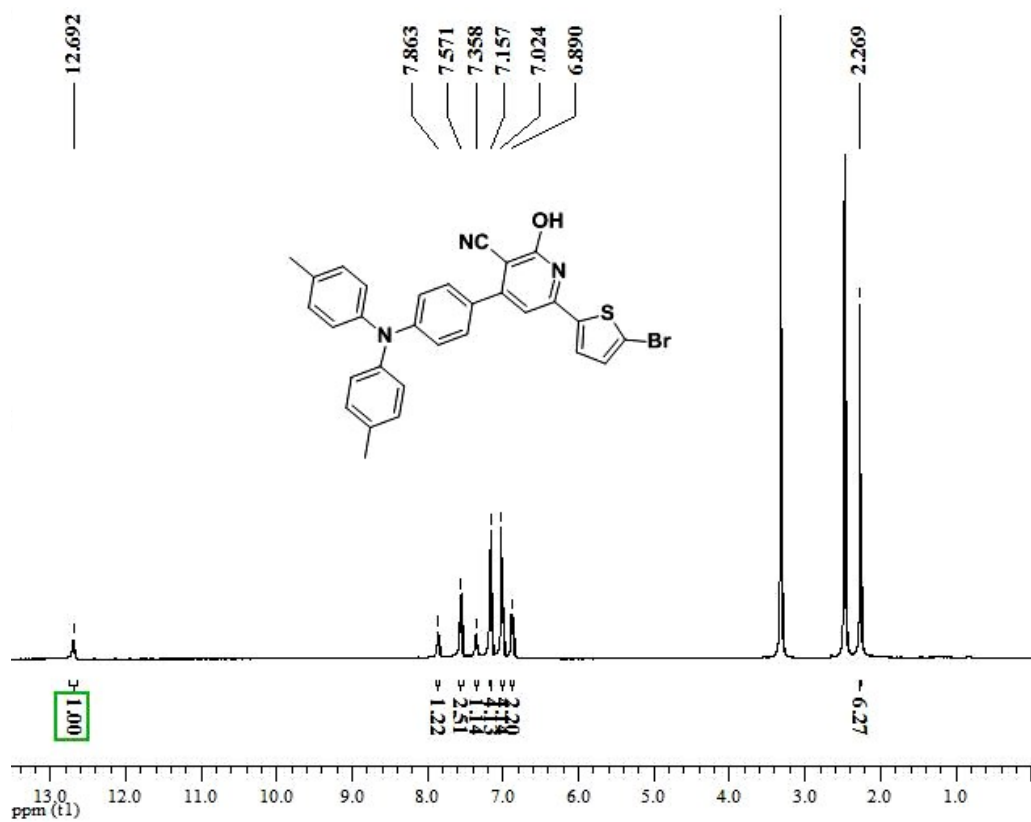


Figure S1: ¹H-NMR and ¹³C-NMR of compound 2

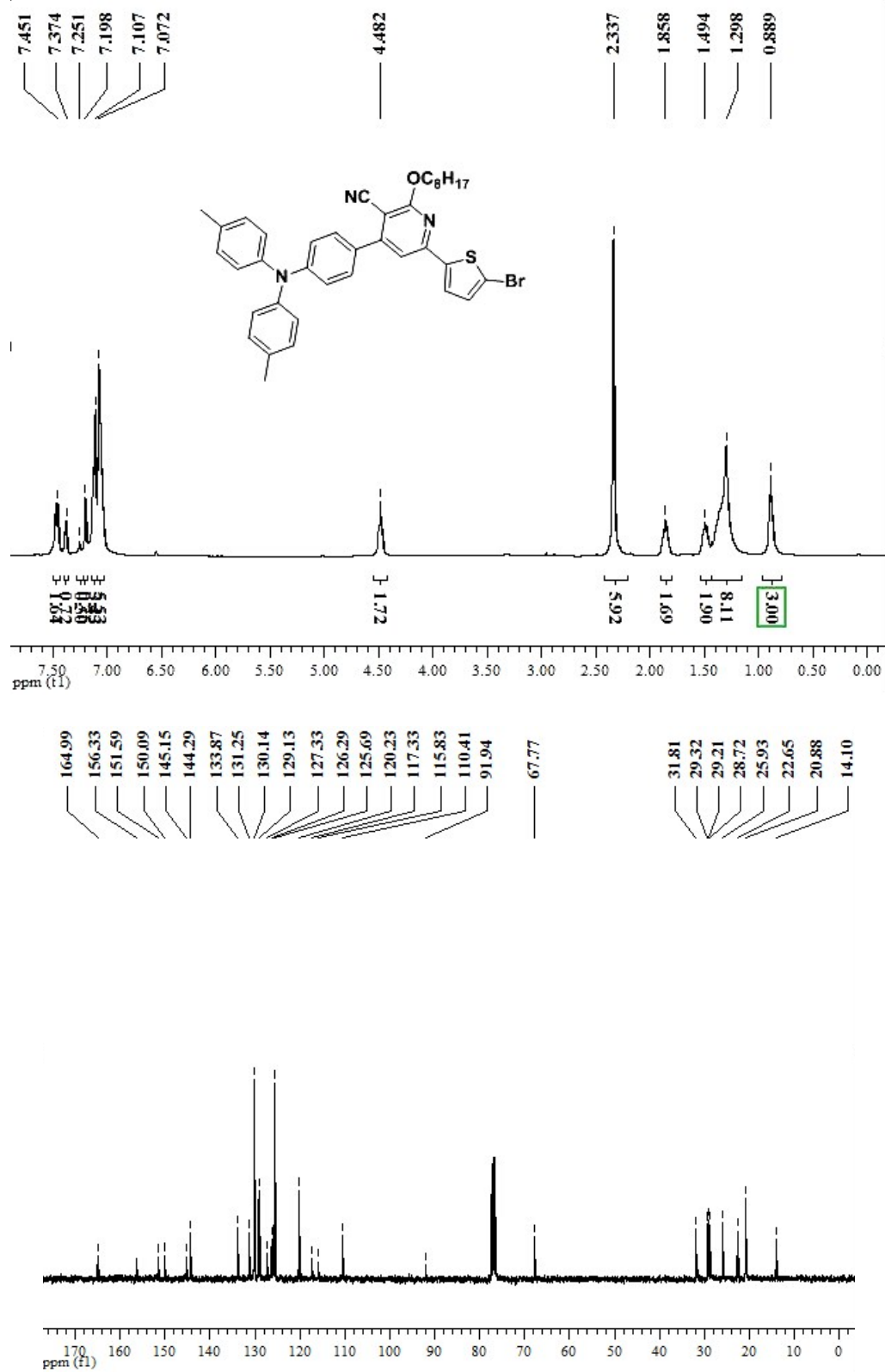


Figure S2: ¹H-NMR and ¹³C-NMR of compound 3

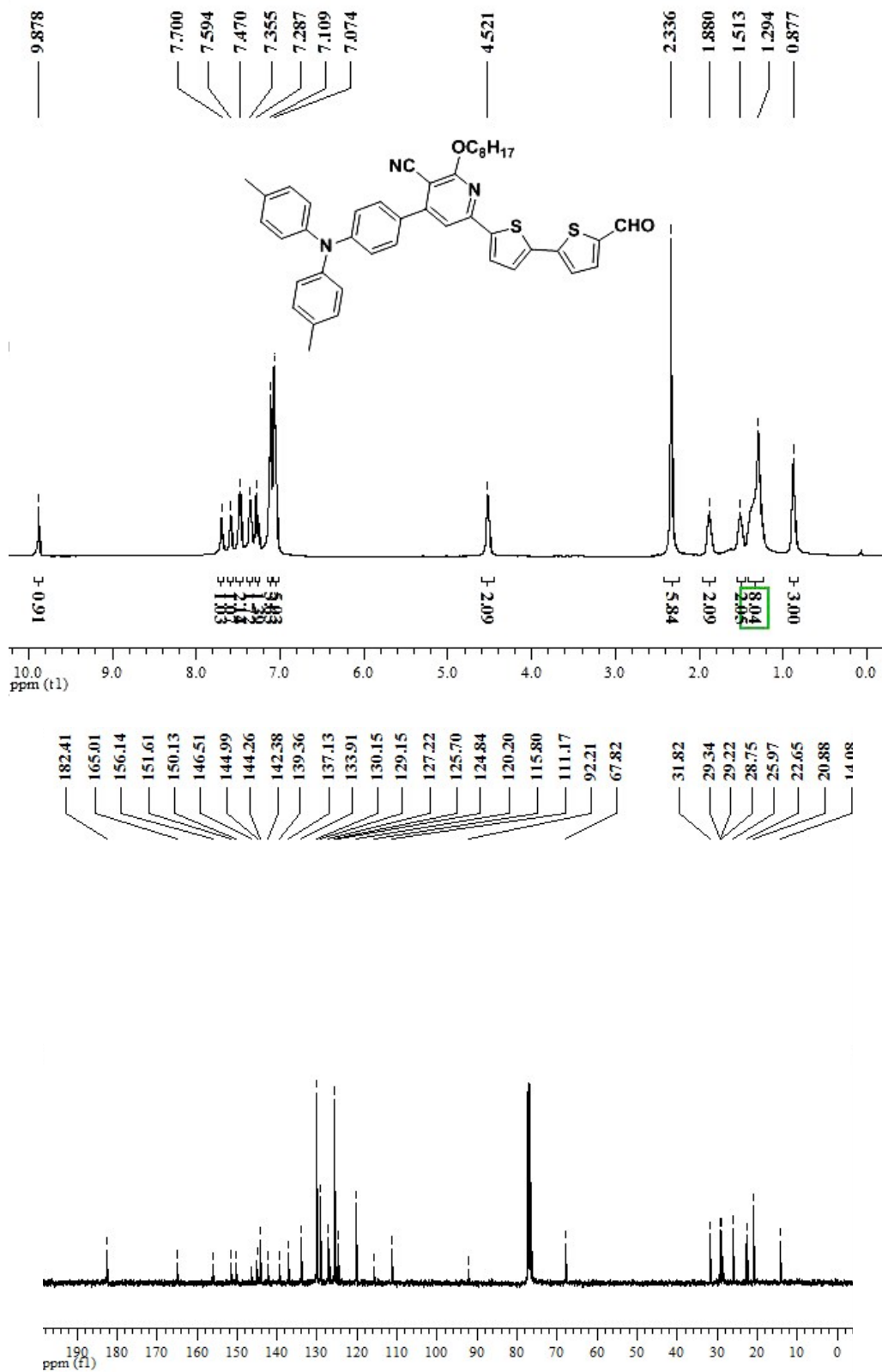


Figure S3: ¹H-NMR and ¹³C-NMR of compound 4

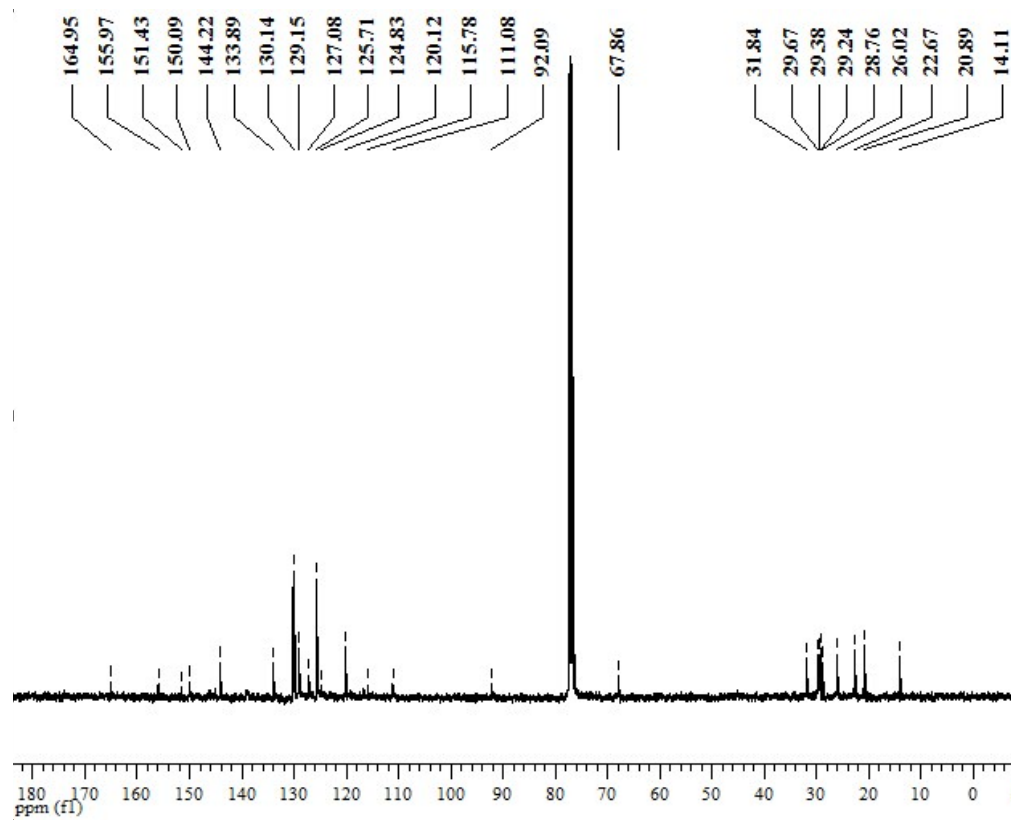
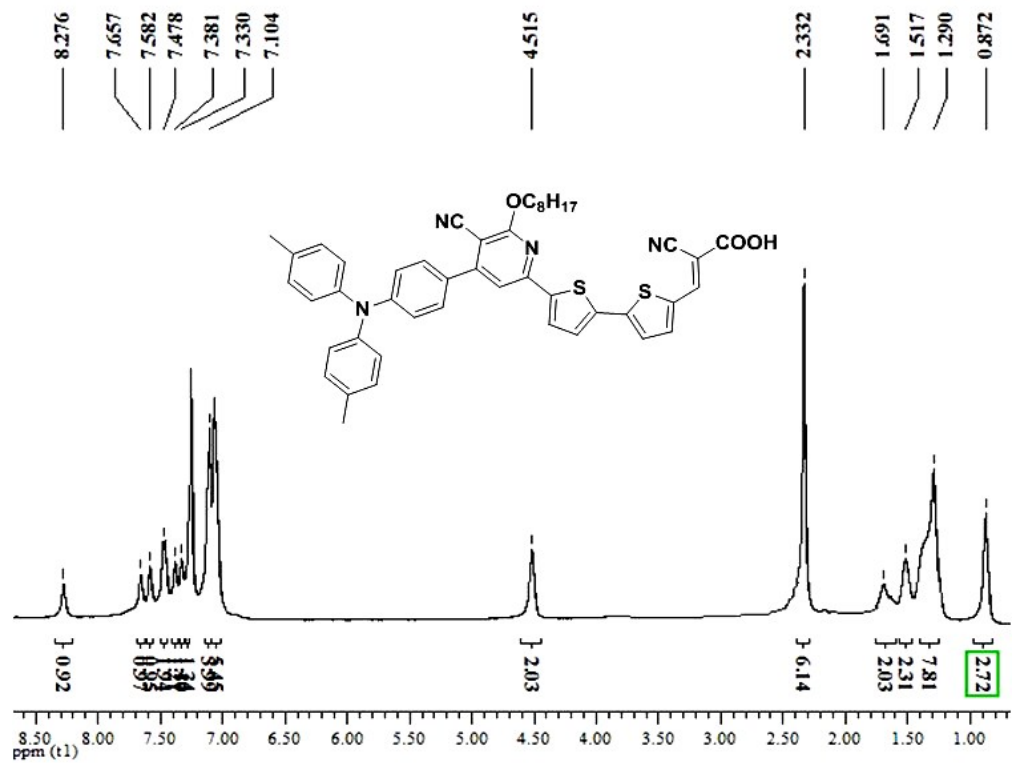


Figure S4: ¹H-NMR and ¹³C-NMR of TPCTh

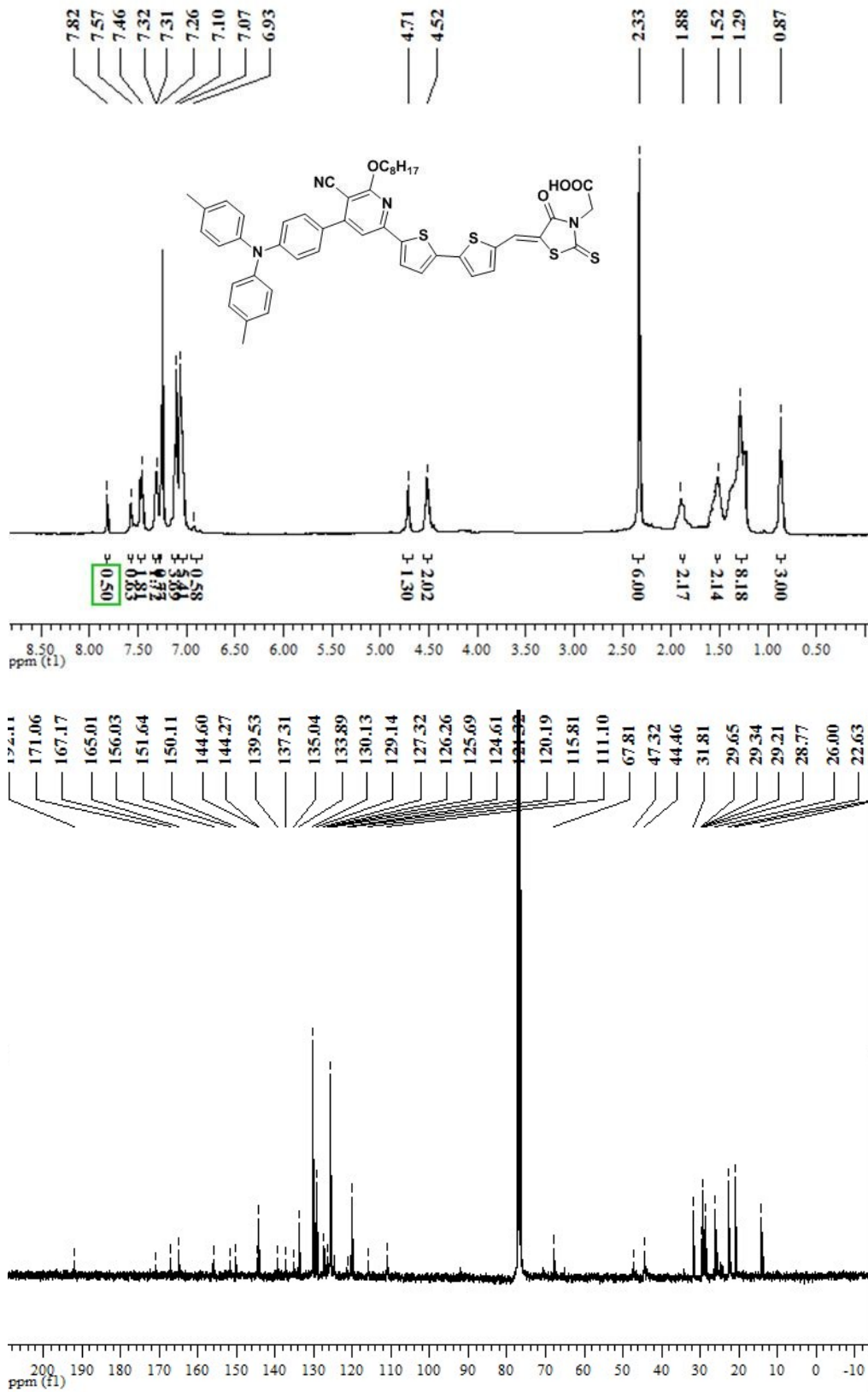


Figure S5: ¹H-NMR and ¹³C-NMR of TPCRh

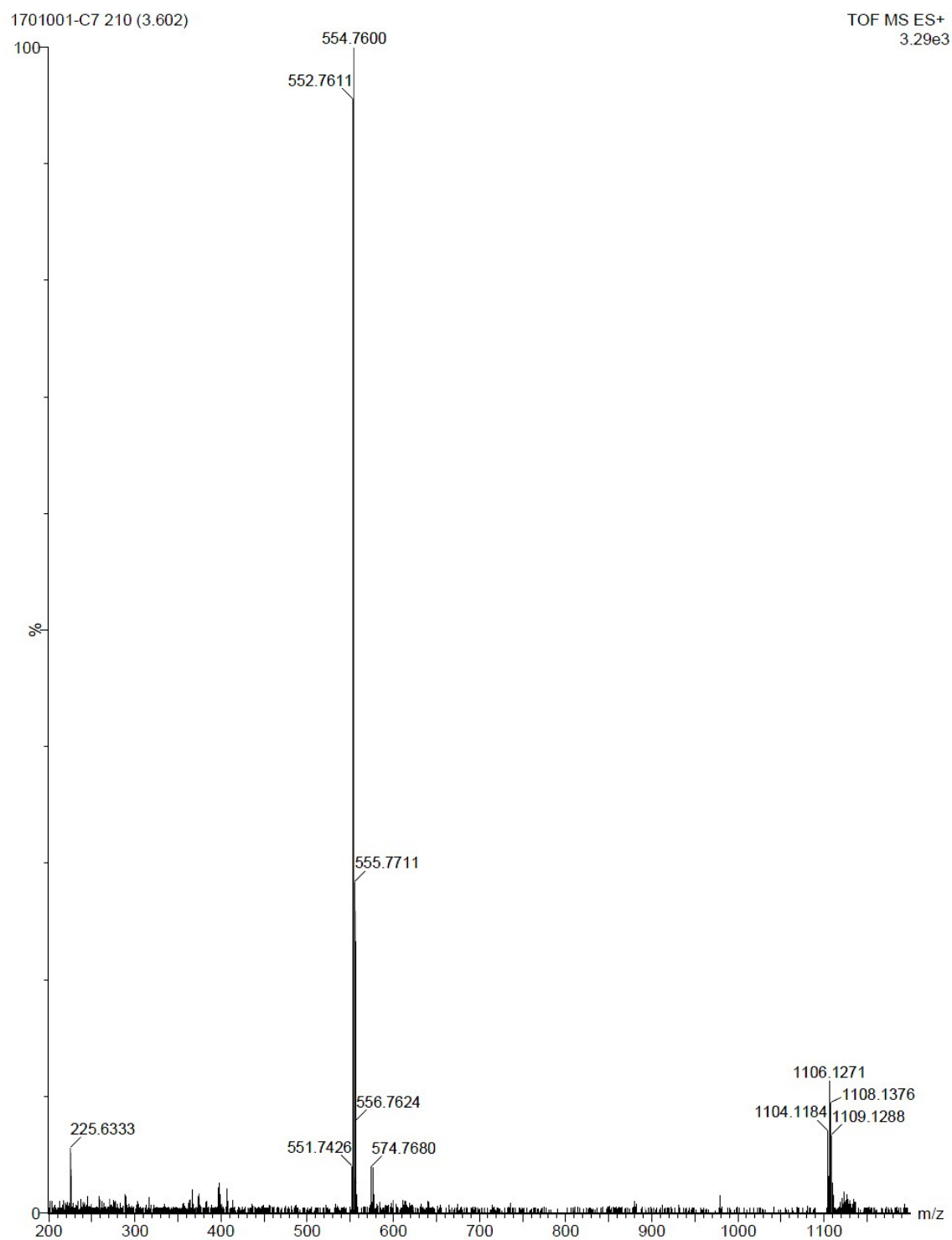


Figure S6: Mass spectrum of compound **2**

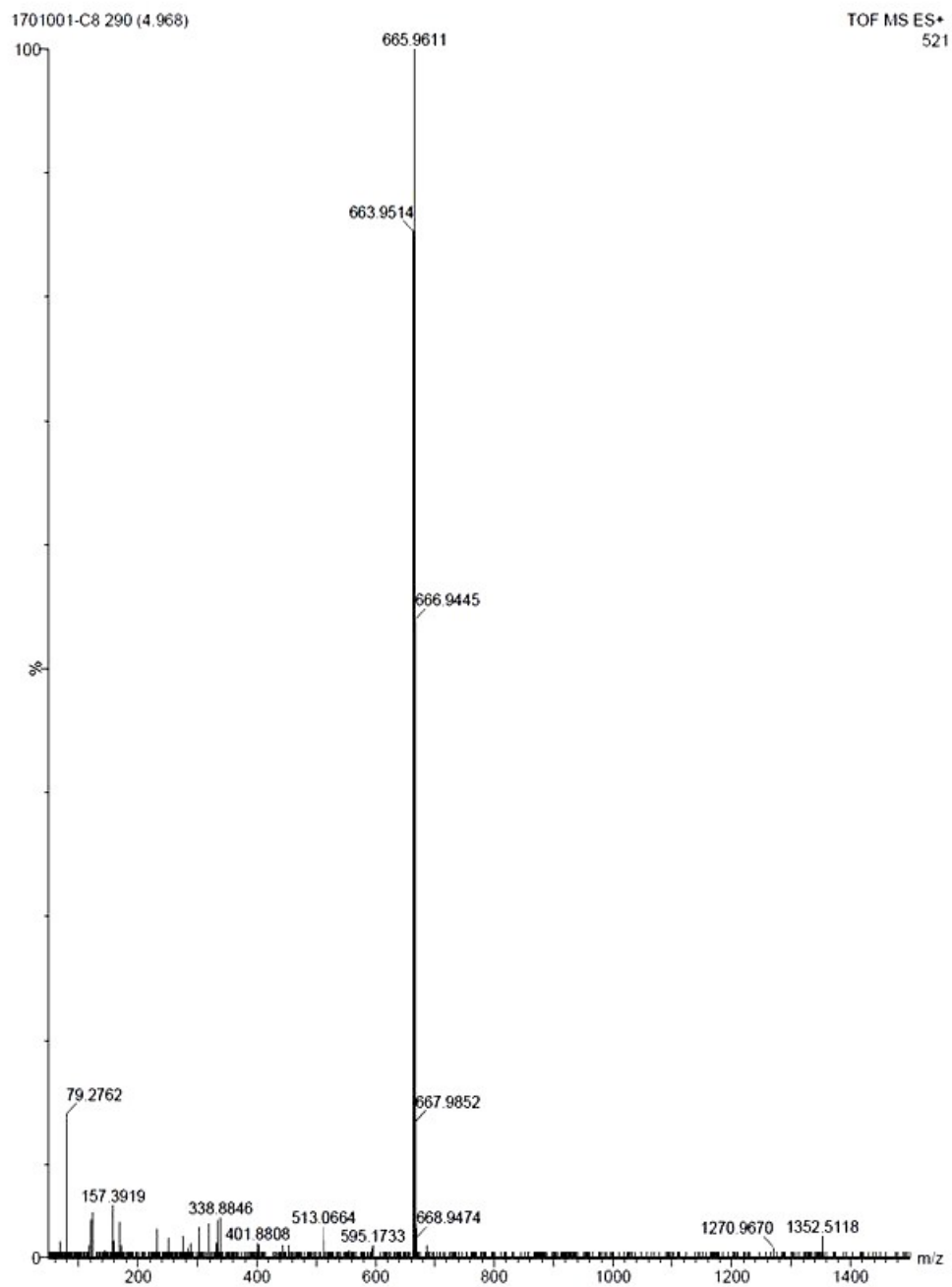


Figure S7: Mass spectrum of compound 3

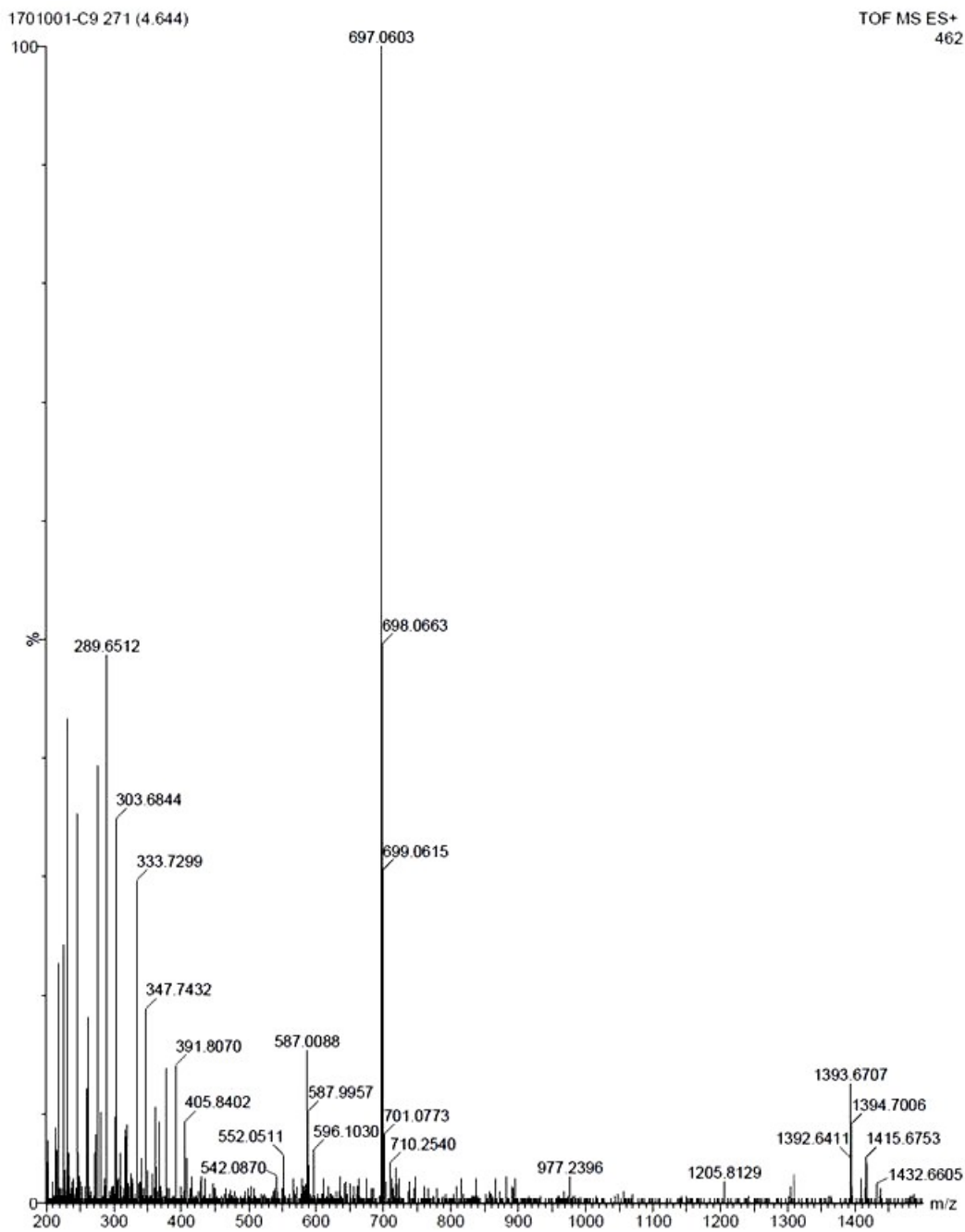


Figure S8: Mass spectrum of compound 4

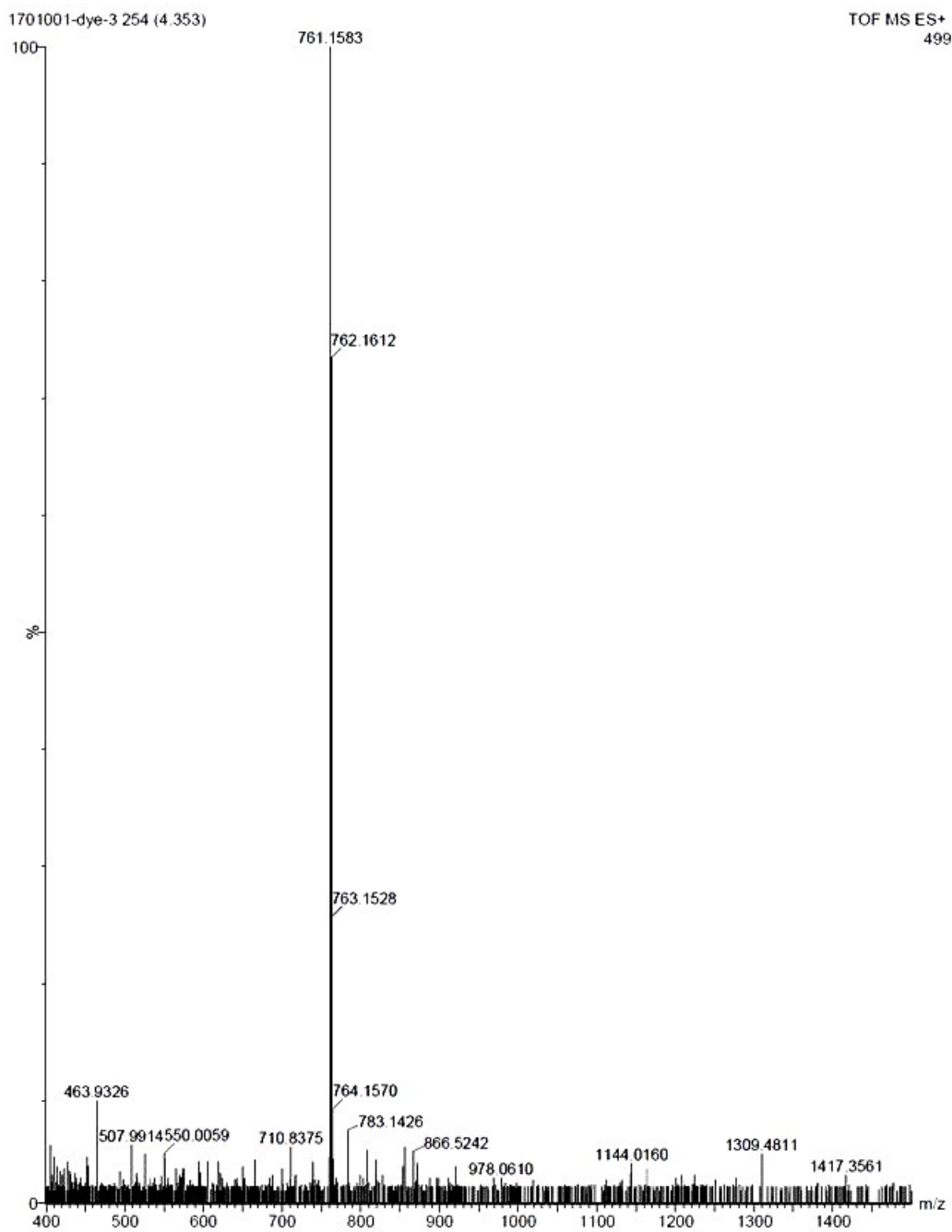


Figure S9: Mass spectrum of TPCTh

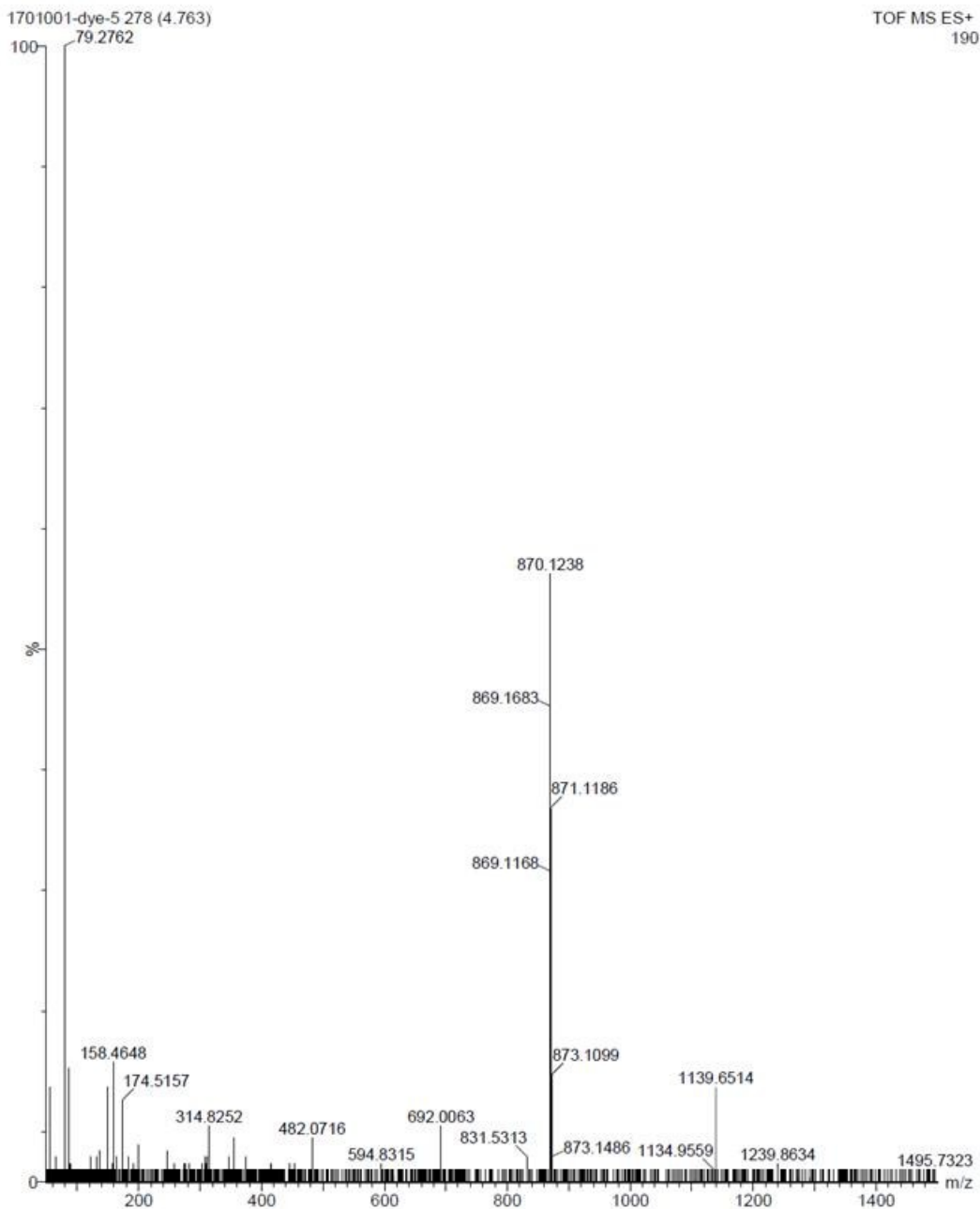


Figure S10: Mass spectrum of TPCRh

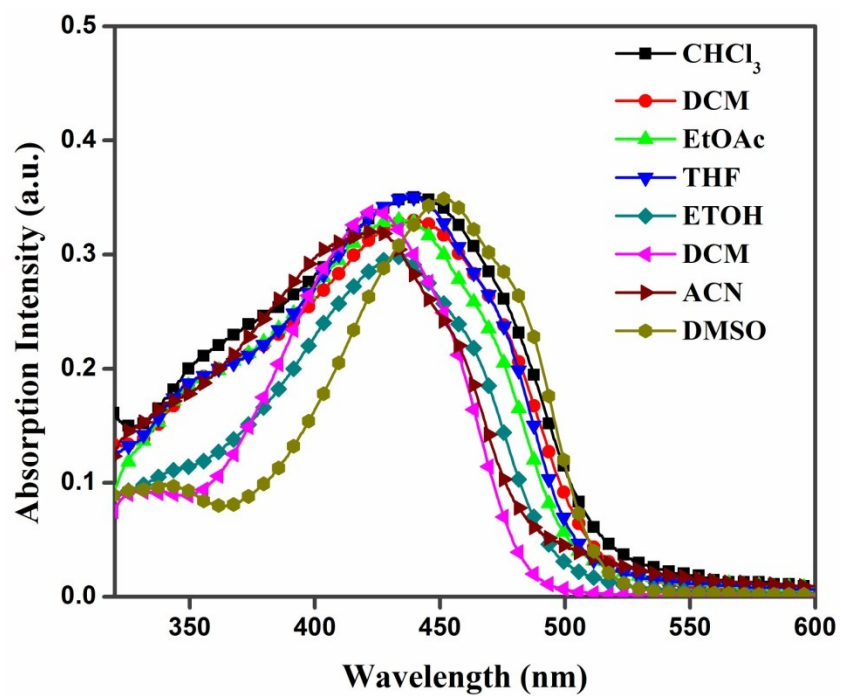


Figure S11: Solvatochromism of TPCTh

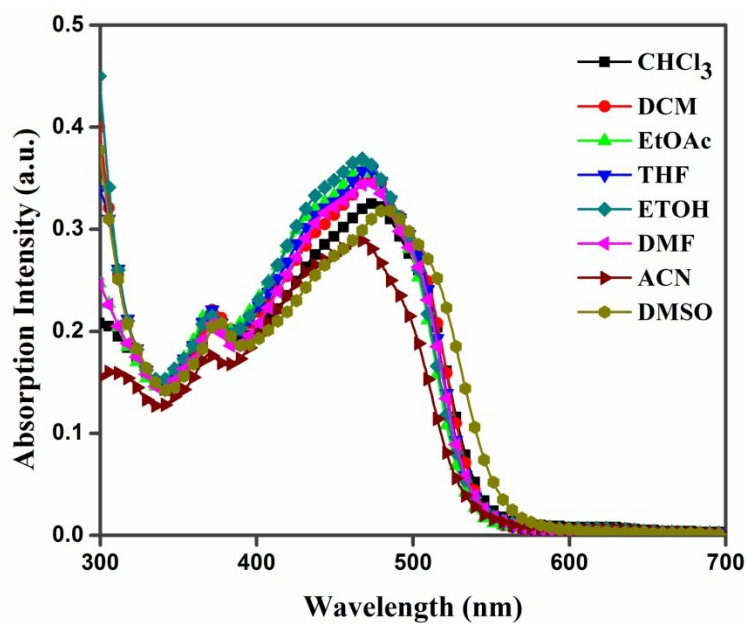


Figure S12: Solvatochromism of TPCRh

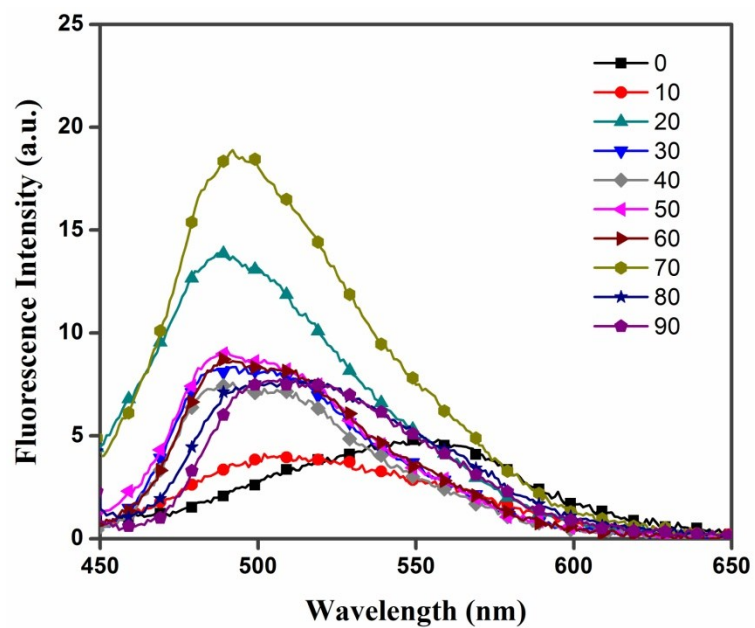


Figure S13: Aggregation study of TPCTh

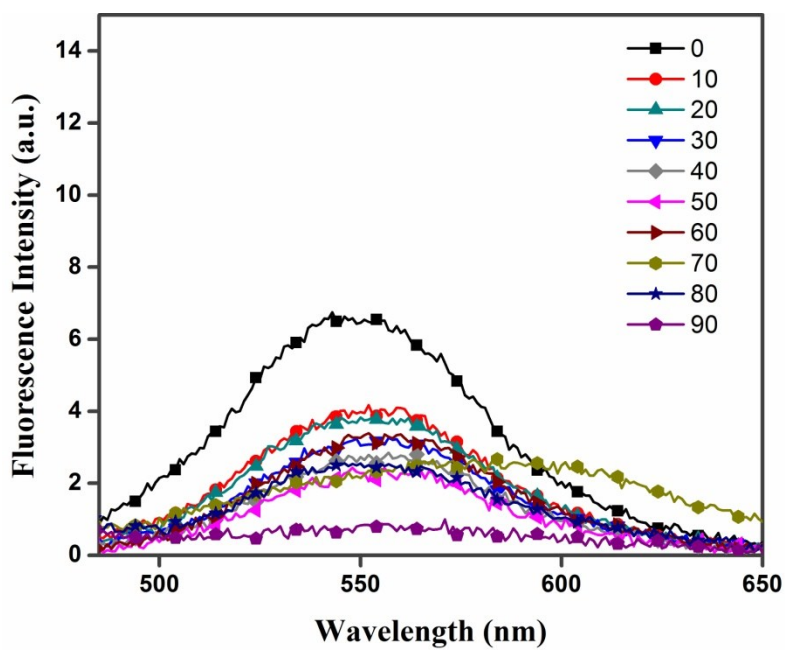


Figure S14: Aggregation of TPCRh

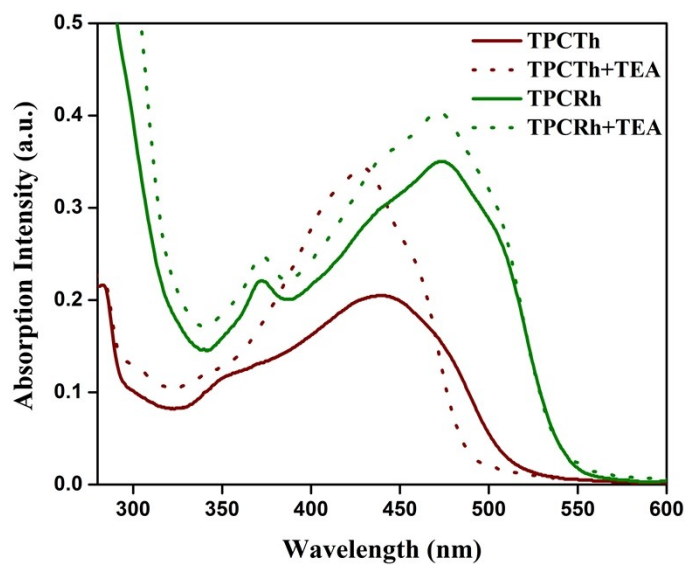


Figure S15: Absorption spectra of dyes in presence TEA.

Table S1: Cartesian coordinates for the optimized geometry of TPCTh

Energy: -1721661.3463998

C	-5.32740	0.15623	-0.04325
C	-4.97806	-1.01978	-0.73519
C	-4.32795	0.80278	0.71019
C	-3.03971	0.29017	0.76227
C	-2.69029	-0.89591	0.09141
C	-3.69290	-1.53663	-0.65780
C	-1.30747	-1.41218	0.16140
C	-0.22629	-0.51815	0.09624
C	1.08573	-0.99106	0.15833
N	1.37305	-2.30778	0.27540
C	0.36948	-3.16375	0.34118
C	-1.00143	-2.78528	0.29852
C	2.23836	-0.09981	0.08808
C	-1.99275	-3.80018	0.45032
C	2.29382	1.27627	-0.02500

C	3.60930	1.78431	-0.06544
C	4.58022	0.79883	0.01981
S	3.84472	-0.78364	0.15617
C	6.01175	0.98913	0.00874
C	6.70143	2.18291	0.20048
C	8.09652	2.05217	0.12831
C	8.52118	0.74882	-0.11734
S	7.12822	-0.31743	-0.27192
C	9.82290	0.18135	-0.25603
C	11.05084	0.78436	-0.19168
C	12.24536	-0.08093	-0.37842
C	11.23166	2.17768	0.04239
N	-6.63679	0.66608	-0.09940
C	-7.75472	-0.20994	-0.24772
C	-6.87859	2.06676	0.02308
C	-7.87473	2.54283	0.88597
C	-8.12594	3.90932	0.98382
C	-7.38772	4.84404	0.24651
C	-6.39258	4.35551	-0.61107
C	-6.14318	2.99103	-0.73300
C	-7.86233	-1.37567	0.52378
C	-8.95780	-2.22103	0.36880
C	-9.98833	-1.92599	-0.53396
C	-9.87303	-0.75316	-1.29126
C	-8.77352	0.09190	-1.16119
C	-11.19273	-2.82718	-0.66515
C	-7.63840	6.32644	0.38709
N	-2.78778	-4.64076	0.58121
N	11.34245	3.32136	0.23572
O	13.39943	0.61539	-0.29326
O	12.20551	-1.27798	-0.58452

O	0.61920	-4.47514	0.46592
C	1.99036	-4.88904	0.53726
H	9.87656	-0.88955	-0.44223
H	-5.72194	-1.52580	-1.33934
H	-4.57316	1.69920	1.26774
H	-2.30071	0.79480	1.37762
H	-3.46070	-2.43660	-1.21561
H	-0.42237	0.53790	-0.03800
H	1.41336	1.90482	-0.08444
H	3.84193	2.83677	-0.17549
H	6.20014	3.12014	0.40939
H	8.78319	2.87795	0.26076
H	-8.45398	1.83723	1.47231
H	-8.90676	4.25568	1.65628
H	-5.81301	5.05402	-1.20974
H	-5.38078	2.63451	-1.41806
H	-7.08246	-1.62114	1.23706
H	-9.01667	-3.12331	0.97222
H	-10.65079	-0.50150	-2.00801
H	-8.69860	0.98892	-1.76712
H	-11.96601	-2.56865	0.06935
H	-11.64740	-2.74552	-1.65689
H	-10.92807	-3.87590	-0.49988
H	-6.98417	6.77158	1.14744
H	-7.44873	6.85577	-0.55173
H	-8.67018	6.53111	0.68741
H	14.11579	-0.02730	-0.42657
H	2.48952	-4.43756	1.39837
H	1.95306	-5.97303	0.64231
H	2.52973	-4.61064	-0.37158

Table S2: Cartesian coordinates for the optimized geometry of **TPCRh**

Energy: -2317467.9254681

C	-5.93997	-0.96129	-0.01491
C	-6.32177	0.11472	0.80972
C	-4.79416	-0.80434	-0.81947
C	-4.06744	0.37693	-0.79160
C	-4.45526	1.46286	0.01453
C	-5.60122	1.30044	0.81290
C	-3.65250	2.70302	0.02823
C	-2.25010	2.62489	-0.00218
C	-1.47238	3.78366	0.00731
N	-2.02235	5.02014	0.05738
C	-3.33817	5.11209	0.08762
C	-4.22107	3.99548	0.06510
C	-0.01111	3.75067	-0.02302
C	-5.62644	4.23872	0.02696
C	0.84292	4.83392	0.02146
C	2.20890	4.48116	-0.02122
C	2.42539	3.11624	-0.10482
S	0.89759	2.25922	-0.13701
C	3.69408	2.42963	-0.17136
C	4.92997	2.97858	-0.48888
C	5.98615	2.05059	-0.46494
C	5.59012	0.75969	-0.13343
S	3.85793	0.72633	0.16894
C	6.32980	-0.45706	-0.00779
C	7.66087	-0.67828	-0.17477
N	-6.68133	-2.15601	-0.03767
C	-6.04443	-3.40153	-0.31992
C	-8.08748	-2.15013	0.20889
C	-4.86702	-3.77281	0.34432

C	-4.25867	-4.99440	0.06604
C	-4.80667	-5.89016	-0.86167
C	-5.99236	-5.51386	-1.50669
C	-6.60135	-4.28774	-1.25188
C	-8.65853	-3.09812	1.06805
C	-10.03351	-3.10584	1.29186
C	-10.87874	-2.16806	0.68576
C	-10.29355	-1.21873	-0.16357
C	-8.92388	-1.21123	-0.41232
C	-4.13092	-7.20411	-1.17317
C	-12.37068	-2.19180	0.91710
S	8.94172	0.45588	-0.60580
C	10.19046	-0.80758	-0.54825
N	9.61056	-2.01149	-0.23244
C	8.21793	-2.03098	0.00742
O	7.61426	-3.04822	0.29720
C	10.38315	-3.21287	-0.00839
C	10.91747	-3.27092	1.43085
S	11.78198	-0.52050	-0.85877
N	-6.76973	4.45661	-0.00941
O	11.76550	-4.29918	1.67131
O	10.60075	-2.50290	2.29721
O	-3.92037	6.32147	0.13179
C	-3.06626	7.47102	0.13269
H	5.77271	-1.35267	0.26188
H	-7.18711	0.01408	1.45418
H	-4.48695	-1.60908	-1.47719
H	-3.20604	0.47610	-1.44539
H	-5.91998	2.09933	1.47252
H	-1.77891	1.64912	0.00349
H	0.46906	5.84673	0.09325

H	3.01704	5.20099	0.03222
H	5.05571	4.02125	-0.75411
H	7.00886	2.32036	-0.69670
H	-4.43487	-3.10284	1.08053
H	-3.34782	-5.26386	0.59495
H	-6.44409	-6.18776	-2.23038
H	-7.51570	-4.01296	-1.76741
H	-8.02127	-3.82617	1.55911
H	-10.45501	-3.84889	1.96424
H	-10.92149	-0.47697	-0.65073
H	-8.49676	-0.47256	-1.08251
H	-3.43757	-7.10571	-2.01808
H	-3.55150	-7.56844	-0.31965
H	-4.85912	-7.97554	-1.44119
H	-12.89169	-2.71773	0.10709
H	-12.62228	-2.70229	1.85120
H	-12.78526	-1.17998	0.96311
H	9.71340	-4.06318	-0.17029
H	11.20870	-3.24254	-0.72476
H	11.94363	-4.80075	0.86208
H	-2.41216	7.47123	1.00866
H	-2.45015	7.50095	-0.76989
H	-3.74151	8.32600	0.16175

Table S3: Lifetime measured for **CCTh**, **TPCTh** and **TPCRh** as sensitizers.

Dye	Frequency Max (Hz)	Lifetime (S)
CCTh	83.77	1.90×10^{-3}
TPCTh	119.38	1.33×10^{-3}
TPCRh	492.39	3.23×10^{-4}

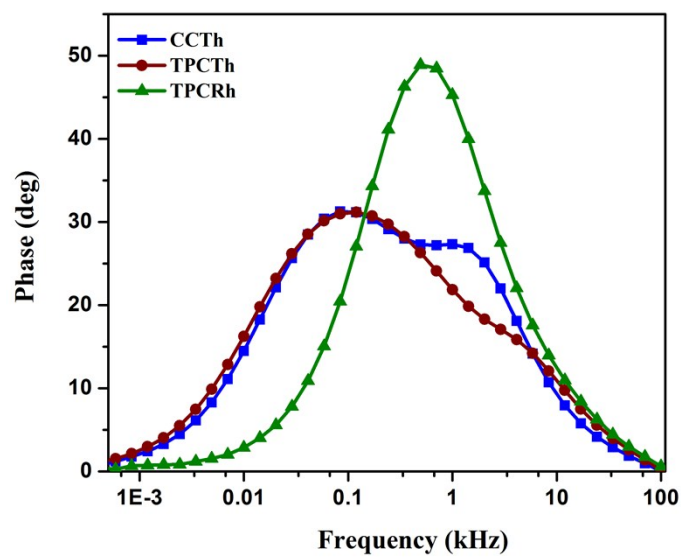


Figure S16. Bode plots of DSSCs fabricated with **CCTh**, **TPCTh** and **TPCRh** as sensitizers at - 0.60 V under forward bias in dark.

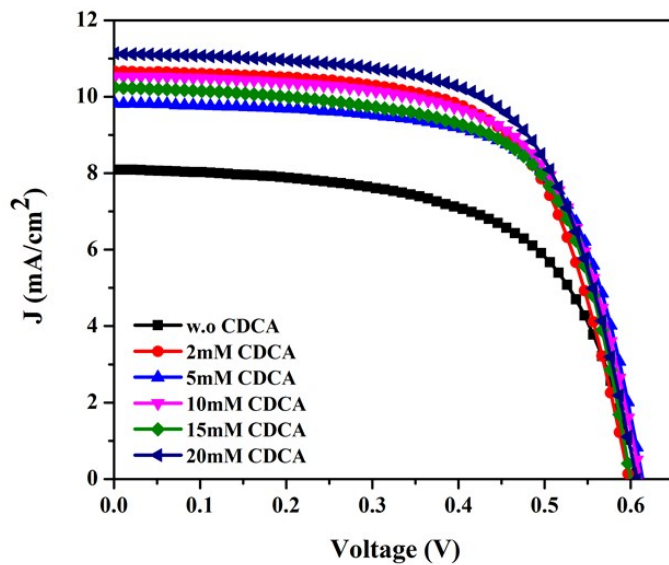


Figure S17. DSSCs fabricated with CDCA with dye **TPCTh**.

Table S4: DSSC device parameters of **TPCTh** fabricated with CDCA.

	Voc (mV)	Jsc (mAcm⁻²)	FF (%)	Efficiency (%)
w.o CDCA	609	8.1	60.78	2.99
2mM CDCA	598	10.67	64.56	4.12
5mM CDCA	614	9.81	67.11	4.04
10mM CDCA	611	10.55	64.67	4.17
15mM CDCA	599	10.25	65.4	4.02
20mM CDCA	607	11.14	64.56	4.36

Table S5: Dye loading.

Dye	Dye-loading (X10⁻⁷) Mol cm⁻²
CCTh	1.92
TPCTh	0.92
TPCRh	0.96

Reference

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3. L. M. Peter, N. W. Duffy, R. L. Wang and K. G. U. Wijayantha, *Journal of Electroanalytical Chemistry*, 2002, **524-525**, 127-136.
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