Supporting Information

Dithienothiophene (DTT)-based Dyes for Dye-Sensitized Solar Cells: Synthesis of 2,6-Dibromo-DTT

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Solar Cells Assembly

Working electrodes were screen printed on clean 4 mm NSG F:SnO_2 glass (13 ohm/square, Nippon Sheet Glass, Japan), using TiO_2 paste (PST-18NR, JGC- Catalysts and Chemicals Ltd., Japan). A homemade scattering paste (see later) was applied on the transparent film. Films were dried at 125 ºC before subsequent prints were applied. A full sinter followed:

	Step1	Step2	Step3	Step4	Step5
Ramp (º/min)	10	15	5	7	5
Temperature (ºC)	150	325	375	450	500
Duration (min)	10	5	5	30	15

Prior to device construction, the electrode was re-sintered at 500 ˚C for 30 minutes in air. After the electrode was allowed to cool around 80 ºC, it was immersed in a dye solution containing organic dye **13** (0.2 mM) with or without 3α, 7α-dihydroxy-5β-cholic acid (10 mM) in $CHCl_3$/EtOH (1:1) and maintained in darkness at room temperature for 12 h. The electrode was then rinsed with EtOH and dried.

Counter electrodes were prepared by drilling a hole to be used as a filling port in a piece of 3 mm NSG F:SnO_2 glass (13 ohm/square), before applying one drop of a solution of H_2PtCl_6 in 2-propanol (10 mM) with a pipette. The drop was smeared over the full surface and allowed to dry. This glass was then fired at about 400 ºC for 15 minutes using a heat gun.

The working and counter electrodes were sandwiched with 25 μm Surlyn (Solaronix, Switzerland) and sealed using a pneumatic finger and resistive heater (150 °C) for 26 s. The electrolyte [0.6 M 1,2-dimethyl-3-propylimidazolium iodide,[1] 0.025 M LiI, 0.04 M I_2, 0.05 M guanidinium thiocyanate (GuSCN), and 0.28 M *tert*-butylpyridine (TBP) in the mixture of dry acetonitrile and valeronitrile (v/v = 85/ 15)] was introduced into the

cavity through pre-drilled holes in the counter electrode by vacuum backfilling. The filling port was sealed using 25 μm Surlyn and a microscope coverslip. Electrode contact was achieved using Cerasol CS186 solder at 220 °C with an oscillation frequency of 60 kHz prior to attaching copper wires using standard 60–40 tin–lead solder.

Solar cells were tested using simulated sunlight (AM 1.5, 1000 W/m^2) provided by an Oriel solar simulator with an AM 1.5 filter. Current-voltage characteristics were measured using a Keithley 2400 source meter. Cells were biased from high to low, with 10 mV steps and 40 ms settling time.

Incident photon to charge carrier conversion efficiency (IPCE) was conducted with the cell held under short circuit conditions and illuminated by monochromatic light. A cornerstone 260 monochromator was used in conjunction with an optical fibre, Keithly 2400 source meter and 150W Oriel Xe lamp.

Fabrication of Scattering Paste

The scattering paste was produced by completing a solvent exchange of water for ethanol with commercial 400 nm and 18 nm titania sols (HPW-400C and HPW-18NR, JGC- Catalysts and Chemicals Ltd., Japan). These are mixed together with ethanolic ethyl cellulose solution (10 wt %) and terpineol with a weight ratio of 5:1:35:30. The ethanol is then removed by rotary evaporation.

Synthesis of 1,2-dimethyl-3-propylimidazolium iodide

1,2-Dimethyl-3-propylimidazolium iodide was synthesized according to literature method.[1]

Summary of device results using different solvents to adsorb the dye 13 on titania.

A dye solution (0.2 mM) was made up in various solvents. The device results were obtained using sandwich cells with a standard electrolyte composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.025 M lithium iodide, 0.04 M iodine, 0.05 M guanidinium thiocyanate (GuSCN), and 0.28 M *tert*-butylpyridine (TBP) in dry acetonitrile and valeronitrile (v/v = 85/15) with combination of the 12 μm + 6 μm scattering layer (12 + 6s) without a coadsorbent.

1) $CH_3CN/CHCl_3$ (1:1)

Light Intensity	**38.5 % sun**	**68.0 % sun**	**100.0 % sun**
Voltage o/c (mV)	614.89	633.53	646.35
Current s/c (mA/cm^2)	3.26	6.06	9.2
Fill Factor	0.75	0.72	0.70
Efficiency (%)	3.89	4.07	4.15

2) Dichloroethane

Light Intensity	**38.5 % sun**	**68.0 % sun**	**100.0 % sun**
Voltage o/c (mV)	657.66	673.96	683.22
Current s/c (mA/cm^2)	3.48	6.37	9.33
Fill Factor	0.74	0.73	0.72
Efficiency (%)	4.41	4.61	4.57

3) CH_2Cl_2

Light Intensity	**38.5 % sun**	**68.0 % sun**	**100.0 % sun**
Voltage o/c (mV)	649.24	667.87	678.82
Current s/c (mA/cm^2)	3.53	6.43	9.21
Fill Factor	0.66	0.65	0.63

Efficiency (%)	3.95	4.08	3.97

4) MeOH/$CHCl_3$(1:1)

Light Intensity	**38.5 % sun**	**68.0 % sun**	**100.0 % sun**
Voltage o/c (mV)	657.49	673.27	682.55
Current s/c (mA/cm^2)	4.17	7.44	10.54
Fill Factor	0.74	0.72	0.7
Efficiency (%)	5.24	5.28	5.04

5) THF/$CHCl_3$ (1:1)

Light Intensity	**38.5 % sun**	**68.0 % sun**	**100.0 % sun**
Voltage o/c (mV)	628.97	648.38	660.83
Current s/c (mA/cm^2)	3.48	6.38	9.4
Fill Factor	0.73	0.71	0.7
Efficiency (%)	4.16	4.34	4.32

6) $CHCl_3$

Light Intensity	**38.5 % sun**	**68.0 % sun**	**100.0 % sun**
Voltage o/c (mV)	667.03	684.77	695.77
Current s/c (mA/cm^2)	3.72	6.84	10.02
Fill Factor	0.76	0.75	0.75
Efficiency (%)	4.92	5.18	5.2

7) Chlorobenzene

Light Intensity	**38.5 % sun**	**68.0 % sun**	**100.0 % sun**
Voltage o/c (mV)	655.52	674.1	685.77
Current s/c (mA/cm^2)	3.69	6.8	9.96
Fill Factor	0.75	0.73	0.72
Efficiency (%)	4.69	4.94	4.93

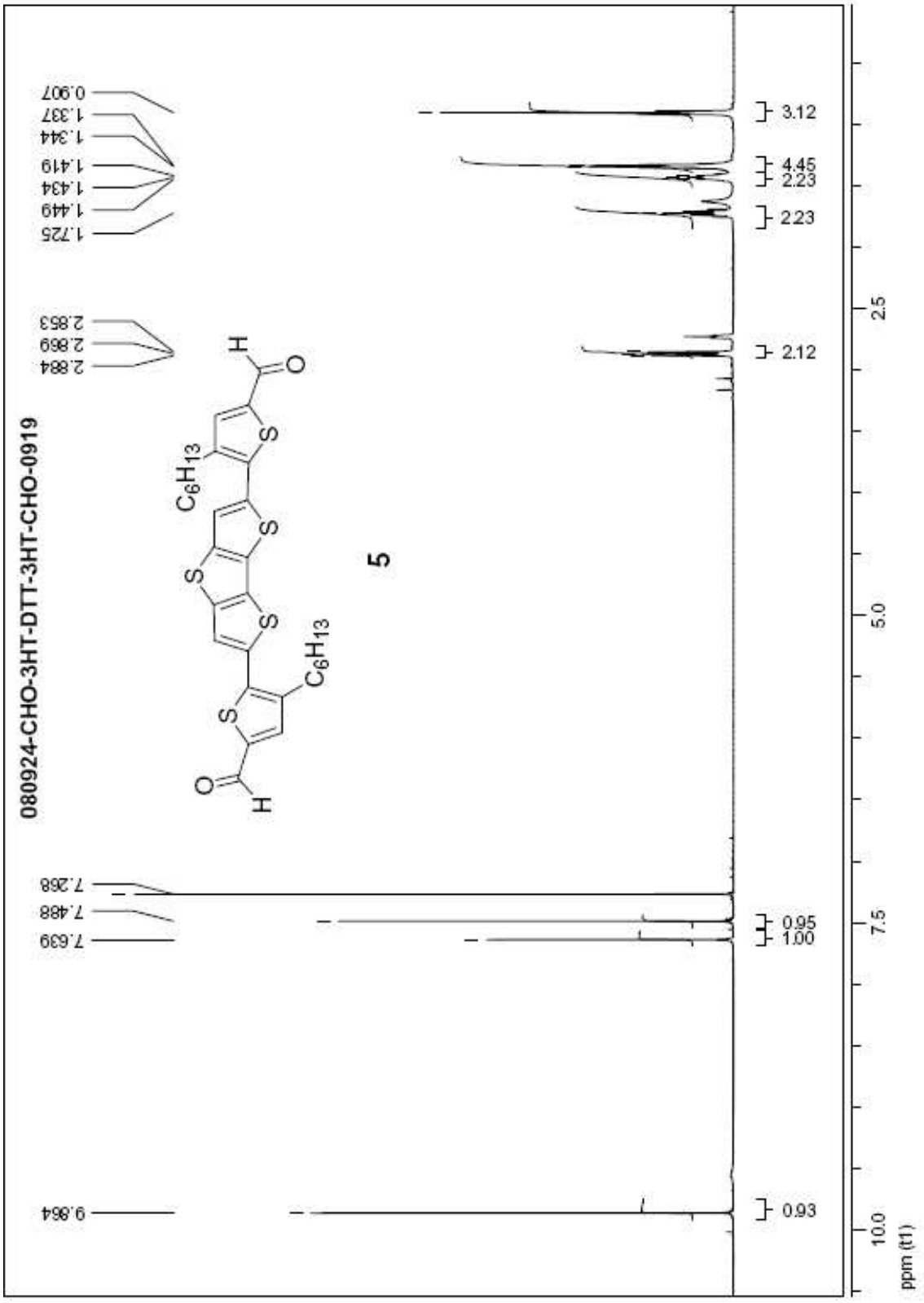


Figure S1. ^{1}H NMR spectrum of **10** (500 MHz, $CDCl_3$).

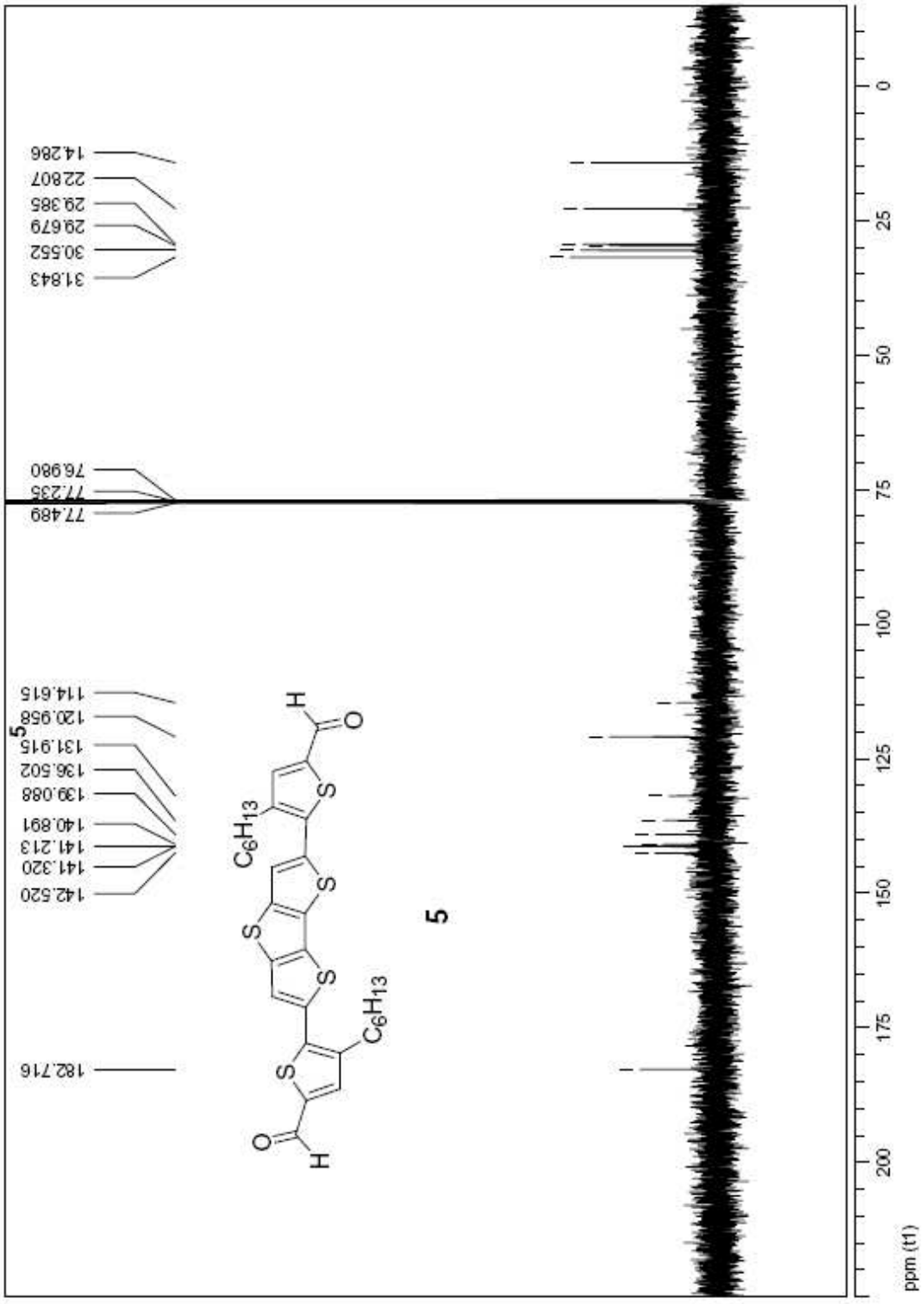


Figure S2. ^{13}C NMR spectrum of **10** (125 MHz, $CDCl_3$).

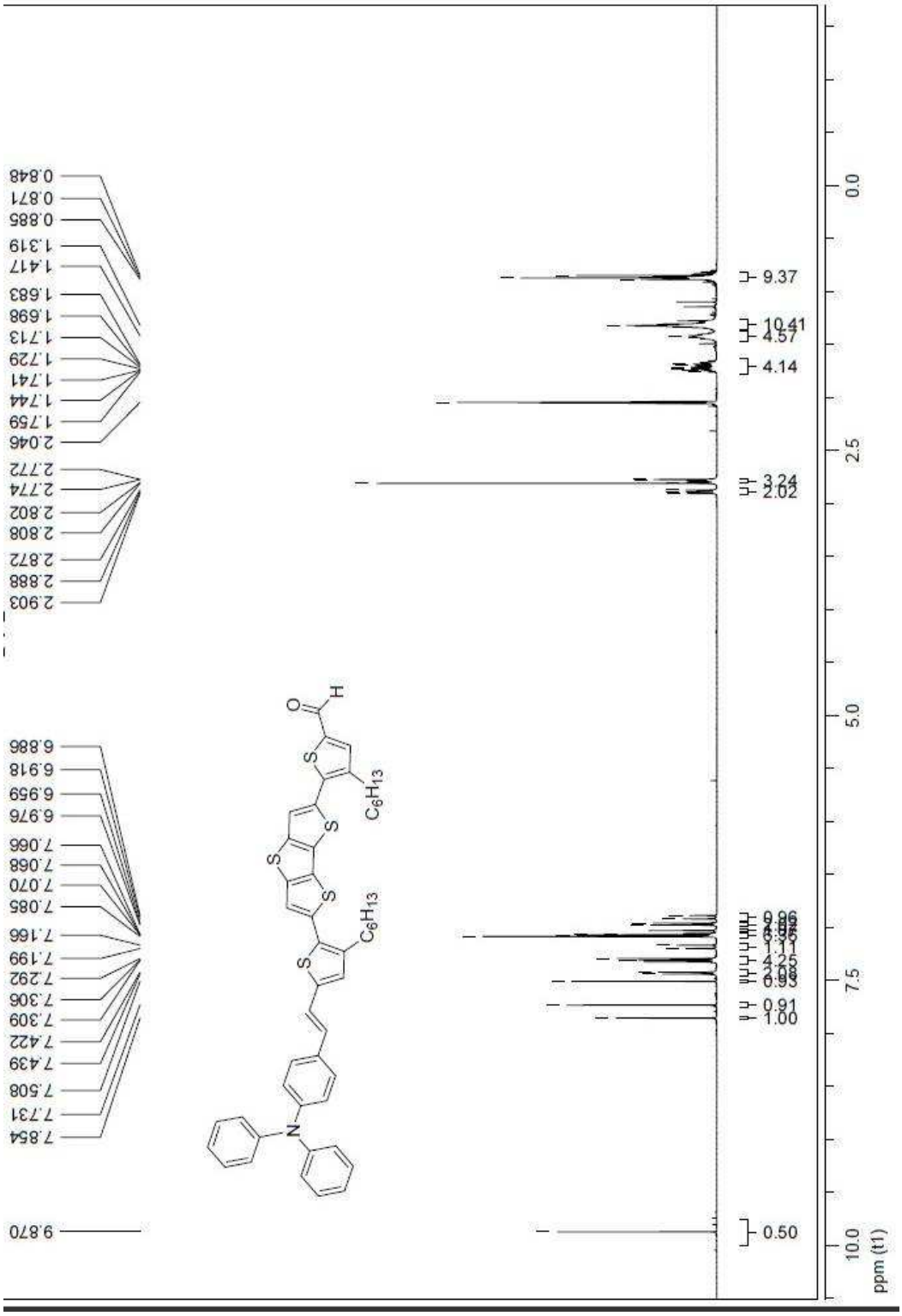


Figure S3. ^{1}H NMR spectrum of **12** (500 MHz, Acetone-d_6).

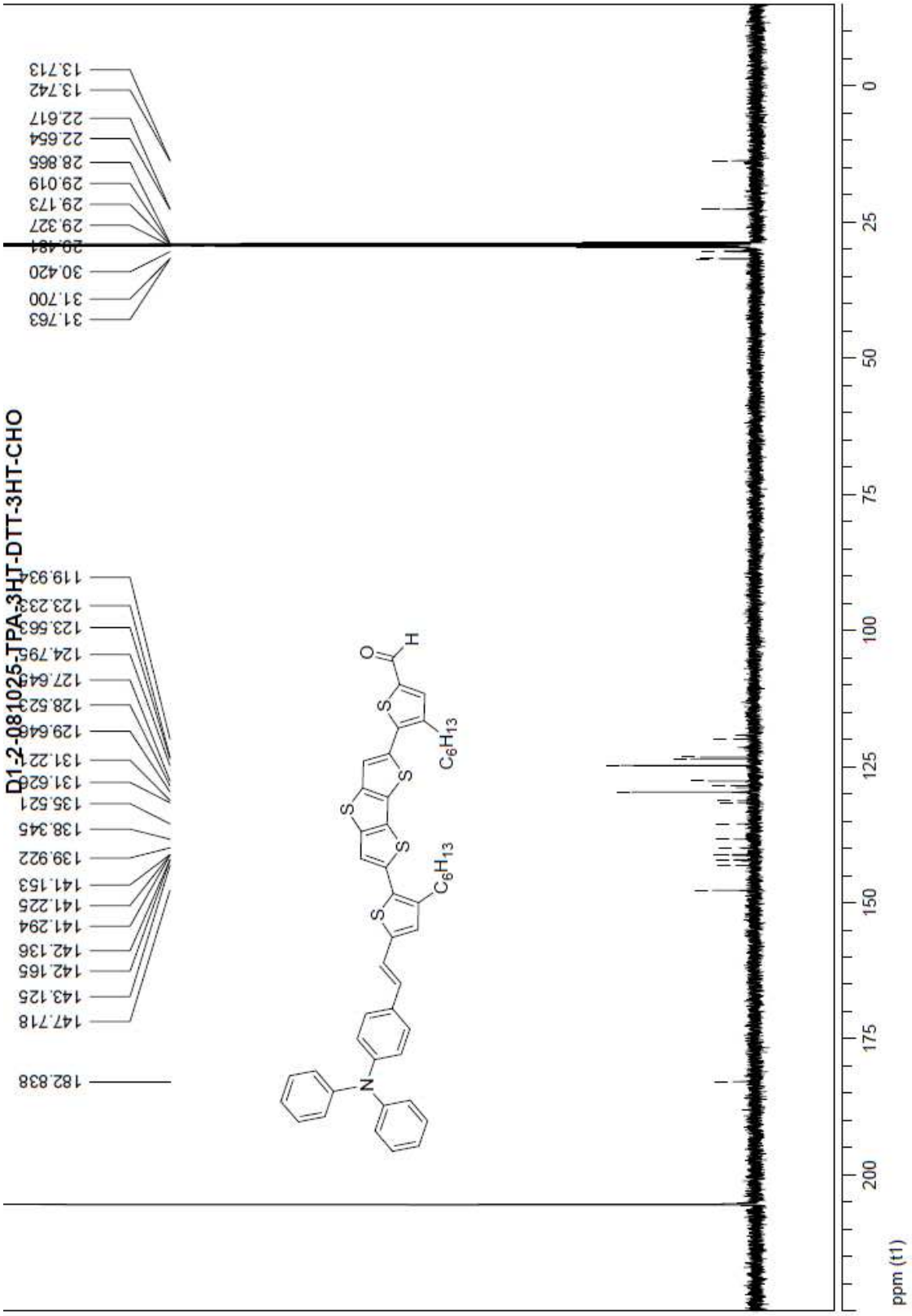


Figure S4. ^{13}C NMR spectrum of **12** (125 MHz, Acetone-d_6).

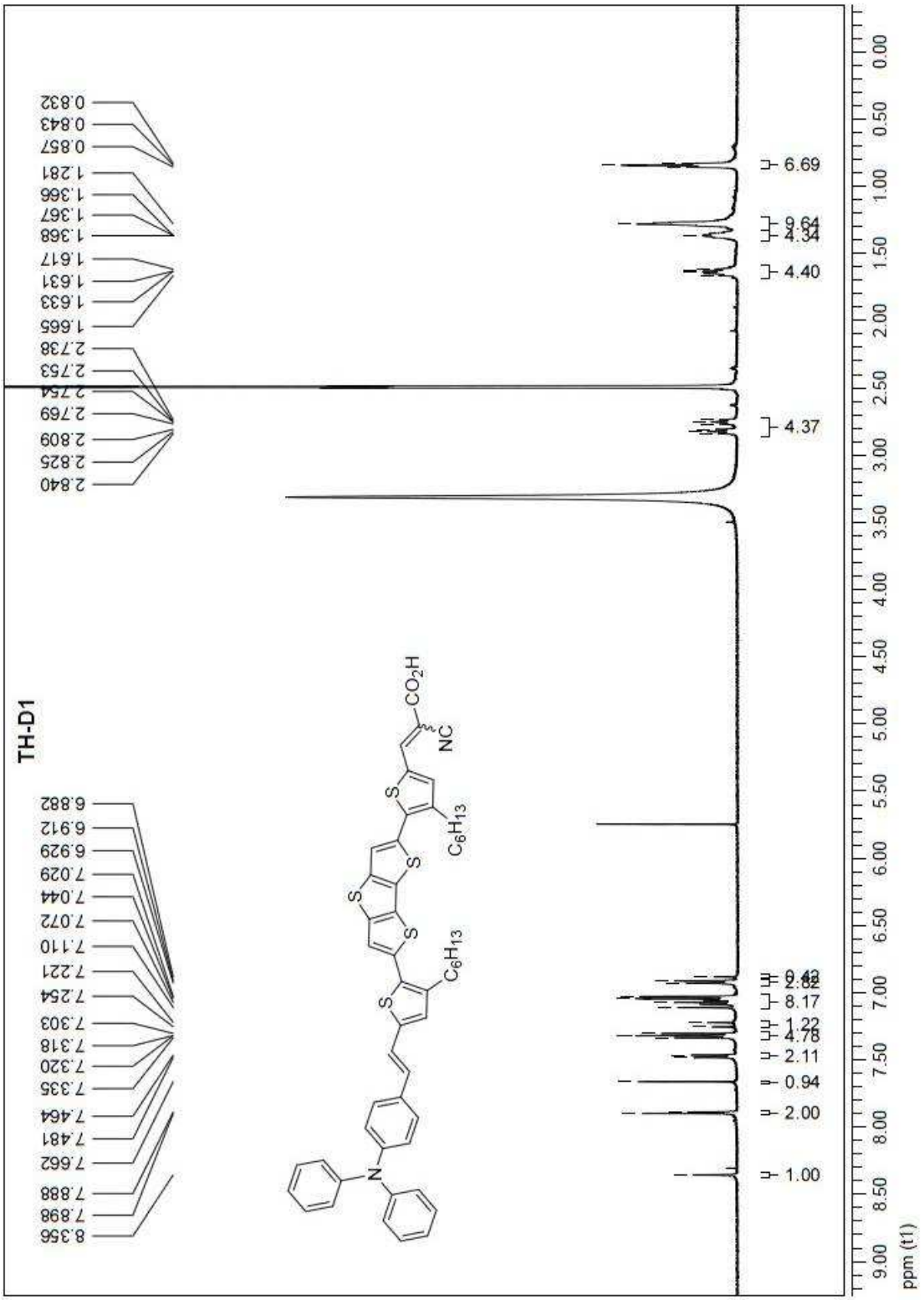


Figure S5. ^{1}H NMR spectrum of **13** (500 MHz, DMSO- d_6).

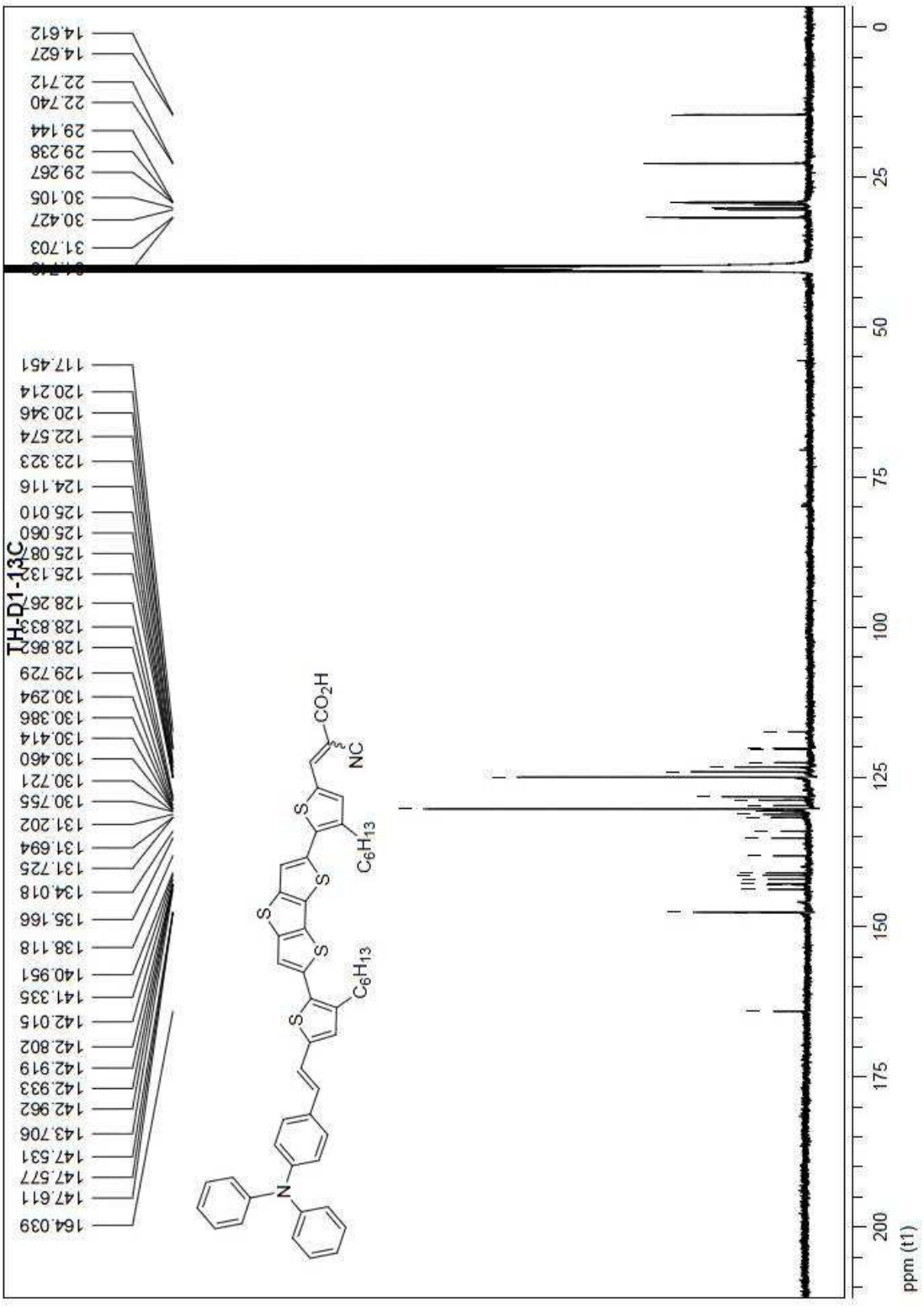


Figure S6. ^{13}C NMR spectrum of **13** (125 MHz, DMSO- d_6)

TABLE 1. Observed and Calculated (DFT) Absorption Maxima and Orbital Contributions to Optical Transitions for the Organic Donor Acceptor Dye 13

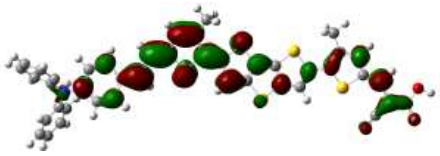
	Abs / cm^{-1} (ε / x10^4 L mol^{-1} cm^{-1})	Calculated Abs / cm^{-1} (Oscillator strength *f*)	Calculated Orbital Contributions
13	20 450 (3.0)	19 549 (2.62)	H-1→L (-0.26), H→L (0.51), H→L+1 (-0.12) [87% L, 13% L+1]
		24 513 (0.41)	H-2→L (0.14), H-1→L (-0.18), H→L+1 (0.56) [36% L, 64% L+1]
	23 641 (3.0)		

*H = HOMO, HOMO-1 = H-1, HOMO-2 = H-2, L = LUMO, LUMO+1 = L+1

TABLE 2. DFT-calculated HOMO and LUMO energy levels *in vacuo* and with a contribution from the dichloromethane solvent environment as well as calculated difference between onset oxidation potential E_{ox} and the $E_{0\text{-}0}$ transition energy for 13

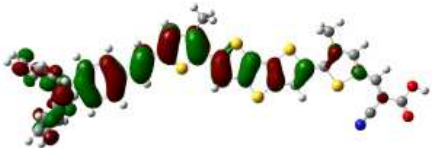
	HOMO vs *Vac* (CH_2Cl_2) / eV	LUMO vs *Vac* (CH_2Cl_2) / eV	LUMO+1 vs *Vac* (CH_2Cl_2) / eV	E_{ox}-$E_{o\text{-}o}$ vs *Vac* $_{[Calc]}$ / eV
13	-4.67 (-5.94)	-2.75 (-1.90)	-1.92 (-0.97)	-3.51

LUMO



LUMO+1

HOMO-1



HOMO

A DFT calculation of the dye **13** was carried out at the B3-LYP level of theory with a 6-31G(d) basis set on all atoms using Gaussian09W.[2] A polarizable continuum model was utilized to accurately account for the solvent environment (calculated with CH_2Cl_2 as a

solvent). The calculated orbital levels are in good agreement with those determined from cyclic voltammetry and approximated in conjunction with emission spectroscopy. The calculated values that include a contribution from the solvent environment match those determined experimentally much better than those calculated *in vacuo.*

TABLE 3. DFT-calculated atom coordinates for 13[a].

Center	Atomic Number	(Angstroms)		
		X	Y	Z
1	S	1.835364	-0.20844	1.718276
2	S	-1.57135	-1.8727	-0.1371
3	S	-0.99337	1.993798	-0.50753
4	C	0.429332	-2.73159	1.316993
5	H	1.088782	-3.37398	1.888629
6	C	-0.71205	-3.19876	0.683683
7	C	1.21538	2.491967	0.808981
8	H	2.05411	3.008189	1.262242
9	C	0.241055	3.143886	0.0657
10	C	-0.17281	0.67103	0.260753
11	C	-0.38023	-0.72114	0.391845
12	C	0.614776	-1.34253	1.150084
13	C	0.983228	1.107575	0.916746
14	C	0.197716	4.547707	-0.25865
15	C	-0.82694	5.321808	-0.82038
16	S	1.620444	5.51792	0.080295
17	C	-0.4458	6.670771	-0.94618
18	C	0.837581	6.974786	-0.50612
19	C	-1.17573	-4.56395	0.620866
20	C	-2.40836	-5.09698	0.255332
21	S	-0.05348	-5.8473	1.077157
22	C	-2.43118	-6.51152	0.364372
23	C	-1.25605	-7.09138	0.800908
24	H	-3.31225	-7.10167	0.13058
25	C	-3.61382	-4.31299	-0.19541
26	H	-3.8469	-3.48748	0.486465

27	H	-3.47331	-3.88067	-1.19437
28	H	-4.49188	-4.96419	-0.24319
29	C	-2.18727	4.827398	-1.23873
30	H	-2.1316	4.146383	-2.09694
31	H	-2.69674	4.292075	-0.42949
32	H	-2.82127	5.669892	-1.53084
33	H	-1.10595	7.432449	-1.35063
34	C	-1.01603	-8.49725	1.003519
35	H	-1.86936	-9.12724	0.757531
36	C	0.128816	-9.0635	1.456185
37	H	0.961746	-8.40573	1.706428
38	C	0.392414	-10.4809	1.662641
39	C	1.63428	-10.8795	2.195615
40	C	-0.52869	-11.5053	1.357664
41	C	1.942054	-12.2135	2.427471
42	H	2.36845	-10.1182	2.44936
43	C	-0.22778	-12.8408	1.572666
44	H	-1.49367	-11.2564	0.925564
45	C	1.014354	-13.2233	2.117965
46	H	2.90316	-12.4809	2.853817
47	H	-0.95292	-13.6049	1.312607
48	N	1.316168	-14.5854	2.341584
49	C	2.64219	-15.0709	2.154011
50	C	3.219247	-15.9382	3.094522
51	C	3.385104	-14.6984	1.022606
52	C	4.510219	-16.4261	2.900126
53	H	2.650608	-16.2262	3.973029
54	C	4.682013	-15.1769	0.846068
55	H	2.94076	-14.0353	0.286934
56	C	5.251366	-16.0461	1.779356
57	H	4.942413	-17.097	3.637924
58	H	5.243824	-14.879	-0.03533
59	H	6.259818	-16.4228	1.63447
60	C	0.300688	-15.4846	2.77653
61	C	0.191189	-16.7606	2.202121
62	C	-0.59683	-15.1122	3.789599

63	C	-0.79282	-17.6452	2.639665
64	H	0.880755	-17.0515	1.416
65	C	-1.58904	-15.9971	4.2081
66	H	-0.51026	-14.1304	4.244348
67	C	-1.69133	-17.2689	3.640394
68	H	-0.86419	-18.6297	2.184781
69	H	-2.27586	-15.6938	4.993949
70	H	-2.46118	-17.9586	3.974363
71	C	1.398971	8.282401	-0.54489
72	H	0.734682	9.033478	-0.96397
73	C	2.627018	8.742709	-0.14372
74	C	3.00789	10.16742	-0.27835
75	O	4.076354	10.63238	0.059461
76	O	2.023466	10.92949	-0.83054
77	H	2.387577	11.83282	-0.86574
78	C	3.622988	7.897343	0.429893
79	N	4.416802	7.183543	0.895669

[a]Ground state energy = -3868.1992993 Hartrees

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