Donor-acceptor-acceptor (D-A-A) type of 1,8–naphthalimides as Non-fullerene Small Molecule Acceptors for Bulk Heterojunction Solar Cells

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I. Experimental Section

Device fabrication and characterization

The OSCs were fabricated in the configuration of ITO/PEDOT:PSS/P:**SM1** or **SM2**/PFN/Al. Indium tin oxide (ITO) coated glass substrates were cleaned sequentially with deionized water, acetone, ethanol and iso-propanol in a ultrasonic bath for 10 min each and then treated and then dried in ambient conditions. After drying the substrates, a thin layer (40 nm) of

poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) was spin coated ITO coated glass substrate and baked at 110° C for 10 min. The blends photoactive layer of different weight ratios of P and **SM1** or **SM2** were prepared from chloroform solvent and then spin cast on the top of PEDOT:PSS film and then dried in ambient conditions for 5 hrs to remove the residue of solvent. For solvent additive different concentration of DIO (1, 2, 3 and 4 v%) was added to host chloroform solvent. The concentration of solution was kept 18 mg/mL for all the blends. A methanol solution of PFN with concentration of 1.5 mg/mL was then spin coated onto the top of the photoactive layer at 3000 rpm for 30 s and dried in a vacuum oven for 2hr. Finally, aluminum (Al) top electrode was deposited onto the top of PFN buffer layer by thermal evaporation at a base pressure of $1x10^{-5}$ Pa through a shadow mask area of 20 mm^2.

The current–voltage (*J–V*) characteristics of the BHJ organic solar cells were measured using a computer controlled Keithley 2400 source meter in the dark and under simulated AM1.5G illumination of 100 mW cm^{-2}. A xenon light source coupled with an optical filter was used to provide stimulated irradiance at the surface of the devices. The incident photon-to-current efficiency (IPCE) of the devices was measured by illuminating the devices through the light source and a monochromator and the resulting current was measured using a Keithley electrometer under short-circuit conditions. All the measurements were performed in ambient conditions with encapsulation.

In order to measure the charge carrier mobilities in the active layers, the hole-only and electron-only devices with architectures of ITO/PEDOT:PSS/active layer/Au (hole mobility) and ITO/Al/active layer/Al (electron mobility) were also fabricated in a similar way in order to measure the hole and electron mobility, respectively.

Experimental details. Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere. ^{1}H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard {$CDCl_3$, 7.26 ppm}. ^{13}C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent

as internal standard {$CDCl_3$, 77.0 ppm}. The ^1H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". UV-visible absorption spectra of all compounds were recorded in choloroform solution. Cyclic voltamograms and differential pulse voltamograms were recorded on electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. The scan rate was $100mVs^{-1}$ for Cyclic Voltammetry. A 0.1 M solution of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) in chloroform was used as supporting electrolyte.

Preparation of SM1. TCNE (0.038 g, 0.30 mmol) was added to a solution of compound **3** (0.30 mmol) in CH_2Cl_2 (50 mL). The mixture was refluxed at 40 ºC for 20 h. The solvent was removed in vacuo, and the product was purified by SiO_2 column chromatography with DCM as the eluent to yield **SM1** as deep brown solid (0.126 g; 65%): ^1H NMR (400 MHz, δ in ppm): 8.74 (d, J = 8 Hz, 1H), 8.62 (d, J = 8 Hz, 1H), 8.36 (d, J = 8 Hz, 1H), 7.99 (t, 1H), 7.72 (d, J = 8 Hz, 1H), 7.62 (d, J = 8 Hz, 2H), 7.42-7.39 (m, 4H), 7.29-7.27 (m, 3H), 7.25-7.21 (m, 4H), 6.74 (d, J = 12 Hz, 2H), 4.18 (t, 2H), 1.75-1.67 (m, 2H), 1.47-1.42 (m, 2H), 0.98 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm):165.88, 163.73, 163.17, 162.79, 153.99,144.40, 135.01, 132.64, 131.93, 130.48, 130.19, 129.51, 129.31, 129.14, 128.67, 128.09, 126.96, 126.90, 123.88, 121.61, 118.29, 113.28, 112.91, 110.92, 110.45, 94.86, 80.16, 40.62, 30.11, 20.36, 13.80 ; HRMS (ESI-TOF) *m/z* calcd for $C_{42}H_{28}N_2O_2$ + H: 649.234 $[M + H]^+$, found 649.236 $[M+ H]^+$.

Preparation of SM2. TCNQ (0.061g, 0.30 mmol) was added to a solution of compound **3** (0.30 mmol) in $C_2H_4Cl_2$ (50 mL). The mixture was refluxed at 100 ºC for 48 h. The solvent was removed in vacuo, and the product was purified by SiO_2 column chromatography with (0.1:10) ethylacetate:DCM as the eluent to yield SM2 as black solid (0.13 g; 60%): ^1H NMR (400 MHz, δ in ppm): 8.72 (d, 1H), 8.63-8.61 (d, J = 7.8 Hz, 1H), 8.60 (d, J = 7.5 Hz, 1H), 7.92 (t, 1H), 7.76 (d, J = 7.76 Hz, 1H), 7.39-7.30 (m, 7H), 7.22-7.18 (m, 3H), 7.10 (d, J = 8 Hz, 6H), 6.88 (d, J = 8 Hz, 2H), 4.19 (t, 2H), 1.76-1.69 (m, 2H), 1.49-1.43 (m, 2H), 0.99 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 169.08, 163.19, 162.85, 153.16, 151.54, 149.99, 145.19, 138.31, 135.74, 135.60, 133.49, 133.39, 132.17, 129.86, 129.72, 129.50, 128.98, 128.57, 128.32, 126.87, 126.69,

126.40, 126.06, 125.87, 123.95, 119.19, 113.65, 112.21, 11.60, 93.42, 40.56, 30.06, 20.31, 13.76; HRMS (ESI-TOF) *m/z* calcd for $C_{48}H_{32}N_6O_2$: 724.2659 $[M]^+$, found 724.2581 $[M]^+$

II. Copies of ^{1}H NMR, ^{13}C NMR spectra and HRMS of 3, SM1 and SM2.

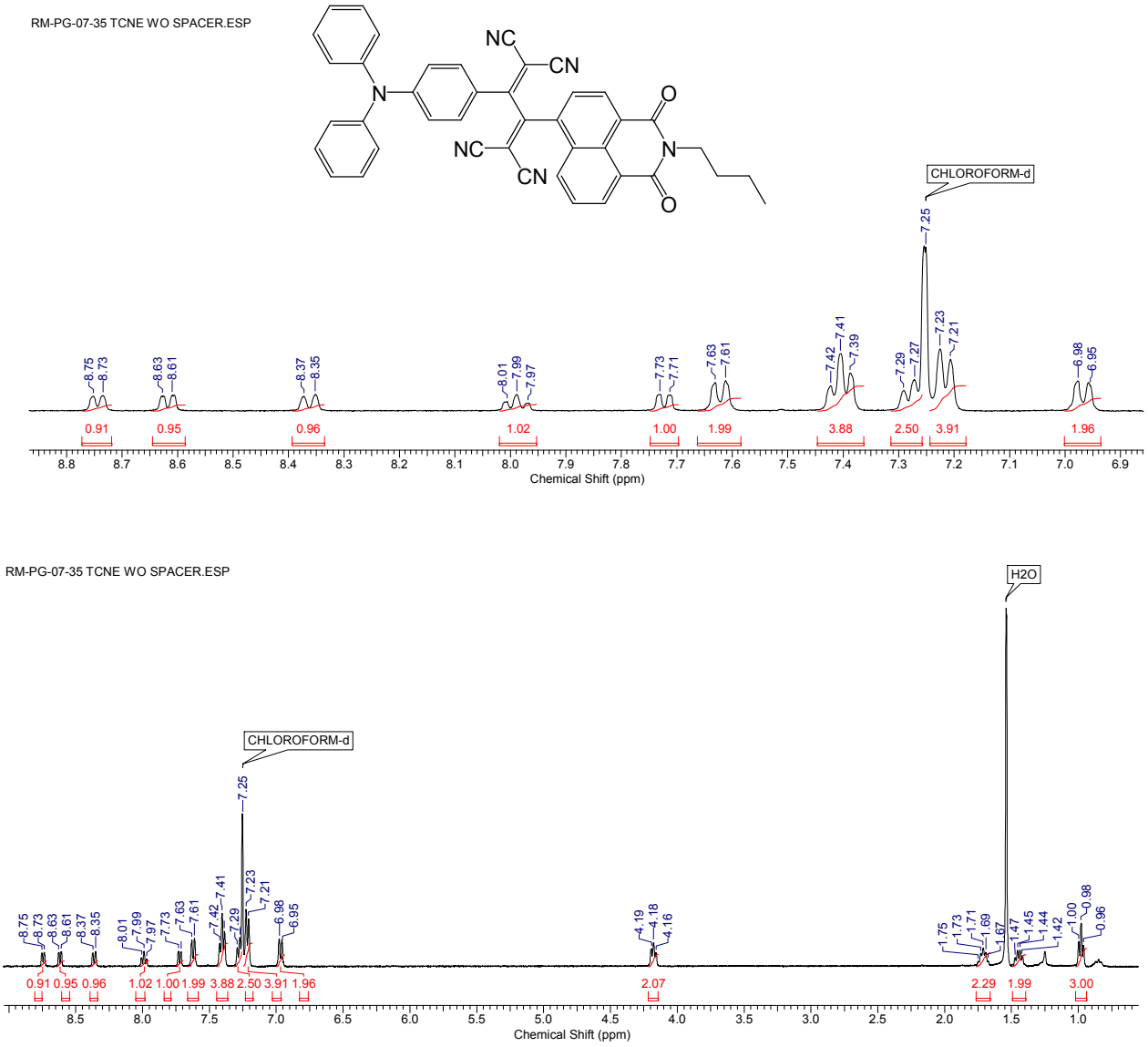

Figure S1. ^{1}H NMR spectra of **SM1**

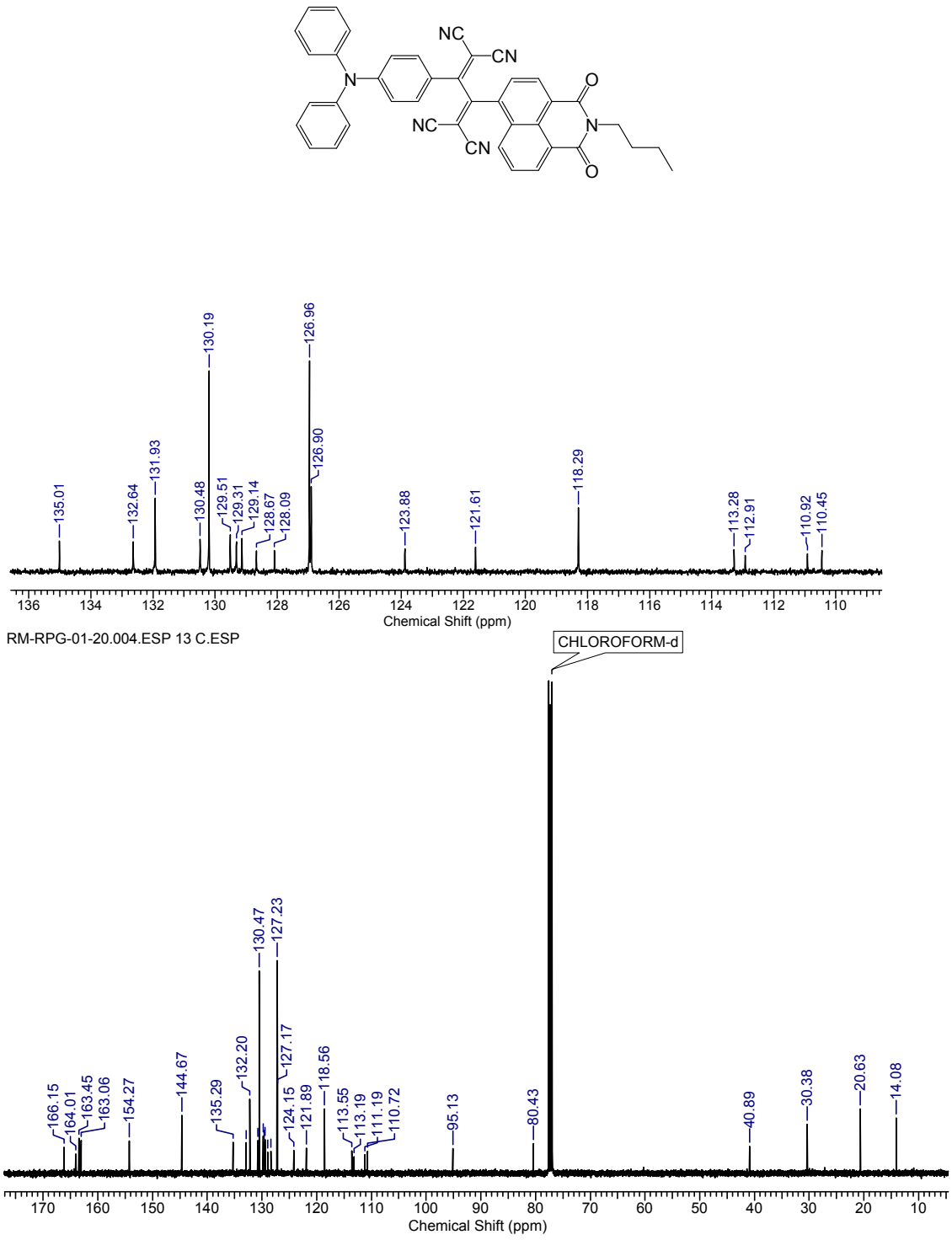

Figure S2. ^{13}C NMR spectra of **SM1**

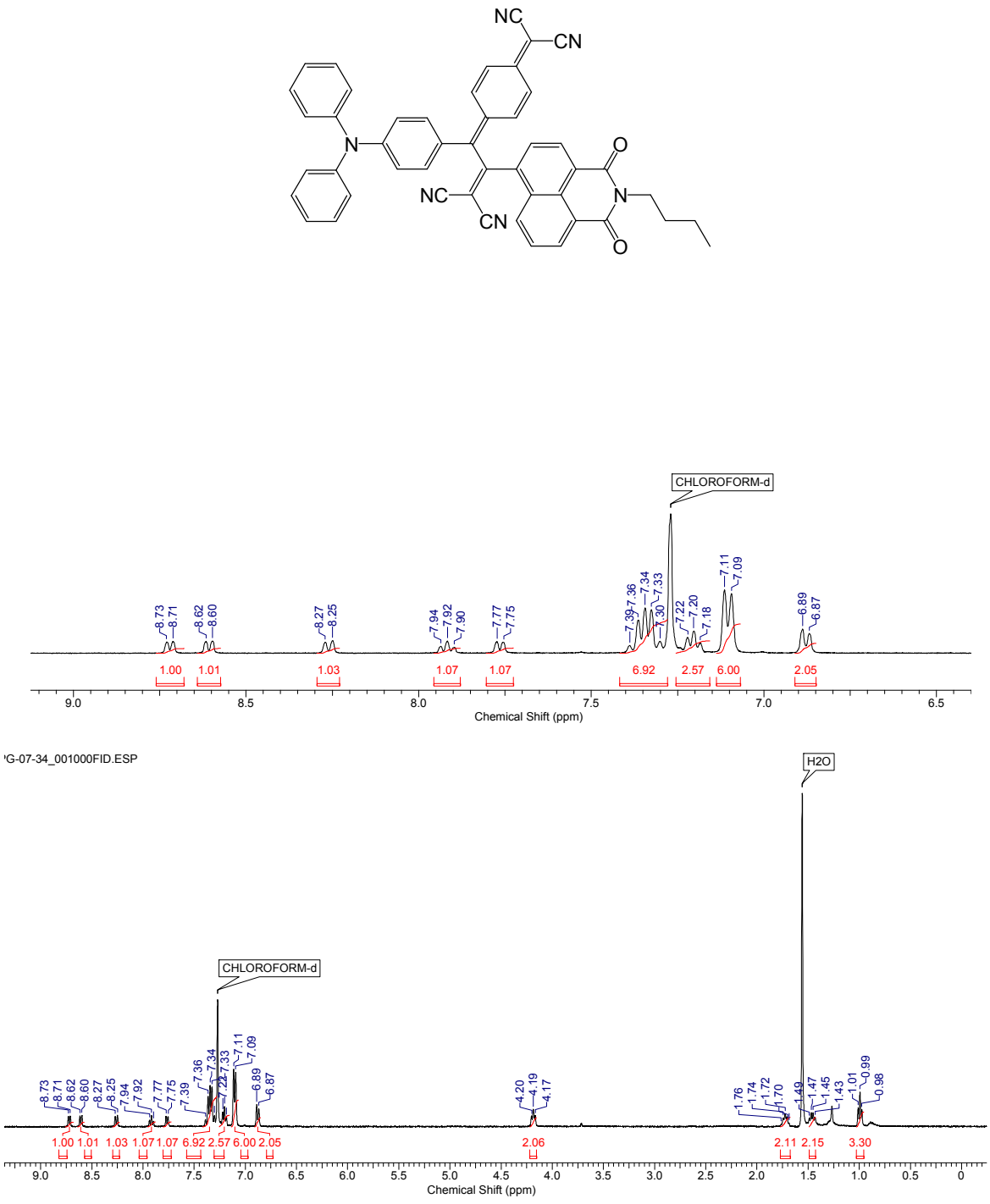

Figure S3. ^{1}H NMR spectra of **SM2**

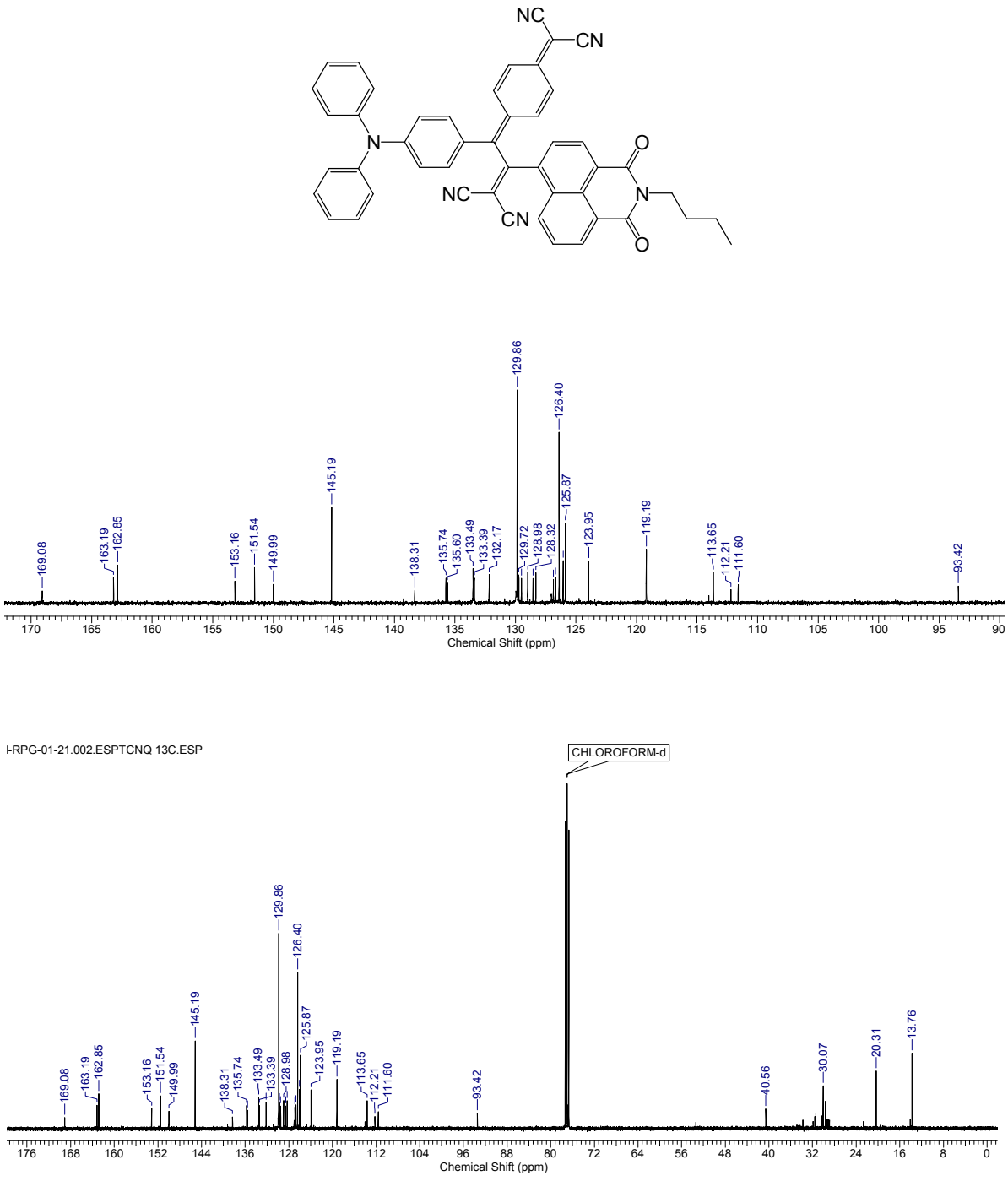

Figure S4. ^{13}C NMR spectra of **SM2**

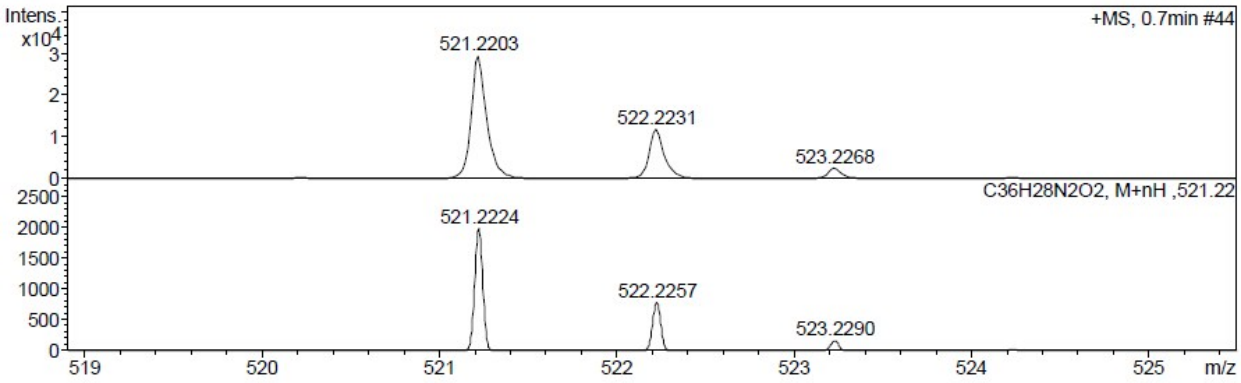

Figure S5. HRMS spectra of **3**

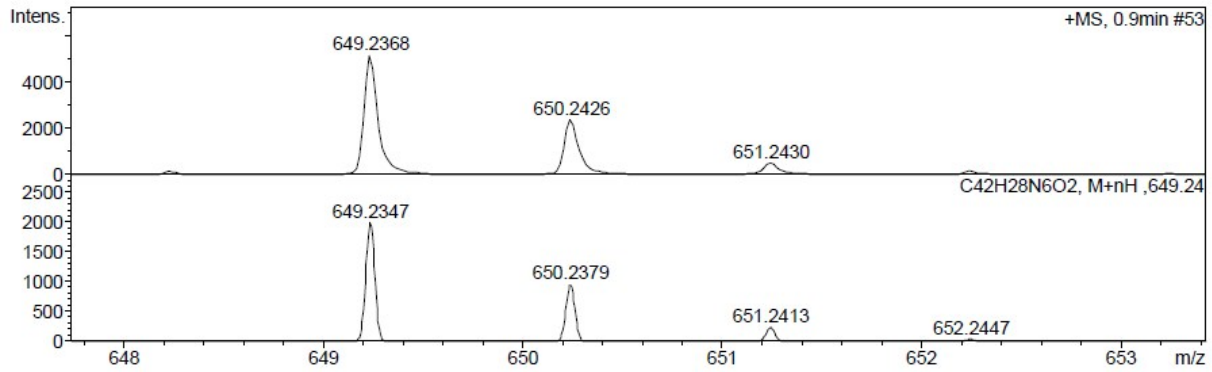

Figure S6. HRMS spectra of **SM1**

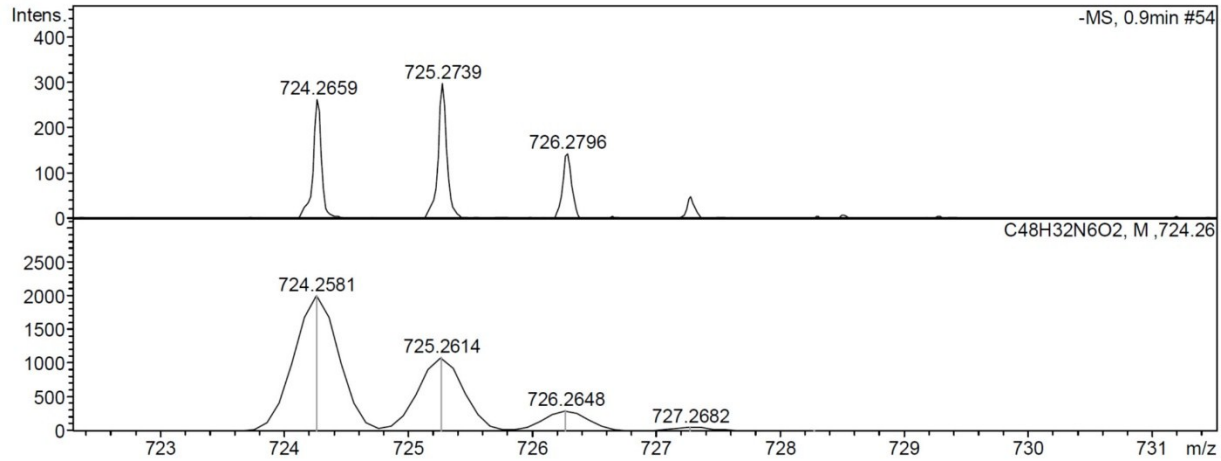

Figure S7. HRMS spectra of **SM2**

III. DFT calculations for SM1 and SM2

For SM1: Calculation method: B3LYP/6-31G** for C, H, N, O, with Gaussian 09.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.822717	0.272155	0.321794
2	6	0	-7.806052	0.886699	1.107177
3	6	0	-7.063073	-0.993612	-0.229972
4	6	0	-9.017522	0.237316	1.338342
5	6	0	-8.271834	-1.641627	0.019046
6	1	0	-6.305467	-1.462479	-0.849490
7	6	0	-9.253740	-1.029170	0.800216
8	1	0	-9.774269	0.719966	1.949318
9	1	0	-8.449737	-2.622471	-0.411227
10	1	0	-10.196349	-1.534222	0.986411
11	6	0	-5.660328	2.295714	-0.435635
12	6	0	-6.494623	2.598070	-1.519395
13	6	0	-4.919970	3.316407	0.176598
14	6	0	-6.583294	3.908903	-1.984693
15	6	0	-5.003890	4.621865	-0.304641
16	1	0	-4.287463	3.082463	1.026775
17	6	0	-5.836590	4.924226	-1.383878
18	1	0	-7.231671	4.134109	-2.826013
19	1	0	-4.427696	5.406574	0.176274
20	1	0	-5.905152	5.943199	-1.751590
21	6	0	-4.364482	0.320574	0.248576
22	6	0	-3.218256	0.714195	-0.479437
23	6	0	-4.228975	-0.749025	1.164415
24	6	0	-2.013968	0.061013	-0.304861
25	1	0	-3.290226	1.519129	-1.200400

26	6	0	-3.015154	-1.380627	1.348495
27	1	0	-5.090074	-1.081888	1.730581
28	6	0	-1.861876	-0.997778	0.623455
29	1	0	-1.167592	0.381847	-0.903059
30	1	0	-2.970717	-2.203303	2.050024
31	7	0	-5.589318	0.953979	0.060287
32	6	0	0.386608	-1.624394	-0.374032
33	6	0	1.657372	-0.880561	-0.203289
34	6	0	2.938352	-1.371984	-0.637328
35	6	0	1.574747	0.377970	0.390781
36	6	0	3.173098	-2.697836	-1.087608
37	6	0	4.063241	-0.491206	-0.544716
38	6	0	2.688829	1.225036	0.480133
39	1	0	0.618043	0.732126	0.759526
40	6	0	4.430309	-3.105042	-1.481262
41	1	0	2.360848	-3.413149	-1.094744
42	6	0	5.344204	-0.928484	-0.971116
43	6	0	3.915082	0.808510	-0.001102
44	1	0	2.606356	2.215170	0.913782
45	6	0	5.520433	-2.215372	-1.441943
46	1	0	4.582301	-4.125804	-1.815541
47	1	0	6.511823	-2.522521	-1.755832
48	6	0	5.074661	1.738848	0.086658
49	6	0	6.517645	-0.019543	-0.905250
50	8	0	7.632613	-0.362960	-1.271506
51	8	0	4.967132	2.862296	0.560457
52	7	0	6.296722	1.274198	-0.405012
53	6	0	7.451806	2.191441	-0.347243
54	1	0	7.059146	3.199970	-0.484092
55	1	0	8.097846	1.933362	-1.187171
56	6	0	8.223735	2.091514	0.972369
57	1	0	8.569371	1.059307	1.105145
58	1	0	7.543229	2.319006	1.801585
59	6	0	9.421868	3.047846	1.007487
60	1	0	9.069869	4.076751	0.853368

61	1	0	10.089969	2.822883	0.165422
62	6	0	10.208643	2.968522	2.319121
63	1	0	10.602624	1.959489	2.483743
64	1	0	11.056599	3.660767	2.317878
65	1	0	9.574491	3.219980	3.176562
66	1	0	-7.616001	1.867854	1.529610
67	1	0	-7.068098	1.805673	-1.988718
68	6	0	-0.571422	-1.658182	0.786229
69	6	0	-0.139972	-2.303278	1.931048
70	6	0	-0.001875	-2.193676	-1.560618
71	6	0	1.075506	-3.058702	1.942627
72	6	0	-0.834667	-2.289016	3.180646
73	6	0	0.728631	-2.049245	-2.786056
74	6	0	-1.214068	-2.953053	-1.683287
75	7	0	2.050664	-3.695268	1.962356
76	7	0	-1.354781	-2.288662	4.222588
77	7	0	1.268582	-1.931220	-3.809545
78	7	0	-2.177364	-3.590305	-1.821655

E(HF) = -2096.28898801

For SM2: Calculation method: B3LYP/6-31G** for C, H, N, O, with Gaussian 09.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.126944	-0.076246	0.166700
2	6	0	-8.258728	0.411771	-0.499318
3	6	0	-7.037830	0.035953	1.561678
4	6	0	-9.290358	1.005667	0.225488

5	6	0	-8.068139	0.645668	2.275470
6	1	0	-6.165711	-0.351550	2.078632
7	6	0	-9.198333	1.129435	1.613183
8	1	0	-10.163719	1.381733	-0.298794
9	1	0	-7.990894	0.728636	3.355298
10	1	0	-10.001366	1.597204	2.174104
11	6	0	-6.439920	-1.742536	-1.500825
12	6	0	-7.326744	-2.755898	-1.113060
13	6	0	-5.926709	-1.733583	-2.805695
14	6	0	-7.692073	-3.747291	-2.021878
15	6	0	-6.285878	-2.737701	-3.702963
16	1	0	-5.253210	-0.938950	-3.109864
17	6	0	-7.170935	-3.746425	-3.317229
18	1	0	-8.378720	-4.528939	-1.711212
19	1	0	-5.883669	-2.721582	-4.711491
20	1	0	-7.454132	-4.522882	-4.020864
21	6	0	-4.744052	-0.376686	-0.357551
22	6	0	-3.712392	-1.321810	-0.560708
23	6	0	-4.383149	0.911936	0.095667
24	6	0	-2.396916	-0.997690	-0.289648
25	1	0	-3.959423	-2.318245	-0.906342
26	6	0	-3.060704	1.231671	0.341619
27	1	0	-5.153729	1.653157	0.269457
28	6	0	-2.023078	0.287835	0.166245
29	1	0	-1.634755	-1.757560	-0.432871
30	1	0	-2.822721	2.218845	0.722477
31	7	0	-6.080908	-0.710983	-0.577360
32	6	0	0.181082	-0.433332	1.148873
33	6	0	1.542223	-0.734280	0.621665
34	6	0	2.714346	-0.829971	1.449842
35	6	0	1.656033	-0.953514	-0.747300
36	6	0	2.740440	-0.508798	2.834027
37	6	0	3.948113	-1.213965	0.833160
38	6	0	2.871519	-1.336240	-1.336367
39	1	0	0.776040	-0.851700	-1.373714

40	6	0	3.905569	-0.598363	3.567016
41	1	0	1.831155	-0.181831	3.324965
42	6	0	5.130019	-1.313765	1.611865
43	6	0	4.003539	-1.477667	-0.558014
44	1	0	2.942195	-1.529726	-2.400796
45	6	0	5.106192	-1.014507	2.960440
46	1	0	3.896728	-0.346705	4.622438
47	1	0	6.026847	-1.096834	3.527262
48	6	0	5.277970	-1.888868	-1.208786
49	6	0	6.415960	-1.729496	0.990643
50	8	0	7.450492	-1.823503	1.635631
51	8	0	5.348750	-2.108563	-2.410340
52	7	0	6.397987	-2.018930	-0.381901
53	6	0	7.667928	-2.437008	-1.008915
54	1	0	7.406159	-3.097007	-1.836923
55	1	0	8.219904	-2.998590	-0.254218
56	6	0	8.497867	-1.250247	-1.508201
57	1	0	8.710383	-0.584633	-0.662979
58	1	0	7.904538	-0.680042	-2.233258
59	6	0	9.813247	-1.700224	-2.155511
60	1	0	9.593680	-2.376717	-2.992445
61	1	0	10.392255	-2.287562	-1.430212
62	6	0	10.661401	-0.527496	-2.655892
63	1	0	10.925314	0.148585	-1.835068
64	1	0	11.593045	-0.876318	-3.112476
65	1	0	10.121589	0.059415	-3.407306
66	1	0	-8.323346	0.321502	-1.578596
67	1	0	-7.723679	-2.759972	-0.103484
68	6	0	-0.626708	0.609872	0.476711
69	6	0	-0.361293	-1.203953	2.160407
70	6	0	0.275515	-2.385398	2.661589
71	6	0	-1.608117	-0.905437	2.803356
72	7	0	0.747675	-3.363393	3.080541
73	7	0	-2.593249	-0.700109	3.388516
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75	6	0	1.144623	2.345477	0.763914
76	6	0	-0.661302	2.719144	-0.845863
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78	1	0	1.628357	1.746690	1.525417
79	6	0	-0.138606	3.937210	-1.155419
80	1	0	-1.529136	2.364172	-1.388367
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83	6	0	1.040472	4.434040	-0.496468
84	6	0	1.573589	5.691323	-0.801142
85	6	0	0.963329	6.543532	-1.764704
86	7	0	0.447401	7.225618	-2.557255
87	6	0	2.750570	6.175755	-0.163110
88	7	0	3.714742	6.554924	0.371785

E(HF) = -2327.33640305