Supplementary Information

Exploration of naphtho[*c*]dithiophenes: synthesis, optical and electrochemical properties of naphtho[1,2-*c*:5,6-*c*']dithiophenes

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Experimental Section:

General

Melting points were measured with an AS ONE ATM-02. IR spectra were recorded on a SHIMADZU IRTracer-100 spectrometer by the ATR method. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-400 or -500 FT NMR spectrometer. High-resolution mass spectral data were acquired by APCI on a Thermo Fisher Scientific LTQ Orbitrap XL. Photoabsorption spectra were observed with a SHIMADZU UV-3600 plus. Fluorescence spectra of solutions and solids were measured with a HORIBA FluoroMax-4 spectrofluorometer. The fluorescence quantum yields in solution and in solid state were determined using a HORIBA FluoroMax-4 spectrofluorometer with a calibrated integrating sphere system. Fluorescence decay measurements were performed on a HORIBA DeltaFlex modular fluorescence lifetime system, using a Nano LED pulsed diode excitation source (370 nm). Cyclic voltammetry (CV) curves were recorded in DMF/Bu_4NClO_4 (0.1 M) solution with a three-electrode system consisting of Ag/Ag^+ ($AgNO_3$ in acetonitrile/Bu_4NClO_4) as the reference electrode, a Pt plate as the working electrode and a Pt wire as the counter electrode using an Electrochemical Measurement System HZ-7000 (HOKUTO DENKO).

Synthesis

2,6-Dimethylnaphthalene-1,5-dicarbaldehyde

To a diethyl ether (25 mL)/toluene (75 mL) solution of 1,5-dibromo-2,6-dimethylnaphthalene (3.85 g, 12.3 mmol) under a nitrogen atmosphere at 0 °C was added dropwise a 1.6 M hexane solution of *n*BuLi (38.3 mL, 61.3 mmol). After stirring for 1 h at 0 °C, the reaction mixture was allowed to warm to room temperature and stirred for a futher 2 h. Then, *N*,*N*-dimethylformamide (7.58 mL, 98.4 mmol) was added dropwise. After stirring for 1 h at 0 °C, the reaction mixture was quenched with NH_4Cl aq, and then the solution was extracted with ethyl acetate. The ethyl acetate extract was concentrated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane as eluent) to give 2,6-dimethylnaphthalene-1,5-dicarbaldehyde (1.10 g, yield 42 %) as a yellow solid; m.p. 173–174 °C; FT-IR (ATR): $\tilde{\nu}$ = 3095 (aromatic C–H str.), 2956 (methyl C–H str.), 2929 (methyl C–H str.), 2872 (methyl C–H str.), 1670 (C=O str.) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 2.82 (s, 6H), 7.49 (d, J = 8.9 Hz, 2H), 9.14 (d, J = 8.8 Hz, 2H), 10.93 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.66, 128.60, 130.45, 130.94, 132.60, 142.44, 193.50 ppm; HRMS (APCI): m/z (%): $[M+H]^+$ calcd for $C_{14}H_{13}O_2$, 213.0910; found 213.0907.

1,2,5,6-Tetramethylnaphthalene (1)

A solution of 2,6-dimethylnaphthalene-1,5-dicarbaldehyde (0.50 g, 2.36 mmol) and hydrazine monohydrate (0.45 mL, 9.44 mmol) in diethylene glycol (25 mL) was stirred for 30 min at 110 °C. Next, potassium hydroxide (1.54 g, 28.3 mmol) was added to the reaction mixture, and the reaction mixture was stirred at 150 °C for 2 h. The reaction mixture was quenched with 10% HCl aq, and then the solution was extracted with dichloromethane. The dichloromethane extract was concentrated under reduced pressure to afford **1** (0.303 g, yield 70%) as a white solid; m.p. 112–114 °C; FT-IR (ATR): $\tilde{\nu}$ = 3066 (aromatic C–H str.), 2920 (methyl C–H str.), 2862 (methyl C–H str.) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 2.48 (s, 6H), 2.59 (s, 6H), 7.30 (d, J = 8.7 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.88, 20.72, 121.50, 128.93, 131.59, 131.69, 131.78 ppm; HRMS (APCI): m/z (%): $[M+H^+]$ calcd for $C_{14}H_{17}$, 185.1324; found 185.1322.

1,2,5,6-Tetrakis(bromomethyl)naphthalene (2)

A solution of **1** (1.93 g, 10.5 mmol) and *N*-bromosuccinimide (7.48 g, 42.0 mmol) in carbon tetrachloride (300 ml) was stirred at room temperature under ambient light. After 3 h, to a reaction mixture was added $Na_2S_2O_3$ aq, and then the solution was extracted with dichloromethane. The dichloromethane extract was concentrated under reduced pressure. The residue was dissolved in dichloromethane, and then compound **2** was recrystallized from dichloromethane solution as a while solid (2.03 g, yield 40 %); m.p. 238–240 °C; FT-IR (ATR): $\tilde{\nu}$ = 3026 (aromatic C–H str.), 546 (C–Br str.), 2862 (methyl C–H str.) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 4.75 (s, 4H), 5.06 (s, 4H), 7.5936 (d, J = 11.0 Hz, 2H), 8.15 (d, J = 11.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.19, 29.98, 125.69, 129.33, 132.27, 133.05, 135.55 ppm; HRMS (APCI): m/z (%): [$M^{+\bullet}$] calcd for $C_{14}H_{12}Br_4$, 499.7626; found 499.7637.

1,3,6,8-Tetrahydronaphtho[1,2-*c*:5,6-*c*']dithiophene (3)

An ethanol solution (100 mL) of Na_2S (0.937 g, 12.00 mmol) was refluxed, and a ethenol solution (150 ml) of **2** (1.00 g, 2.00 mmol) was added dropwise. After stirring for 3 h, the solution was evapolated. The resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was concentrated to afford **3** (0.21 g, yield 44 %) as a white solid; decomp.p. 228–230 °C; FT-IR (ATR): $\tilde{\nu}$ = 2912 (methylene C–H str.), 2841 (methylene C–H str.), 736 (C–S str.) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 4.48–4.49 (m, 4H), 4.67–4.68 (m, 4H), 7.44 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 37,84, 39.44, 123.60, 124.15, 129.29, 136.35, 137.55 ppm; HRMS (APCI): m/z (%): $[M-H]^+$ calcd for $C_{14}H_{11}S_2$, 243.0296; found 243.0295.

1,3,6,8-Tetrahydronaphtho[1,2-*c*:5,6-*c*']dithiophene 2,7-dioxide (4)

To a THF (180 mL) solution of **3** (0.664 g, 2.72 mmol) was added dropwise a water solution (90 mL) of $NaIO_4$ (2.32 g, 10.9 mmol) at room temperature. After stirring for 19 h, the solution was extracted with dichloromethane. The dichloromethane extract was concentrated to afford **4** (0.445 g, yield 59 %) as a light-yellow solid; decomp.p. 178–180 °C; FT-IR (ATR): $\tilde{\nu}$ = 2964 (methylene C–H str.), 2912 (methylene C–H str.), 1016 (S=O str.) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 4.32–4.71 (m, 8H), 7.55–7.58 (m, 2H), 7.80–7.82 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 58.78, 59.05, 60.63, 60.84, 125.11, 125.57, 130.87, 132.47, 133.48 ppm; HRMS (APCI): m/z (%): $[M+H]^+$ calcd for $C_{14}H_{13}O_2S_2$, 277.0351; found 274.0348.

Naphtho[1,2-*c*:5,6-*c*']dithiophene (N[*c*]DT-1)

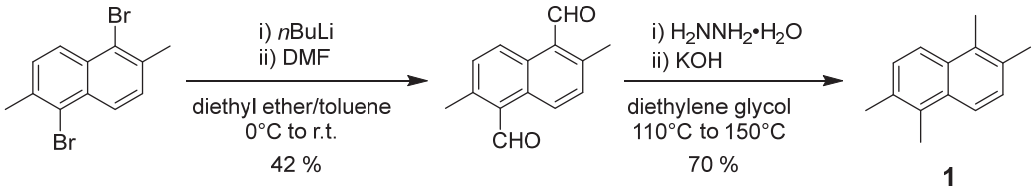
To a THF solution (50 ml) of **4** (0.380 g, 1.38 mmol) under a nitrogen atmosphere at –80 °C was added tetramethylethylenediamine (2.46 mL, 16.5 mmol). After stirring for 30 min, a 1.6 M hexane solution of *n*BuLi (2.46 ml, 16.5 mmol) was added dropwise for 30 min. After stirring for 2 h at room temperature, the reaction mixture was quenched with water, and then the solution was extracted with dichloromethane. The dichloromethane extract was concentrated. The residue was chromatographed on silica gel (dichloromethane : hexane = 1 : 1 as eluent) to give **N[*c*]DT-1** (0.176 g, yield 53 %) as an yellow solid; decomp.p. 140–142 °C; FT-IR (ATR): $\tilde{\nu}$ = 3103 (aromatic C–H str.), 763 (C–S str.) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.69 (d, J = 8.9 Hz, 2H), 7.75 (d, J = 3.2 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 8.08 (dd, J = 3.2, 1.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.20, 118.07, 121.41, 121.43, 123.47, 136.53, 137.31 ppm; HRMS (APCI): m/z (%): $[M+H]^+$ calcd for $C_{14}H_9S_2$, 241.0140; found 241.0138.

To a THF solution (5 mL) of **4** (0.021 g, 0.076 mmol) under a nitrogen atmosphere at 0 °C was added dropwise a 1.3 M THF solution of lithium hexamethyldisilazide (0.70 mL, 0.912 mmol). After stirring for 3 h, the reaction mixture was

quenched with water, and then, the solution was extracted with ethyl acetate. The ethyl acetate extract was concentrated. The residue was chromatographed on silica gel (dichloromethane : hexane = 1 : 1 as eluent) to give **N[*c*]DT-1** (0.005 g, yield 30 %) as an yellow solid.

1,3,6,8-Tetrakis(tert-butyldimethylsilyl)-naphtho[1,2-*c*:5,6-*c*']dithiophene (N[*c*]DT-Si4)

To a THF solution (3 mL) of **N[*c*]DT-1** (0.030 g, 0.125 mmol) under a nitrogen atmosphere at 0 °C was added dropwise a 2.0 M THF/heptane/ethylbenzene solution of lithium diisopropylamide (0.75 mL, 1.50 mmol). After stirring for 3 h, a THF solution (3.0 mL) of *tert*-butyldimethylsilyl chloride (0.226 g, 1.50 mmol) was added dropwise. The reaction mixture was further stirred for 15 h. The reaction mixture was quenched with water, and then, the solution was extracted with dichloromethane. The dichloromethane extract was concentrated. The residue was chromatographed on silica gel (dichloromethane : hexane = 1 : 1 as eluent) to give **N[*c*]DT-Si4** (0.044 g, yield 49 %) as an yellow solid; decomp.p. 218–220 °C; FT-IR (ATR): $\tilde{\nu}$ = 2953 (methyl C–H str.), 2962 (methyl C–H str.), 2881 (methyl C–H str.), 2854 (methyl C–H str.), 1359 (aromatic C–Si str.), 1247 (aliphatic C–Si str.), 767 (C–S str.) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 0.56 (s, 12H), 0.68 (s, 12H), 0.96 (s, 18H), 1.00 (s, 18H), 7.78 (d, J = 9.3 Hz, 2H), 8.29 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = −3.65, −0.34, 18.39, 19.30, 26.92, 28.01, 121.37, 124.69, 125.85, 134.96, 135.58, 144.89, 146.41 ppm; HRMS (APCI): m/z (%): $[M+H]^+$ calcd for $C_{38}H_{65}S_2Si_4$, 697.3599; found 697.3597.



Scheme S1 Synthesis of 2,6-dimethylnaphthalene-1,5-dicarbaldehyde and **1**.

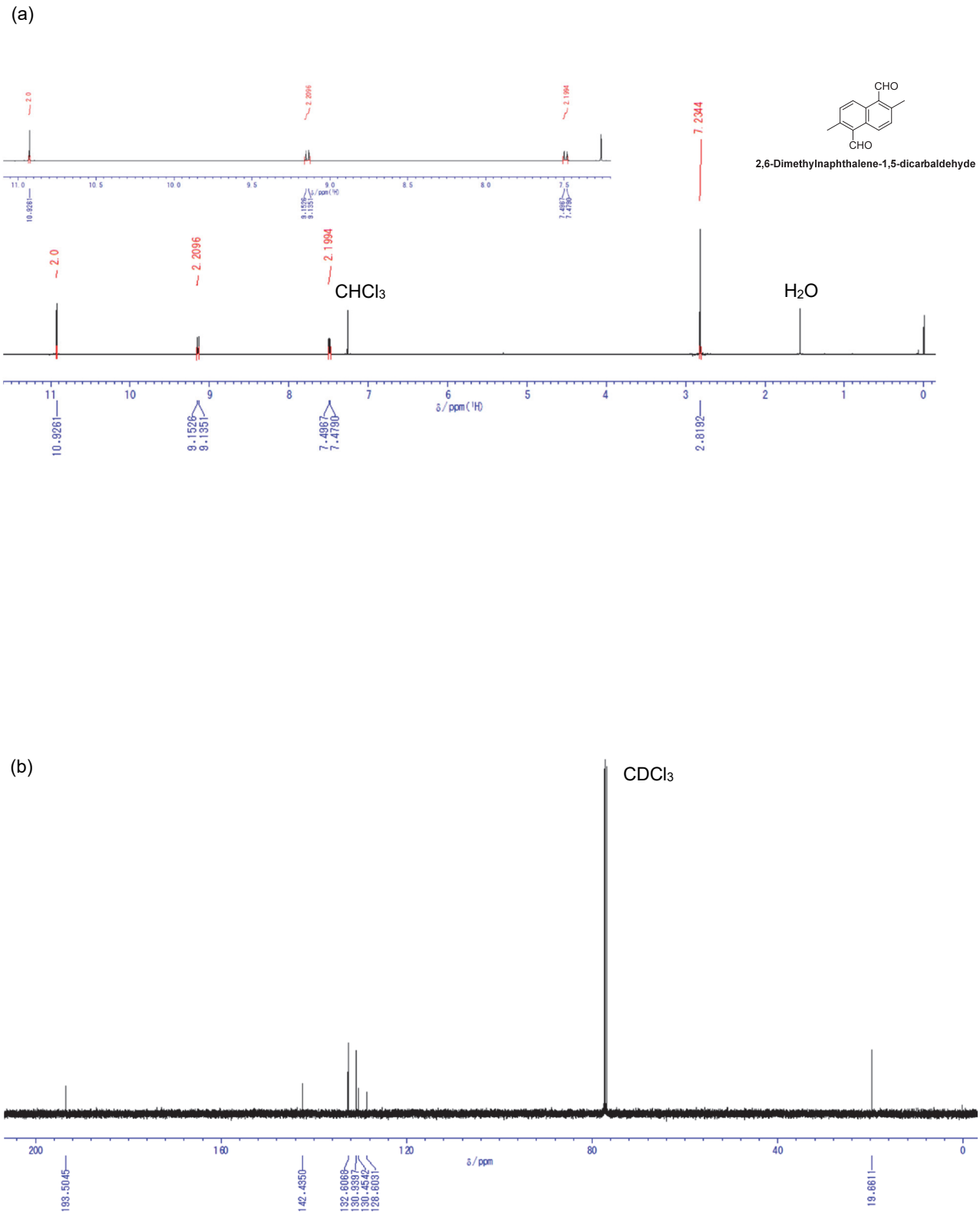


Fig. S1 (a) ^{1}H NMR (500 MHz) spectrum of 2,6-dimethylnaphthalene-1,5-dicarbaldehyde in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of 2,6-dimethylnaphthalene-1,5-dicarbaldehyde in $CDCl_3$.

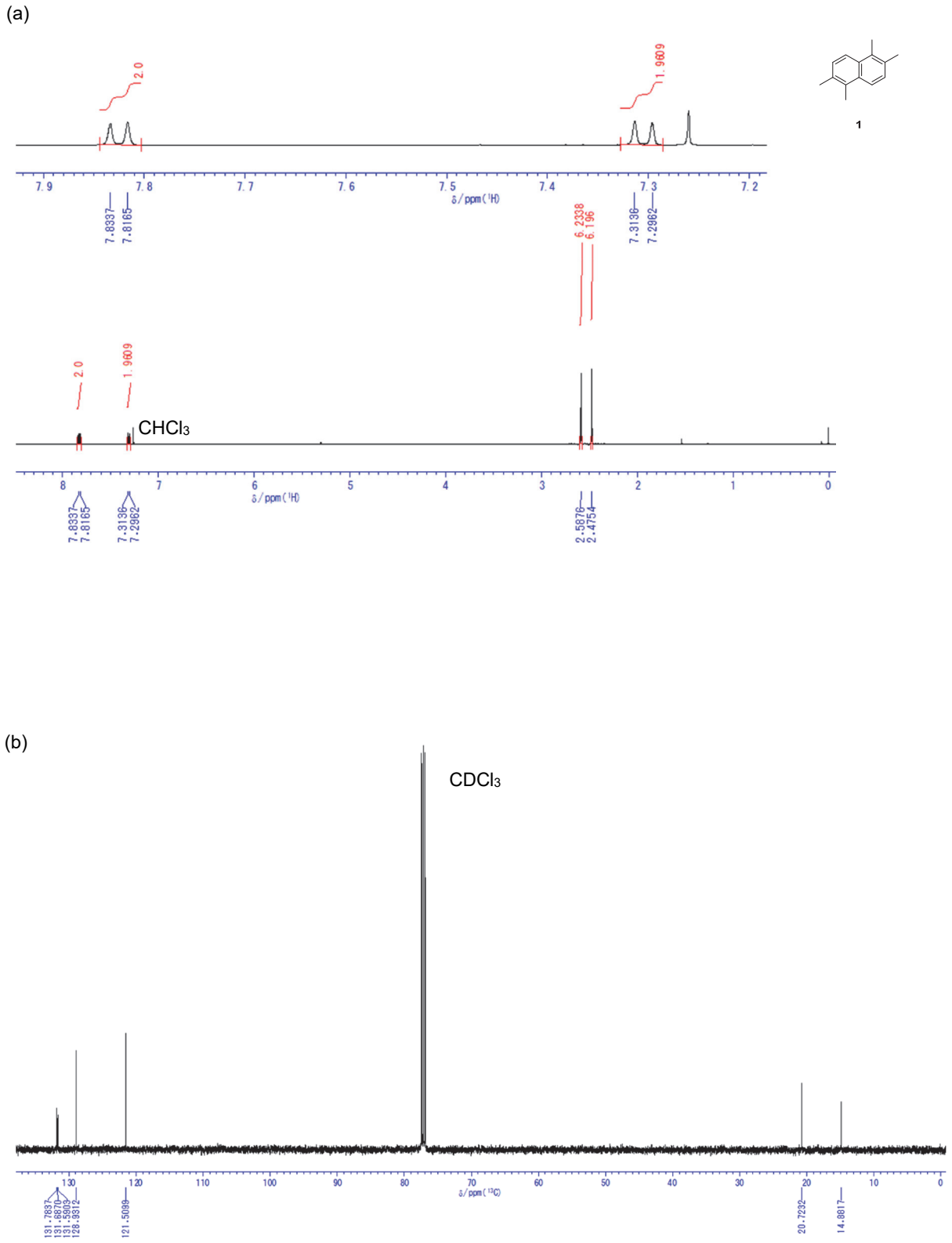


Fig. S2 (a) ^{1}H NMR (500 MHz) spectrum of **1** in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of **1** in $CDCl_3$.

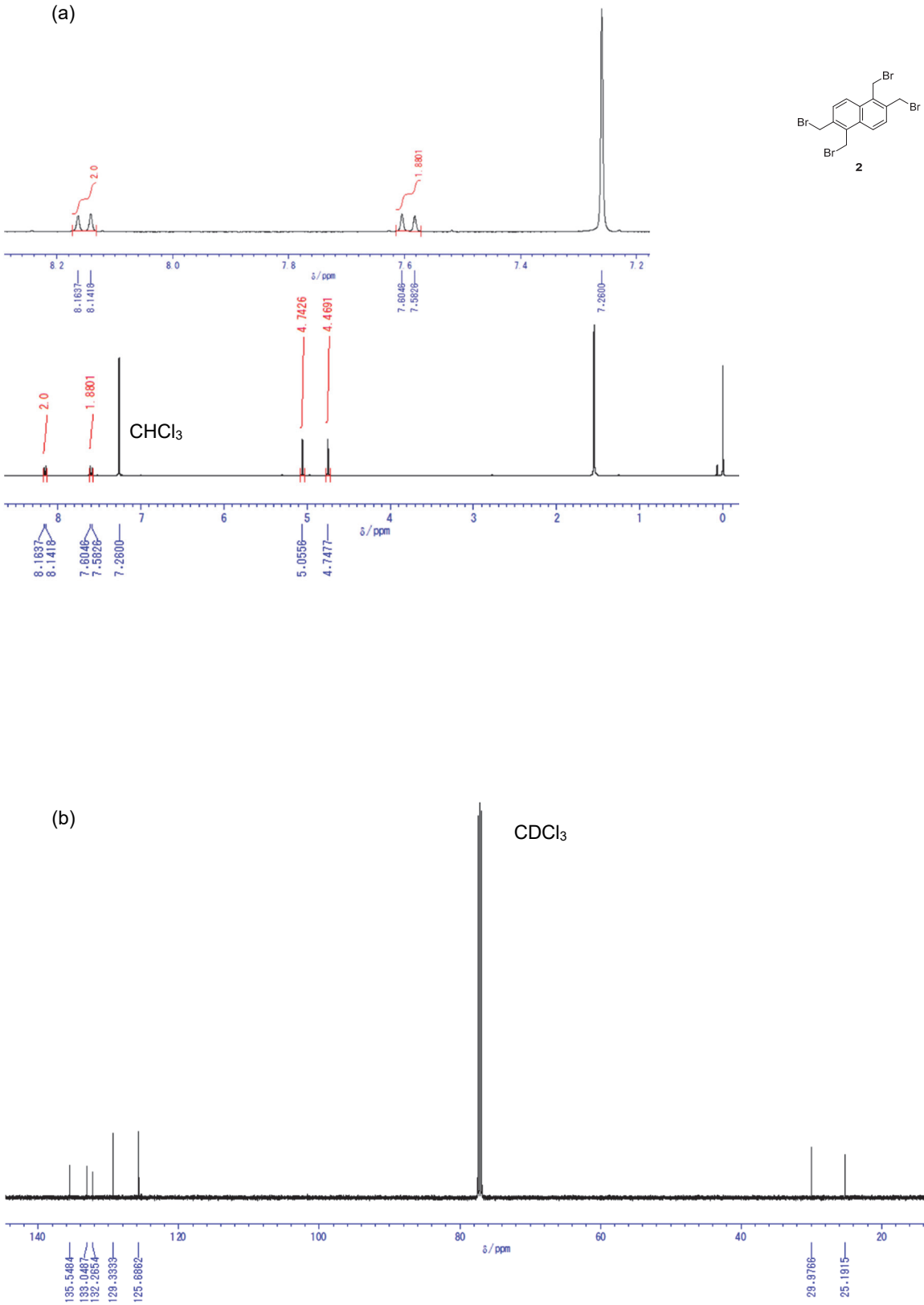


Fig. S3 (a) ^{1}H NMR (500 MHz) spectrum of **2** in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of **2** in $CDCl_3$.

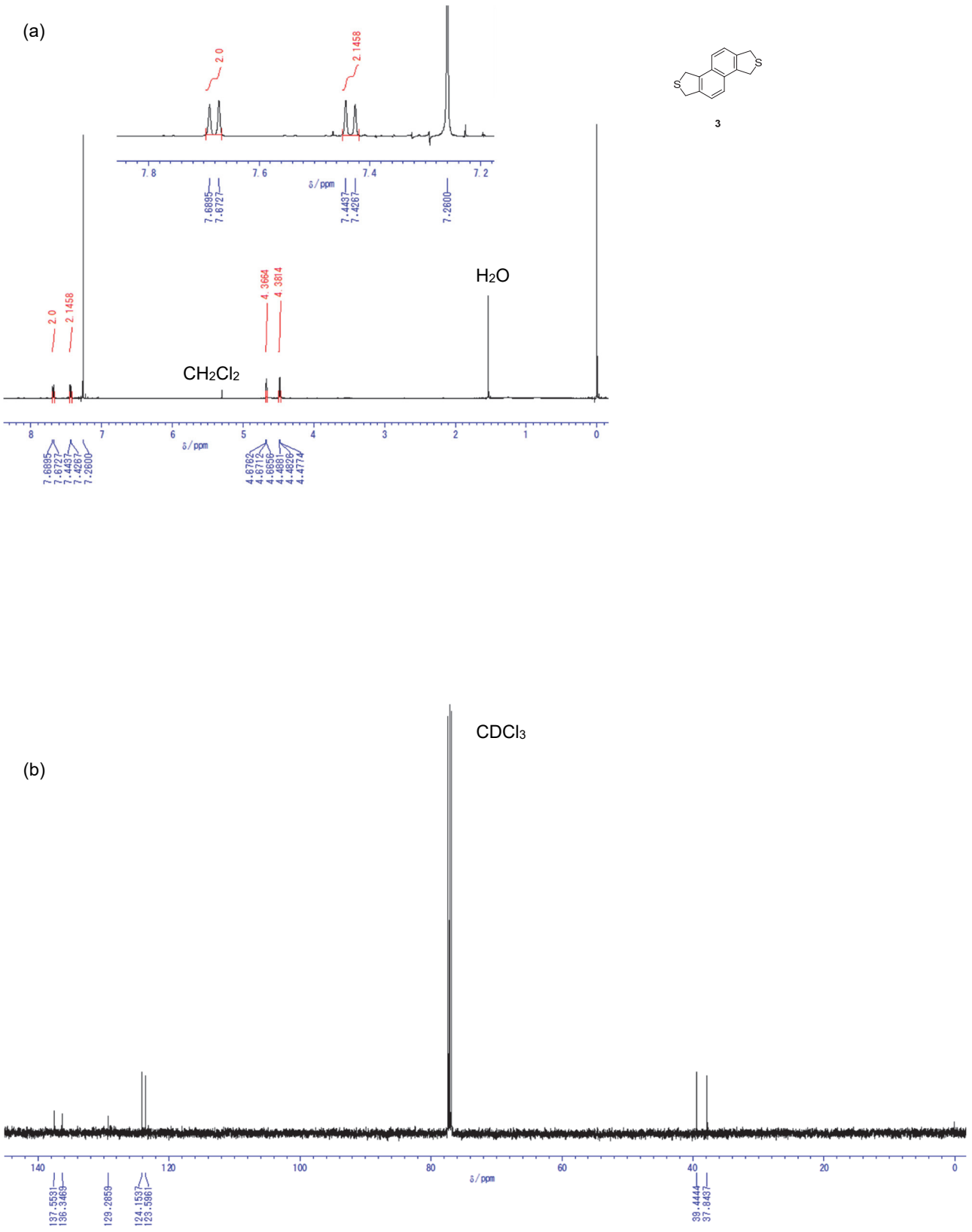


Fig. S4 (a) ^{1}H NMR (500 MHz) spectrum of **3** in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of **3** in $CDCl_3$.

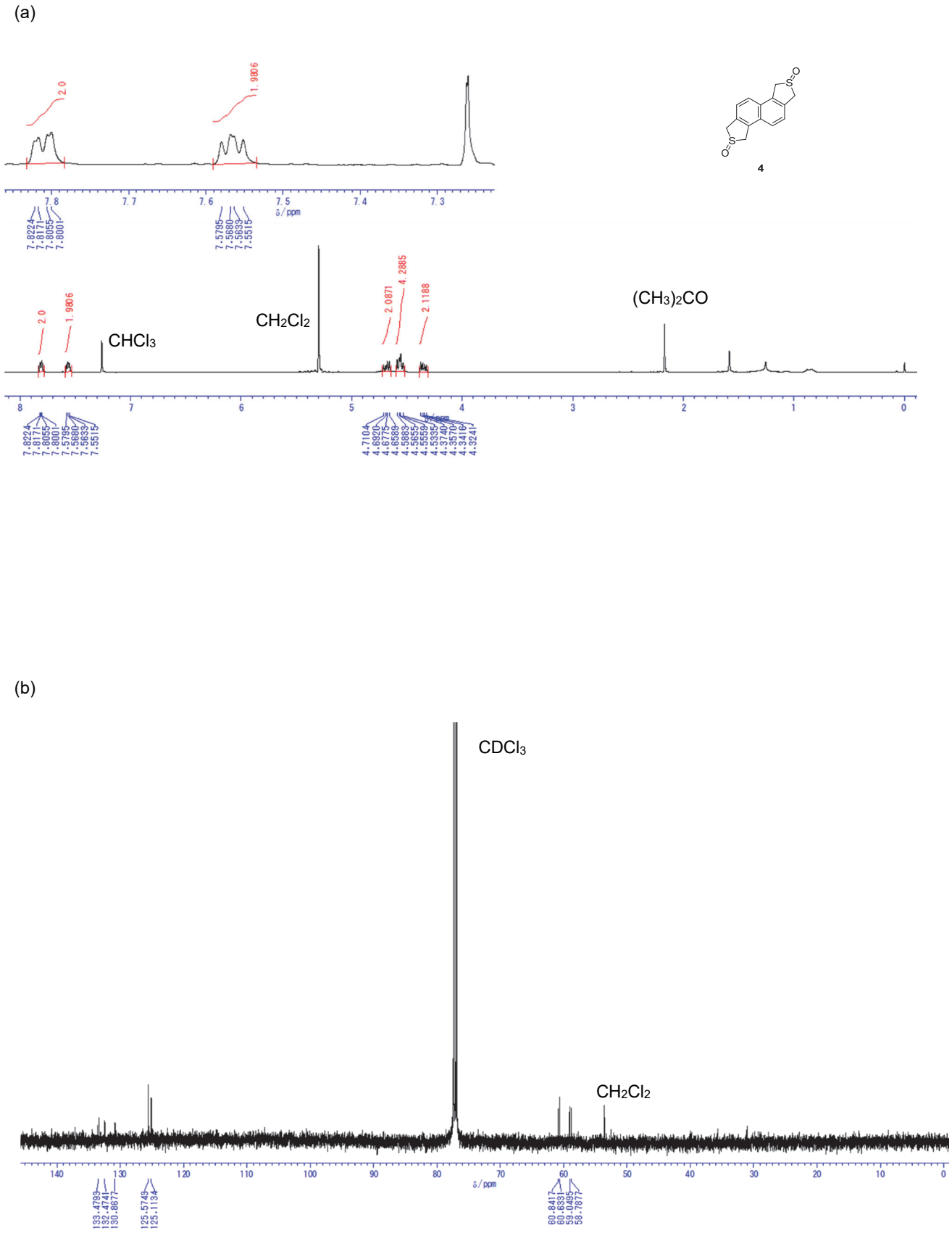


Fig. S5 (a) ^{1}H NMR (500 MHz) spectrum of **4** in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of **4** in $CDCl_3$.

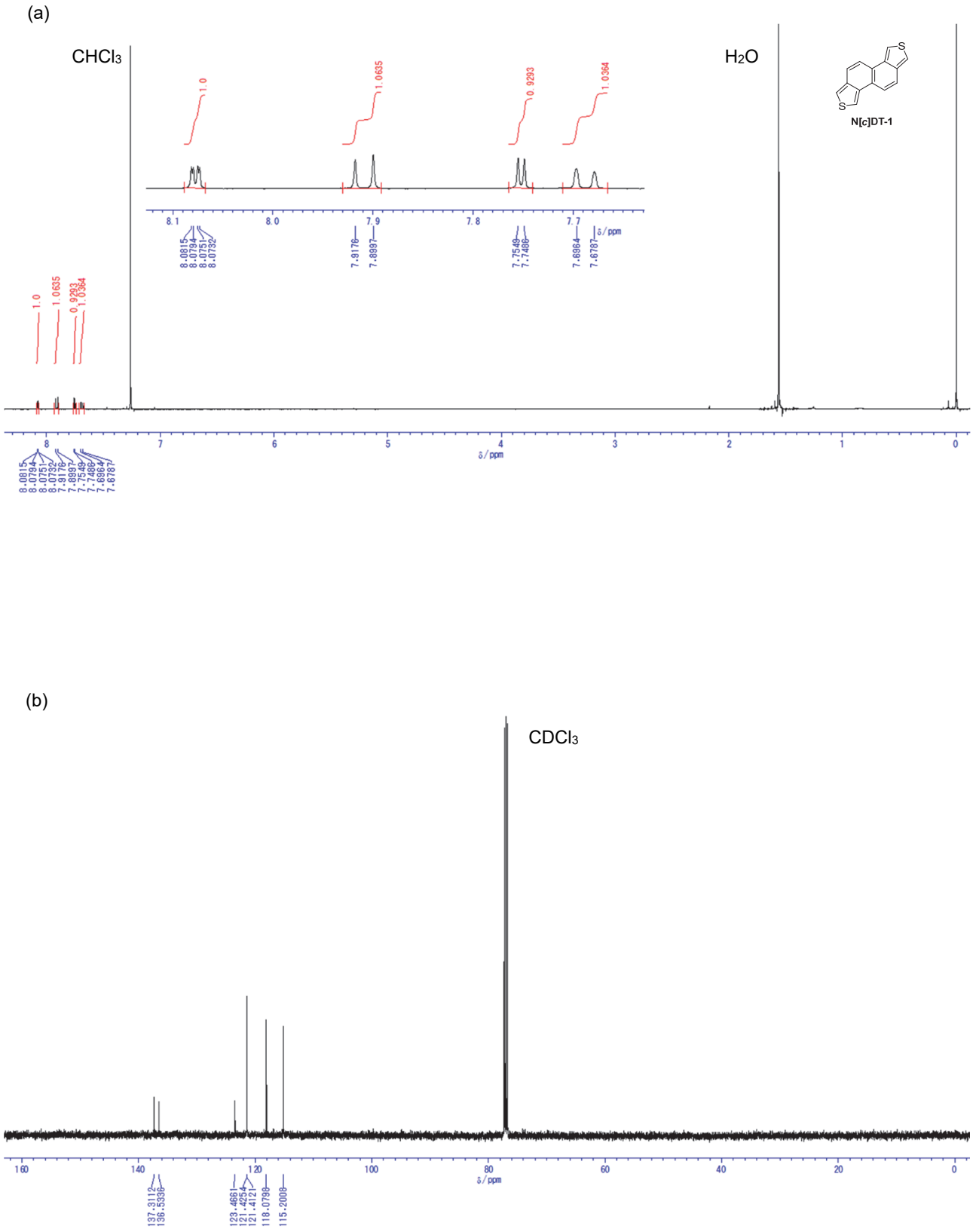


Fig. S6 (a) ^{1}H NMR (500 MHz) spectrum of **N[*c*]DT-1** in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of **N[*c*]DT-1** in $CDCl_3$.

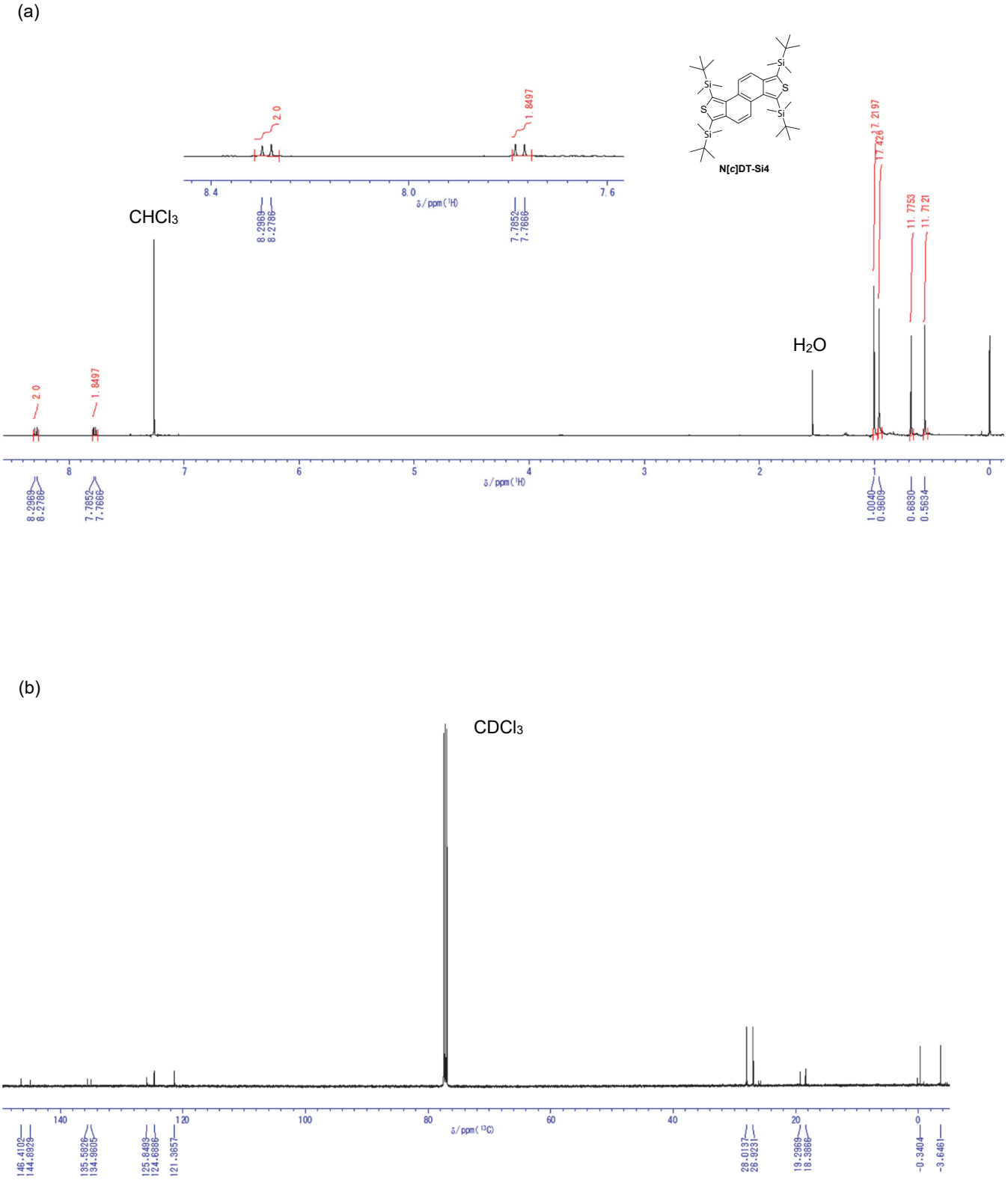


Fig. S7 (a) ^{1}H NMR (500 MHz) spectrum of **N[*c*]DT-Si4** in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of **N[*c*]DT-Si4** in $CDCl_3$.

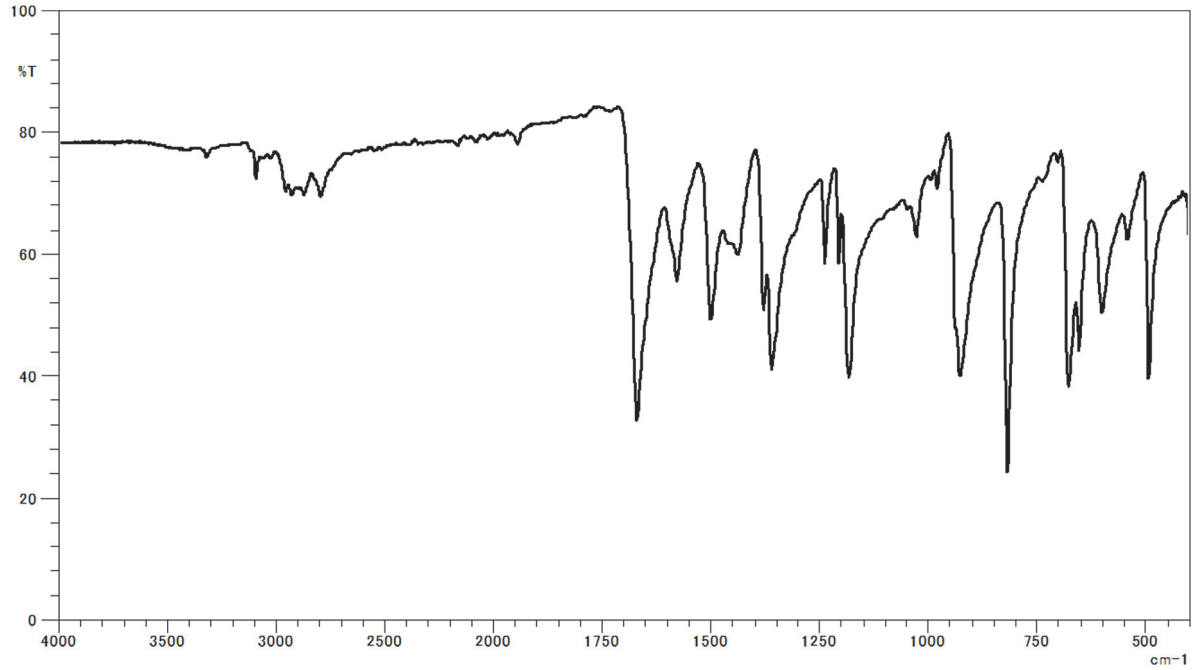


Fig. S8 FTIR (ATR) spectrum of 2,6-dimethylnaphthalene-1,5-dicarbaldehyde.

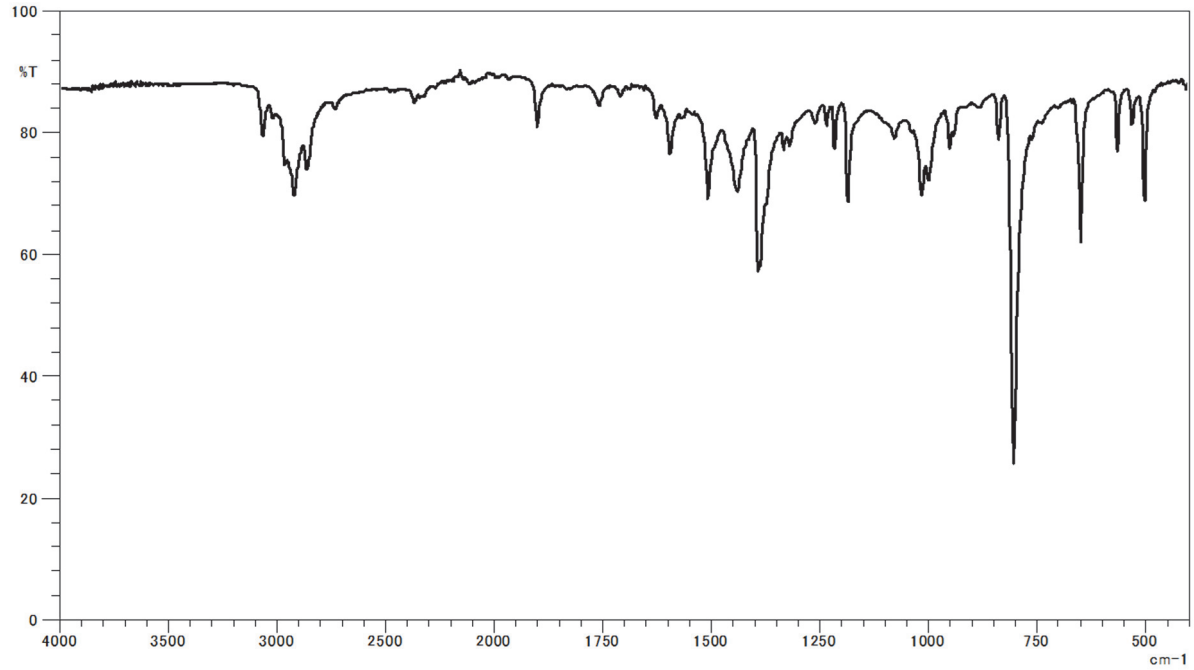


Fig. S9 FTIR (ATR) spectrum of **1**.

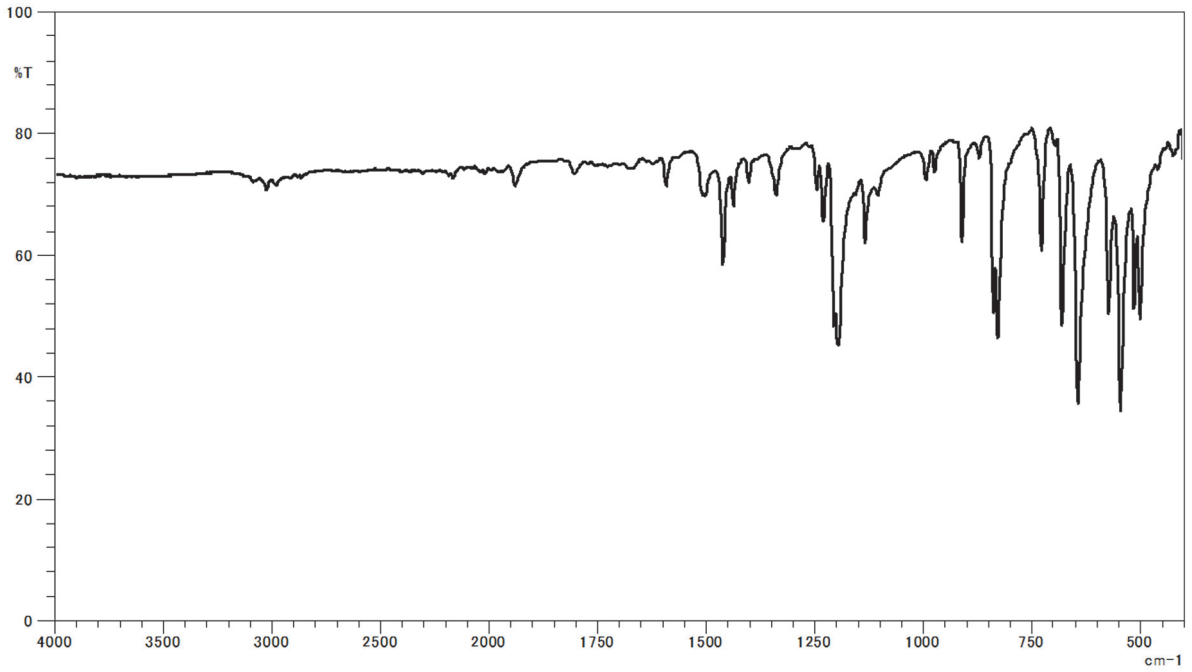


Fig. S10 FTIR (ATR) spectrum of **2**.

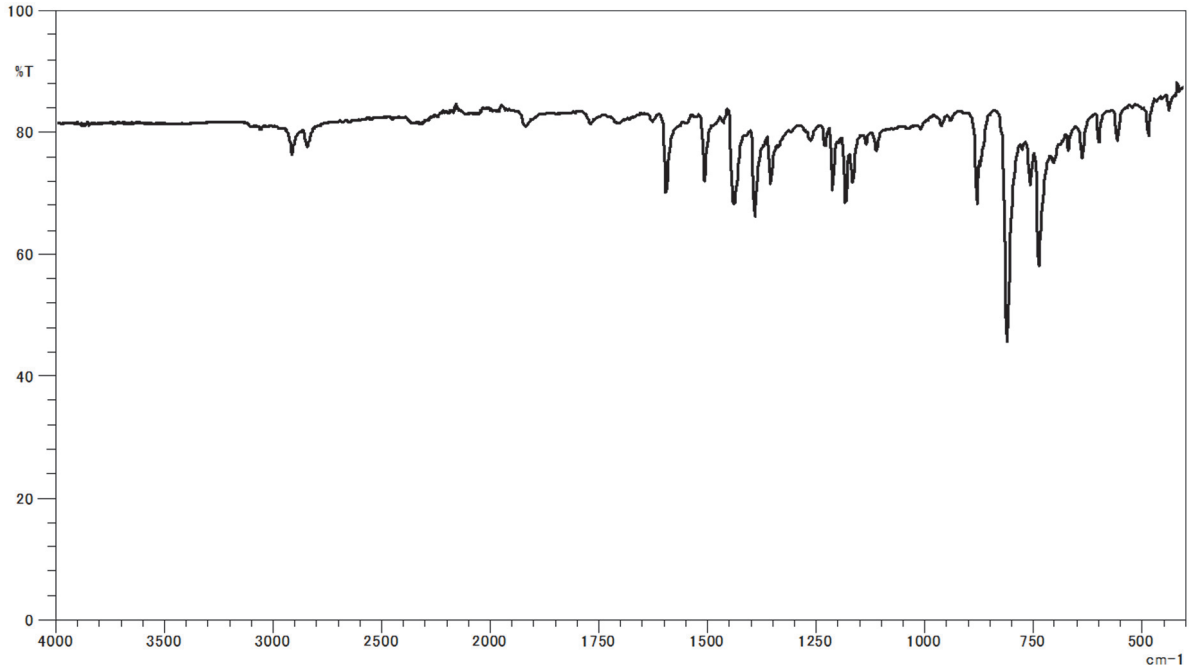


Fig. S11 FTIR (ATR) spectrum of **3**.

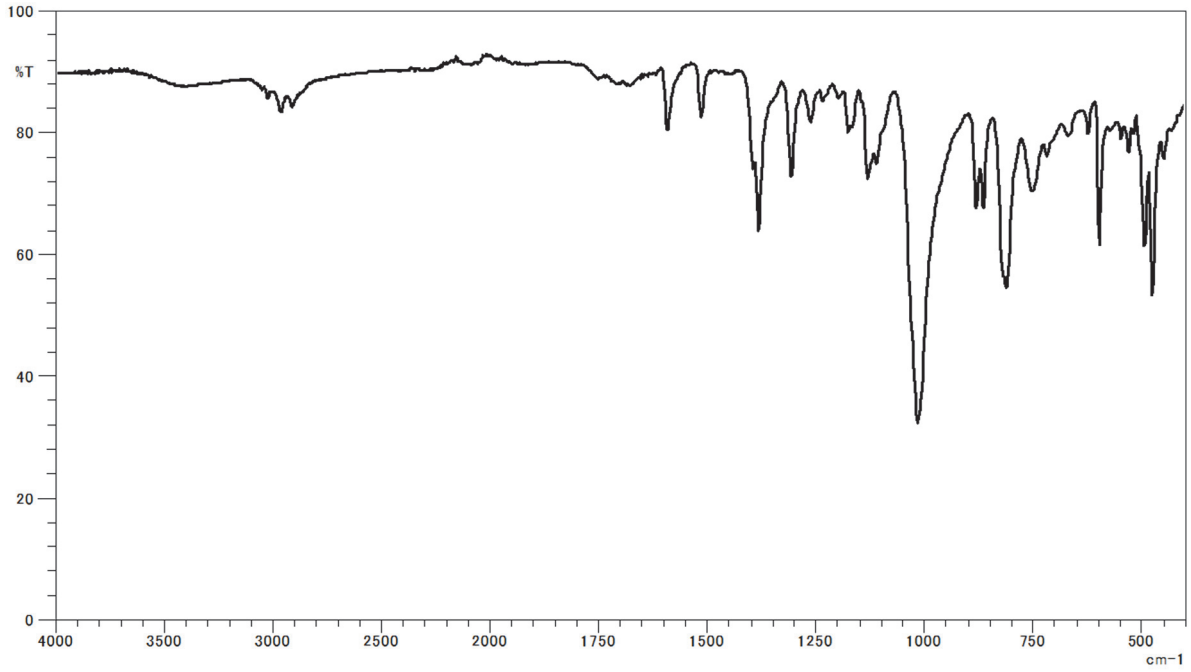


Fig. S12 FTIR (ATR) spectrum of **4**.

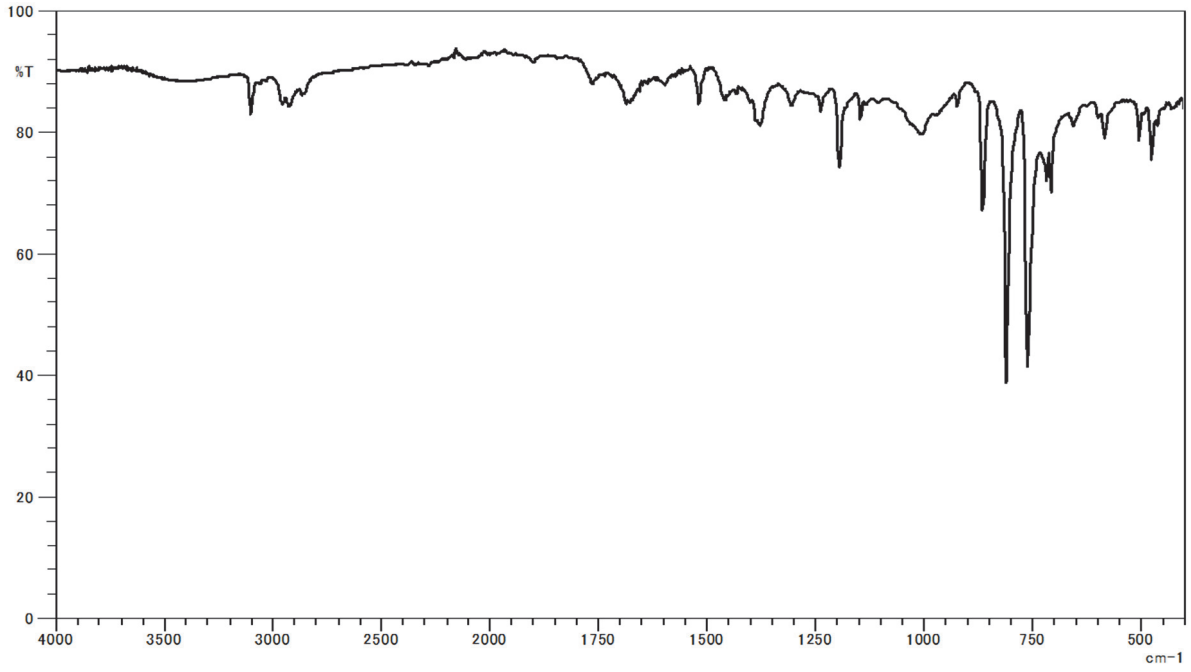


Fig. S13 FTIR (ATR) spectrum of **N[*c*]DT-1**.

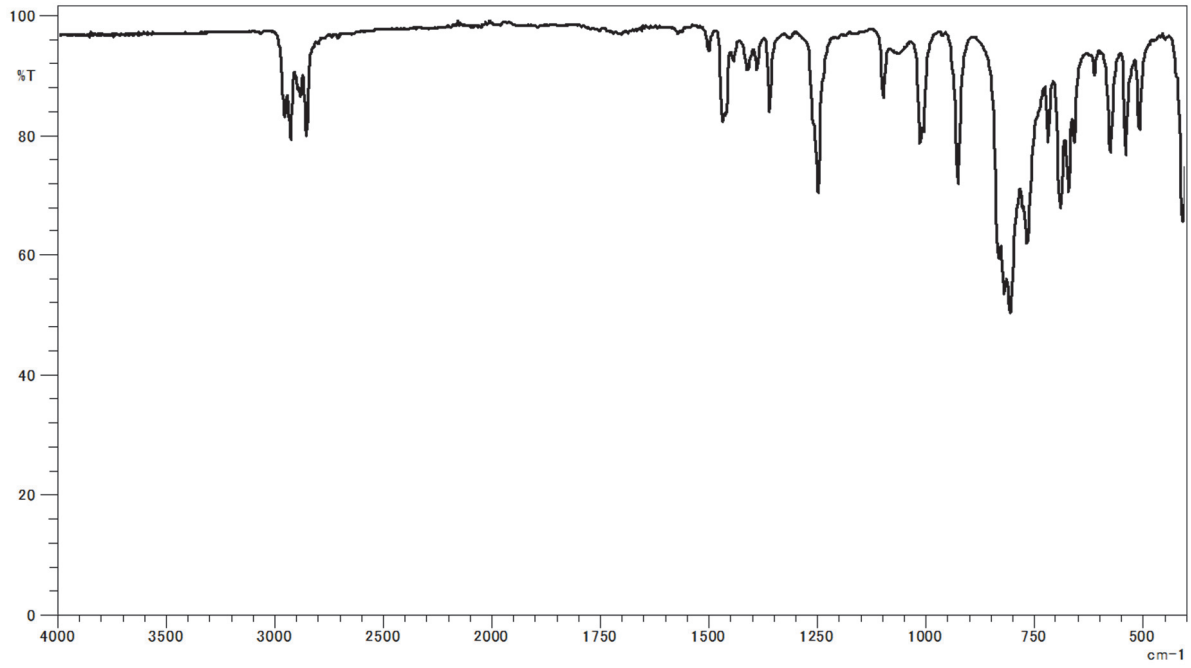


Fig. S14 FTIR (ATR) spectrum of **N[*c*]DT-Si4**.

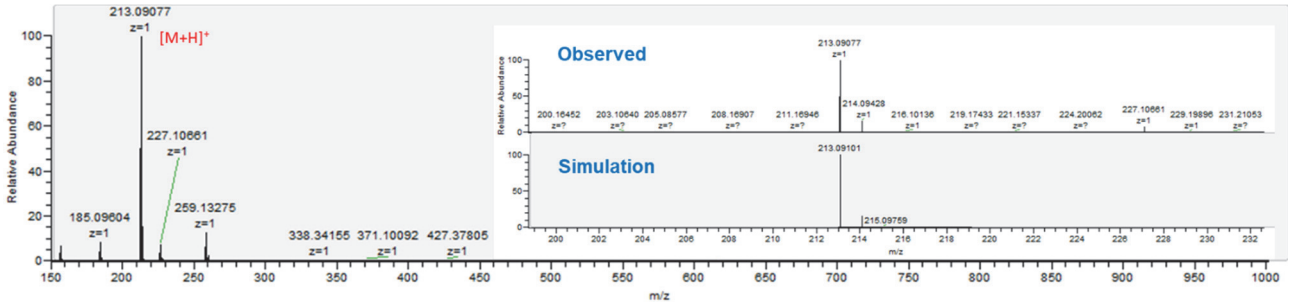


Fig. S15 HRMS spectrum of 2,6-dimethylnaphthalene-1,5-dicarbaldehyde.

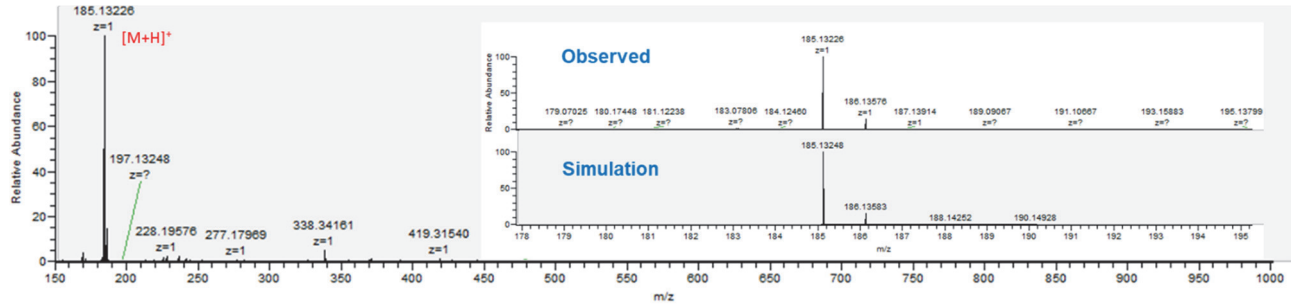


Fig. S16 HRMS spectrum of **1**.

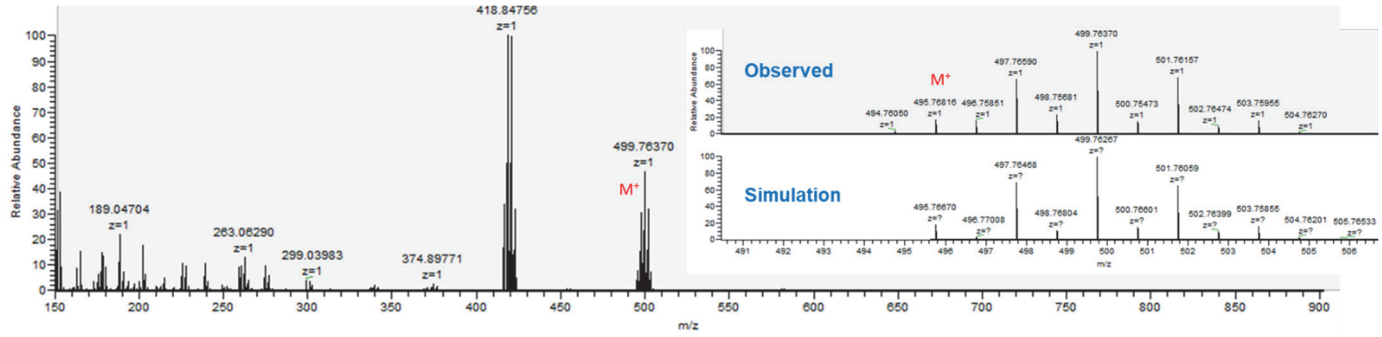


Fig. S17 HRMS spectrum of **2**.

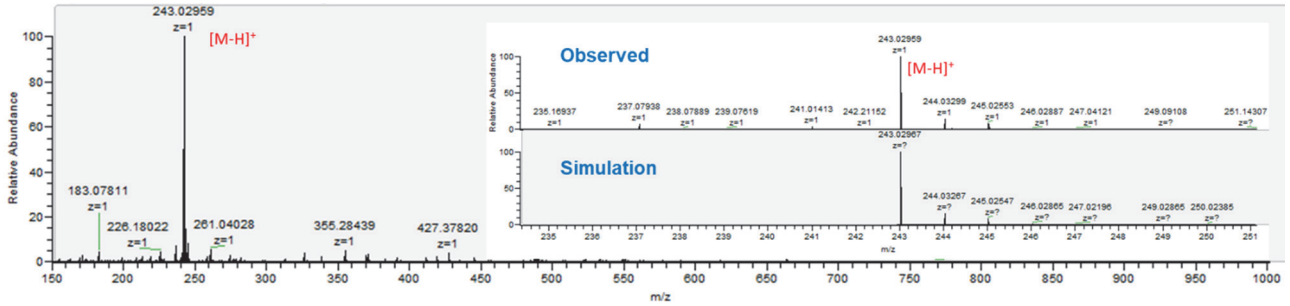


Fig. S18 HRMS spectrum of **3**.

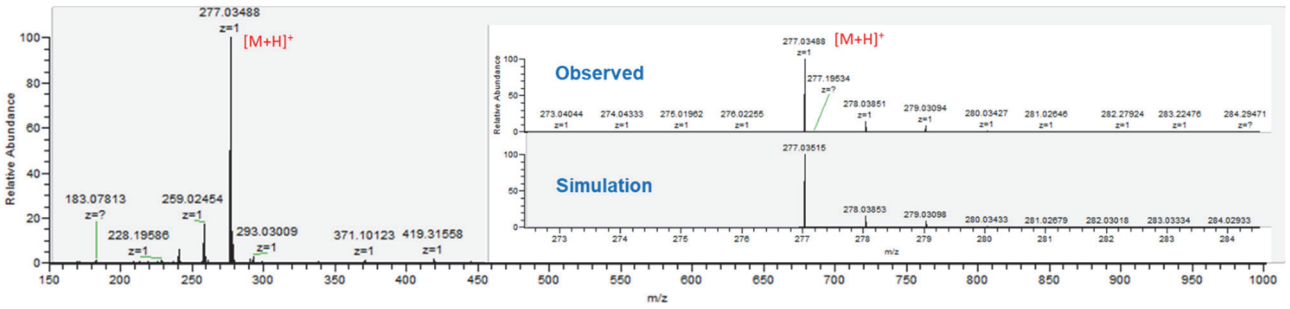


Fig. S19 HRMS spectrum of **4**.

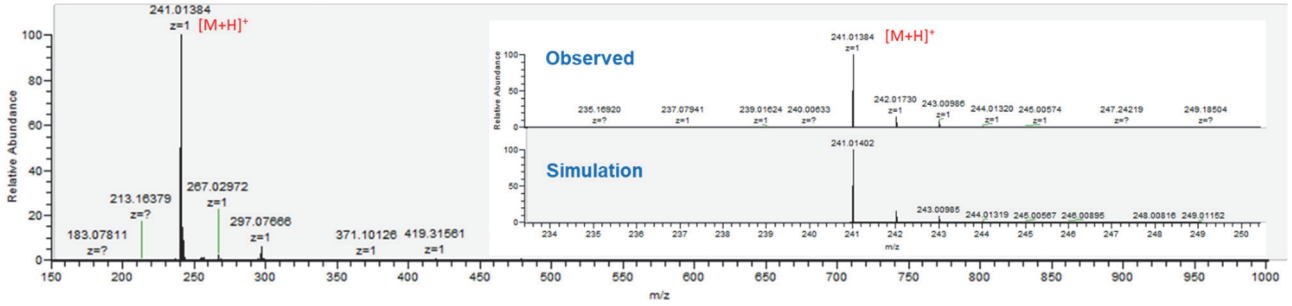


Fig. S20 HRMS spectrum of **N[*c*]DT-1**.

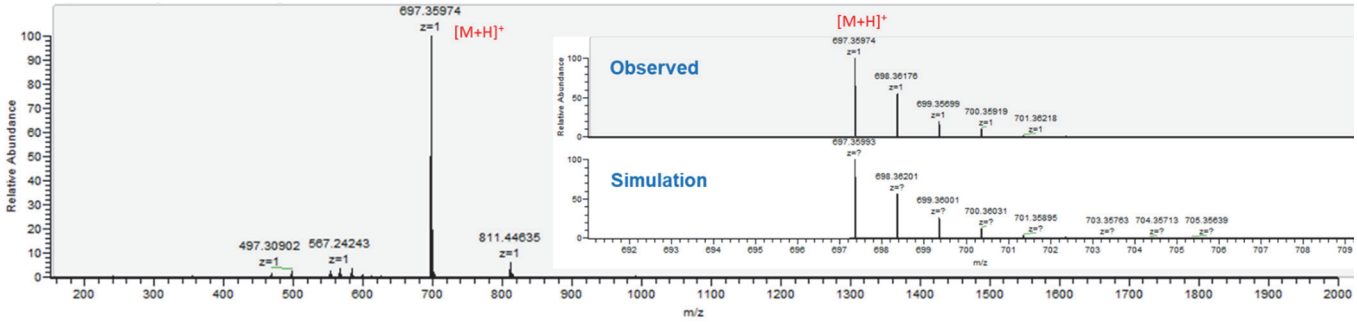


Fig. S21 HRMS spectrum of **N[*c*]DT-Si4**.

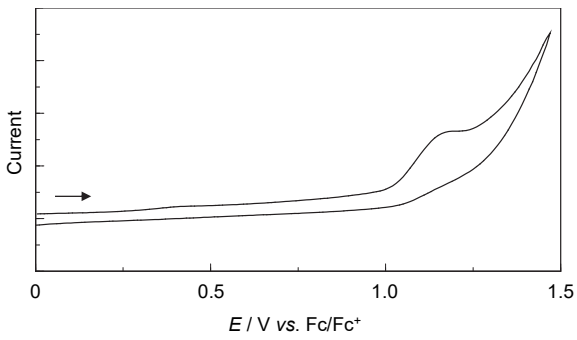


Fig. S22 Cyclic voltammogram of chrysene in DMF containing 0.1 M Bu_4NClO_4 at a scan rate of 100 mV s^{-1}. The arrow denotes the direction of the potential scan.

Table S1 Geometrical coordinates of the optimized **N[*c*]DT-1** by DFT at the B3LYP/6-31G(d,p) level

Cartesian coordinates:

Tag	Symbol	Coordinates(Angstroms)		
		X	Y	Z
1	C	1.4658934	-2.1247416	0.0002477
2	C	2.3776918	-1.0194724	0.0000802
3	C	1.8563427	0.3353284	-0.0000913
4	C	0.4241013	0.5592761	-0.0000109
5	C	-0.4241013	-0.5592761	0.0000543
6	C	0.1243744	-1.8906112	0.0001582
7	C	-0.1243744	1.8906112	-0.0000057
8	C	-1.4658934	2.1247416	0.0001118
9	C	-2.3776918	1.0194724	0.0000759
10	C	-1.8563427	-0.3353284	0.0000061
11	C	-3.7597113	1.0555773	0.0000793
12	S	-4.4255776	-0.5297351	-0.0000003
13	C	-2.873061	-1.2735684	-0.0000197
14	C	3.7597113	-1.0555773	0.0000365
15	S	4.4255776	0.5297351	-0.0002092
16	C	2.873061	1.2735684	-0.0002379
17	H	1.8531354	-3.1391775	0.0003336
18	H	-0.5606691	-2.7322219	0.0002709
19	H	0.5606691	2.7322219	0.0000071
20	H	-1.8531354	3.1391775	0.0001213
21	H	4.4048838	-1.9224519	0.0001415
22	H	2.8013599	2.3509554	-0.0004351
23	H	-4.4048838	1.9224519	0.0001304
24	H	-2.80136	-2.3509554	-0.0001236

Table S2 Geometrical coordinates of the optimized **N[*c*]DT-Si4** by DFT at the B3LYP/6-31G(d,p) level

Cartesian coordinates:

Tag	Symbol	Coordinates(Angstroms)		
		X	Y	Z
1	C	1.5356105	2.0324154	-0.5131067
2	C	2.4217365	0.9177807	-0.3863522
3	C	1.8652195	-0.4138202	-0.2039381
4	C	0.4156144	-0.5716385	-0.2594587
5	C	-0.4156205	0.5716388	-0.2594572
6	C	0.188967	1.8609563	-0.4154813
7	C	-0.1889728	-1.8609544	-0.415498
8	C	-1.5356162	-2.0324134	-0.5131299
9	C	-2.4217427	-0.9177797	-0.3863677
10	C	-1.8652256	0.4138201	-0.2039476
11	C	-3.8213378	-0.9730452	-0.4011017
12	S	-4.4082898	0.6200111	-0.1360187
13	C	-2.8612447	1.394764	-0.0027983
14	C	3.8213312	0.9730464	-0.4010911
15	S	4.4082846	-0.6200106	-0.1360147
16	C	2.861239	-1.3947642	-0.0027896
17	H	1.9375806	3.0239737	-0.6862859
18	H	-0.4507167	2.7214501	-0.5294414
19	H	0.450712	-2.7214471	-0.5294594
20	H	-1.9375854	-3.0239706	-0.6863191
21	Si	-4.9283972	-2.4968325	-0.6421566
22	Si	-2.8701964	3.2406585	0.5035113
23	Si	4.9283902	2.496833	-0.6421529
24	Si	2.8702135	-3.2406768	0.5034563
25	C	4.5879684	-3.8471625	1.1893999
26	C	1.6119537	-3.5141934	1.8991703
27	H	0.6596114	-3.0110683	1.7248675
28	H	1.4066025	-4.5824018	2.0272321
29	H	2.0118938	-3.1386299	2.846708
30	C	2.4877945	-4.3189213	-1.0171697
31	H	2.4806643	-5.3811495	-0.7502505
32	H	1.5268053	-4.093975	-1.4866099
33	H	3.2568071	-4.173504	-1.78288
34	C	-4.5488305	-3.7218298	0.7561573
35	H	-5.0928457	-4.6625877	0.6198706
36	H	-3.4818834	-3.9598712	0.7997715
37	H	-4.8279207	-3.3097102	1.7310451
38	C	-6.8137534	-2.0736235	-0.625
39	C	-4.58798	3.847184	1.1893411
40	C	-1.6120245	3.5140324	1.8993287
41	H	-0.6596157	3.0110617	1.7249402
42	H	-1.4068065	4.5822373	2.0276308
43	H	-2.0119457	3.1382083	2.8467708
44	C	4.5488392	3.7218287	0.7561665
45	H	5.0928552	4.6625855	0.619876
46	H	3.4818932	3.9598725	0.7997913
47	H	4.827938	3.309707	1.731051
48	C	6.8137459	2.0736212	-0.6250154
49	C	4.4844068	3.2836214	-2.3108092
50	H	3.4140907	3.4982909	-2.3820608

51	H	5.0214263	4.2262171	-2.4611344
52	H	4.7355153	2.617258	-3.1421697
53	C	-2.4876032	4.3189899	-1.0170192
54	H	-2.4802018	5.381186	-0.7499783
55	H	-1.5266907	4.0938652	-1.4865307
56	H	-3.2566882	4.173856	-1.7827096
57	C	-4.4844289	-3.2836189	-2.310818
58	H	-4.7355457	-2.6172552	-3.1421758
59	H	-3.4141131	-3.4982874	-2.3820796
60	H	-5.0214489	-4.2262151	-2.4611387
61	C	7.5974633	3.3886288	-0.8519076
62	H	8.6769018	3.1857965	-0.844292
63	H	7.3624826	3.8503973	-1.8168211
64	H	7.402571	4.128396	-0.0679845
65	C	7.2535158	1.482721	0.7323555
66	H	6.7626682	0.530387	0.9539526
67	H	8.33656	1.2981953	0.7299093
68	H	7.0435337	2.165837	1.5624932
69	C	7.1870935	1.0919629	-1.757253
70	H	8.2704733	0.9093807	-1.7559208
71	H	6.6938889	0.1212722	-1.6501085
72	H	6.9271858	1.4890854	-2.7445253
73	C	5.6900771	-3.8838291	0.1072414
74	H	5.9327304	-2.892939	-0.2858094
75	H	6.6150176	-4.2991527	0.5304966
76	H	5.4098609	-4.5188376	-0.7397484
77	C	4.382213	-5.2997987	1.6901123
78	H	5.3336834	-5.6957147	2.0697968
79	H	3.6581643	-5.3594253	2.5085636
80	H	4.0490462	-5.9746001	0.894417
81	C	5.0764146	-3.0081269	2.3905796
82	H	5.9964179	-3.4452763	2.8024017
83	H	5.3000343	-1.9739537	2.1170832
84	H	4.340048	-2.9853058	3.2011982
85	C	-5.0765044	3.008204	2.3905276
86	H	-5.9965367	3.4453692	2.8022683
87	H	-5.3001032	1.9740171	2.1170642
88	H	-4.3401912	2.9854245	3.2011954
89	C	-5.6900319	3.8838231	0.1071236
90	H	-5.9327056	2.8929161	-0.2858705
91	H	-6.614976	4.2992138	0.530305
92	H	-5.4097517	4.5187611	-0.7398982
93	C	-4.3822239	5.2998375	1.6900026
94	H	-5.33371	5.6957957	2.0696032
95	H	-3.6582303	5.3594814	2.5085016
96	H	-4.0489816	5.9745927	0.8942999
97	C	-7.1871136	-1.0919636	-1.757232
98	H	-8.2704938	-0.9093838	-1.7558894
99	H	-6.6939102	-0.121272	-1.65009
100	H	-6.9272141	-1.4890833	-2.7445076
101	C	-7.2535109	-1.4827265	0.7323762
102	H	-6.7626615	-0.5303929	0.9539706
103	H	-8.3365552	-1.2982012	0.7299404
104	H	-7.043521	-2.1658442	1.5625106

105	C	-7.5974707	-3.3886321	-0.8518874
106	H	-7.4025691	-4.1284008	-0.0679679
107	H	-8.6769096	-3.1858018	-0.8442604
108	H	-7.3624989	-3.8503978	-1.8168044

Table S3 Geometrical coordinates of the optimized **4,4′-BBT** by DFT at the B3LYP/6-31G(d,p) level

Cartesian coordinates:

Tag	Symbol	Coordinates(Angstroms)		
		X	Y	Z
1	C	3.014613	0.092656	0.246587
2	C	3.469568	1.192933	1.038642
3	C	2.586725	2.181467	1.372708
4	C	1.21901	2.12832	0.956653
5	C	0.713504	1.089175	0.210163
6	C	1.622641	0.033794	-0.17567
7	S	2.781034	-2.035549	-1.172737
8	C	-1.622642	0.033794	0.17567
9	C	-0.713504	1.089175	-0.210163
10	C	-1.21901	2.128319	-0.956655
11	C	-2.586726	2.181466	-1.372709
12	C	-3.469569	1.192933	-1.038641
13	C	-3.014613	0.092656	-0.246585
14	S	-2.781033	-2.035551	1.172734
15	H	4.506637	1.23322	1.358132
16	H	2.916292	3.02579	1.971013
17	H	0.549238	2.927872	1.258602
18	H	-0.549238	2.927871	-1.258604
19	H	-2.916292	3.025789	-1.971014
20	H	-4.506638	1.23322	-1.35813
21	C	3.751548	-0.981598	-0.225472
22	H	4.800145	-1.191301	-0.070182
23	C	1.369808	-1.078593	-0.963293
24	H	0.437756	-1.375725	-1.419233
25	C	-1.369809	-1.078591	0.963295
26	H	-0.437757	-1.375723	1.419236
27	C	-3.751549	-0.981596	0.225475
28	H	-4.800146	-1.191299	0.070187

Table S4 Geometrical coordinates of the optimized **4,4′-BBT-Si4** by DFT at the B3LYP/6-31G(d,p) level

Cartesian coordinates:

Tag	Symbol	Coordinates(Angstroms)		
		X	Y	Z
1	C	4.218161	-0.33767	-0.016252
2	C	3.066512	-0.77509	0.653943
3	C	3.009221	-1.909125	1.51953
4	H	3.910183	-2.480712	1.707261
5	C	1.826697	-2.26251	2.105088
6	H	1.773574	-3.118151	2.771738
7	C	0.656908	-1.493972	1.862646
8	H	-0.261931	-1.769139	2.369861
9	C	0.637633	-0.390744	1.036687
10	C	1.866232	0.024955	0.386908
11	C	2.114446	1.088983	-0.514497
12	C	6.809855	-0.307254	-1.620217
13	H	6.802518	0.785533	-1.678026
14	H	7.853335	-0.633829	-1.684102
15	H	6.290831	-0.688549	-2.505699
16	C	6.041037	-2.86158	-0.122845
17	H	5.34186	-3.226144	-0.882163
18	H	7.04384	-3.200161	-0.405932
19	H	5.787633	-3.348789	0.823057
20	C	6.970751	-0.33548	1.509924
21	C	8.420041	-0.867745	1.459713
22	H	8.985098	-0.512927	2.332474
23	H	8.457503	-1.962788	1.473604
24	H	8.955707	-0.525105	0.56745
25	C	6.303838	-0.827547	2.811122
26	H	5.273994	-0.468341	2.904417
27	H	6.285945	-1.921581	2.876675
28	H	6.860867	-0.462198	3.684818
29	C	7.001599	1.207344	1.520032
30	H	7.549511	1.571454	2.399883
31	H	7.502412	1.61494	0.63493
32	H	5.993996	1.634556	1.560787
33	C	1.916458	2.515077	-3.191008
34	H	1.474095	3.334924	-3.768268
35	H	3.003072	2.617719	-3.251161
36	H	1.646205	1.579186	-3.691998
37	C	-0.639894	2.357931	-1.619016
38	H	-0.921469	1.343743	-1.912766
39	H	-1.205427	2.61625	-0.722451
40	H	-0.95275	3.034042	-2.422946
41	C	1.658739	4.242796	-0.610874
42	C	3.144123	4.60451	-0.82185
43	H	3.816352	3.883698	-0.345652
44	H	3.410277	4.660591	-1.882733
45	H	3.356494	5.588106	-0.380499
46	C	1.363225	4.252281	0.901551
47	H	1.603609	5.235979	1.328893
48	H	0.308586	4.051797	1.113043
49	H	1.961625	3.50643	1.435645
50	C	0.792869	5.329558	-1.289518

51	H	1.03961	6.318106	-0.878443
52	H	0.962508	5.379704	-2.371199
53	H	-0.277122	5.166474	-1.124974
54	C	-4.218199	0.337696	-0.01623
55	C	-3.066543	0.775158	0.653922
56	C	-3.009278	1.90918	1.519525
57	H	-3.910269	2.4807	1.70732
58	C	-1.826754	2.262597	2.105064
59	H	-1.773638	3.118237	2.771718
60	C	-0.656959	1.49407	1.862627
61	H	0.261867	1.769224	2.369871
62	C	-0.63765	0.390855	1.036651
63	C	-1.866239	-0.024847	0.386848
64	C	-2.11446	-1.088901	-0.51452
65	C	-6.809806	0.307577	-1.620348
66	H	-6.802379	-0.785193	-1.678443
67	H	-7.853311	0.634084	-1.684188
68	H	-6.290778	0.689149	-2.505709
69	C	-6.041244	2.861592	-0.122269
70	H	-5.34176	3.226545	-0.881112
71	H	-7.043971	3.200087	-0.405734
72	H	-5.788418	3.348522	0.823933
73	C	-6.970791	0.335081	1.509822
74	C	-6.303554	0.826421	2.811127
75	H	-5.273783	0.466915	2.904103
76	H	-6.28536	1.920421	2.877146
77	H	-6.860539	0.460843	3.684755
78	C	-8.419941	0.867762	1.460035
79	H	-8.45709	1.962805	1.474463
80	H	-8.955802	0.525708	0.567662
81	H	-8.985003	0.51267	2.332681
82	C	-7.002046	-1.207739	1.519275
83	H	-7.549808	-1.572088	2.39912
84	H	-7.503215	-1.614811	0.634134
85	H	-5.994546	-1.635247	1.559566
86	C	-1.91645	-2.51493	-3.191073
87	H	-1.47409	-3.334782	-3.768334
88	H	-3.003066	-2.617585	-3.251208
89	H	-1.646206	-1.579043	-3.692072
90	C	0.639921	-2.357663	-1.619065
91	H	0.921517	-1.343309	-1.912209
92	H	1.205474	-2.616495	-0.722658
93	H	0.952745	-3.033314	-2.423393
94	C	-1.658631	-4.242688	-0.611001
95	C	-1.363302	-4.2521	0.901461
96	H	-0.308742	-4.051353	1.1131
97	H	-1.961957	-3.506391	1.435461
98	H	-1.603502	-5.235853	1.328779
99	C	-0.79254	-5.329345	-1.289527
100	H	-1.039207	-6.317926	-0.878487
101	H	-0.962019	-5.379518	-2.371234
102	H	0.277411	-5.166123	-1.124846
103	C	-3.143944	-4.60458	-0.822158
104	H	-3.816323	-3.883816	-0.346099

105	H	-3.409941	-4.660748	-1.883076
106	H	-3.356256	-5.588174	-0.380777
107	S	3.790812	1.023678	-0.967463
108	S	-3.79085	-1.0237	-0.967374
109	Si	6.003406	-0.96692	-0.03706
110	Si	1.228135	2.52939	-1.417205
111	Si	-1.228105	-2.529245	-1.417284
112	Si	-6.003452	0.966909	-0.037005

Table S5 Geometrical coordinates of the optimized **N[*b*]DT-3** by DFT at the B3LYP/6-31G(d,p) level

Cartesian coordinates:

Tag	Symbol	Coordinates(Angstroms)		
		X	Y	Z
1	C	1.3493332	-2.1768314	0.0003766
2	C	2.3018626	-1.122762	0.0001937
3	C	1.8476048	0.2062904	0.0000859
4	C	0.4658727	0.5441183	0.0000778
5	C	-0.4658727	-0.5441183	0.0001447
6	C	0.0085115	-1.8893493	0.000317
7	C	-0.0085115	1.8893494	0.0001541
8	C	-1.3493331	2.1768314	0.0002457
9	C	-2.3018626	1.122762	0.0001944
10	C	-1.8476048	-0.2062904	0.0001822
11	C	-3.7368012	1.2115612	-0.0001336
12	C	3.7368012	-1.2115612	-0.0001876
13	H	1.6908486	-3.2077915	0.000526
14	H	-0.7149525	-2.6992408	0.0003939
15	H	0.7149525	2.6992408	0.0001302
16	H	-1.6908486	3.2077916	0.0003205
17	H	4.2789131	-2.1504516	-0.0000132
18	H	-4.2789131	2.1504516	-0.0000174
19	S	3.1980803	1.3275891	-0.0003024
20	S	-3.1980804	-1.3275892	-0.0000516
21	C	-4.341265	-0.0053343	-0.0002678
22	C	4.341265	0.0053342	-0.0004528
23	H	-5.4002839	-0.2237069	-0.0005046
24	H	5.4002838	0.2237069	-0.0007535

Table S6 Geometrical coordinates of the optimized **N[*b*]DT-4** by DFT at the B3LYP/6-31G(d,p) level

Cartesian coordinates:

Tag	Symbol	Coordinates(Angstroms)		
		X	Y	Z
1	C	1.6917038	1.9250514	-0.000057
2	C	2.4282741	0.7223093	-0.0000076
3	C	1.8037139	-0.5359173	0.0000771
4	C	0.3711846	-0.611109	0.000044
5	C	-0.3711846	0.611109	-0.000022
6	C	0.3185596	1.8578367	-0.0000615
7	C	-0.3185596	-1.8578367	0.0001042
8	C	-1.6917038	-1.9250514	0.0000821
9	C	-2.4282741	-0.7223093	0.0000016
10	C	-1.8037139	0.5359173	-0.0000161
11	C	-2.7657729	1.605965	-0.0000468
12	C	2.7657729	-1.605965	0.0001693
13	H	2.1986423	2.8847239	-0.0001116
14	H	-0.2550394	2.7784596	-0.0001141
15	H	0.2550394	-2.7784596	0.0001512
16	H	-2.1986423	-2.8847239	0.0001049
17	H	2.5086419	-2.6581052	0.0001952
18	H	-2.5086419	2.6581052	-0.000113
19	S	-4.1747696	-0.5740717	-0.0000875
20	S	4.1747696	0.5740717	-0.0000412
21	C	-4.0529662	1.1669774	-0.0000815
22	C	4.0529662	-1.1669773	0.0001244
23	H	4.9550324	-1.7631371	0.0001842
24	H	-4.9550324	1.7631371	-0.0000989

Table S7 Geometrical coordinates of the optimized chrysene by DFT at the B3LYP/6-31G(d,p) level

Cartesian coordinates:

Tag	Symbol	Coordinates(Angstroms)		
		X	Y	Z
1	C	-4.6726097	0.073772	0.000045
2	C	-3.8048989	1.1446133	0.0000298
3	C	-2.4026163	0.9470746	0.0000152
4	C	-1.8705008	-0.3776312	0.0000042
5	C	-2.7925598	-1.4551164	0.0000272
6	C	-4.1563049	-1.2375904	0.0000475
7	C	-1.5039585	2.0550422	0.0000158
8	C	-0.4295459	-0.564071	-0.0000002
9	C	0.4295576	0.5640628	-0.000011
10	C	-0.152837	1.8711812	0.0000021
11	C	1.870483	0.3776401	-0.0000654
12	C	1.5039663	-2.0550276	0.0000409
13	C	0.1528268	-1.8711657	0.000009
14	H	-1.9183551	3.059692	0.0000202
15	H	-5.7462622	0.2362301	0.0000592
16	H	-4.1855278	2.1626951	0.000035
17	H	-2.4340077	-2.4775932	0.0000363
18	H	-4.8352485	-2.085249	0.000066
19	H	0.4892961	2.7434669	-0.0000037
20	H	-0.4892912	-2.743464	0.000001
21	C	2.4026142	-0.9470859	0.0000002
22	C	2.7925649	1.4551297	-0.0000762
23	H	2.4339975	2.4776019	-0.0000096
24	C	4.1562951	1.2375884	0.0000036
25	H	4.8352629	2.0852291	0.0000551
26	C	4.6726109	-0.0737914	-0.0000779
27	C	3.8049137	-1.1446222	-0.0000527
28	H	5.7462698	-0.2362207	-0.0001101
29	H	4.1855258	-2.1627128	0.0000603
30	H	1.9183369	-3.0596904	0.0000475