

# Supporting Information

## Preparation, Properties, and Reduction of a Novel TCNQ-type Thienoquinoid

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### 1, Synthetic procedure

**General.** Melting points were taken on a Yanako MP J-3 and are uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL Lambda 300, 400 and Bruker Avance 600 spectrometers. Chemical shifts were recorded in units of parts per million downfield from tetramethylsilane as internal standard and all coupling constants are reported in Hz. IR spectra were obtained on a Shimadzu FTIR-8700 spectrometer. Electronic spectra were recorded on a Shimadzu UV-2550 spectrometer using 1 cm quartz cuvettes. Mass spectra and elemental analyses were obtained from the Analytical Center in Osaka City University. TLC was carried out on 0.2 mm Merck silica gel (60 F254) precoated plates. Merck silica gel 60 (0.063-0.200 mm) was used for column chromatography. Commercially available reagents and solvents were purified and dried when necessary.

**Compound 4** A 100 mL round-bottomed flask is charged under nitrogen with benzo[2,1-*b*:3,4-*b'*]dithiophene-4,5-dione **3** (700 mg, 3.32 mmol 50 mL) and dry ethylene glycol (70 mL). Chlorotrimethylsilane (2.10 mL, 16.6 mmol) is added in three portions (0.70 mL, 5.54 mmol), at intervals of 2 days between each addition. After the addition of the third portion the solution was stirred at room temperature for further 2 days. The solution was poured into 1 M sodium hydroxide solution and extracted with dichloromethane. The combined organic layers were washed with water and dried over sodium sulfate. After filtration the solvent was evaporated and the resulting yellow solid was crystallized from ethyl acetate to give **4** as yellow crystals (866 mg, 85%): mp 199-200 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.69-3.75 (m, 4H) 4.14-4.21 (m, 4H) 7.19 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  61.55, 93.67, 123.79, 125.25, 133.29, 135.49; IR (KBr) 3098, 3082, 2970, 1283, 1173, 1099  $\text{cm}^{-1}$ ; HRMS (EI)

$m/z$  calcd for  $C_{14}H_{12}O_4S_2$ , 308.0177, found 308.0175; Anal. Calcd for  $C_{12}H_4O_4S_2$ : C, 54.53; H, 3.92. Found: C, 54.47; H, 3.82.

**Compound 5** To a solution of TMEDA (3.23 mL, 21.43 mmol) in dry THF (25 mL) was added at  $-78\text{ }^{\circ}\text{C}$  under nitrogen  $n\text{-BuLi}$  (3.82 mL, 6.04 mmol). After the solution was stirred for 10 min, compound **4** (806 mg, 2.61 mmol) in dry THF was added. The solution was allowed to warm to  $-30\text{ }^{\circ}\text{C}$  and iodine (1.92 g, 7.58 mmol) in dry THF (25 mL) was added. The solution was allowed to warm to room temperature and stirred for 10 min. Water was added and the organic solvent was evaporated. The resulting solution was extracted with dichloromethane. The combined organic layers were washed with saturated sodium hydrogen carbonate and water and dried over sodium sulfate. After filtration the solvent was evaporated and the resulting yellow solid was crystallized from 1-propanol to give **5** (1.35 g, 93%) as yellow crystals: mp  $243\text{--}244\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.66–3.73 (m, 4H) 4.10–4.17 (m, 4H) 7.31 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  61.61, 72.36, 92.79, 134.85, 137.05, 138.03; IR (KBr) 2980, 2924, 2872, 1285, 1167,  $1094\text{ cm}^{-1}$ ; HRMS (FAB)  $m/z$  calcd for  $C_{14}H_{10}O_4S_2I_2$ , 559.8110, found 559.8108; Anal. Calcd for  $C_{14}H_{10}I_2O_4S_2$ : C, 30.02; H, 1.80. Found for C, 30.15; H, 1.82.

**Compound 6** To the solution of malononitrile (35.4 mg, 0.536 mmol) in dry THF (13 mL) was added under nitrogen at  $0\text{ }^{\circ}\text{C}$  60% sodium hydride (42.8 mg, 1.07 mmol). After the solution was stirred for 20 min, compound **5** (100 mg, 0.179 mmol) and  $\text{Pd(PPh}_3)_4$  (20.5 mg, 0.018 mmol) were added. The mixture was heated to reflux for 3 h and cooled to room temperature. Saturated solution of bromine (8 mL) was added dropwise and the resulting solution was stirred for 10 min. The solution was poured into water and extracted with dichloromethane. The combined organic layers were washed with sodium thiosulfate and water and dried over sodium sulfate. After filtration the solvent was evaporated and the resulting reddish purple solid was separated by a column chromatography on silica gel (dichloromethane) to give **6** (56.2 mg, 72%) as reddish purple solid: mp  $>300\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.70–3.75 (m, 4H) 4.23–4.27 (m, 4H) 7.48 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  61.82, 91.04, 111.76, 112.43, 130.53, 138.18, 152.81, 170.02; IR (KBr) 2218,  $1508\text{ cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $C_{20}H_{10}N_4O_4S_2$  434.0143, found 434.0127.

**Compound 2** To a solution of compound **6** (635 mg, 1.46 mmol) in dichloromethane (535 mL) was added 70% perchloric acid (80 mL). The solution was stirred for 5.5 h at  $0\text{ }^{\circ}\text{C}$  and poured into water. The solution was extracted with dichloromethane. The combined organic layer was washed with water and brine and dried over sodium sulfate. After filtration the solvent was evaporated to give **2** (431 mg, 85%) as black

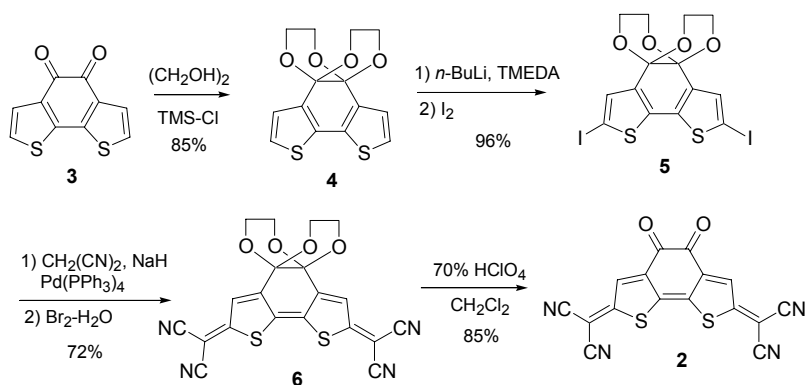
solid: mp >300 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  80.04, 110.98, 112.01, 135.23, 140.12, 143.22, 166.99, 171.92; IR (KBr) 2218, 1697  $\text{cm}^{-1}$ ; HRMS (FAB $^-$ )  $m/z$  calcd for  $\text{C}_{16}\text{H}_2\text{N}_4\text{O}_2\text{S}_2$  345.9619, found 345.9607.

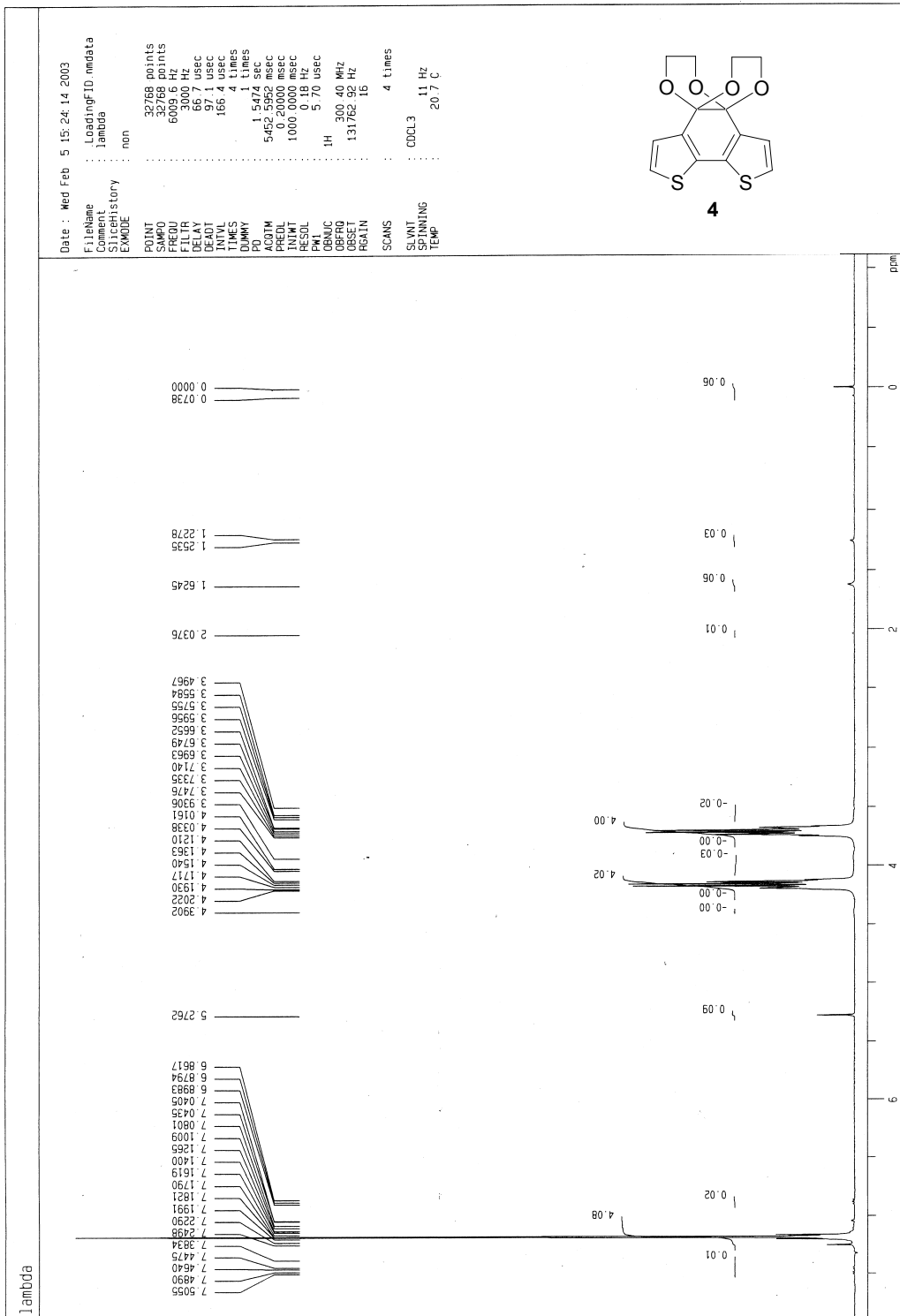
**CT complex TTF-2 (General Procedure)** To a solution of TTF (0.014 mmol) in dichloromethane (0.4 mL) was added **2** (5 mg, 0.014 mmol) in dichloromethane (2 mL). The solution was stirred for 10 min to form black solid. The solid was filtered off and dried to afford **TTF-2** (4 mg) as black powder: mp >300 °C; IR (KBr) 2183, 1663, 1653  $\text{cm}^{-1}$ ; Anal. Calcd. for  $\text{C}_{16}\text{H}_2\text{N}_4\text{O}_2\text{S}_2 \cdot \text{C}_6\text{H}_4\text{S}_4 \cdot 1/2\text{CH}_2\text{Cl}_2$  C, 45.56; H, 1.19; N, 9.45. Found C, 45.55; H, 1.17; N, 9.27.

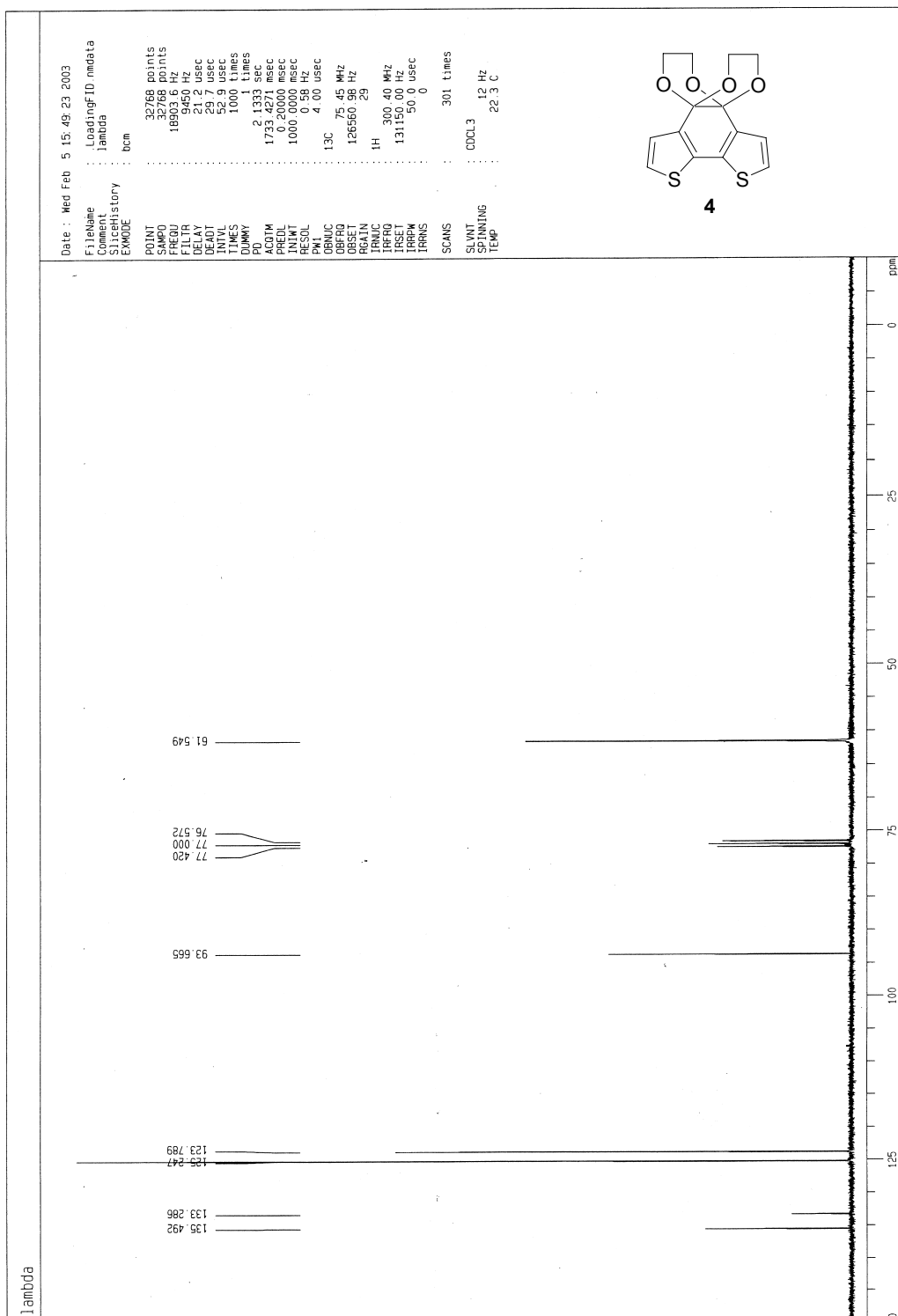
**DEF-2** mp >300 °C ; IR (KBr) 2183, 1663, 1653  $\text{cm}^{-1}$ ; Anal ( $\text{C}_{16}\text{H}_2\text{N}_4\text{O}_2\text{S}_2 \cdot \text{C}_{16}\text{H}_{18}\text{N}_2 \cdot 1/2\text{C}_6\text{H}_5\text{Cl}$ ) Calcd for C; 65.59, H; 3.54, N; 13.11. Found C; 65.57, H; 3.88, N; 12.72.

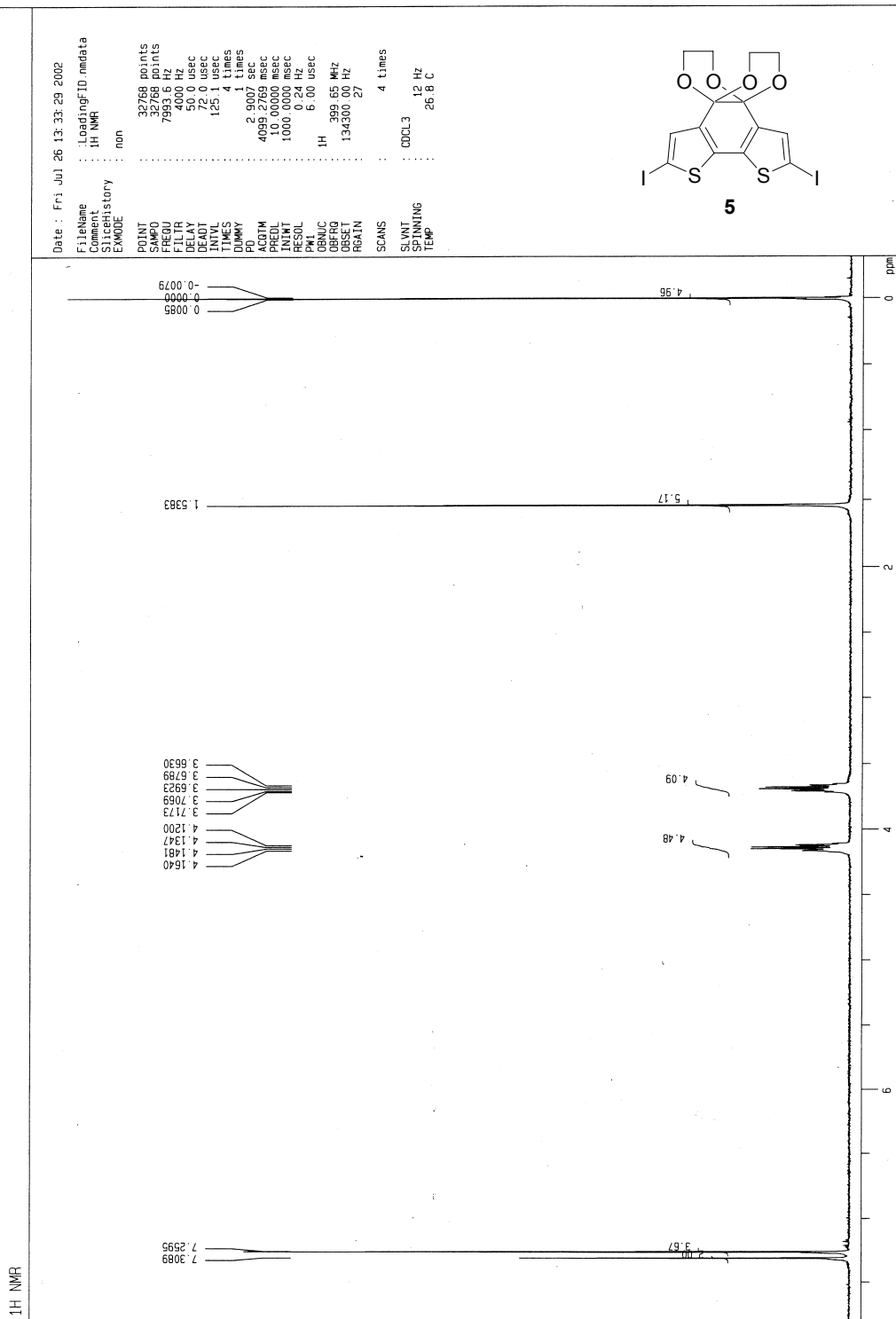
**Preparation of anion radical salts 2•Et<sub>4</sub>N (General Procedure)** To the stirred solution of tetraethylanmonium iodide (2.2 mg, 0.0086 mmol) in dichloromethane (3 mL) was slowly added **2** (3 mg, 0.0086 mmol) in dichloromethane (2 mL). The precipitate which appears is collected by filtration to give **2•Et<sub>4</sub>N** (1.5 mg) as green solid: mp >300 °C; IR (KBr) 2197, 2185, 1668, 1470, 1367, 1315, 1232, 1140  $\text{cm}^{-1}$ . Anal Calcd. for  $\text{C}_{16}\text{H}_2\text{N}_4\text{O}_2\text{S}_2 \cdot \text{Et}_4\text{N} \cdot 1/2\text{H}_2\text{O}$ : C, 59.36; H, 4.77; N, 14.42. Found C, 59.45; H, 4.55, N, 14.33.

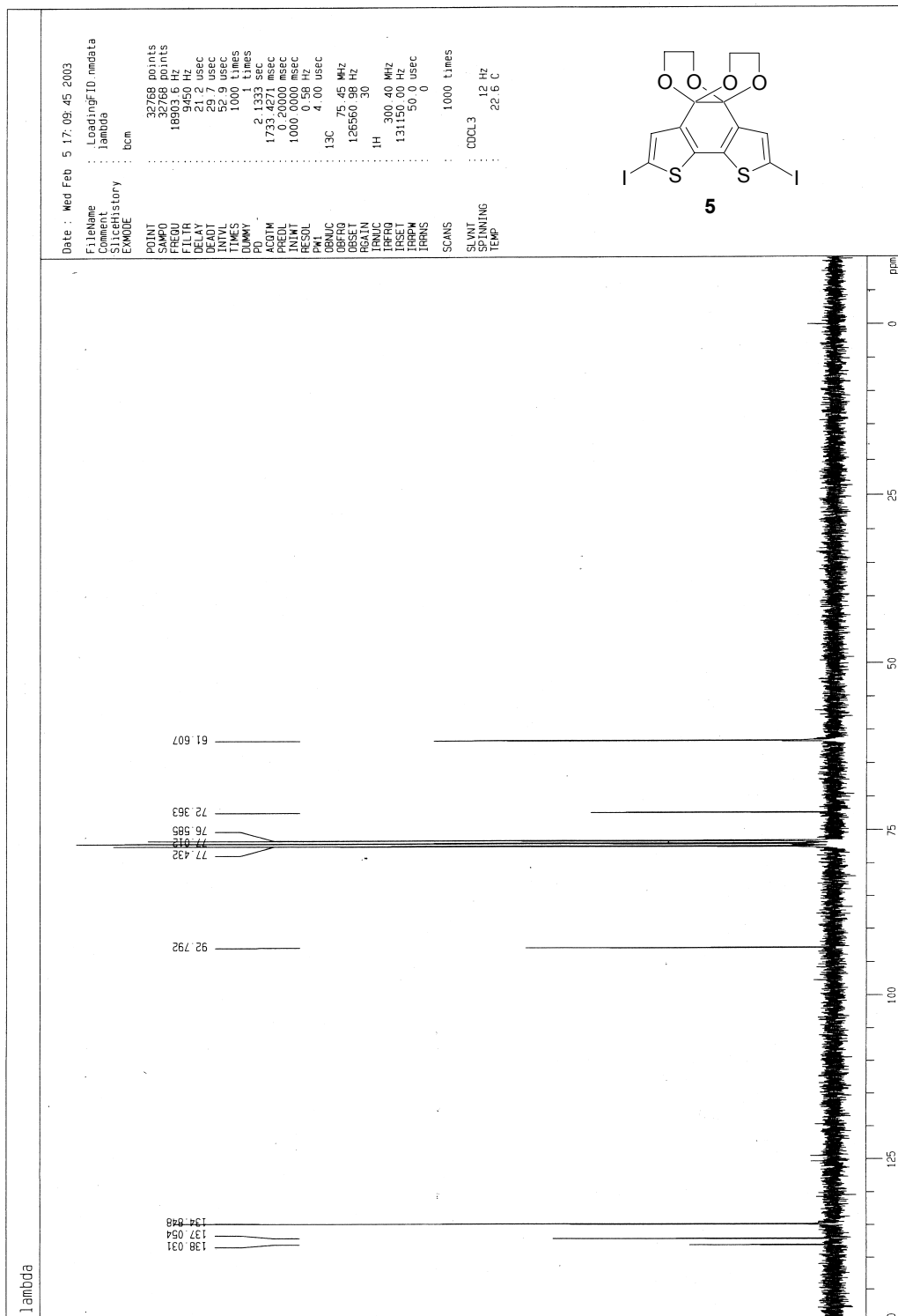
**2•Me<sub>4</sub>P** green solid; mp >300 °C; IR (KBr) 2197, 2185, 1670, 1470, 1366, 1315, 1234, 1140, 984  $\text{cm}^{-1}$ . Anal Calcd. for  $\text{C}_{16}\text{H}_2\text{N}_4\text{O}_2\text{S}_2 \cdot \text{Me}_4\text{P} \cdot \text{H}_2\text{O}$ : C, 52.74; H, 3.54; N, 12.30. Found C, 53.06; H, 3.22; N, 11.93.

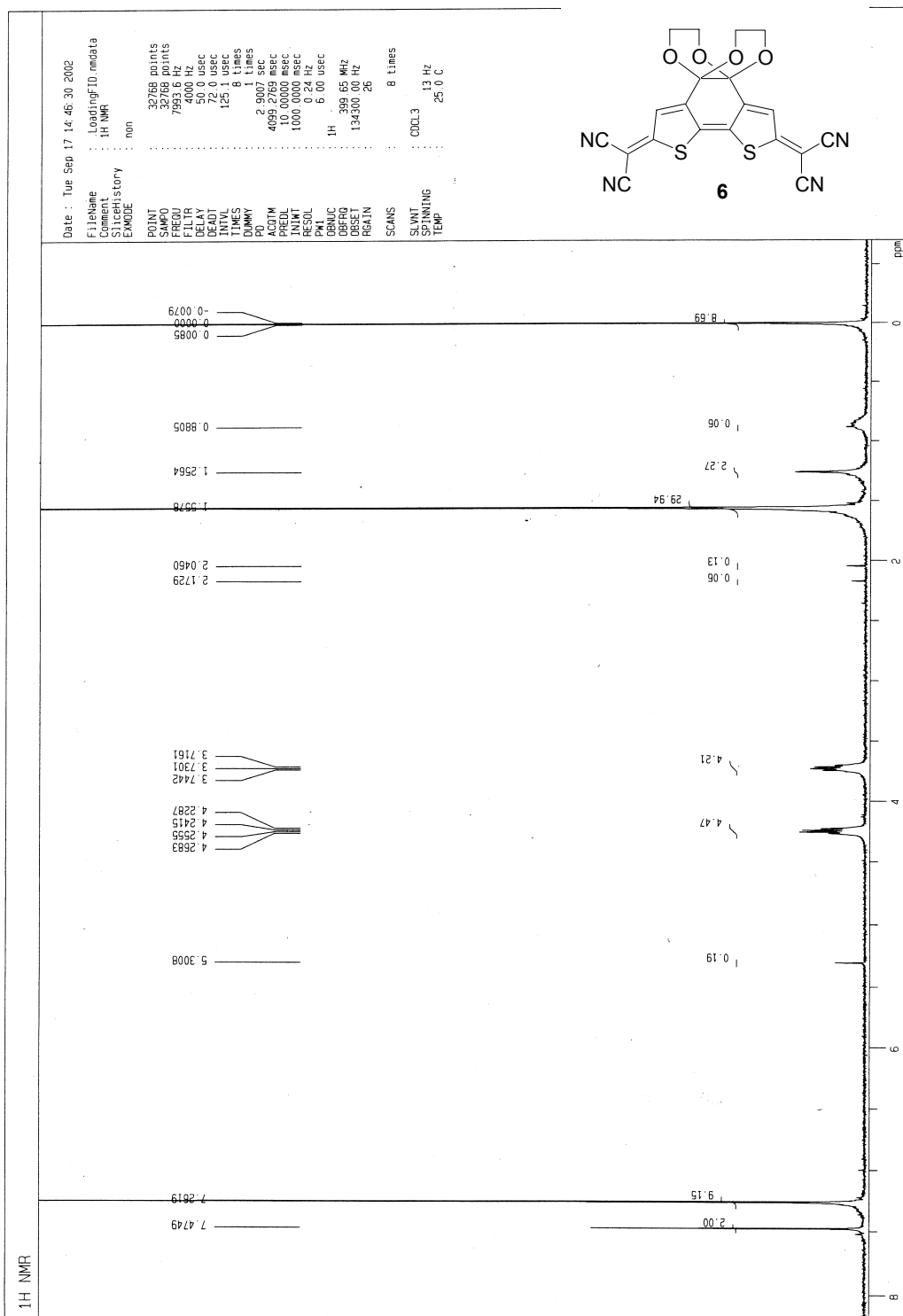








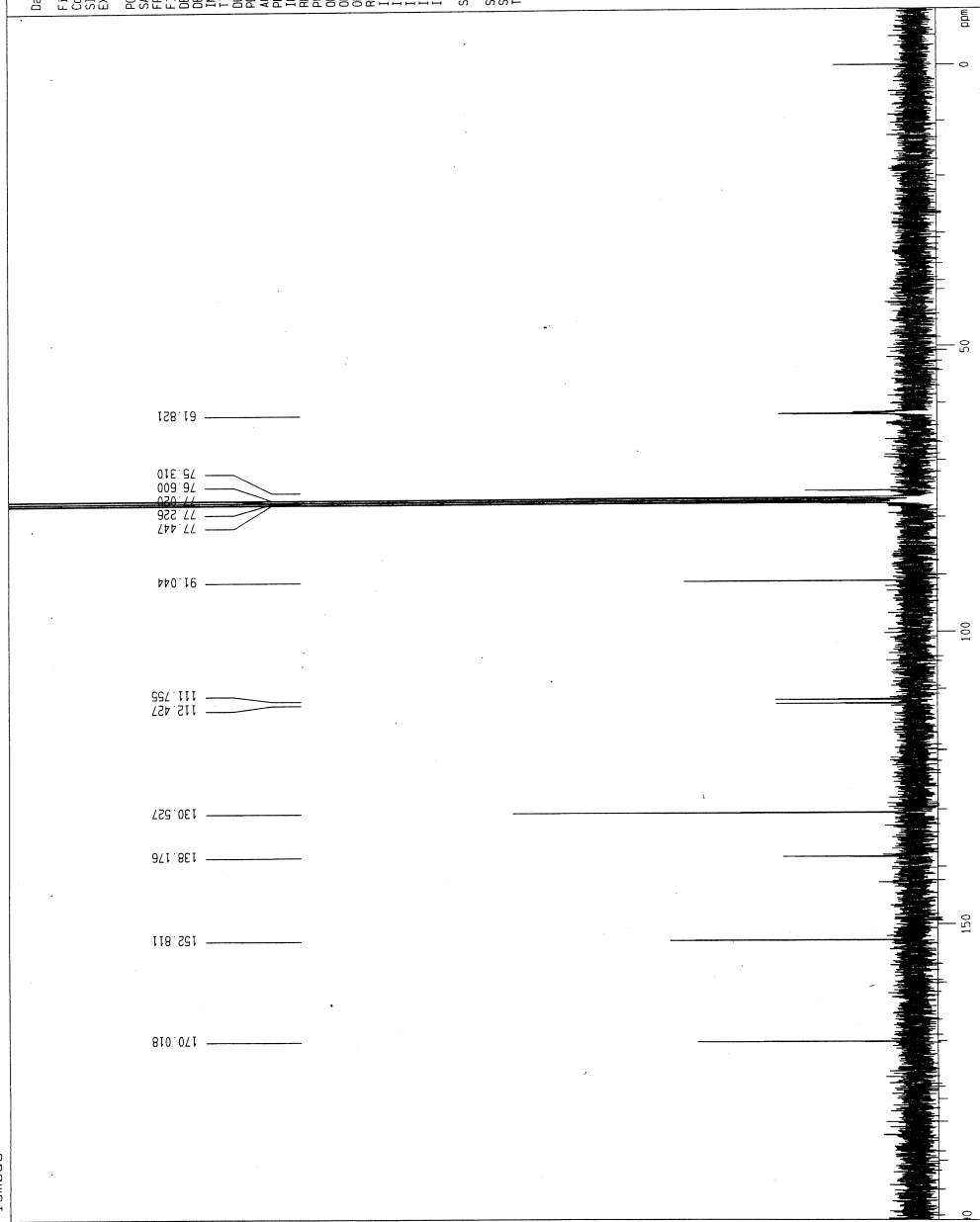
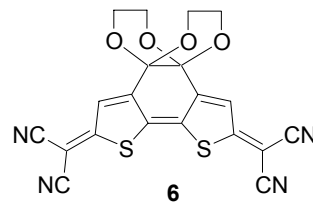


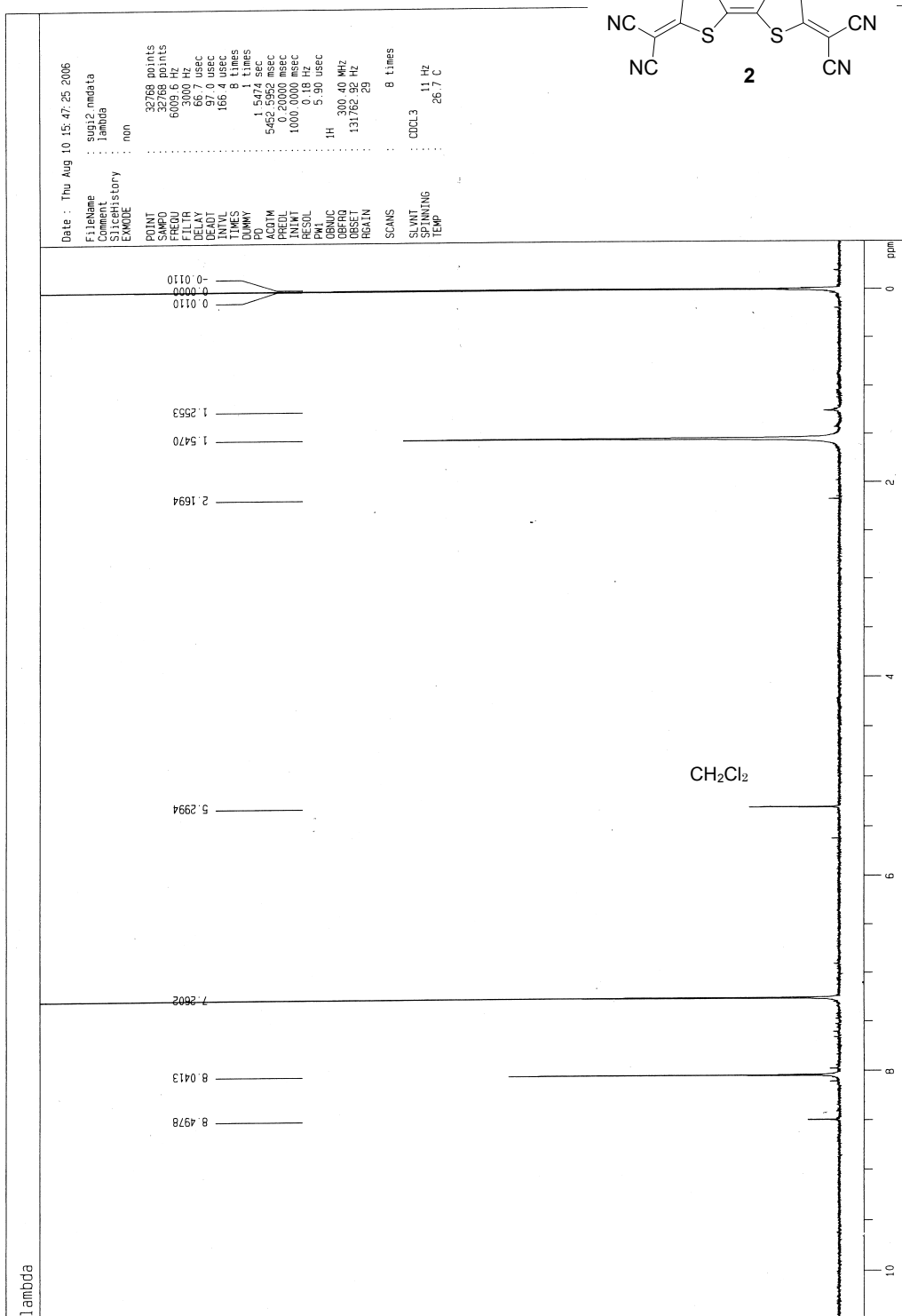




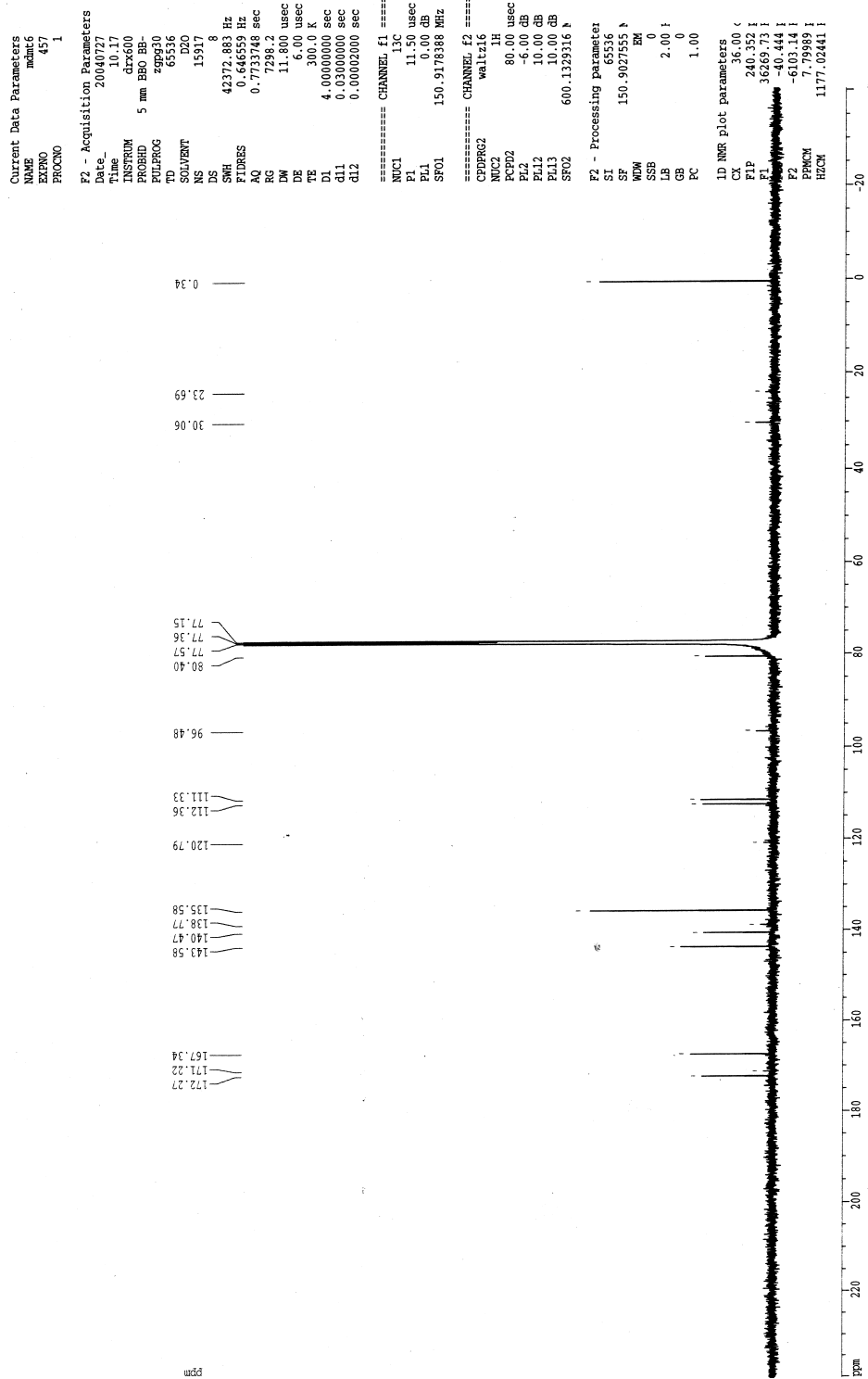
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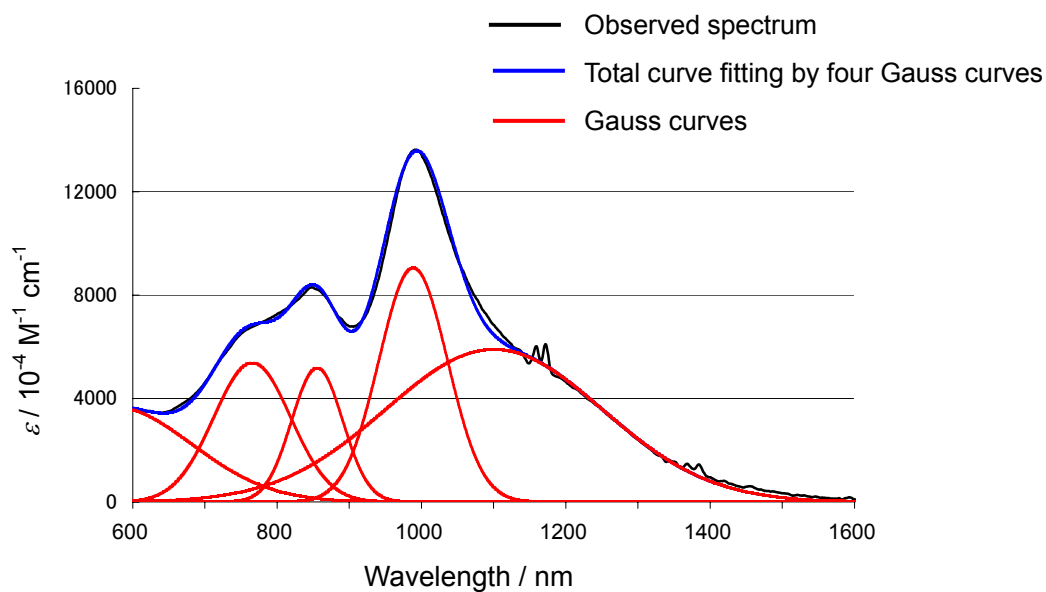




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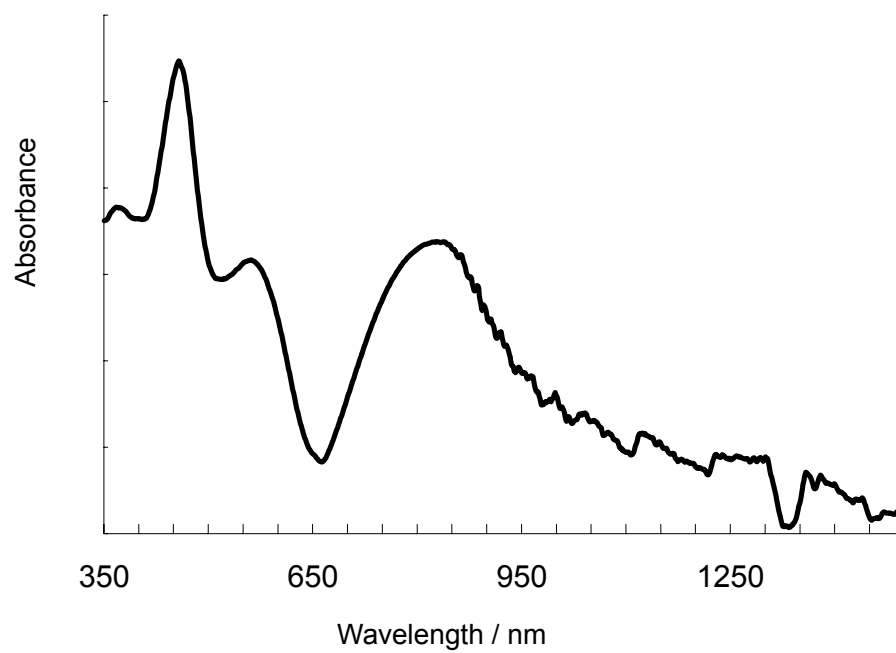
## 2, Vis-NIR and EPR Spectra



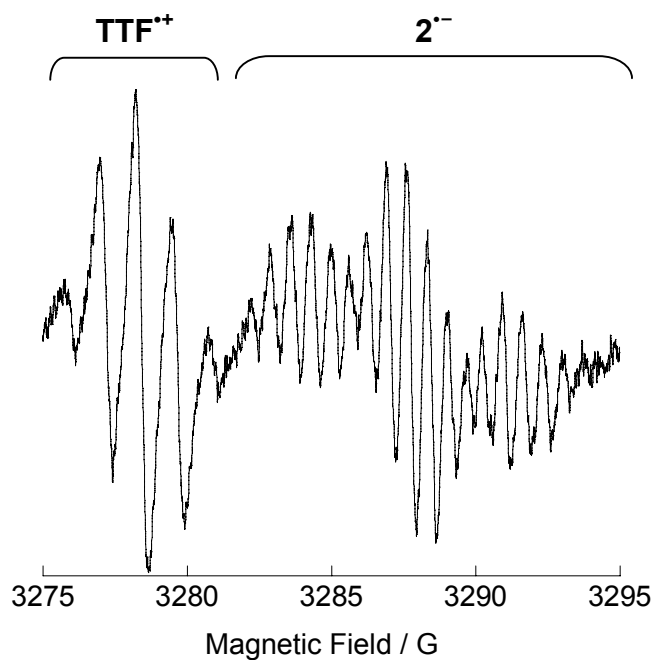
**Figure S1.** Band shape analysis of NIR absorption of  $2^{\bullet-}$  generated by the reduction with Na-Hg.

**Table S1.** Band shape analysis of the observed NIR absorptions

	Band 1	Band 2	Band 3	Band 4
$\lambda_{\max}$ (nm)	765	855	988	1100
$\nu_{\max}$ ( $\text{cm}^{-1}$ )	13072	11696	10121	9091
Half width ( $\text{cm}^{-1}$ )	2163	1142	1148	2996



**Figure S2.** UV-vis-NIR spectrum of **2•TTF** in KBr.

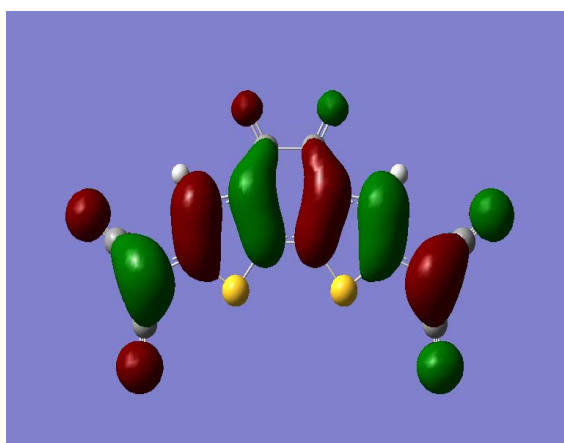


**Figure S3.** EPR spectrum of **2•TTF** measured in dichloromethane-DMF (10:1) at room temperature.

**3, DFT calculations** The molecular structures with  $C_1$  symmetry were fully optimized at the B3LYP/6-31G(d) level theory. The total SCF energies and  $S^2$  for thienoquinoids QT2CN2 $^{\bullet-}$ , **1 $^{\bullet-}$** , and **2 $^{\bullet-}$**  were summarized in Table S2. The optimized Cartesian coordinates for thienoquinoids QT2CN2 $^{\bullet-}$ , **1 $^{\bullet-}$** , and **2 $^{\bullet-}$**  were summarized in Table S3 ~ 5.

**Table S2.** The Total SCF Energies and  $S^2$  for thienoquinoids QT2CN2 $^{\bullet-}$ , **1 $^{\bullet-}$** , and **2 $^{\bullet-}$**

	SCF Energies / Hartree	$S^2$
QT2CN2 $^{\bullet-}$	-1551.27955555	0.7502
<b>1<math>^{\bullet-}</math></b>	-1663.38882541	0.7503
<b>2<math>^{\bullet-}</math></b>	-1776.73568521	0.7507



**Figure S3.** SOMO in **2 $^{\bullet-}$**  obtained using DFT calculations (UB3LYP/6-31G\*).

**Table S3.** The optimized Cartesian coordinates for QT2CN2<sup>•-</sup>

	atom	X	Y	Z
1	S	-1.99179	0.997085	-3.2E-05
2	C	-3.22223	-0.26653	0.000019
3	C	-2.61057	-1.53535	0.000069
4	C	-1.22014	-1.49016	0.000075
5	C	-0.6761	-0.19704	0.000027
6	C	0.676098	0.197039	0.000027
7	S	1.991787	-0.99709	-3.2E-05
8	C	3.222226	0.266534	0.000017
9	C	2.610565	1.535347	0.000068
10	C	1.220137	1.490157	0.000079
11	C	4.604436	-0.03099	-4E-06
12	C	5.551433	1.023777	0.000021
13	N	6.315278	1.9089	0.00002
14	C	5.084807	-1.36242	-4.4E-05
15	N	5.4667	-2.46781	-0.00012
16	C	-4.60444	0.030992	0
17	C	-5.08481	1.362421	-4.4E-05
18	N	-5.4667	2.467811	-0.00012
19	C	-5.55143	-1.02378	0.000022
20	N	-6.31528	-1.9089	0.000018
21	H	-3.19465	-2.4485	0.000108
22	H	-0.59465	-2.37741	0.000122
23	H	3.194652	2.448504	0.000105
24	H	0.594646	2.377412	0.000128

**Table S4.** The optimized Cartesian coordinates for **1<sup>+</sup>**

	atom	X	Y	Z
1	C	-2.56827	1.25516	-3.8E-05
2	C	-1.18604	1.14075	-1.1E-05
3	C	-0.70708	-0.18636	-1.5E-05
4	S	-2.01387	-1.32815	-6.1E-05
5	C	-3.21226	-0.00343	-2.4E-05
6	C	0	2.067843	0.000026
7	O	0	3.284527	-1.5E-05
8	C	1.186043	1.14075	-6E-06
9	C	0.707077	-0.18636	-4E-06
10	S	2.013869	-1.32815	-1.9E-05
11	C	3.212256	-0.00343	0.000003
12	C	2.568267	1.255161	-3.7E-05
13	C	4.599437	-0.27459	0.000024
14	C	5.528196	0.796131	0.000017
15	C	5.100436	-1.59833	0.000037
16	C	-4.59944	-0.27459	-1E-06
17	C	-5.5282	0.796131	0.000046
18	C	-5.10044	-1.59833	0.000021
19	N	6.279047	1.691933	0.000022
20	N	5.493818	-2.69962	0.000044
21	N	-6.27904	1.691935	0.000074
22	N	-5.49382	-2.69962	0.000041
23	H	-3.12208	2.1865	-3.6E-05
24	H	3.122081	2.186501	-4.8E-05



**Table S5.** The optimized Cartesian coordinates for 2<sup>+</sup>

	atom	X	Y	Z
1	C	1.454003	1.256519	-2.4E-05
2	C	0.78333	2.568694	-4.9E-05
3	C	-0.78333	2.568694	-2.9E-05
4	C	-1.454	1.256519	-0.00002
5	C	-0.70014	0.05946	-0.00002
6	C	0.700139	0.05946	-1.8E-05
7	C	2.835971	1.052743	-5E-06
8	C	3.205127	-0.3035	0.000005
9	S	1.762649	-1.33694	-3E-06
10	C	-2.83597	1.052743	-7E-06
11	C	-3.20513	-0.3035	-2E-06
12	S	-1.76265	-1.33694	-9E-06
13	O	1.380616	3.631564	-3E-06
14	O	-1.38062	3.631564	-1.4E-05
15	C	-4.50707	-0.85073	0.000009
16	C	-5.63626	0.007025	0.000023
17	N	-6.55755	0.725545	0.000102
18	C	-4.7286	-2.2491	0.000008
19	N	-4.89255	-3.40656	-4.1E-05
20	C	4.507074	-0.85073	0.000019
21	C	5.636256	0.007025	0.000029
22	N	6.557553	0.725545	0.000063
23	C	4.728596	-2.2491	0.000025
24	N	4.892551	-3.40656	-2.7E-05
25	H	3.559645	1.85892	-4E-06
26	H	-3.55965	1.85892	-3E-06