Electronic Supplementary Material (ESI) for RSC Advances.

Support Information

Colorless Metallodithiolene Oligomers and Polymers with Intense Near- and Mid-Infrared Absorption

Bo Liu, [ab] **Wenqiang Qiao***[a] **and Zhi Yuan Wang***[ac]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China

[b] University of Chinese Academy of Sciences, Beijing, 100049, China

[c] Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

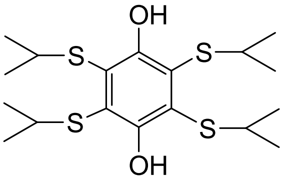
SI-1. General Methods

NMR spectra were recorded on Bruker Avance 300 (300 MHz) and Bruker Avance 400 (400 MHz) NMR spectrometers. Chemical shifts (ppm) are given relative to $CDCl_3$, 7.26 ppm (^1H NMR) and 77.16 ppm (^{13}C NMR), with TMS as internal reference and H_3PO_4 as external reference for ^{31}P NMR spectra, respectively. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), sep (septet), m (multiplet) and br (broad). All the measurements were carried out at room temperature unless otherwise stated. All the compounds were characterized by MS (mass spectroscopy): MALDI-TOF-MS were obtained from Bruker Daltonics Autoflex III time-of-flight (TOF) mass spectrometry; Electron impact mass spectrometry (EI-MS) were recorded on Agilent Technologies 5975 mass spectrometer and Elaectrospray ionization mass spectrometry (ESI-MS) were recorded on Waters Quattro Premier XE. Elemental analysis was performed on Elementar Vario EL cube analyzer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris Diamond TG from 50 to 800 ºC at a heating rate of 10 ºC /min under a continuous nitrogen flow. The analysis of metals (Ni and Pd) was carried on inductive coupled plasma optical emission spectrometer (Thermo Scientific iCAP 6000). Molecular weight of the polymer was determined on a Waters 1515 Gel Permeation Chromatography (GPC). UV-VIS-NIR spectra were recorded using a Shimadu UV-3600 Spectrophotometers. IR spectra (4400–400 cm^{-1}) were recorded using a Shimadu FT-IR Affinity-1 Spectrometer. Cyclic voltammetry was done on a CHI660B electrochemical workstation, using a conventional three-electrode cell consisting of a platinum disk or glass-carbon as the working electrode, a platinum wire as the counter-electrode and Ag/Ag^+ in a 0.01 $mol\cdot dm^{-3}$ of $AgNO_3$ solution as the reference electrode. The experiments were performed at room temperature (25 °C) in dry DCM or CH_3CN containing 0.1 $mol\cdot dm^{-3}$ Bu_4NPF_6 as the supporting electrolyte, at a scan rate of 100 $mV\cdot s^{-1}$.

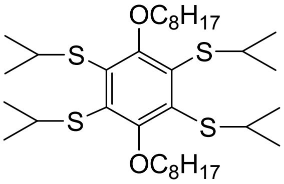
SI-2. Materials

All the reagents were used as received from Alfa Aesar, Acros Organics, and Aldrich. Air- and moisture-sensitive syntheses were carried with the standard Schlenk techniques in a Schlenk tube under argon atmosphere. Compound **1** was obtained according to literature [1]. Ligand **3** was synthesized from **2** according to literature [2,3]. The complexes were prepared according to the literature [4].

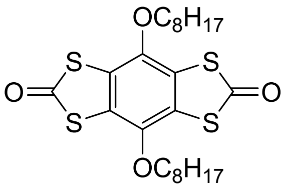
SI-3. Synthesis



2,3,5,6-Tetrakis(isopropylthio)benzene-1,4-dihydroquinone (1). The suspension of sodium hydroxide (7.20 g, 180 mmol) and 2-propanethiol (22.3 mL, 240 mmol) in dry toluene (90 mL) was stirred for 2.5 hours at ambient temperature. Then, 200 mL of toluene solution containing 1,2,4,5-tetrachlorobenzoquinone (9.84 g, 40 mmol) was added dropwise and the resulting yellowish green suspension was stirred at 60 ^{o}C for 6 hours under argon. After the reaction mixture was cooled to ambient temperature, some de-ionized water was added to the mixture. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation and recrystallization of the residue from hot methanol gave **1** as bright yellowish needle crystals (12.09 g, 74.3% yield). ^{1}H NMR (δ, ppm in $CDCl_3$) 7.39 (s, 2H, -OH), 3.54-3.72 (sep, 4H, J = 8.8, 8.8 *Hz*, CH), 1.14-1.31 (d, 24 H, J = 8.8 *Hz*, CH_3); ^{13}C NMR (δ, ppm in $CDCl_3$) 151.54, 124.52, 38.52, 22.04; MS (ESI): 407.2 (M^+); Anal. Calcd for $C_{18}H_{30}O_2S_4$: C, 53.16; H, 7.44; S, 31.54; Found: C, 53.14; H, 7.48; S, 31.45.

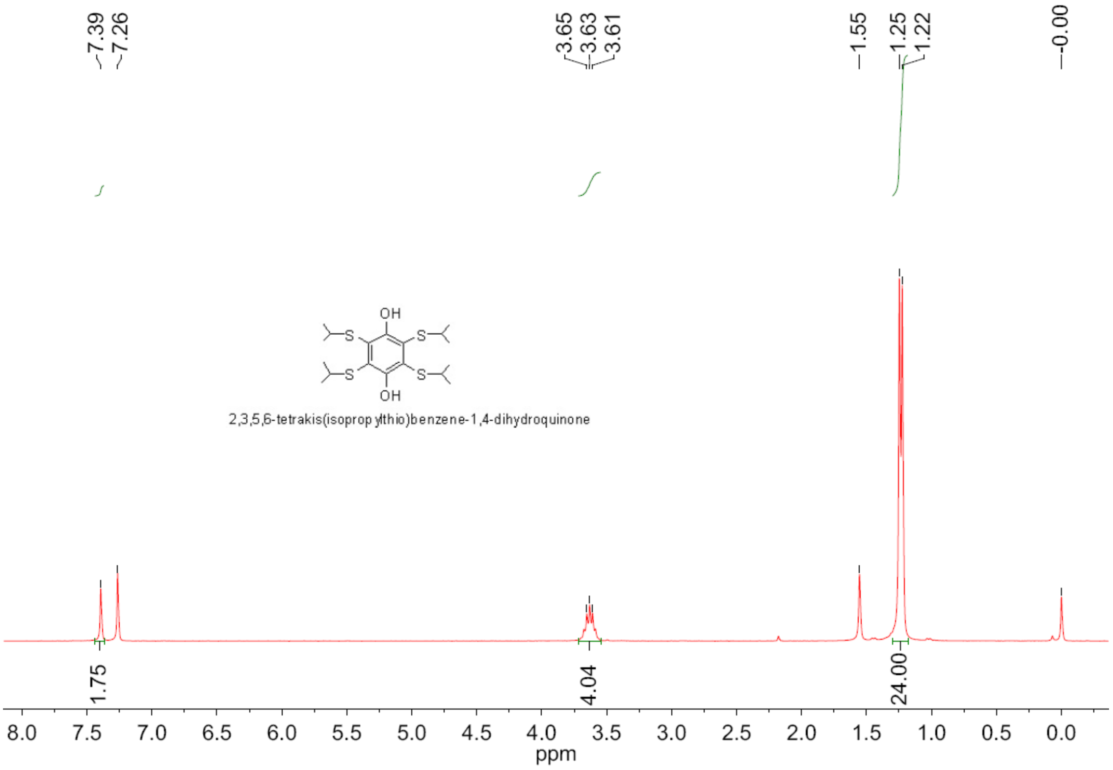


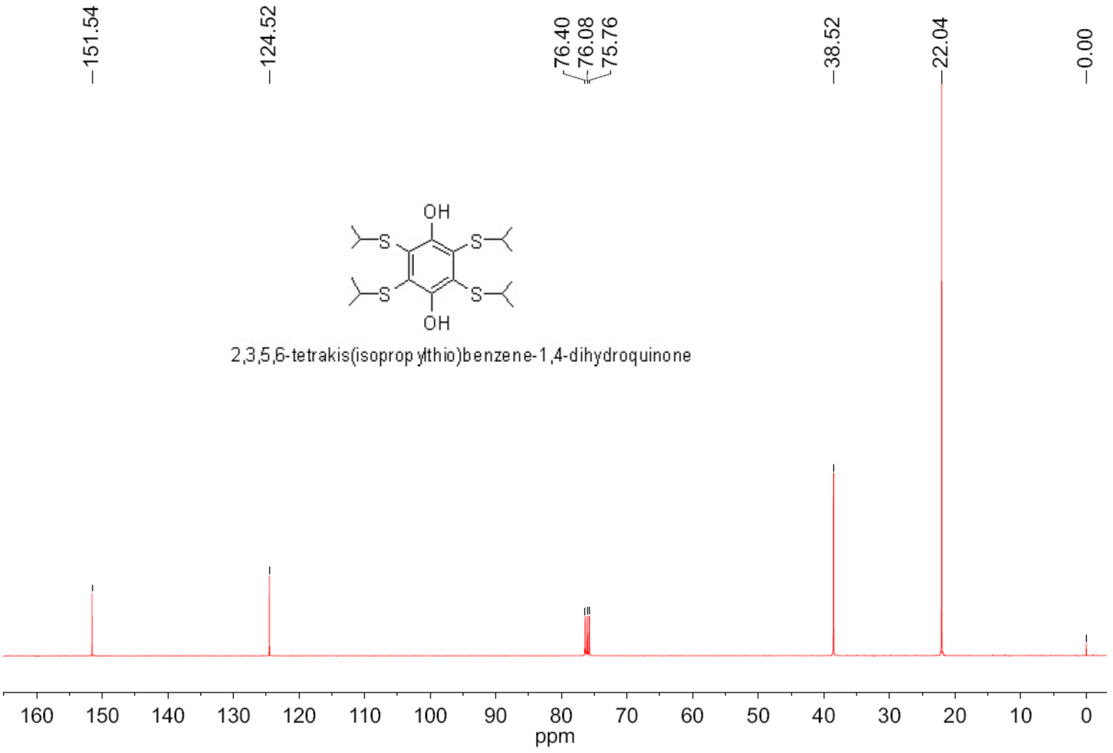
3,6-Bis(octyloxy)-1,2,4,5-tetrakis(isopropylthio)benzene (2). Compound **1** (6.10 g, 15.0 mmol) and potassium carbonate (12.44 g, 90.0 mmol) were mixed in dry toluene/N, N-dimethylformamide (100 mL/100 mL). To the resulting blood-red suspension, was added 1-bromo(-n-)octane (6.95 g, 36.0 mmol) via a syringe. The reaction mixture was heated up to 100 ^{o}C and kept overnight under argon. After cooling to ambient temperature, the reaction mixture was washed with water twice. The aqueous phase was extracted with dichloromethane once, and the organic phase was combined and dried over anhydrous magnesium sulfate. After removal of the solvent, the brown-red sticky residue was purified on a silica gel column eluted with CH_2Cl_2/petroleum ether (1:3 v/v). Compound **2** was obtained as colorless oily liquid (9.23 g, 97.5% yield). ^{1}H NMR (δ, ppm in $CDCl_3$) 3.93-4.01 (t, 4H, J = 6.8 *Hz*, -OCH_2), 3.76-3.87 (sep, 4H, J = 6.8, 6.4, 6.8 *Hz*, CH), 1.73-1.83 (m, 4H, J = 7.6, 6.8 *Hz*, O-CH_2-CH_2), 1.43-1.54 (m, 4H, O-CH_2-CH_2-CH_2), 1.23-1.42 (overlapping br, m, 16H), 1.15-1.22 (d, 24H, J = 6.4 *Hz*), 0.84-0.94 (t, 6H, J = 6.8 *Hz*); ^{13}C NMR (δ, ppm in $CDCl_3$) 157.76, 134.57, 72.55, 38.52, 31.85, 30.43, 29.47, 29.29, 26.05, 22.89, 22.67, 14.08; MS (ESI): 631.5 (M^+); Anal. Calcd for $C_{34}H_{62}O_2S_4$: C, 64.71; H, 9.90; S, 20.32; Found: C, 64.69; H, 10.01; S, 20.34.

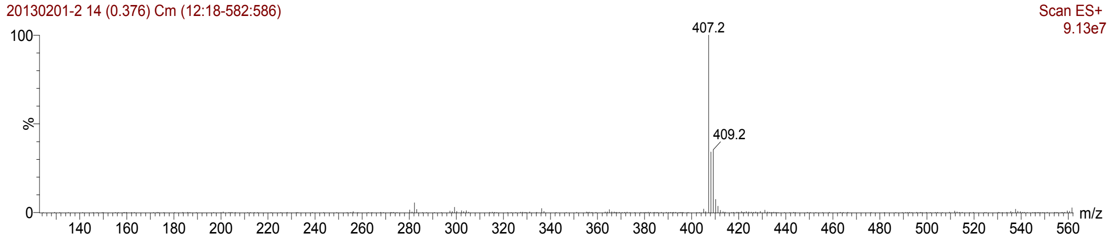


4,8-Bis(octyloxy)-1,3,5,7-tetrathia-s-indacene-2,6-dione (3). Naphthalene (15.38 g, 120 mmol) and sodium (5.52 g, 240 mmol) were stirred in 200 mL of THF at ambient temperature for 0.5 hour under argon. Compound **2** (12.37 g, 19.6 mmol) was added into the dark green solution and the resulting brown solution was stirred under argon at 50 °C for 20 hours. After cooling to -10 °C in an ice-salt bath, 15 mL of triethylamine was introduced. After another 15 minutes while being kept at -5~-10 °C, 110 mL of toluene containing triphosgene (11.87 g, 40 mmol) was added cautiously via addition funnel over 1 hour. The reaction mixture was stirred for one hour afterwards and quenched by adding 30 mL of de-ionized water dropwise over 45 minutes. The aqueous phase was extracted by dichloromethane and the organic phase was combined. The combined organic phase was dried over anhydrous sodium sulfate. After removal of the solvent, the brownish red residue was purified on a silica gel column eluted with CH_2Cl_2/petroleum ether (1:5 v/v) to give bright yellow solids. Recrystallization from dichloromethane gave pure **3** as bright yellow needle crystals (5.13 g, 51.0% yield). ^{1}H NMR (δ, ppm in $CDCl_3$) 3.93-4.05 (t, 4H, J = 6.4 *Hz*, $-OCH_2$), 1.72-1.81 (m, 4H, J = 6.8, 7.2 *Hz*, $O-CH_2-CH_2$), 1.41-1.54 (m, 4H, J = 6.4, 7.2 *Hz*, $O-CH_2-CH_2-CH_2$), 1.24-1.34 (overlapping br, d, 16H), 0.85-0.93 (t, 6H, J = 6.8 *Hz*); ^{13}C NMR (δ, ppm in $CDCl_3$) 188.11, 143.36, 125.06, 73.67, 31.77, 30.08, 29.24, 29.17, 25.79, 22.63, 14.08; MS (EI) m/z: 514 (M^+); Anal. Calcd for $C_{24}H_{34}O_4S_4$: C, 56.00; H, 6.66; S, 24.92; Found: C, 56.01; H, 6.64; S, 25.01.

SI-4. ^{1}H, ^{13}C and ^{31}P NMR and MS spectra of 1-8



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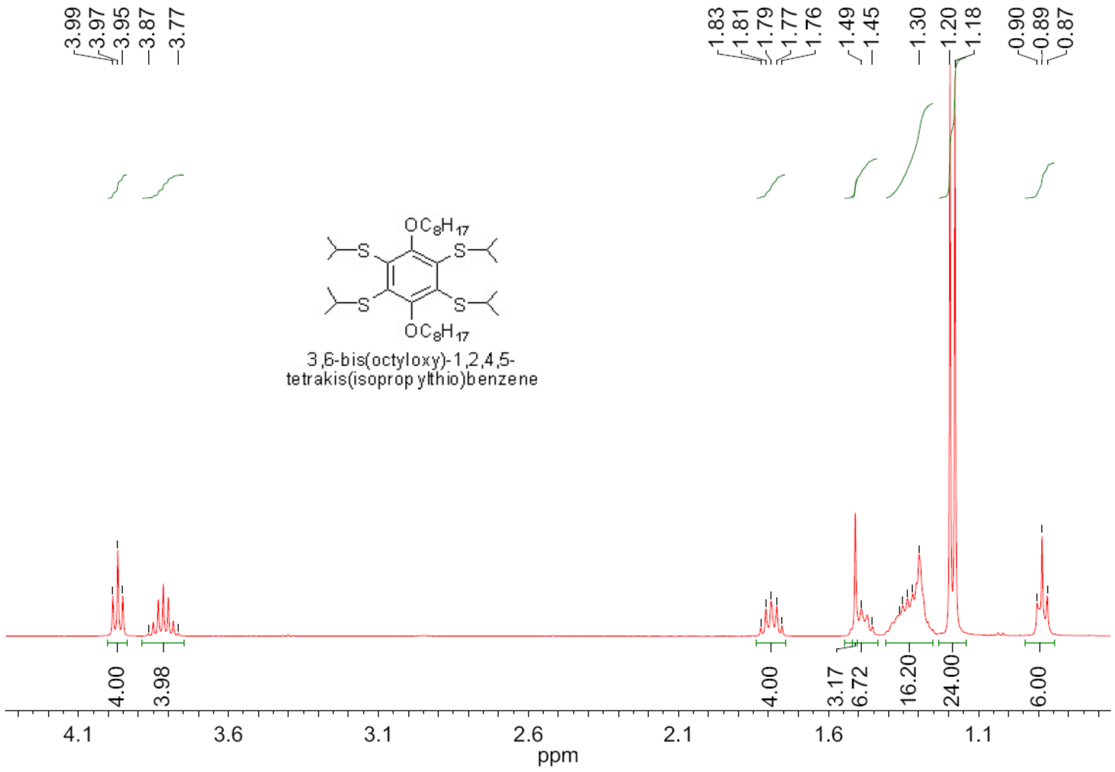
m/z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S
S
S
S
OC8H17
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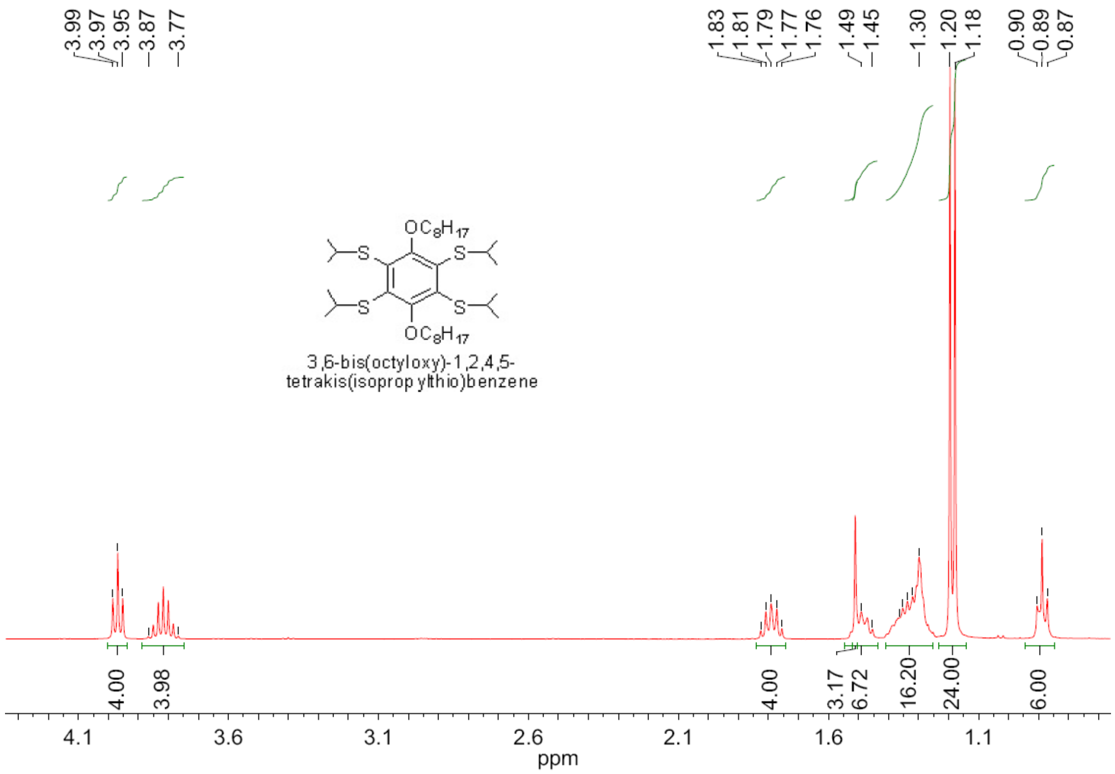
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OC8H17
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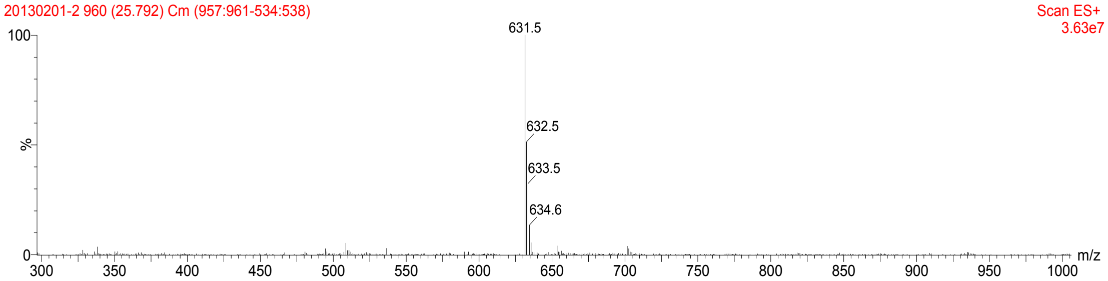
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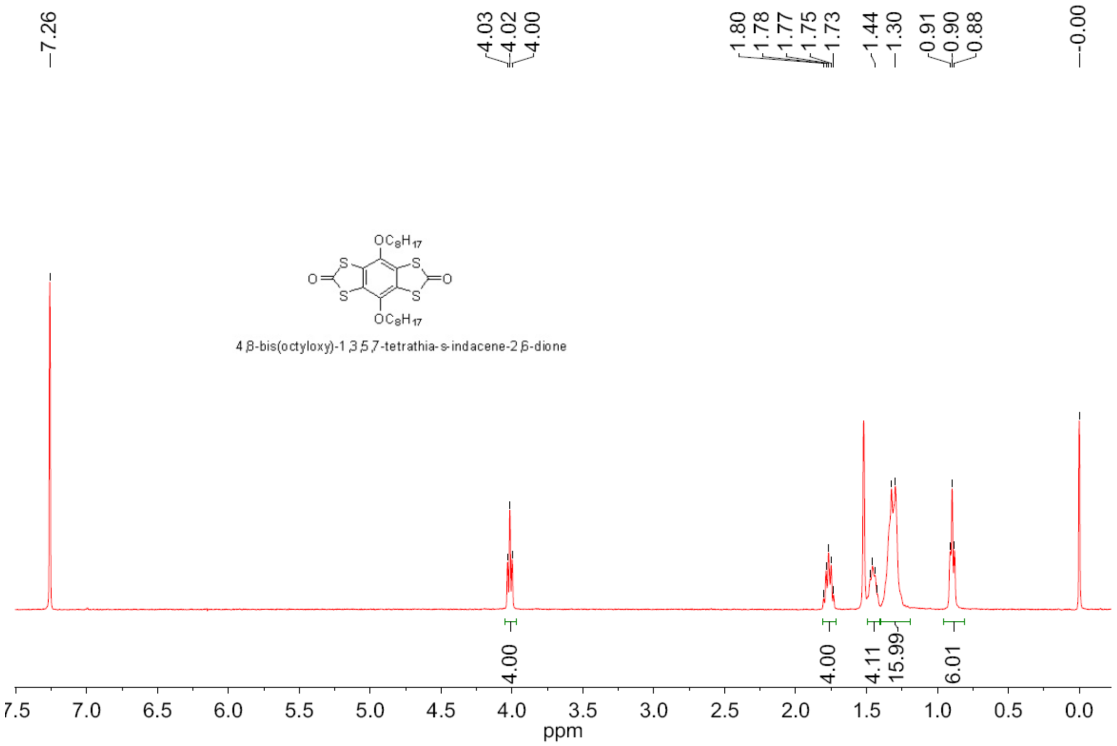
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OC_8H_{17}
4,8-bis(octyloxy)-1,3,5,7-tetrathia-s-indacene-2,6-dione
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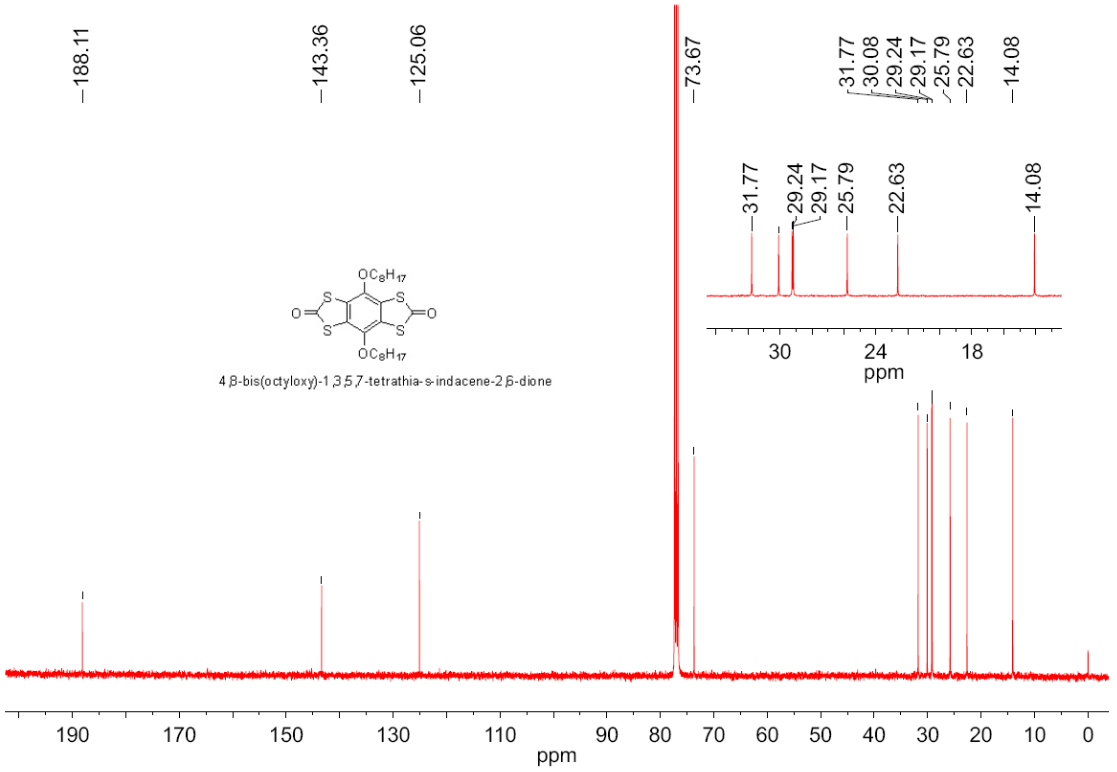
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22.63
14.08
30
24
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ppm
OC_8H_{17}
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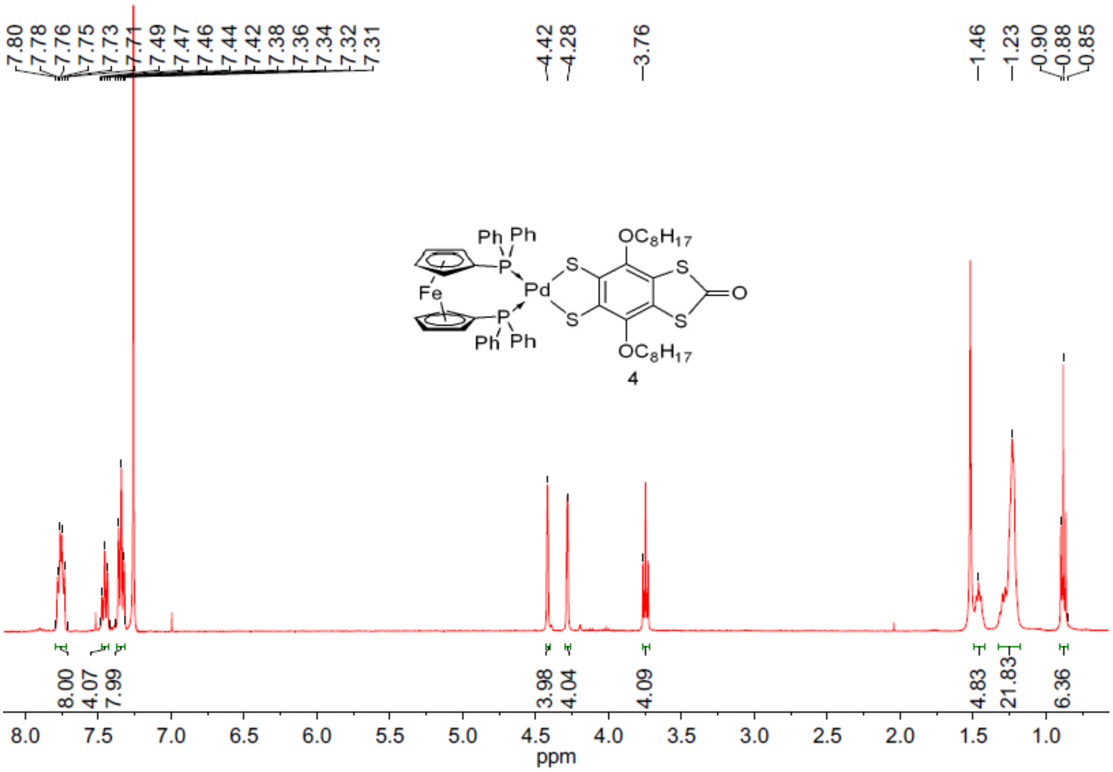
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P
Fe
Pd
S
OC8H17
O
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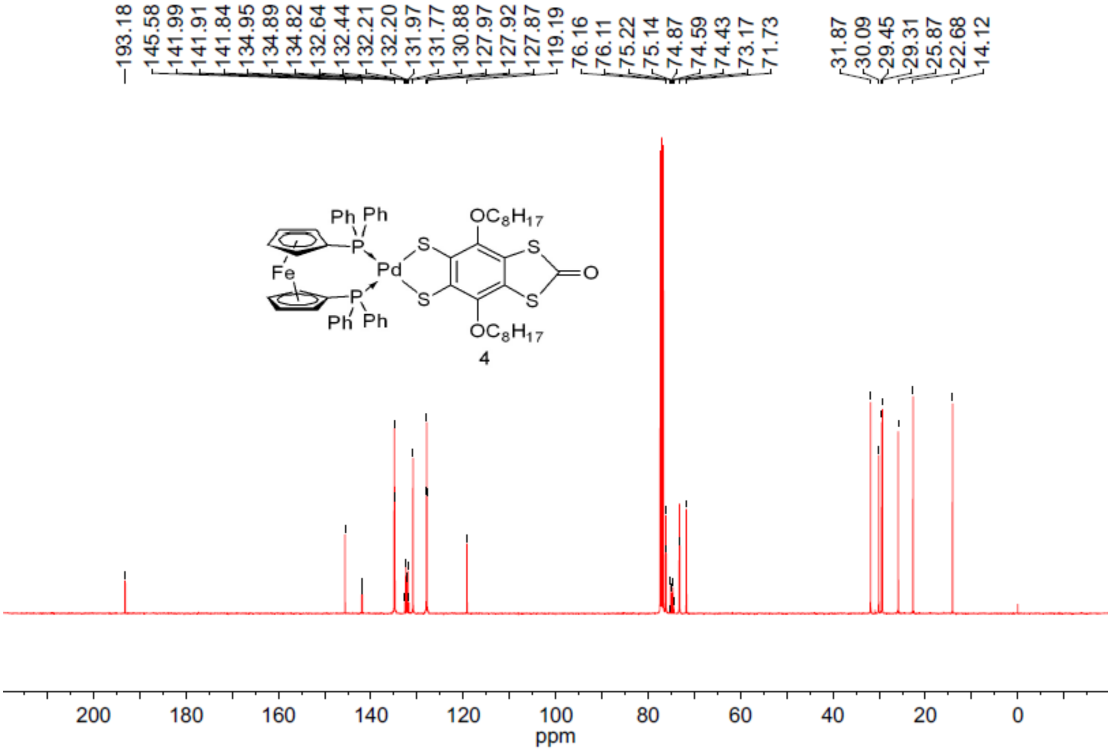
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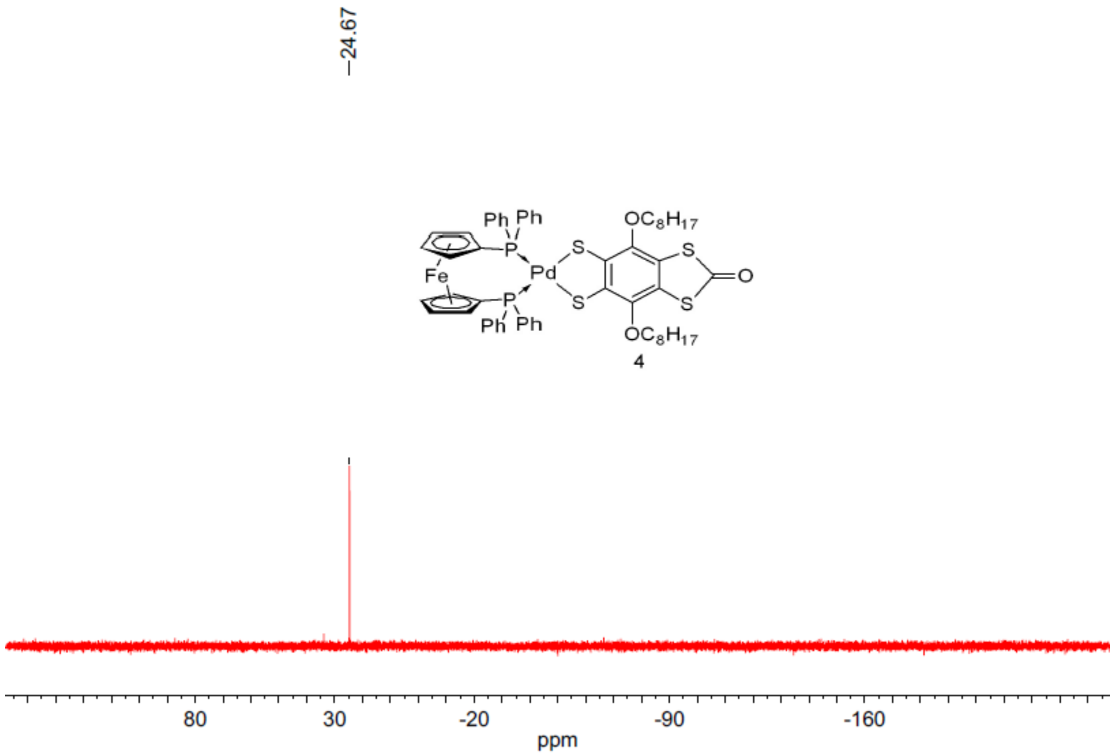
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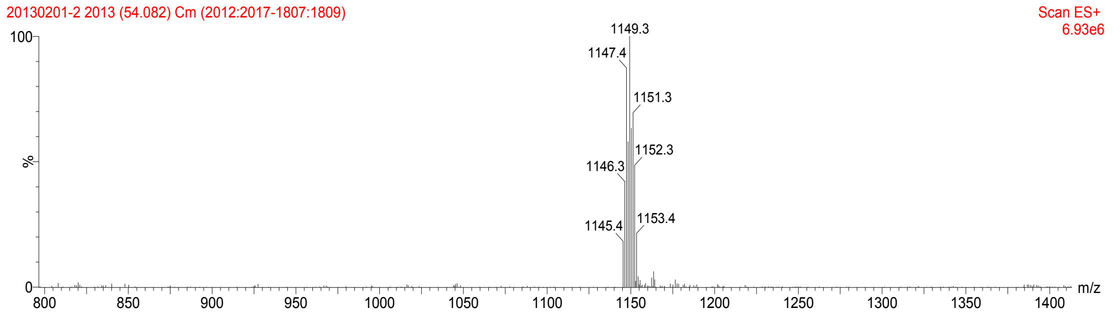
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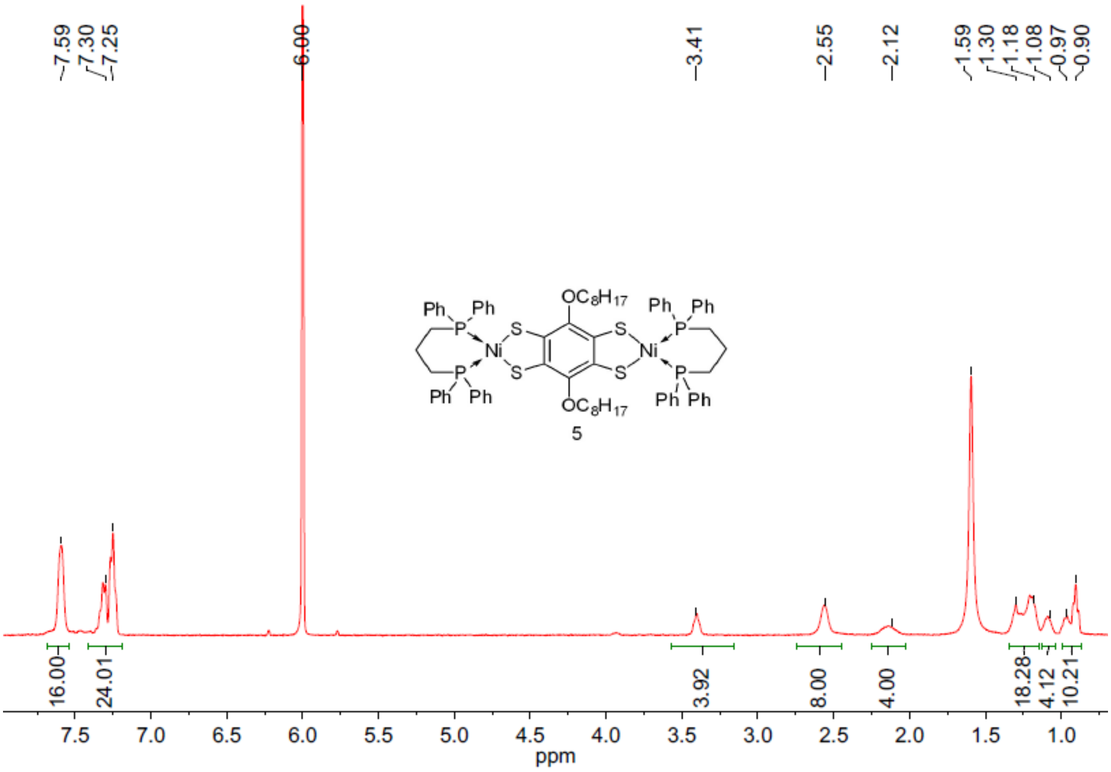
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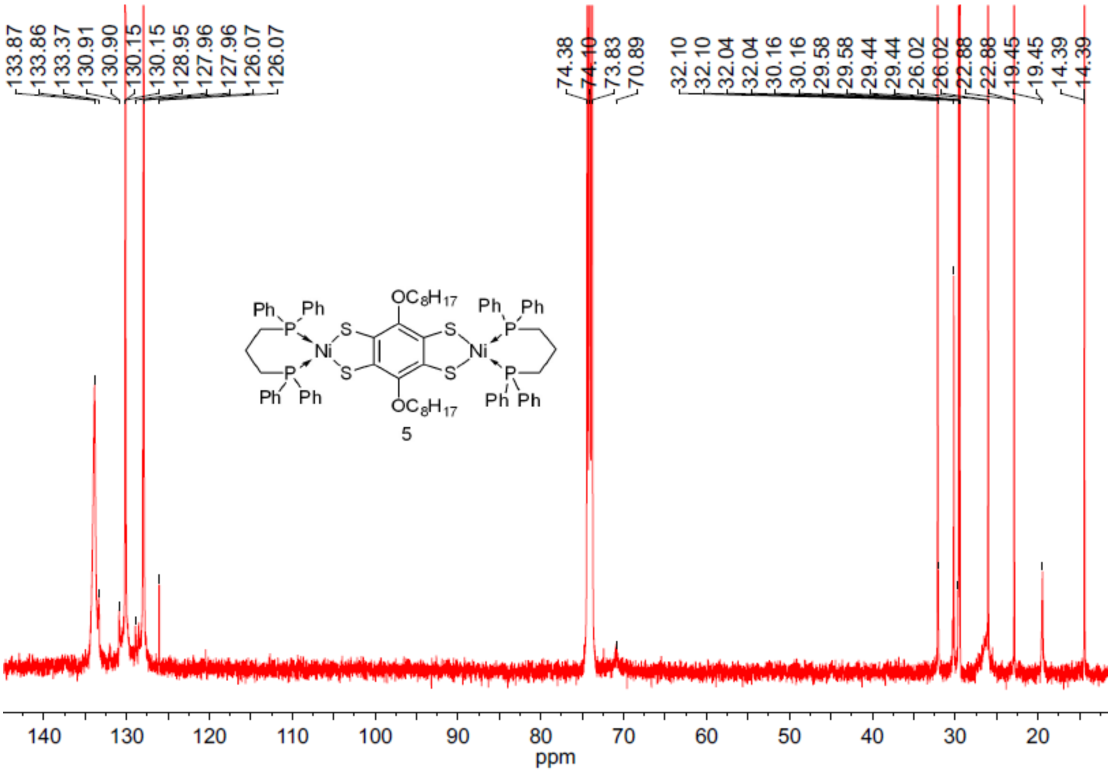
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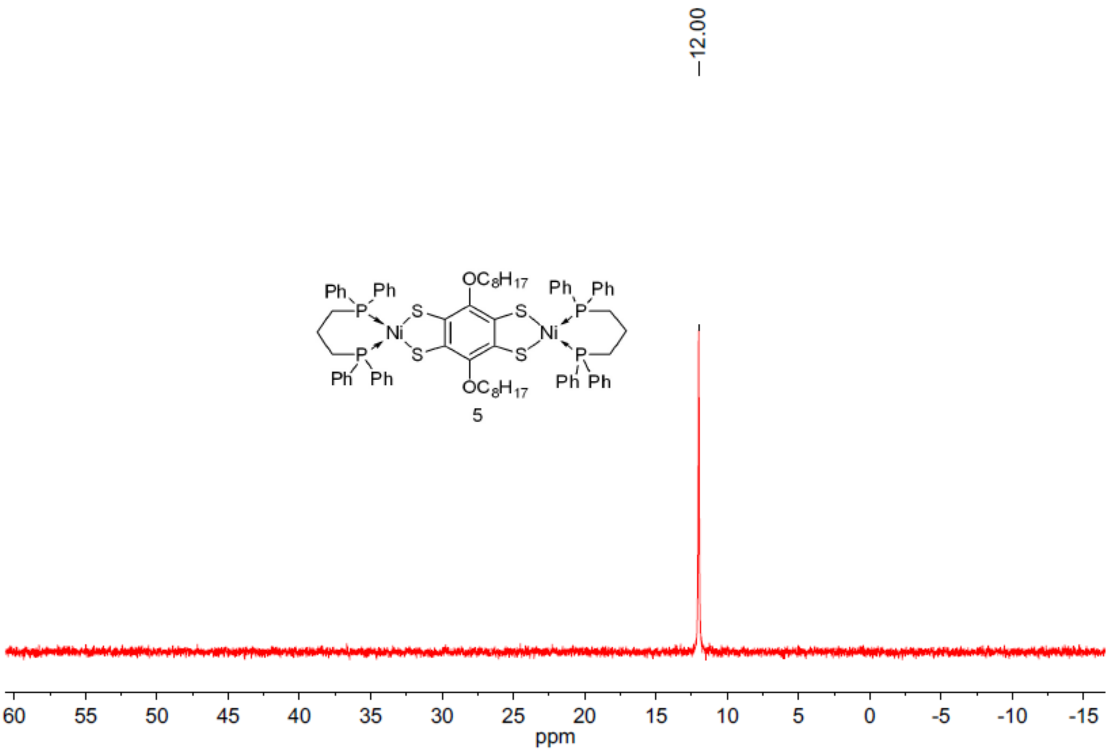

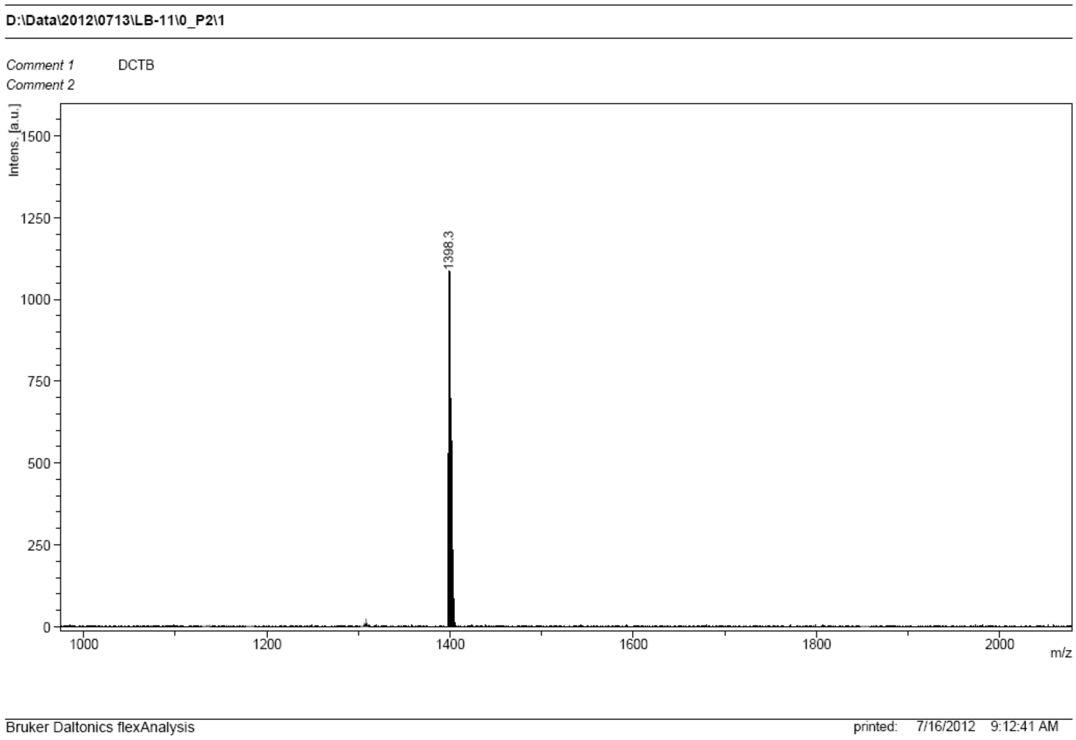

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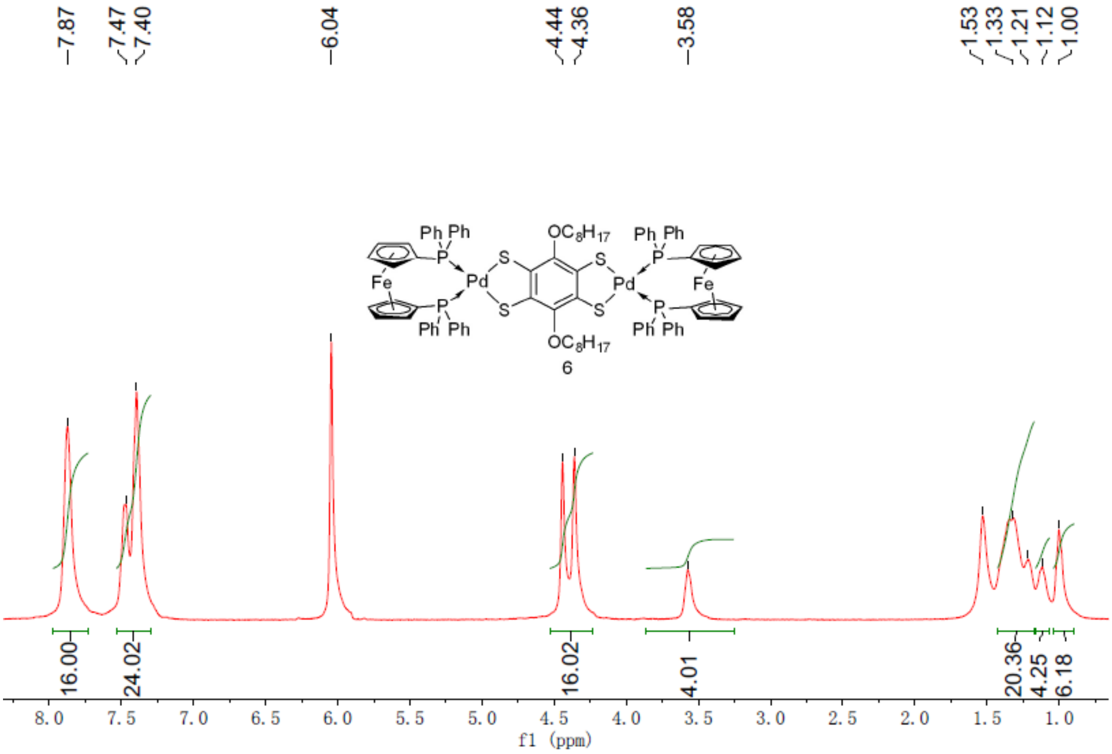
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Fe
Pd
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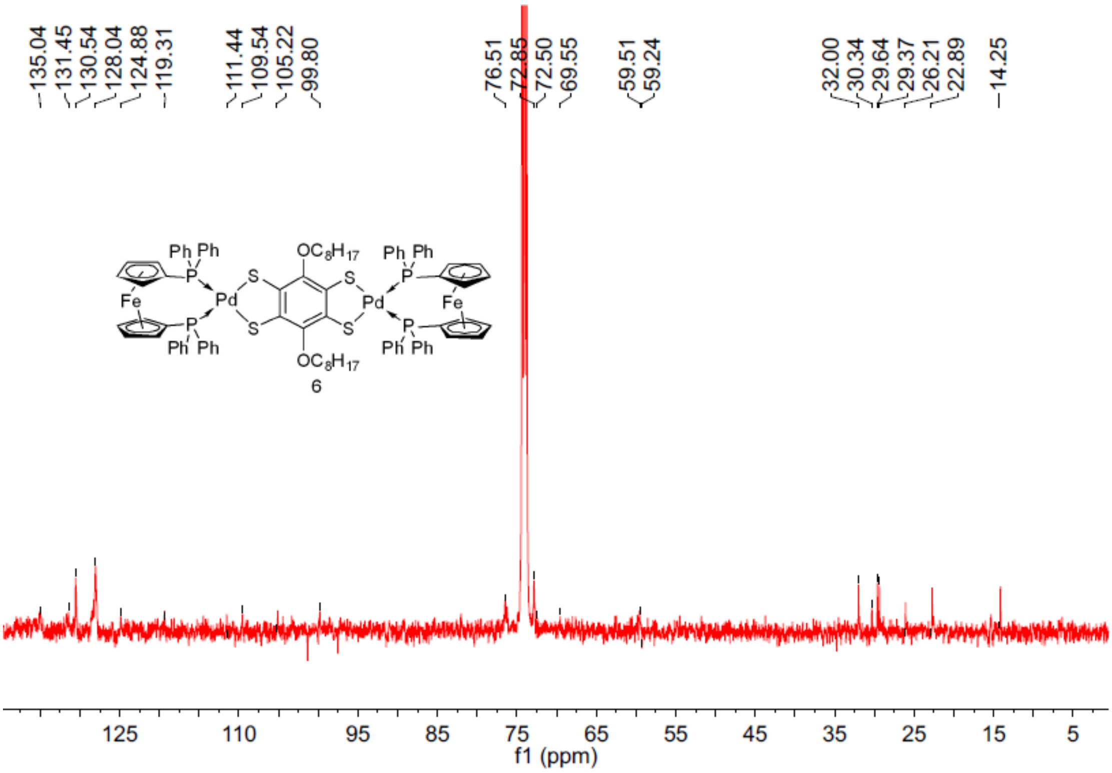
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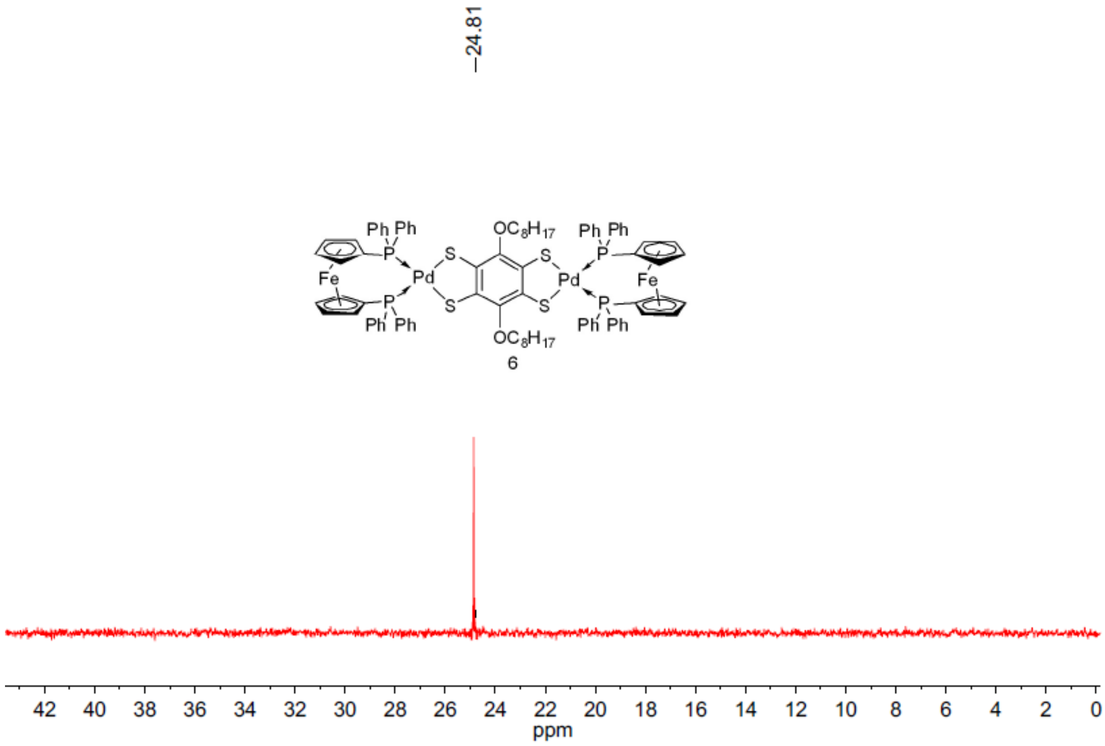

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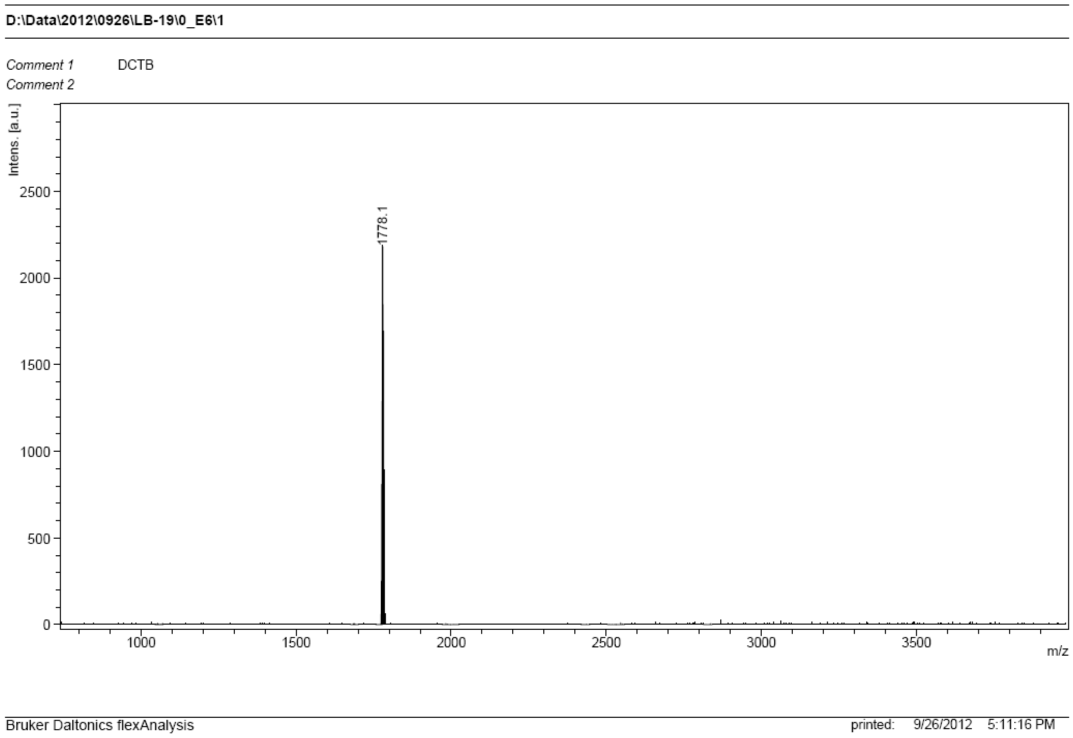
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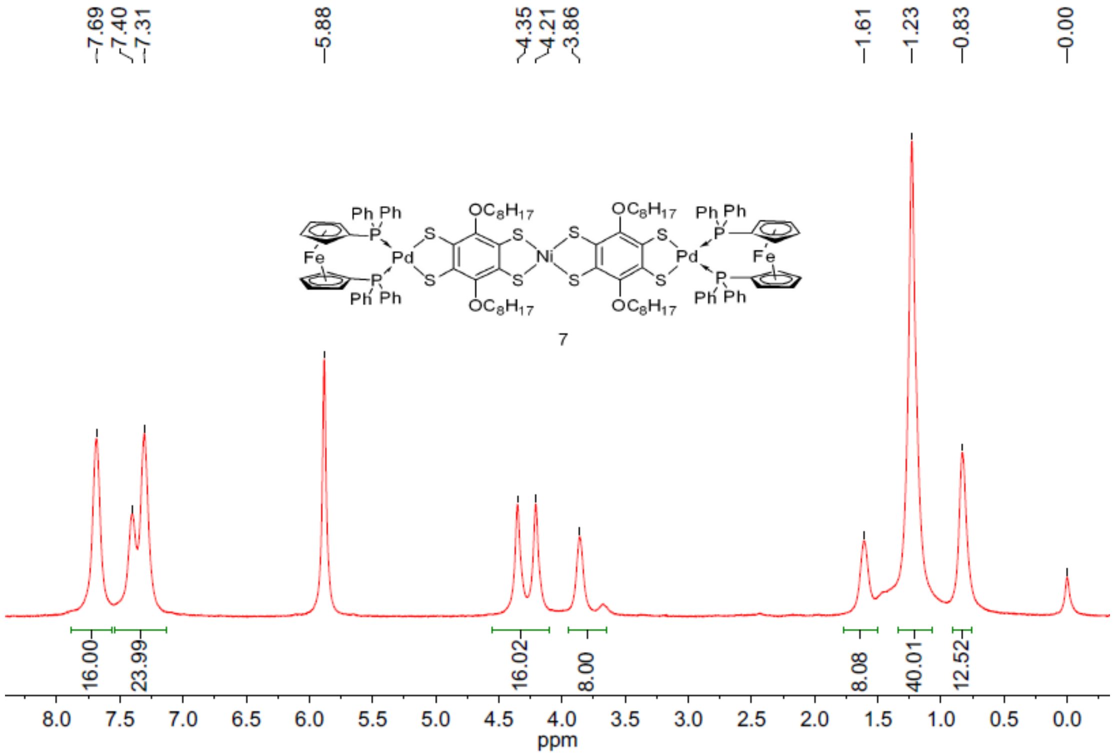
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Pd
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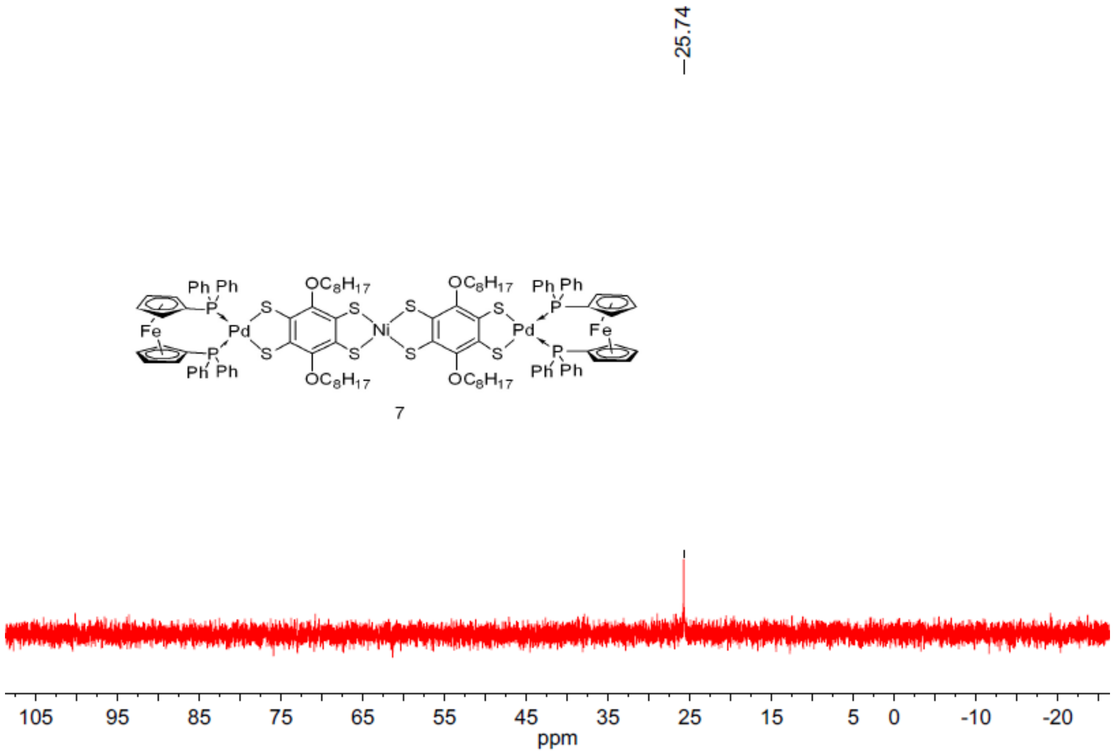
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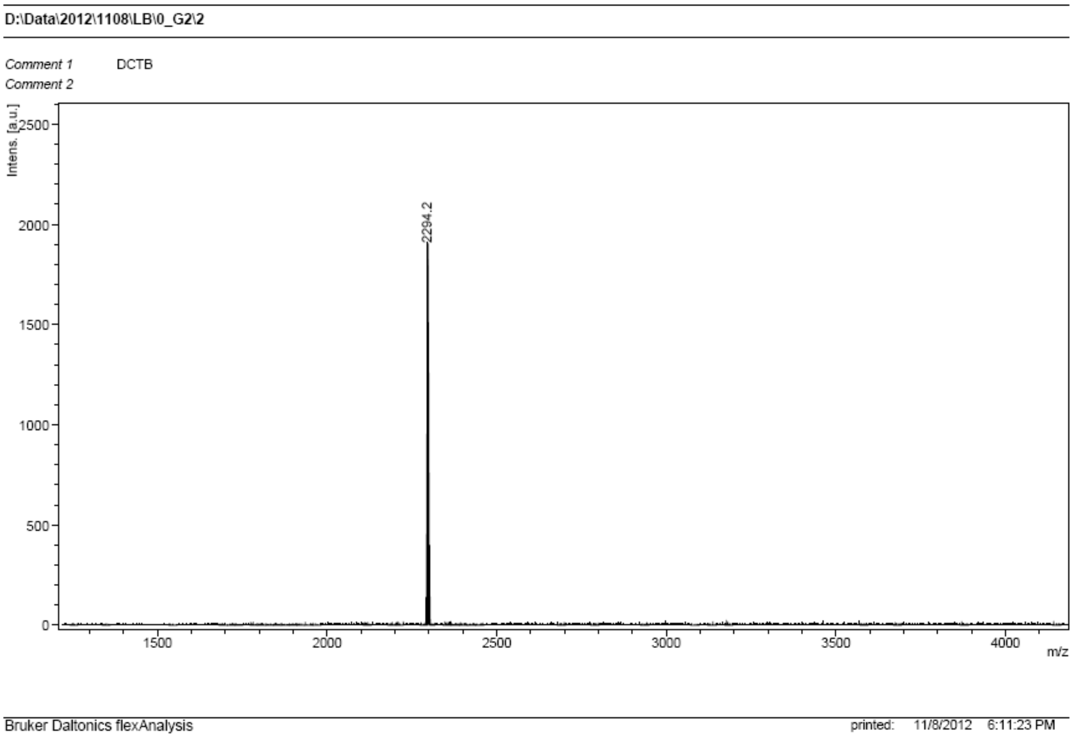
ppm

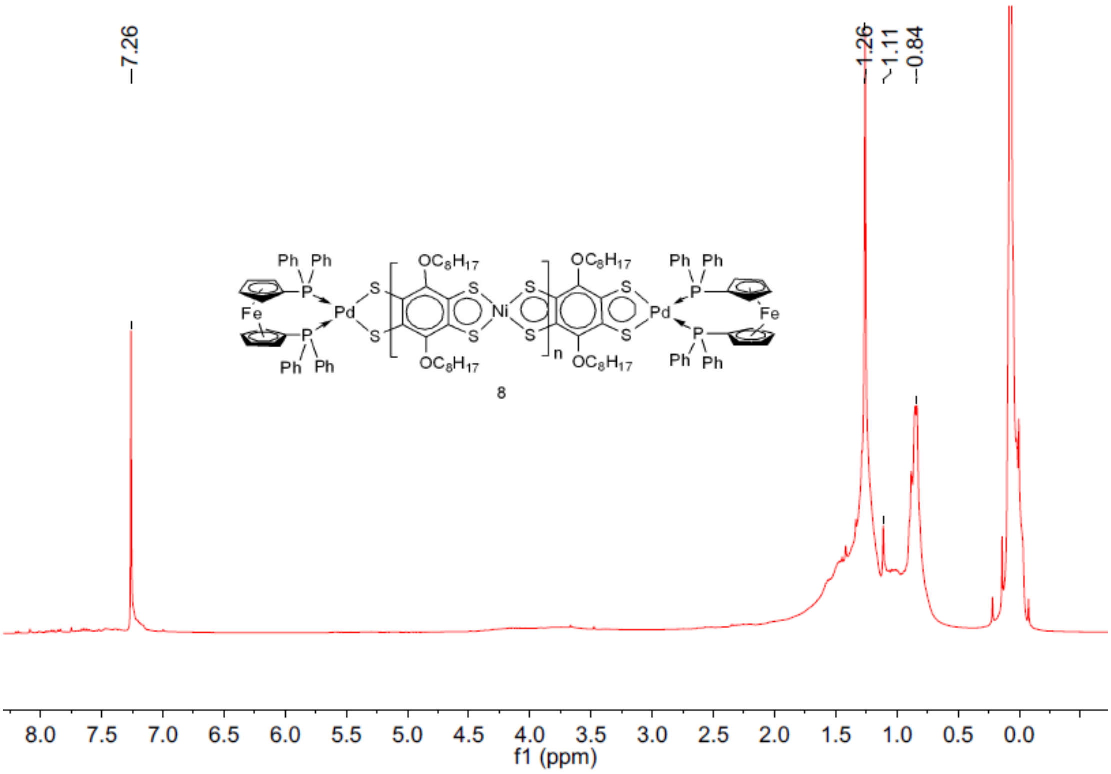
7


D:\Data\2012\1108\LB\0_G2\2

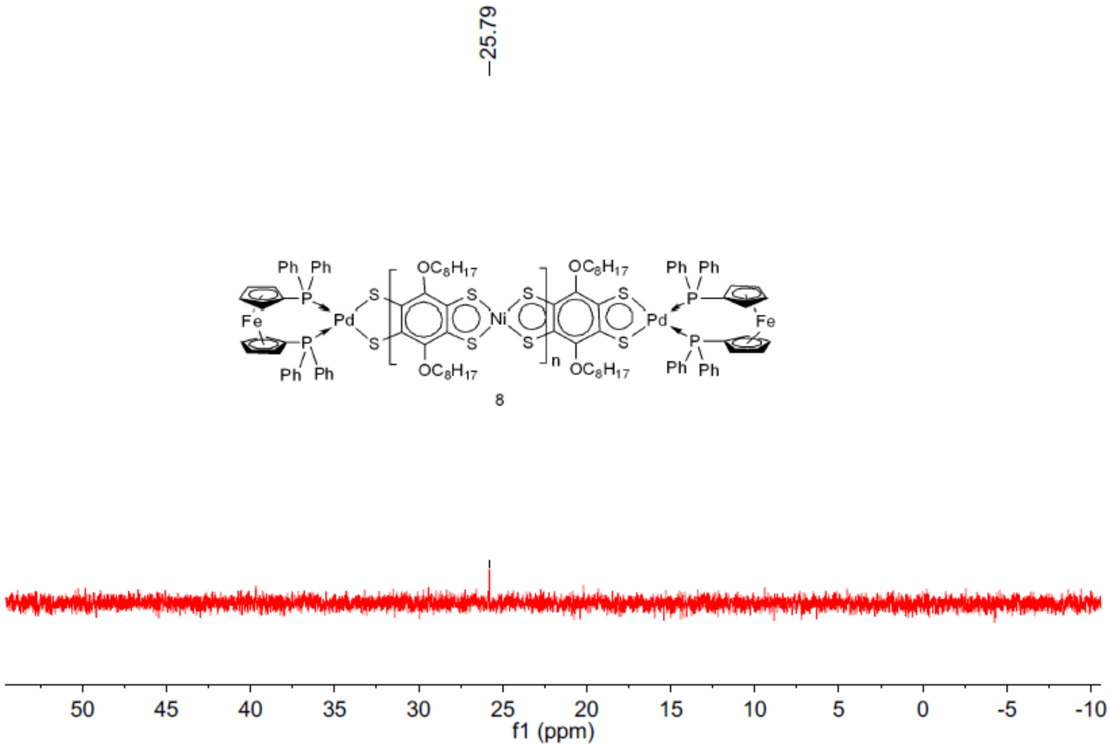
Comment 1 DCTB

Comment 2

Bruker Daltonics flexAnalysis printed: 11/8/2012 6:11:23 PM



8


25.79
Ph
P
Fe
Pd
S
OC_8H_{17}
Ni
n
8
50
45
40
35
30
25
20
15
10
5
0
-5
-10
f1 (ppm)

SI-5. Cyclic voltammograms of complexes 4-7

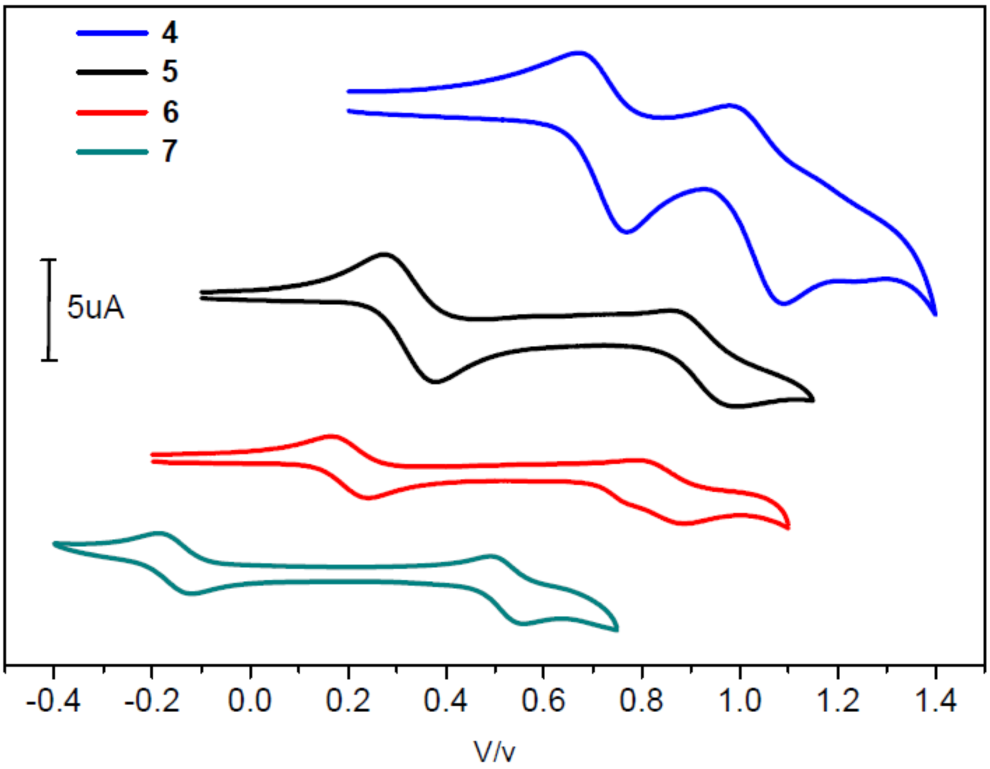


Figure S5. Cyclic voltammograms of complexes **4-7** in DCM.

SI-6. TGA of Polymer 8

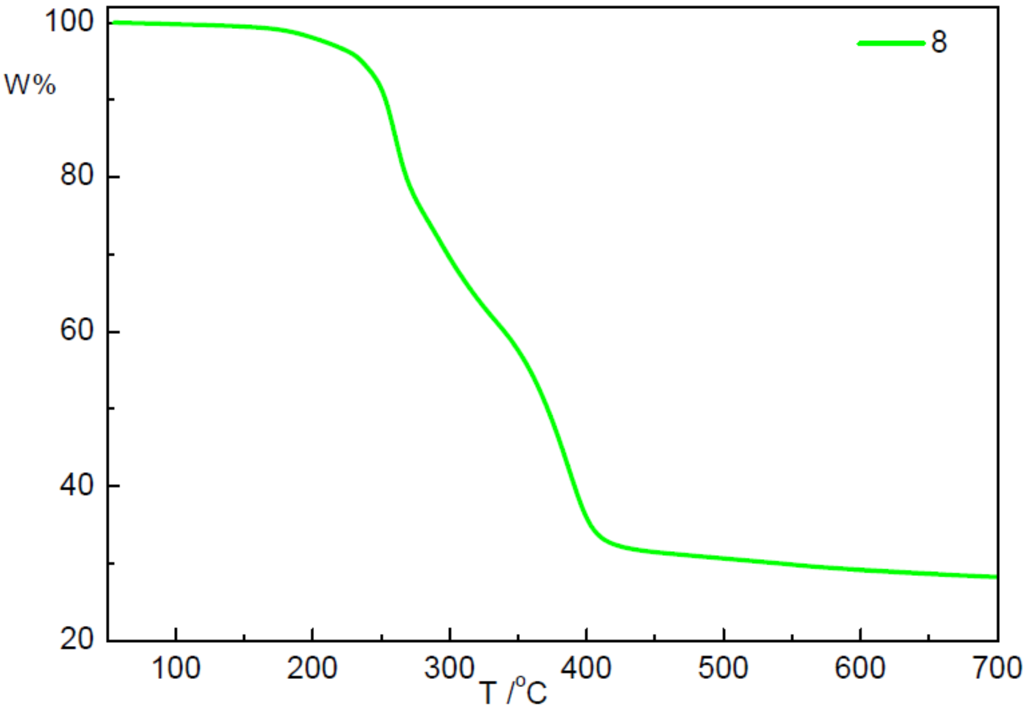


Figure S6. Thermogravimetry of polymer **8** under N_2 with a heating rate of 1 °C/min from 50 to 800 °C.

SI-7. CV for polymer 8

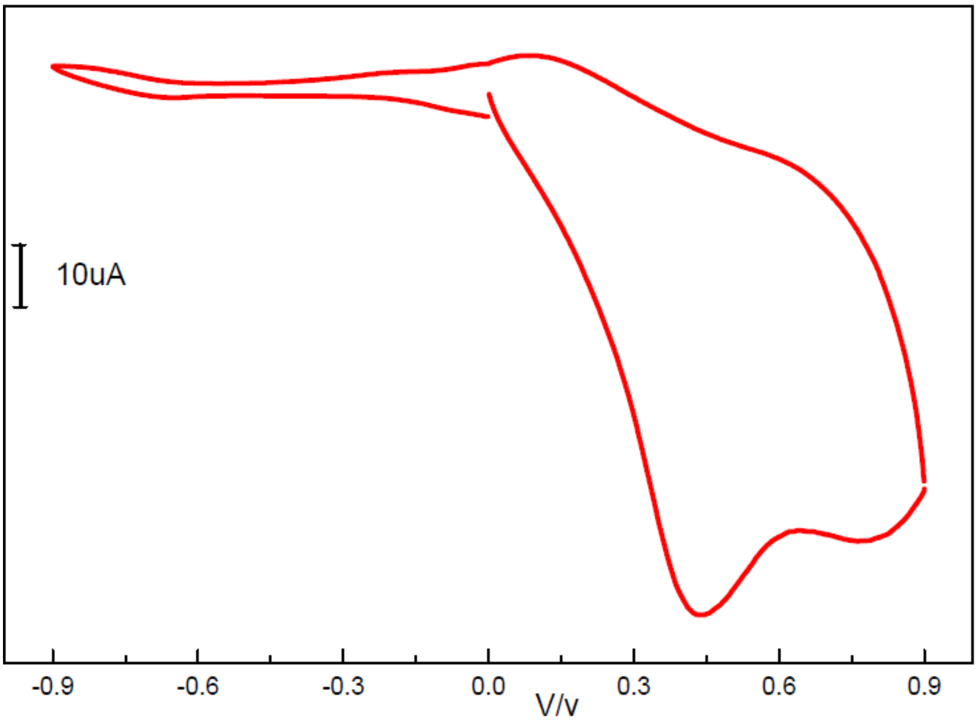
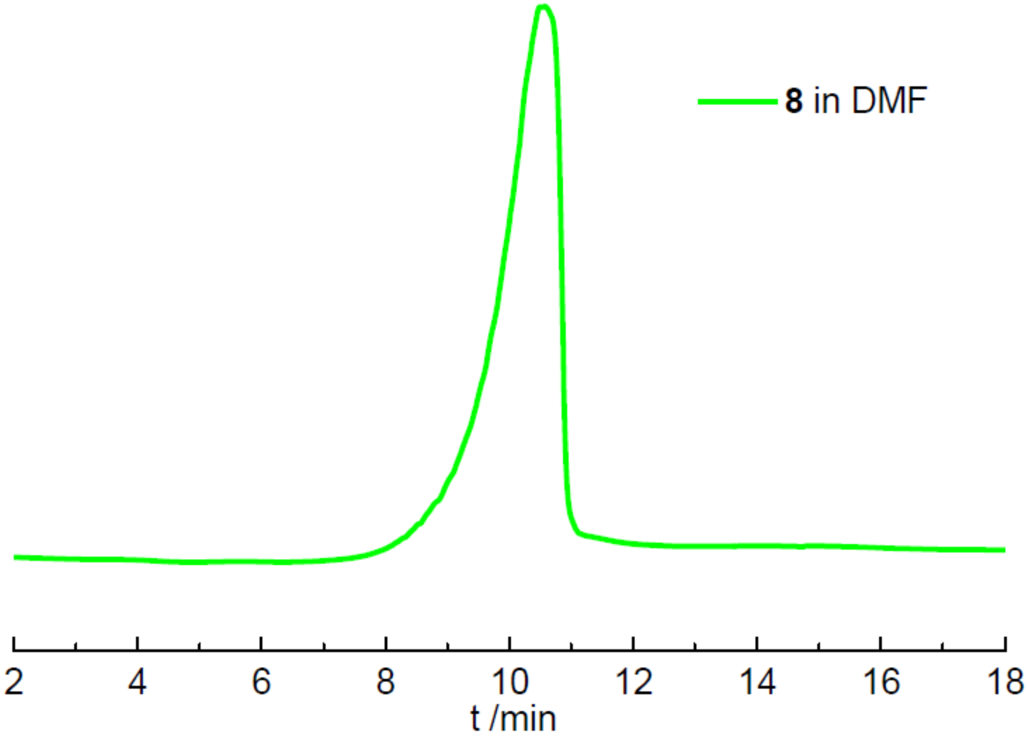


Figure S7. CV of a thin film of polymer **8** coated on the Glass-Carbon electrode in CH_3CN with a scan rate of 100 mv·S^{-1}

SI-8. GPC analysis of polymer 8

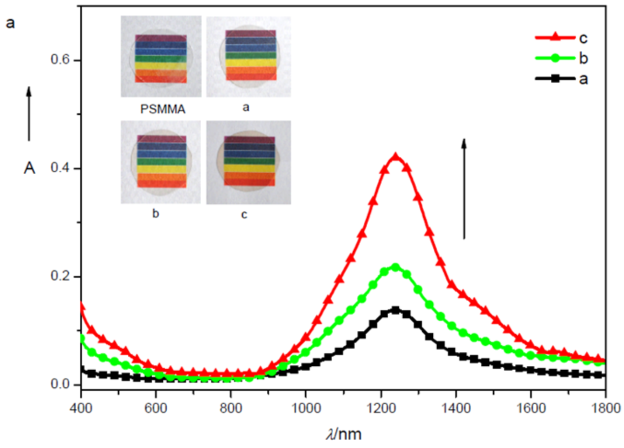


Mn	**Mw**	**Mp**	**Mz**	**Mz+1**	PDI
999052	**1114518**	**776016**	**1303675**	**1594061**	**1.115575**

Figure S8. GPC trace and data of polymer **8**, using DMF as eluting solvent and relative to polystyrene standard.

SI-9. Preparation and characterizations of colorless films from blends of 7 and PSMMA

Complex **7** was blended into poly[styrene-co-(methyl methacrylate)] (PSMMA) with different mass radio (**7**/PSMMA) in chloroform, and the mixture was drop cast on a quartz plate. After evaporation of chloroform, the transparent films were obtained and almost colorless visually. The spectroscopic characterizations and photos of the films placed on color substrate to show visual transparency are shown below.



b:

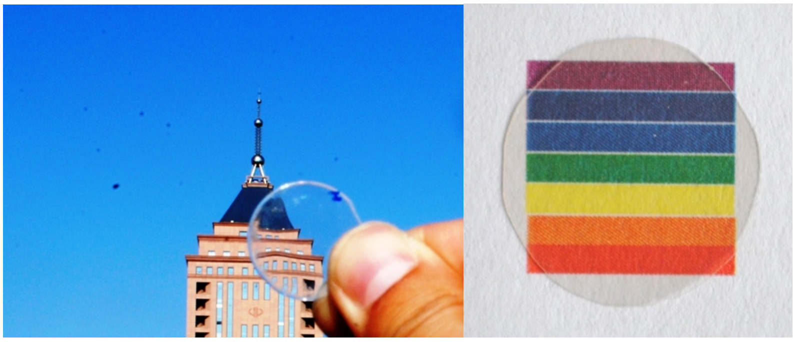


Figure S9. a) Photos of the films of **7** in PSMMA polymer and the absorption of the films with different mass radios of **7**/PSMMA: a (0.3 wt%), b (0.4 wt%), c (0.8 wt%), b) photos of the transparent film b (0.4 wt%) of **7** in PSMMA.

SI-10. Preparation and characterizations of colorless films of 8/PVDF blends

Polymer **8** was dissolved in a different weight together with 75 mg of PVDF in DMF and the polymer solution was then drop cast on a quartz plate. After evaporation of DMF at room temperature in two weeks, the films were obtained in about 0.202~0.204 mm thickness and appear to be light yellow-greenish and transparent visually. The spectroscopic characterizations and photos of the films placed on top of color strips are shown below.

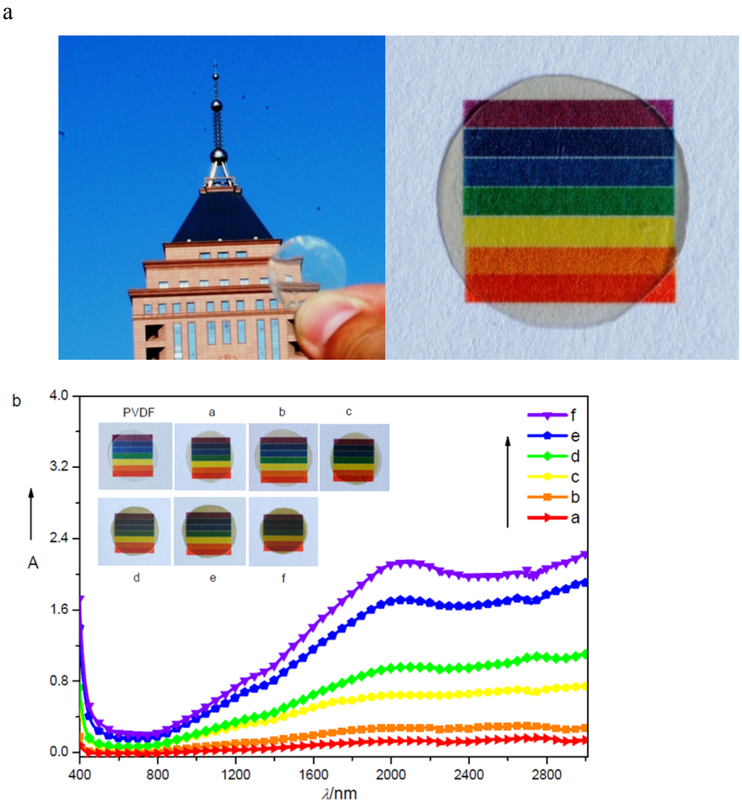


Figure S10. a) Photos of the film d of **8**/PVDF blend. b) Photos and absorption spectra of the films of **8** with a different weight blended in PVDF (75 mg): a (50 µg), b (75 µg), c (125 µg), d (225 µg), e (375 µg), f (475 µg). c) Transmittance (400 – 6400 nm) of polymer **8** blended in PVDF films with different weights of **8** in PVDF (75 mg): a (0.07 wt%), b (0.1 wt%), c (0.17 wt%), d (0.3 wt%), e (0.5 wt%), f (0.63 wt%). Inset: Transparency comparison of PVDF films and **8** blended in PVDF films a-f.

References

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