

Substitution of Thiophene Oligomers with Macrocyclic Endcaps and the Colorimetric Detection of Hg(II)

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Experimental

Elemental analyses were conducted using an Exeter CE-440 Elemental Analyzer. 200 MHz ^1H and 75 MHz ^{13}C (Varian) spectra were obtained at room temperature in CDCl_3 . MS data were collected by directly infusing solutions of each compound into a Thermo-Finnigan Model LCQ MS equipped with an ESI source. Anthracenone **1** was synthesized by a previously reported procedure.⁸ 3-thiophenacetonitrile, 2,2'-bithiophene, 2,2',5',2''-terthiophene, and N-(2-cyanoethyl)-pyrrole were purchased from Aldrich and used without further purification. Melting points were determined in an open capillary and are uncorrected. Low solubility in CDCl_3 and high signal to noise ratio for **4-6** restricted observation of ^{13}C resonances for carbons with no hydrogen atoms attached.

2-(3-thiopheneacetonitrile)-9-(1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-10-one (**2**): 1.00 gram (0.92 mmol) of 3-thiopheneacetonitrile was stirred with 0.085 gram (0.21 mmol) of **1** and warmed to get a clear solution. 3 drops of 70% perchloric acid were added and stirred for 4 hrs. The precipitate was filtered and washed with 5 mL of diethyl ether and air-

dried. The entire crude product was dissolved in CH₂Cl₂-CH₃OH (80:20) and diffused with diethyl ether. A yellow crystalline solid was obtained. Yield: 40 %. Melting point = 223 – 226 °C. Elemental Analyses calculated for C₂₈H₂₆O₆NS: C, 66.52; H, 5.38, N, 2.77 %; Found: C, 65.90; H, 5.14; N, 2.88 %. ¹H NMR ([CD₃]₂CO, 25°C): δ 3.77 – 4.32 (m, 16H, CH₂-O); 4.58 (s, 2H, CH₂-CN); 6.34 (s, 1H, methine); 7.12 (d, 1H, thiophene); 7.25 (d, 2H, anthracenone); 7.42 (t, 2H, anthracenone); 7.52 (d, 1H, thiophene); 7.79 (d, 2H, anthracenone).

5-(2,2'-bithiophene)-9-(1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-10-one (**3**): 0.2 g (0.5 mmol) of **1** and 0.0913 g (0.55 mmol) of 2,2'-bithiophene were mixed with 5 ml of benzonitrile. The solution was stirred for 15 minutes and 5 drops of sulfuric acid were added. The addition of sulfuric acid turned the solution light blue-green with continued stirring for 30 minutes. The benzonitrile solution was mixed with an excess (100 mL) of diethyl ether to precipitate the product. A cream-colored solid was obtained which was filtered off, washed with diethyl ether and air dried. Yield: ~40 %. Melting point = 270-275 °C. Elemental Analyses calculated for C₃₀H₂₈O₆S₂: C, 65.67; H, 5.14; Found: C, 65.64; H, 5.03 %. ESI MS calcd. for [C₃₀H₂₈O₆S₂]⁺ 548.7 m/z; Found 549.0 m/z. ¹H NMR (CDCl₃, 25°C): δ 3.70 – 4.30 (m, 16H, CH₂-O); 6.32 (s, 1H, methine); 6.79 – 7.07 (m, 7H, 2H anthracenone + 5H bithiophene); 7.37 (t, 2H, anthracenone); 7.88 (d, 2H, anthracenone). ¹³C NMR (CDCl₃, 25°C): δ 33.1; 68.1; 69.3; 70.5; 71.1; 115.2; 119.4; 122.6; 122.8; 123.6; 127.3; 127.6; 128.1; 132.3; 133.0; 135.3; 137.9; 145.2; 155.6; 185.2.

Bis(9-(1,8-oxybis(ethyleneoxyethyleneoxy)anthracence-10-one)-5,5'-(2,2'-bithiophene)

(**4**): In an identical procedure substituting 0.5 equivalent of 2,2'-bithiophene (0.0457 g (0.275 mmol)) yields ~20 % of **4**. Melting point = 250 °C (dec). Elemental analyses calculated for C₅₂H₅₀O₁₂S₂: C, 67.08; H, 5.41 %. Found: C, 66.47; H, 5.16 %. ESI-MS calcd. for [C₅₂H₅₀O₁₂S₂]⁺ 930.1 m/z; Found 931.1 m/z. ¹H NMR (CDCl₃, 25°C): δ 3.66 – 4.23 (*m*, 32H, CH₂-O); 6.28 (*s*, 2H, methine); 6.56 (*d*, 2H, thiophene); 6.88 (*d*, 2H, thiophene); 6.97 (*d*, 4H, anthracenone); 7.33 (*t*, 4H, anthracenone); 7.85 (*d*, 4H, anthracenone). ¹³C NMR (CDCl₃, 25°C): δ 68.0; 33.1; 69.3; 70.4; 71.1; 115.2; 119.3; 127.6; 132.2; 155.6.

5-(2,2',5',2''-terthiophene)-9-(1,8-oxybis(ethyleneoxyethyleneoxy)anthracence-10-one (**5**): Compound **5** was synthesized in an identical manner to **3**, using 0.137 g (5.5 mmol) of 2,2',5',2''-terthiophene. Yield: ~60 %. Melting point = 255-258 °C. Elemental analyses calculated for C₃₄H₃₀O₆S₃: C, 64.74; H, 4.79 %. Found: C, 64.23; H, 4.62 %. ESI MS calcd. for [C₃₄H₃₀O₆S₃]⁺ 631.2 m/z; Found 631.1 m/z. ¹H NMR (CDCl₃, 25°C): δ 3.79 – 4.30 (*m*, 16H, CH₂-O); 6.37 (*s*, 1H, methine); 6.81 (*d*, 2H, thiophene); 6.92 – 7.18 (*m*, 7H, 2H anthracenone + 5H thiophene); 7.38 (*t*, 2H, anthracenone); 7.88 (*d*, 2H, anthracenone). ¹³C NMR (CDCl₃, 25°C): δ 33.4; 67.9; 69.4; 70.5; 71.1; 115.2; 119.4; 122.6; 123.3; 124.2; 127.5; 127.8; 128.1; 132.3; 132.9; 145.2; 155.6.

Bis(9-(1,8-oxybis(ethyleneoxyethyleneoxy)anthracence-10-one)-5,5''-(2,2',5',2''-terthiophene) (**6**): 0.2 g (0.5 mmol) of **1** and 0.062 (0.275 mmol) of 2,2',5',2''-terthiophene were combined in ~5 mL of benzonitrile and yields ~70 % of **6**. Melting point = > 300 °C.

Elemental analyses calculated for C₅₆H₅₂O₁₂S₃: C, 65.38 ; H, 5.17 %. Found: C, 65.34; H, 4.98 %. ESI MS calcd. for [C₅₆H₅₂O₁₂S₃]⁺ 1012.2 m/z; Found 1012.2 m/z. ¹H NMR (CDCl₃, 25°C): δ 3.80 – 4.28 (*m*, 32H, CH₂-O); 6.31 (*s*, 2H, methine); 6.70 (*s*, 2H, thiophene); 6.73 (*d*, 2H, thiophene); 6.89 (*d*, 2H, thiophene); 7.01 (*d*, 4H, anthracenone); 7.37 (*t*, 4H, anthracenone); 7.86 (*d*, 4H, anthracenone). ¹³C NMR (CDCl₃, 25°C): δ 33.3; 68.1; 69.4; 70.6; 71.2; 115.2; 119.4; 12.2; 128.1; 132.4; 155.6.

X-ray quality crystals were grown from CH₂Cl₂:CH₃OH mixture (4:1) and diffused with diethyl ether. Crystallographic data were collected at 100 K using MoK_α radiation on a Bruker CCD APEXII diffractometer. Cell constants were determined after integration from typically more than 9,000 reflections.¹² Structures were solved by direct methods using SIR97¹³ and refined using SHELXL-97.¹⁴ Data reduction and refinement were completed using the WinGX suite of crystallographic software.¹⁵ All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. For **6**, the terminal thiophene group is also disordered over two positions in a 2:1 ratio and both positions were refined isotropically. The larger occupancy has the thiophene sulfur atom (S3) facing away from S1 and S2. DFIX restraints were also applied for the thiophene with the lower occupancy. Table S1 below lists additional crystallographic and refinement information.

References:

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Table S1. Crystallographic collection and refinement data.

	2	3	4	5
Empirical formula	C ₂₈ H ₂₇ NO ₆ S	C ₃₀ H ₂₈ O ₆	C ₅₂ H ₅₀ O ₁₂ S ₂	C ₃₄ H ₃₀ O ₆ S ₃
Formula weight	505.57	548.64	931.06	630.76
Temperature, K	125(1)	100(1)	100(1)	100(1)
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P-1	P 21/n	P 21/c	Pna21
<i>a</i> , Å	9.6153(3)	8.2245(4)	13.554(4)	20.811(2)
<i>b</i> , Å	11.8618(6)	17.4342(9)	11.791(3)	17.747(2)
<i>c</i> , Å	12.3299(6)	18.3495(9)	14.702(4)	8.0999(7)
α , °	64.011(1)			
β , °	89.001(1)	92.703(1)	110.179(4)	
γ , °	75.068(1)			
Volume, Å ³	1214	2628	2205	2958
Z	2	4	2	4
Density (calc) g/cm ³	1.383	1.387	1.402	1.416
Absorb.coef.mm ⁻¹	0.179	0.247	0.189	0.298
<i>F</i> (000)	532	1152	980	1320
θ range	1.85-25.05	1.61-25.00	2.27-25.00	1.96-25.00
Index ranges	$\pm 11 \pm 14 \pm 14$	$\pm 9 \pm 20 \pm 21$	$\pm 16 \pm 14 \pm 17$	$\pm 11 \pm 15 \pm 15$
Reflections collected	12029	25448	21043	28177
Independent reflections	4304	4630	3876	5212
Observed reflections	3508	3692	2620	4404
Max/Min trans.	0.922/0.974	0.885/0.973	0.963/0.991	0.835/0.927
Restr./ Param.	6/334	0/343	0/298	7/385
Goodness-of-fit	1.021	1.081	1.034	1.051
Final indices [<i>I</i> >2 σ (<i>I</i>)]	0.0498	0.0427	0.0526	0.0447
R indices (all data)	0.1132	0.1140	0.1245	0.1028
Peak/hole	0.66/-0.62	0.37/-0.48	0.79/-0.38	0.44/-0.37
CCDC #	806525	806528	806527	806529

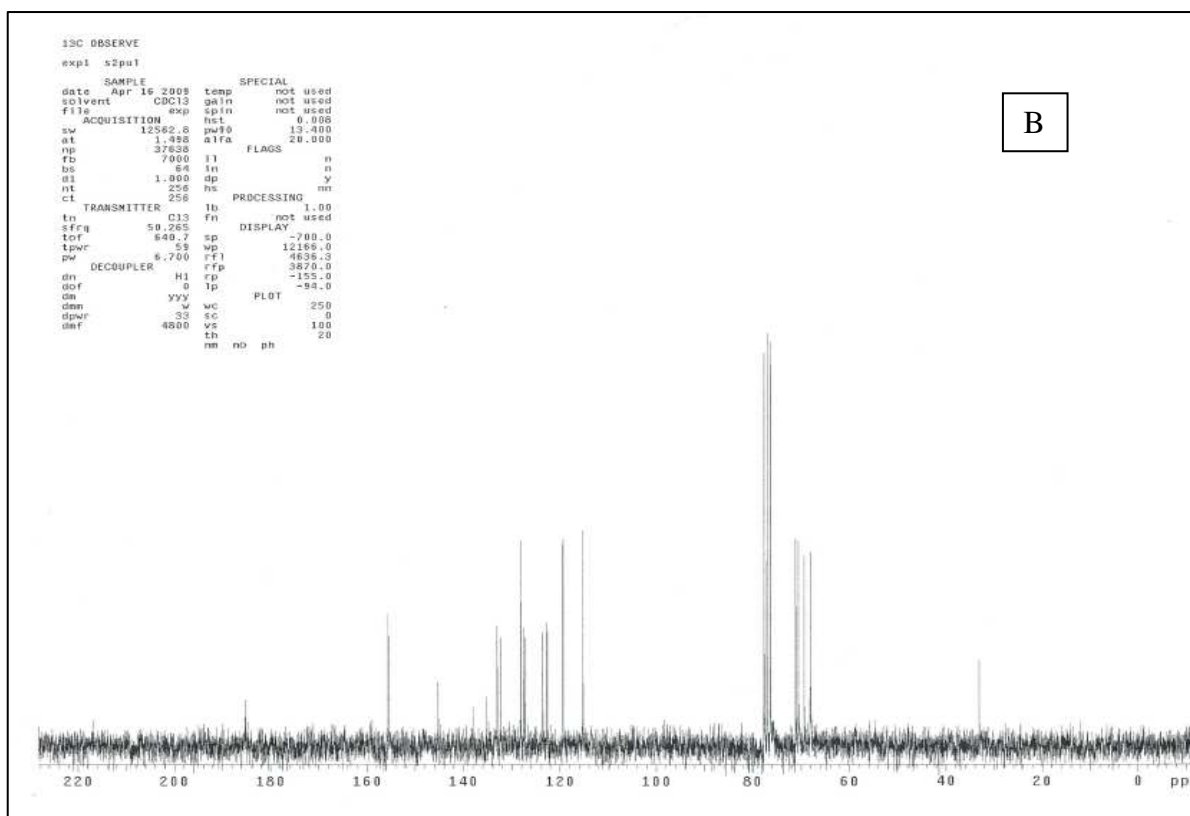
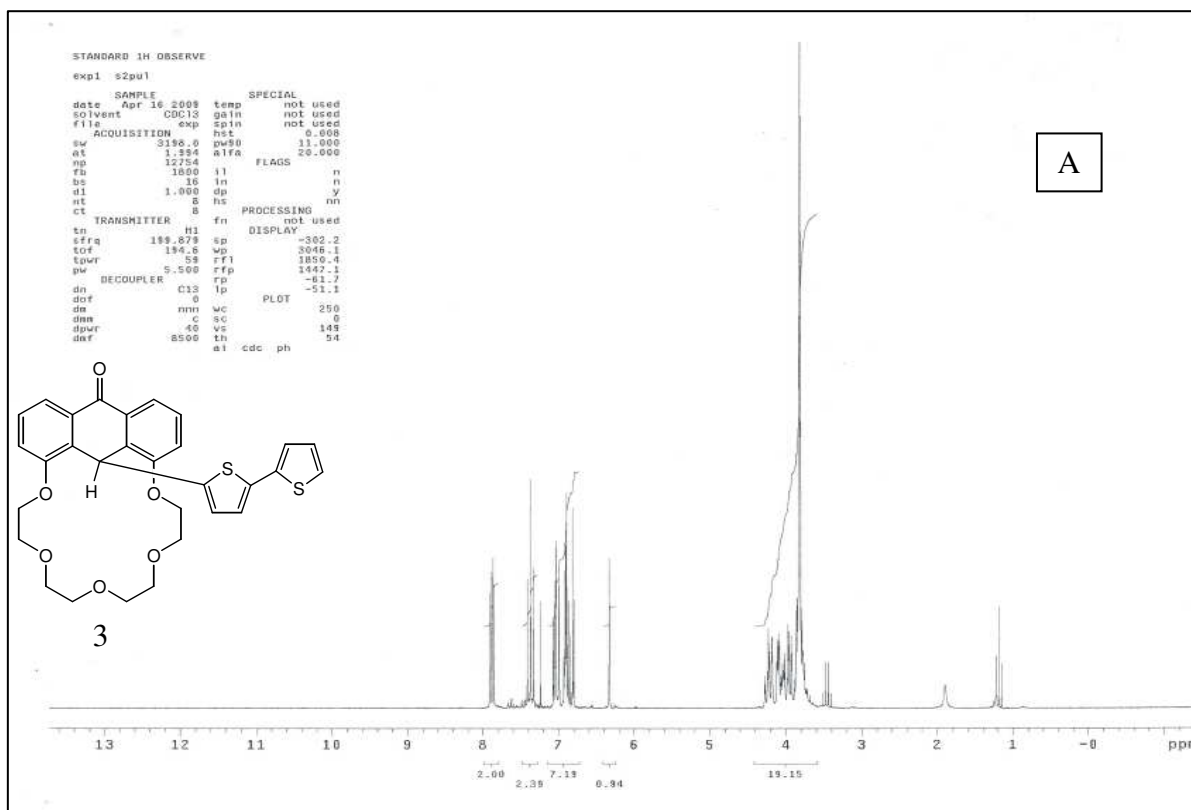


Figure S1: 200 MHz ^1H NMR (A) and ^{13}C NMR (B) spectra of Compound **3** in CDCl_3 .

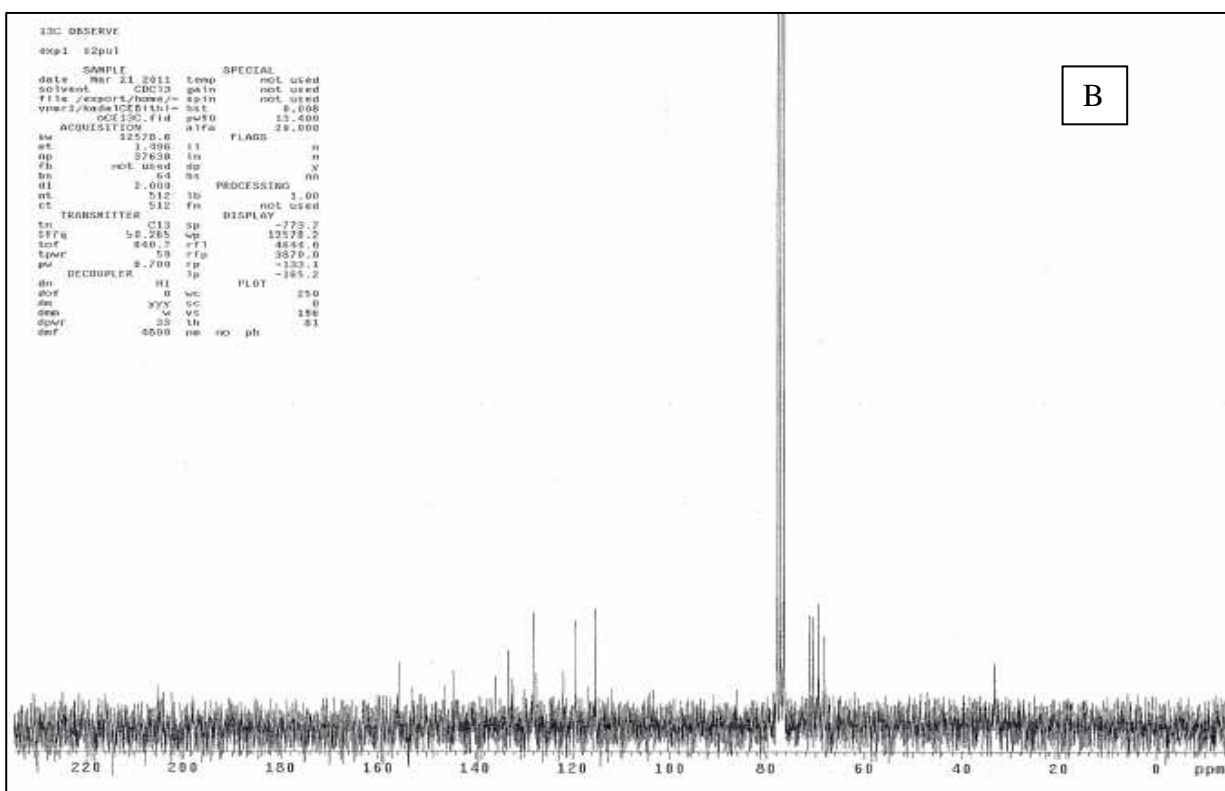
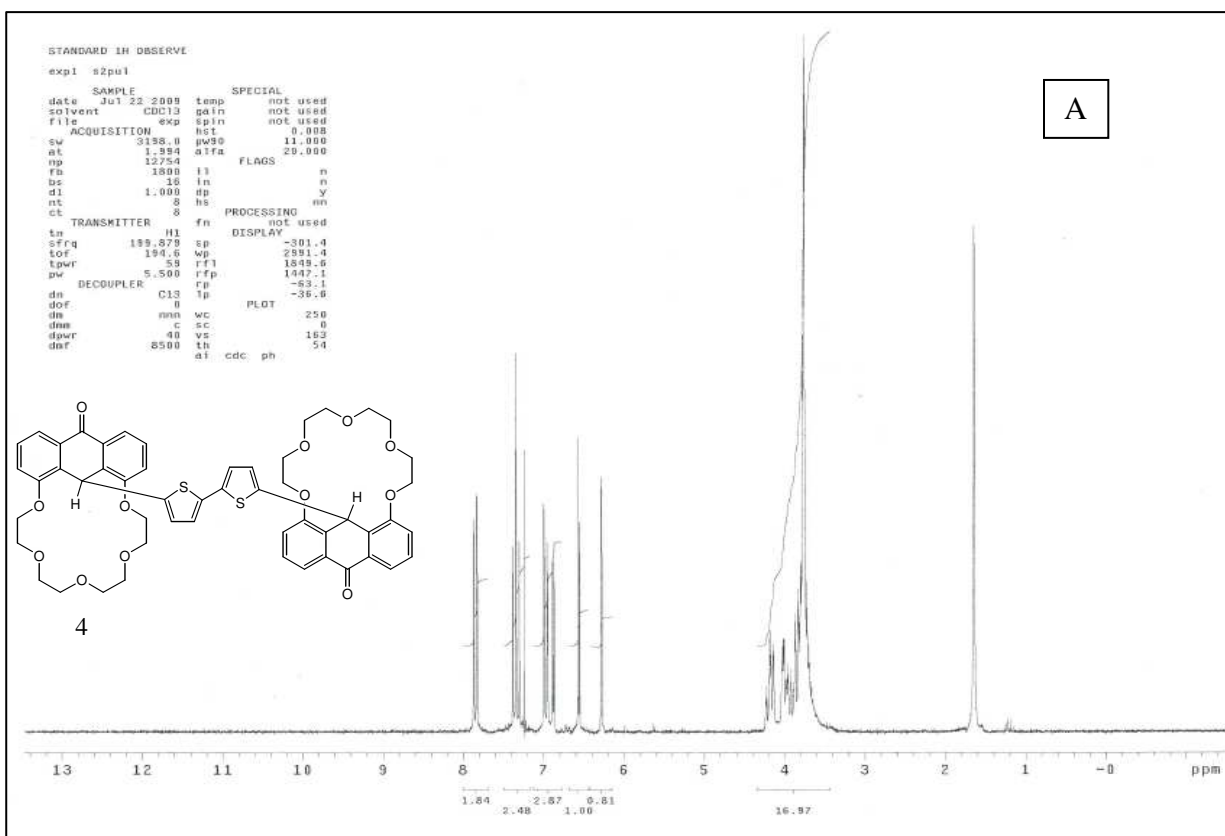


Figure S2: 200 MHz ^1H NMR (A) and ^{13}C NMR (B) spectra of Compound **4** in CDCl_3 .

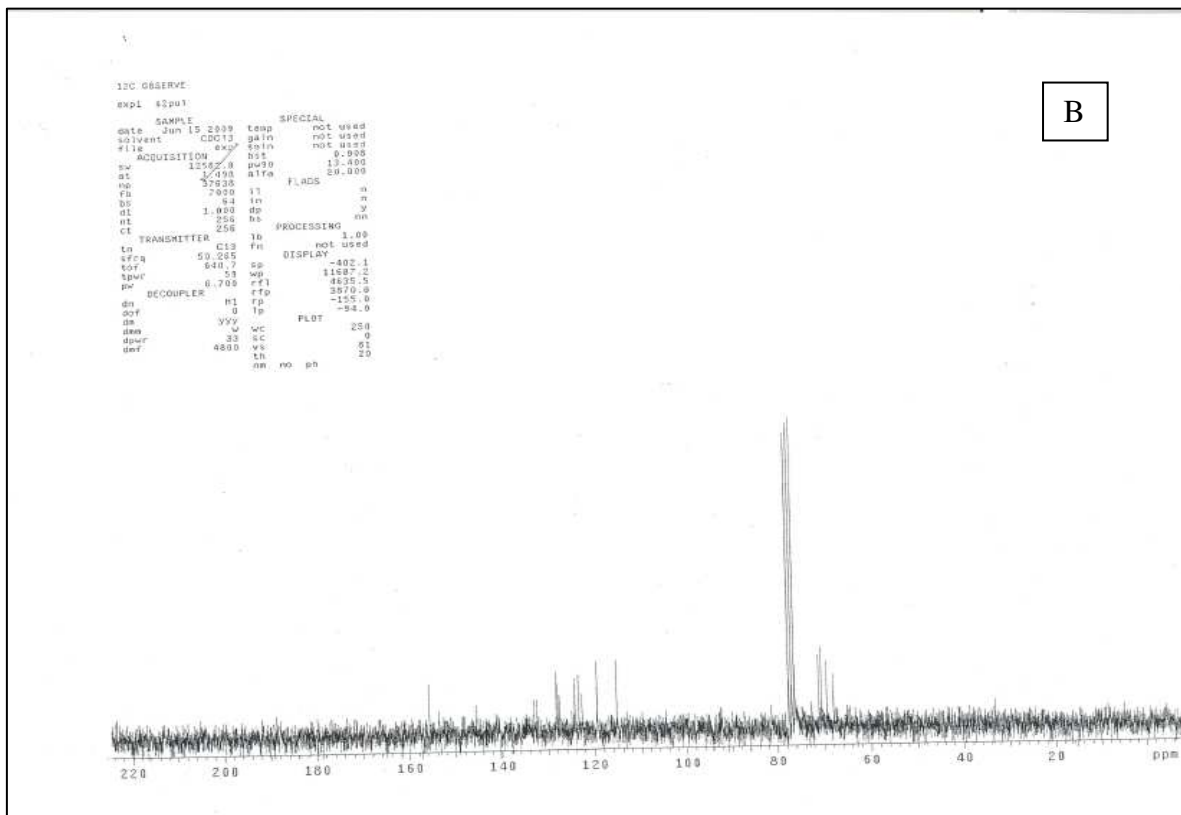
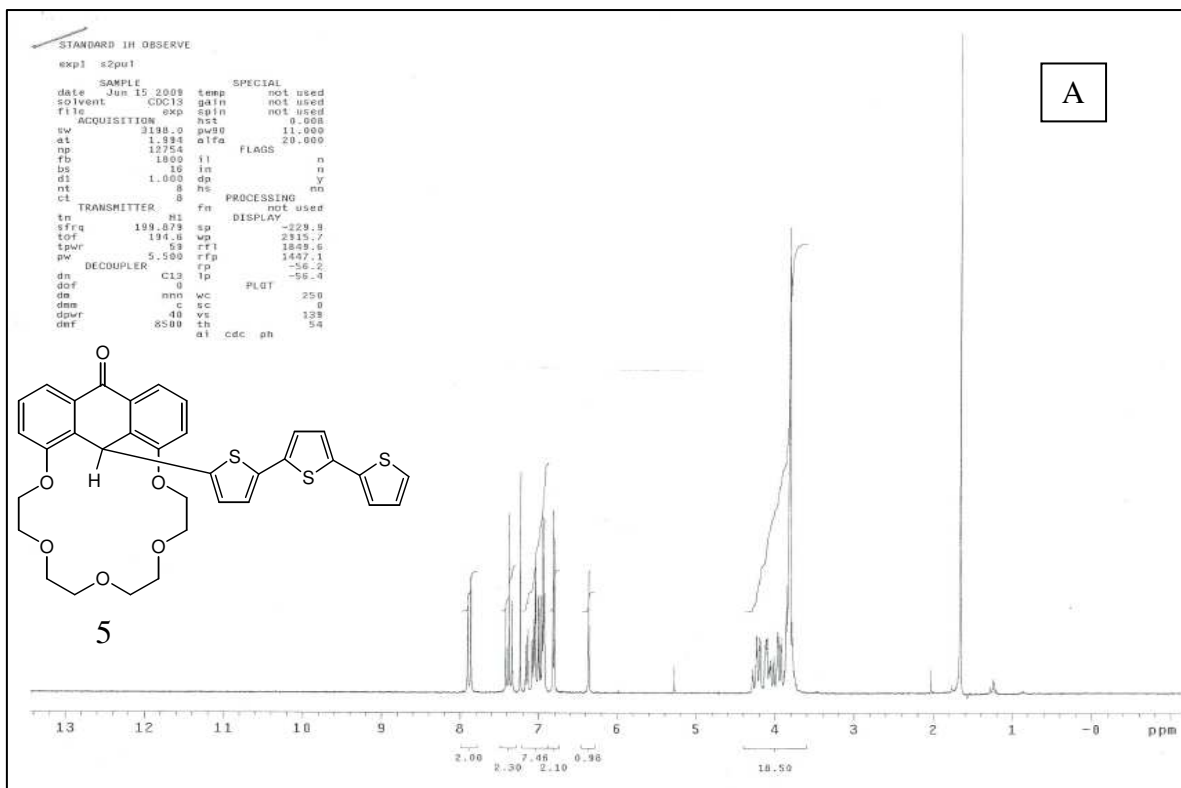


Figure S3: 200 MHz ^1H NMR (A) and ^{13}C NMR (B) spectra of Compound **5** in CDCl_3 .

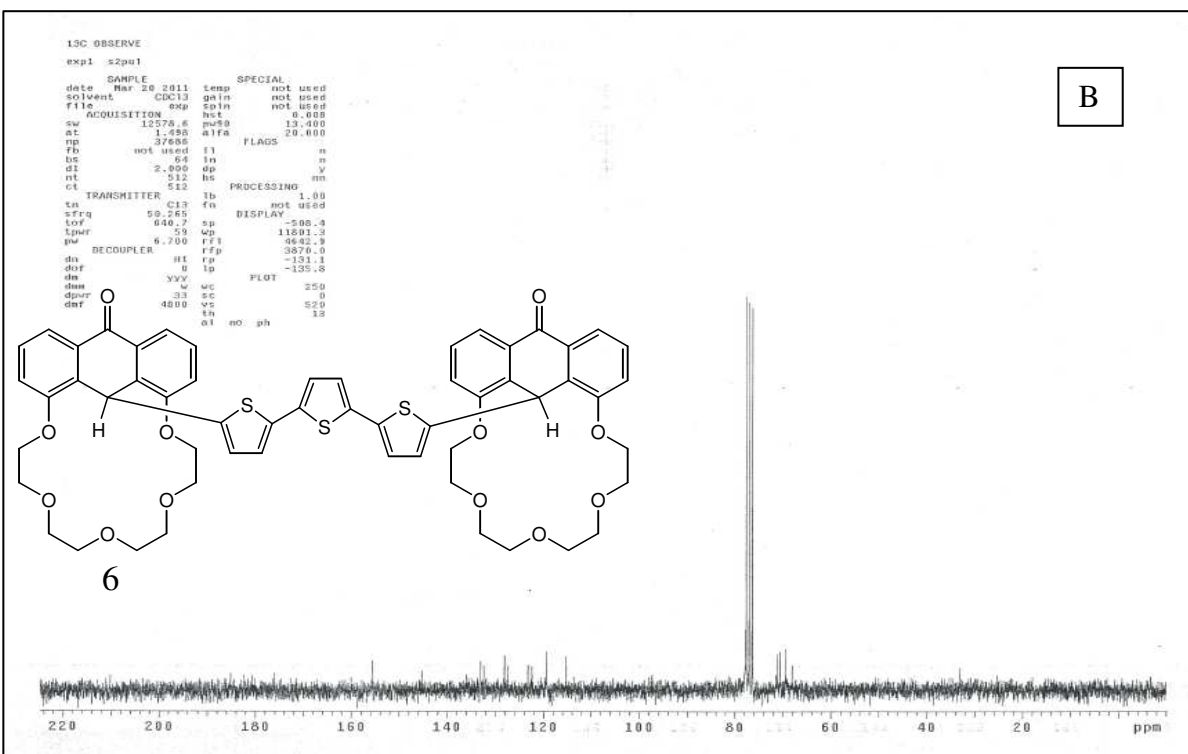
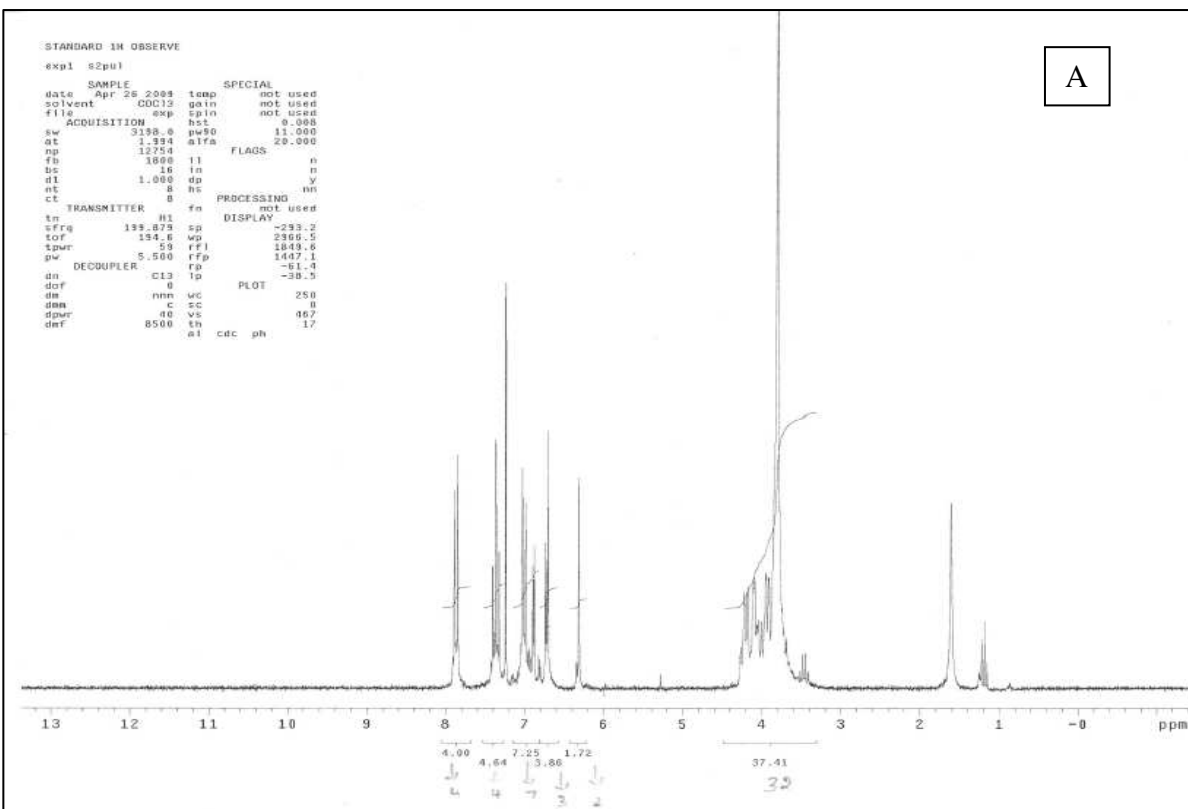


Figure S4: 200 MHz ^1H NMR (A) and ^{13}C NMR (B) spectra of Compound **6** in CDCl_3 .

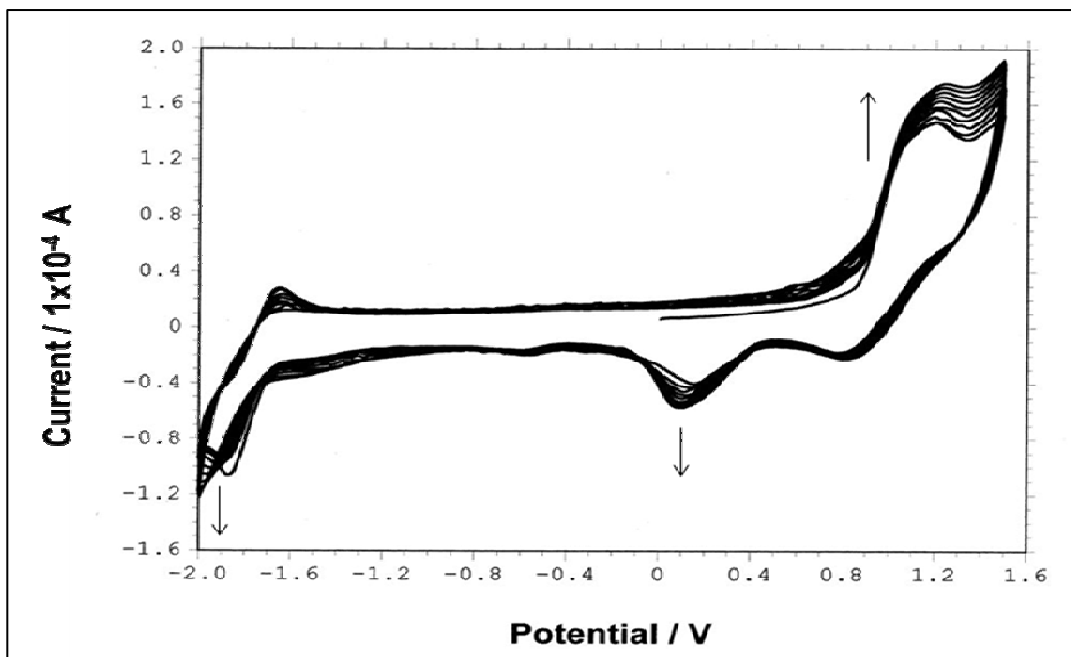


Figure S5. Cyclic voltammogram of the monosubstituted terthiophene adduct, compound **6**, showing film growth with repeated cycling on glassy carbon. 5 mM in 0.05 M TBAH/CH₂Cl₂ vs. Ag/AgCl.

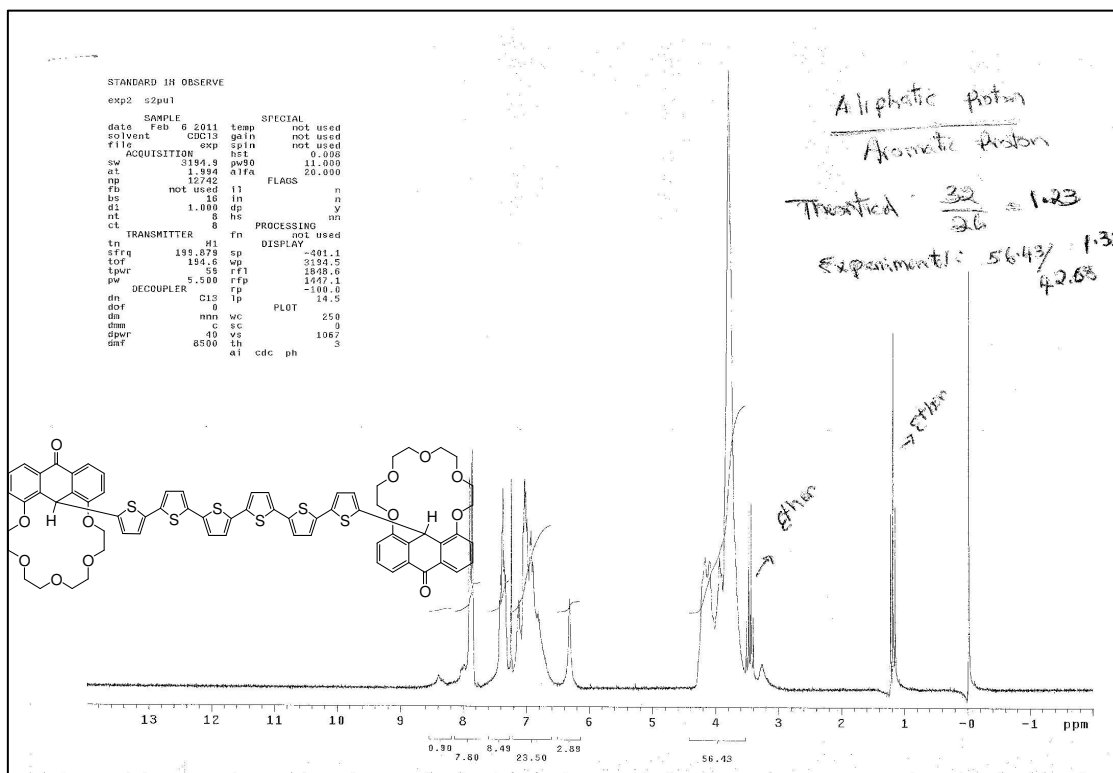


Figure S6. 200 MHz ¹H NMR in CDCl₃. Reaction of compound **5** with Fe(III).

AS_hexathiophene #2 RT: 0.03 AV: 1 NL: 2.30E5
T: + c Full ms2 1259.00@35.00 [345.00-1400.00]

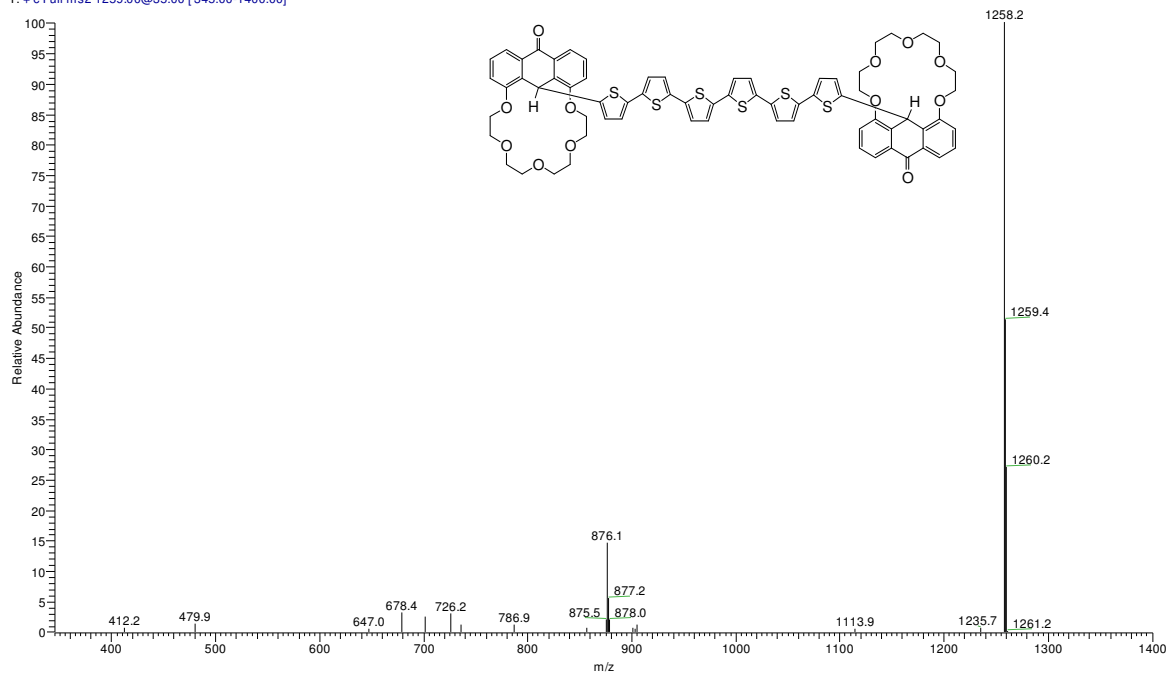


Figure S7. MS-MS with low energy input of 1258 m/z peak. 1258 = diendcapped-hexathiophene.

AS_hexathiophene #52 RT: 1.47 AV: 1 NL: 9.90E4
T: + c Full ms2 1259.00@40.00 [345.00-1400.00]

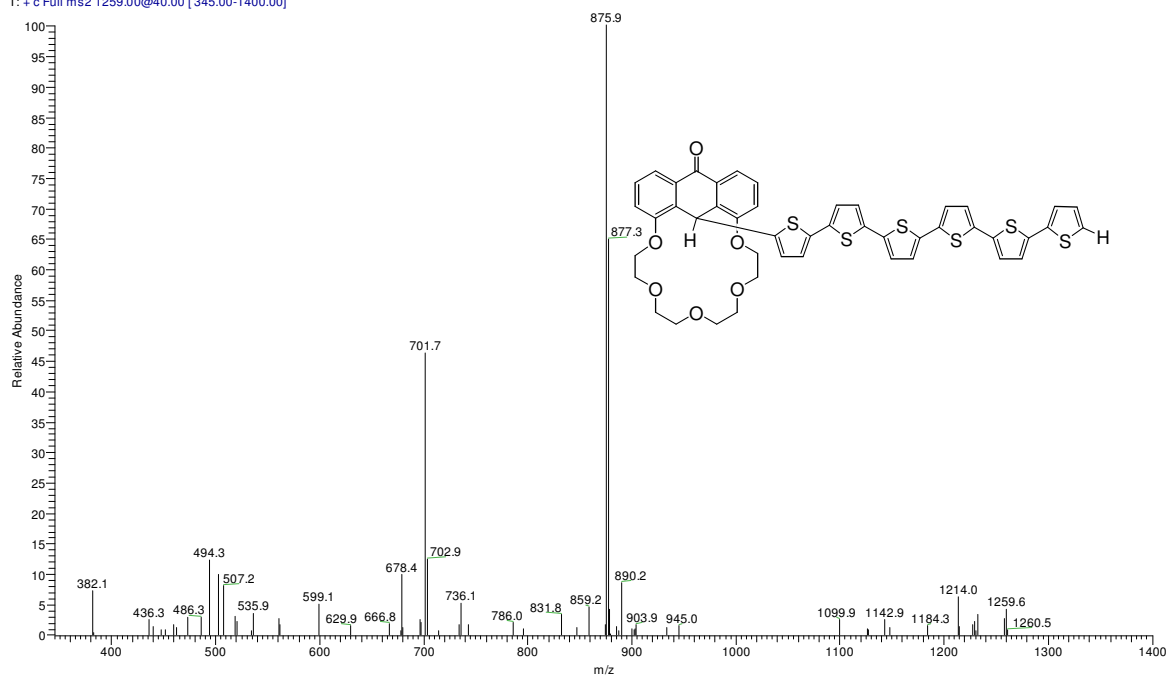


Figure S8. MS-MS at high energy of 1258 m/z peak showing 876 m/z = monocapped hexathiophene fragment

AS_hexathiophene #71-75 RT: 2.11-2.22 AV: 5 NL: 4.75E4
T: +c Full ms3 1259.00@40.00 876.00@35.00 [240.00-900.00]

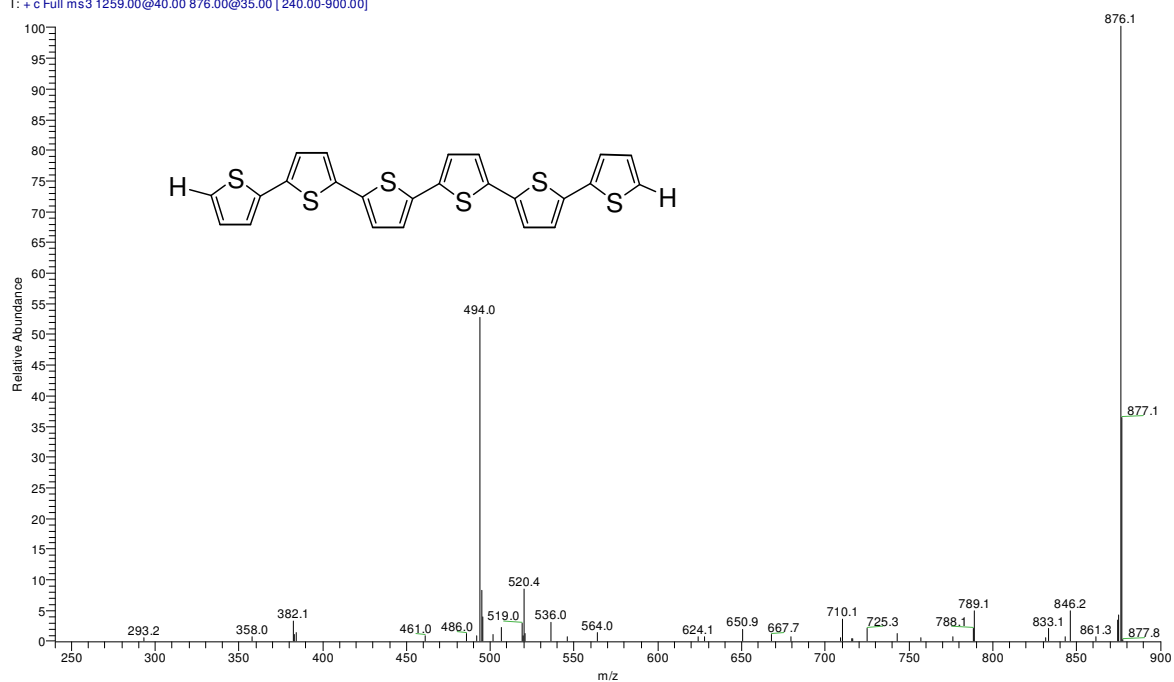


Figure S9. MS-MS-MS of 876 peak showing 494 m/z = hexathiophene fragment.

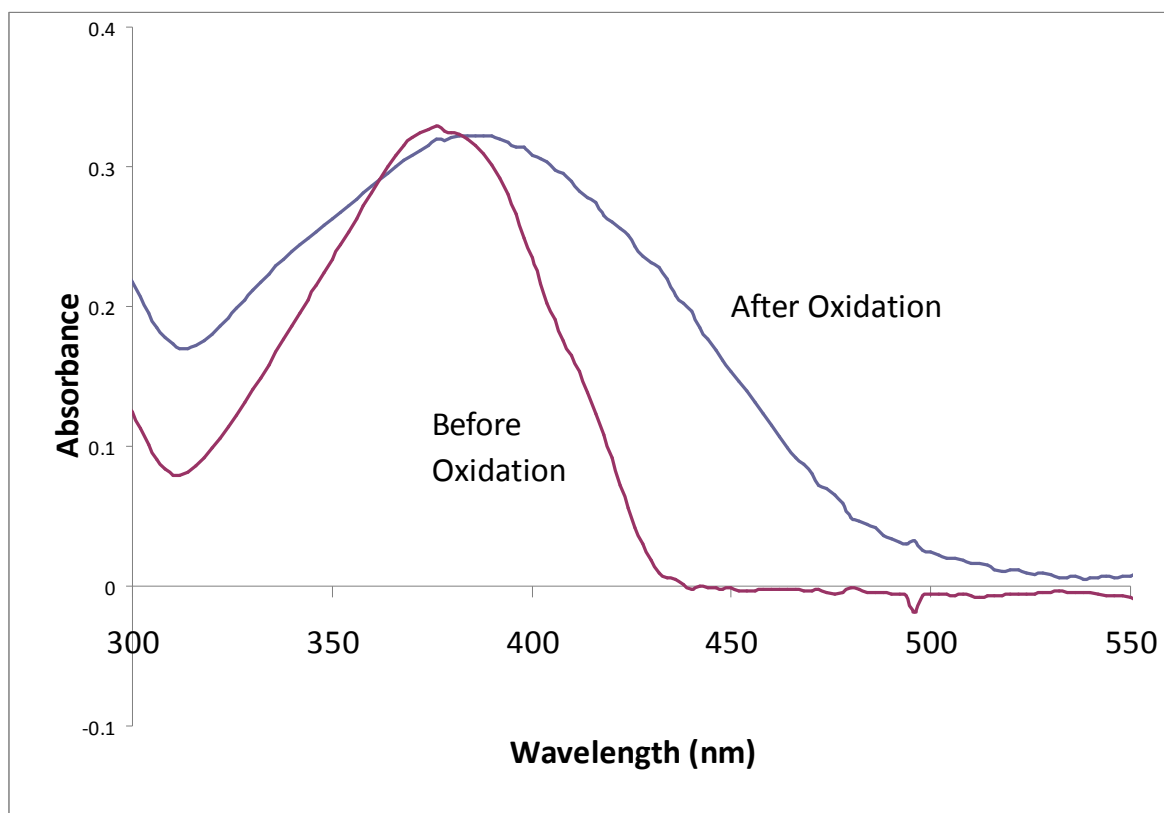


Figure S10. UV/Vis spectrum of compound 5 before and after oxidation by Fe(III).