# Supporting Information

# For

# Near IR absorbing planar aromatic [34]octaphyrins(1.1.0.1.1.0.0.0) containing a quaterthiophene subunit

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## Experimental

### General

All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran and n-hexane were purified and distilled by standard procedure. Electronic spectra were recorded on Perkin-Elmer Lambda 20 UV/Vis spectrophotometer. Proton NMR spectra were obtained on a 400 MHz JEOL spectrometer in $CDCl_3$. FAB-MS spectra were obtained on a JEOL-SX-120/DA6000 spectrometer. Tripyrrane **8 – 11** were synthesized using methods described in reference in the manuscript and stored under inert atmosphere.

### Syntheses

**5,5’’’-bis(mesitylhydroxymethyl)-2,5’: 2’,2’’: 5’’,2’’’-quaterthiophene (7):** An established procedure was used for the synthesis of **7**. Grignard reagent of 2-Bromothiophene (6ml, 62 mmol) was added slowly to 5,5'-dibromo-2,2'-bithiophene (0.55g, 30 mmol), catalyzed by $Ni(dppp)Cl_2$ (0.14 g, 0.26 mmol) in dry THF:Ether (40:40 ml). After conventional workup in ether, column chromatography (silica gel 100-200 mesh, petroleum ether) gave bright yellow solid identified as tetrathiophene. Yield 0.17g, 30%. To a solution of N,N,N’,N’-tetramethylethylenediamine (2.7 ml, 18 mmol) in dry tetrahydrofuran (40 ml), n-butyllithium (11 ml, 18 mmol) was added followed by tetrathiophene (1 g, 3 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for one hour and later heated under reflux for one hour. The reaction mixture was then allowed to attain 25°C. Mesitaldehyde (0.8ml, 7 mmol) in dry tetrahydrofuran was added drop wise to the reaction mixture at 0°C. After addition was over the reaction mixture was allowed to attain 25°C and saturated ammonium chloride was added and it was extracted with ether or chloroform (100 ml). The organic layers were combined and washed with brine (100 ml) and dried over anhydrous sodium sulfate. The crude product obtained on evaporation was recrystalized from dry toluene, which afforded the pale solid, identified as **7,** Yield: 0.8g; $^1$H NMR (300 MHz, $CDCl_3$, δ): 7.02-6.97(m, 4H), 6.97(d, J = 4.5Hz, 2H), 6.88 (s, 4H), 6.54(d, J = 4.2Hz, 2H), 6.42(d, J = 4.2Hz, 2H), 2.35 (s, 12H), 2.29 (s, 6H). EI MS (*m/z*): 626.9(80%)[$M^+$].

**Octaphyrin (12):** A mixture of **7** (0.17g, 0.27 mmol) and tetrapyrrane **8** (0.18g, 0.27 mmol) were dissolved in dry dichloromethane (200 ml) and stirred under nitrogen atmosphere for 5 min. *Para*-toluenesulfonic acid (PTSA) (0.01g, 0.05 mmol) was added and the stirring was continued for 90 min. Chloranil (0.20g, 0.81 mmol) was added and the reaction mixture was exposed to air and refluxed for a further 90 min. The solvent was evaporated in vacuum. The residue was purified by chromatography on a basic alumina column, first red band which eluted with dichloromethane/petroleum ether (1:5) gave **12** in (0.07g, 20.2%); $^1$H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ = 8.75 (d, J = 4.2 Hz, 2H), 8.72 (d, J = 4.2 Hz, 2H), 8.55 (d, J = 4.2 Hz, 2H), 7.91 (d, J = 4.5 Hz, 2H), 7.29 (d, J = 4.5 Hz, 2H), 7.13 (s, 4H), 7.10 (s, 4H), 6.97 (d, J = 4.2 Hz, 2H), 5.57 (d, J = 4.2 Hz, 2H), 4.05 (d, J = 4.2 Hz, 2H), 2.50 (s, 6H), 2.46 (s, 6H), 2.22 (s, 12H), 2.13 (s, 12H); FAB-MS: m/z (%): 1238.70 (100) [M]; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (ε x $10^{-4}$ $M^{-1}cm^{-1}$): 578 (9.7), 766 (2.7), 842 (5.1); ($CH_2Cl_2$/TFA): $\lambda_{max}$ (ε x $10^{-4}$ $M^{-1}cm^{-1}$): 650 (22.6), 985 (1.9), 1090 (7.8); elemental analysis: calcd (%) for $C_{72}H_{60}N_2S_4Se_2$: C 69.77, H 4.88, N 2.26; found: C 69.61, H 4.79, N 2.23.

**Octaphyrin (13): 7** (0.17g, 0.27 mmol) and tetrapyrrane **9** (0.14g, 0.27 mmol) were subjected to conditions similar to those mentioned above with PTSA (0.01g, 0.05 mmol) and Chloranil (0.20g, 0.81 mmol). Purification by column chromatography on basic alumina gave a red colored band with dichloromethane/petroleum ether (1:5), which yielded a green brownish metallic solid on evaporation of solvent identified as **13** in (0.136 g, 18%); $^1$H NMR (300 MHz, $CDCl_3$, 25° C, TMS): $\delta$ = 9.09 (d, J = 4.1 Hz, 2H), 9.04 (d, J = 4.1 Hz, 2H), 8.85 (d, J = 4.2 Hz, 2H), 8.15 (d, J = 4.5 Hz, 2H), 7.46 (d, J = 4.5 Hz, 2H), 7.21 (d, J = 4.5 Hz, 2H), 7.17 (s, 4H), 7.15 (s, 4H), 4.69 (d, J = 4.2 Hz, 2H), 3.33 (d, J = 4.2 Hz, 2H), 2.53 (s, 6H), 2.50 (s, 6H), 2.18 (s, 12H), 2.13 (s, 12H); FAB-MS: m/z (%): 1144.25 (100) [M]; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$ x $10^{-4}$ $M^{-1}cm^{-1}$): 578 (9.5), 766 (2.6), 820 (4.1); ($CH_2Cl_2$/TFA): $\lambda_{max}$ ($\varepsilon$ x $10^{-4}$ $M^{-1}cm^{-1}$): 662 (13.5), 1076 (5.2); elemental analysis: calcd (%) for $C_{72}H_{60}N_2S_6$: C 75.48, H 5.28, N 2.45; found: C 75.39, H 5.32, N 2.43.

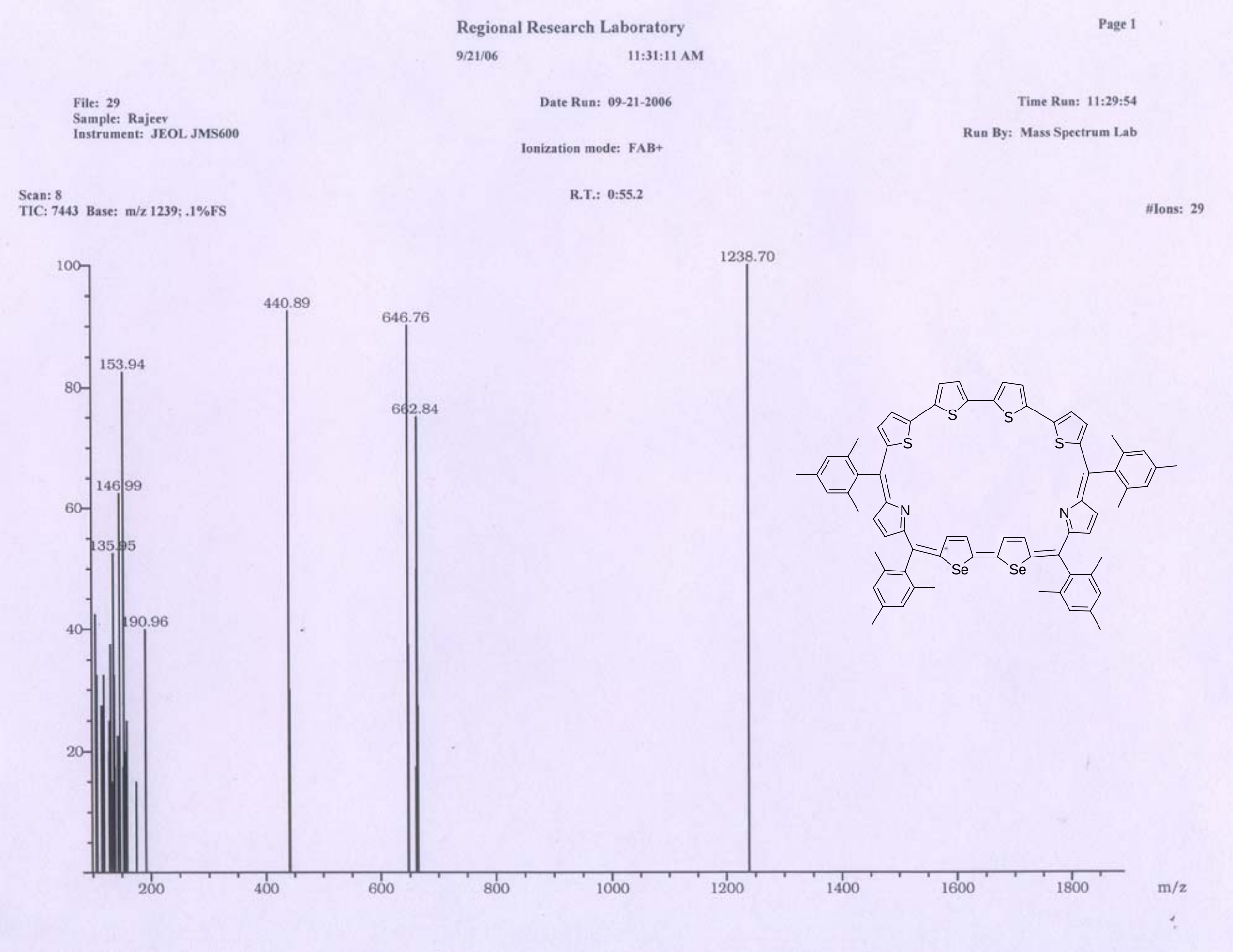
**Octaphyrin (14): 7** (0.17g, 0.27 mmol) and tetrapyrrane **10** (0.13g, 0.27 mmol) were subjected to conditions similar to those mentioned above with PTSA (0.01g, 0.05 mmol) and Chloranil (0.20g, 0.81 mmol). Purification by column chromatography on basic alumina gave a red colored band with dichloromethane/petroleum ether (1:5), which yielded a green brownish metallic solid on evaporation of solvent identified as **14** in (0.124 g, 19%); $^1$H NMR (300 MHz, $CDCl_3$, 25° C, TMS): $\delta$ = 9.19 (t, 4H), 9.00 (d, J =

4.2 Hz, 2H), 8.29 (s, 2H), 8.02 (d, J = 6.9 Hz, 4H), 7.70–7.61 (m, 8H), 7.51 (d, J = 4.4 Hz, 2H), 7.20 (s, 4H), 4.11 (s, 2H), 3.01 (d, J = 4.2 Hz, 2H), 2.55 (s, 6H), 2.12 (s, 12H); FAB-MS: m/z (%): 1060.54 (100) [M]; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$ x $10^{-4}$ $M^{-1}cm^{-1}$): 577 (9.4), 764 (2.7), 838 (5.1); ($CH_2Cl_2$/TFA): $\lambda_{max}$ ($\varepsilon$ x $10^{-4}$ $M^{-1}cm^{-1}$): 650 (22.4), 985 (2.0), 1090 (7.8); elemental analysis: calcd (%) for $C_{66}H_{48}N_2S_6$: C 74.68, H 4.56, N 2.64; found: C 74.79, H 4.49, N 2.59.

**Octaphyrin (15):** **7** (0.17g, 0.27 mmol) and tetrapyrrane **11** (0.12g, 0.27 mmol) were subjected to conditions similar to those mentioned above with PTSA (0.01g, 0.05 mmol) and Chloranil (0.20g, 0.81 mmol). Purification by column chromatography on basic alumina gave a red colored band with dichloromethane/petroleum ether (1:5), which yielded a green brownish metallic solid on evaporation of solvent identified as **15** in (0.110 g, 17%); $^1H$ NMR (300 MHz, $CDCl_3$, 25° C, TMS): $\delta$ = 9.20 (d, J = 4.4 Hz, 4H), 9.03 (d, J = 4.1 Hz, 2H), 8.31 (s, 2H), 7.97 (d, J = 6.6 Hz, 4H), 7.64 (d, J = 4.4 Hz, 2H), 7.57 (d, J = 4.4 Hz, 4H), 7.21 (m, 6H), 4.01 (s, 6H), 3.90 (s, 2H), 2.88 (d, J = 4.2 Hz, 2H), 2.55 (s, 6H), 2.12 (s, 12H); FAB-MS: m/z (%): 1120.68 (100) [M]; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$ x $10^{-4}$ $M^{-1}cm^{-1}$): 580 (9.6), 766 (2.7), 842 (4.9); ($CH_2Cl_2$/TFA): $\lambda_{max}$ ($\varepsilon$ x $10^{-4}$ $M^{-1}cm^{-1}$): 652 (22.4), 985 (2.1), 1090 (7.9); elemental analysis: calcd (%) for $C_{68}H_{52}N_2O_2S_6$: C 72.82, H 4.67, N 2.50; found: C 72.75, H 4.61, N 2.59.

**Crystallography information for 12.**

X-ray single-crystal diffraction data for 12 was collected on a Bruker SMART Apex CCD diffractometer at 100K with MoK$_\alpha$ radiation (0.71073Å).Semi-empirical absorption corrections were applied using SADABS, and the program SAINT was used for integration of the diffraction profiles. The structure was solved by direct methods using SHELXTL package. After the complete convergence of the two macrocyclic ligand moiety present in the asymmetric unit, large number of diffused scatterd peaks with maximum electron density of 4.2 Å$^{-3}$ was present in the differene Fourier map. This may be due to the presence of disorderd solvent molecule used for the crystalisation (n-hexane and methanol). Attempts were made to model this, but were unsuccessful since residual electron density peaks obtained was diffused and there were no obvious major site occupations for the solvent molecules. PLATON/SQUEEZE was used to correct the data for the presence of the disordered solvents. A potential solvent volume of 2036.3 Å$^3$ was found. 198 electrons per unit cell worth of scattering were located in the void. This electron counts corresponds to approximately 4 molecules of n-hexane present per unit cell.. The full-matrix refinement with anisotropic thermal parameters was carried out in blocks. Each macrocyclic molecule present in the asymmetric unit is included in two different blocks. All the H atoms were positioned geometrically and treated as riding atoms



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Ionization mode: FAB+

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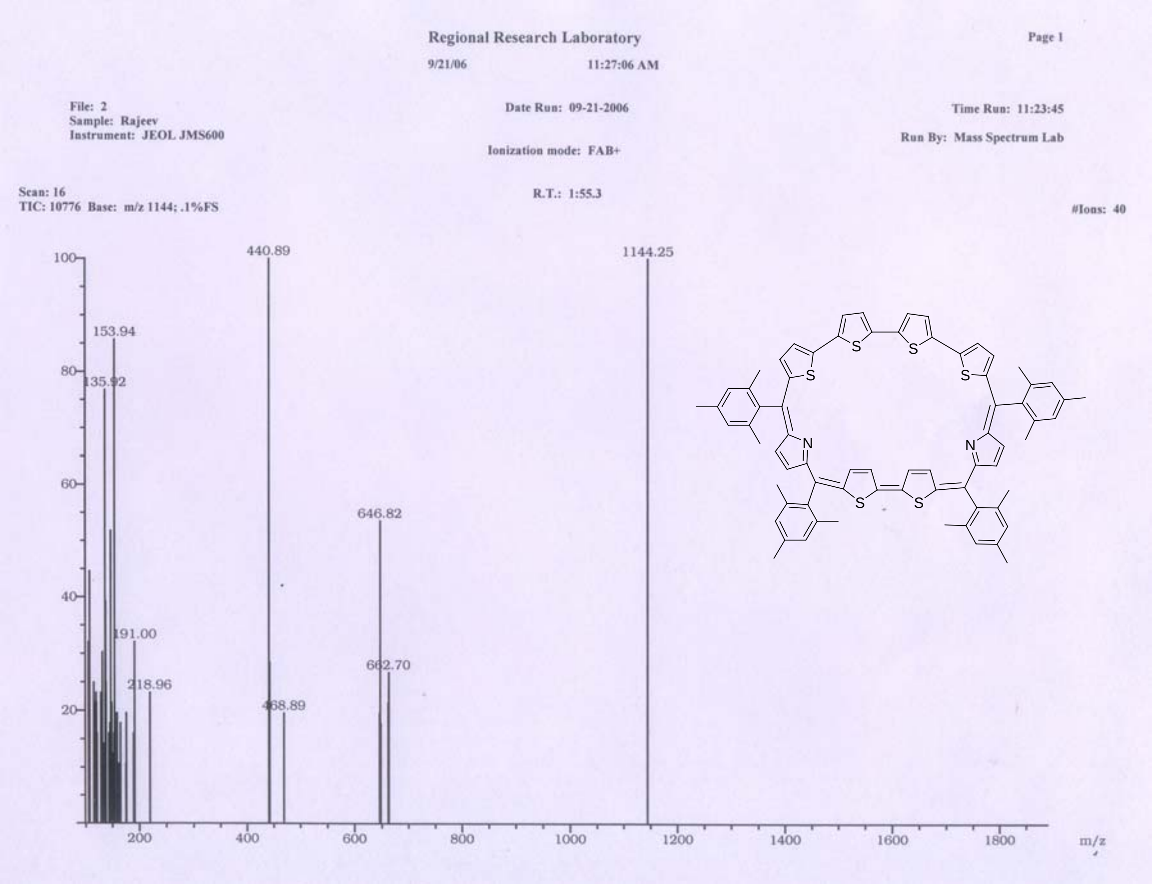
Figure 1: FAB mass spectrum of **12**



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9/21/06 11:27:06 AM
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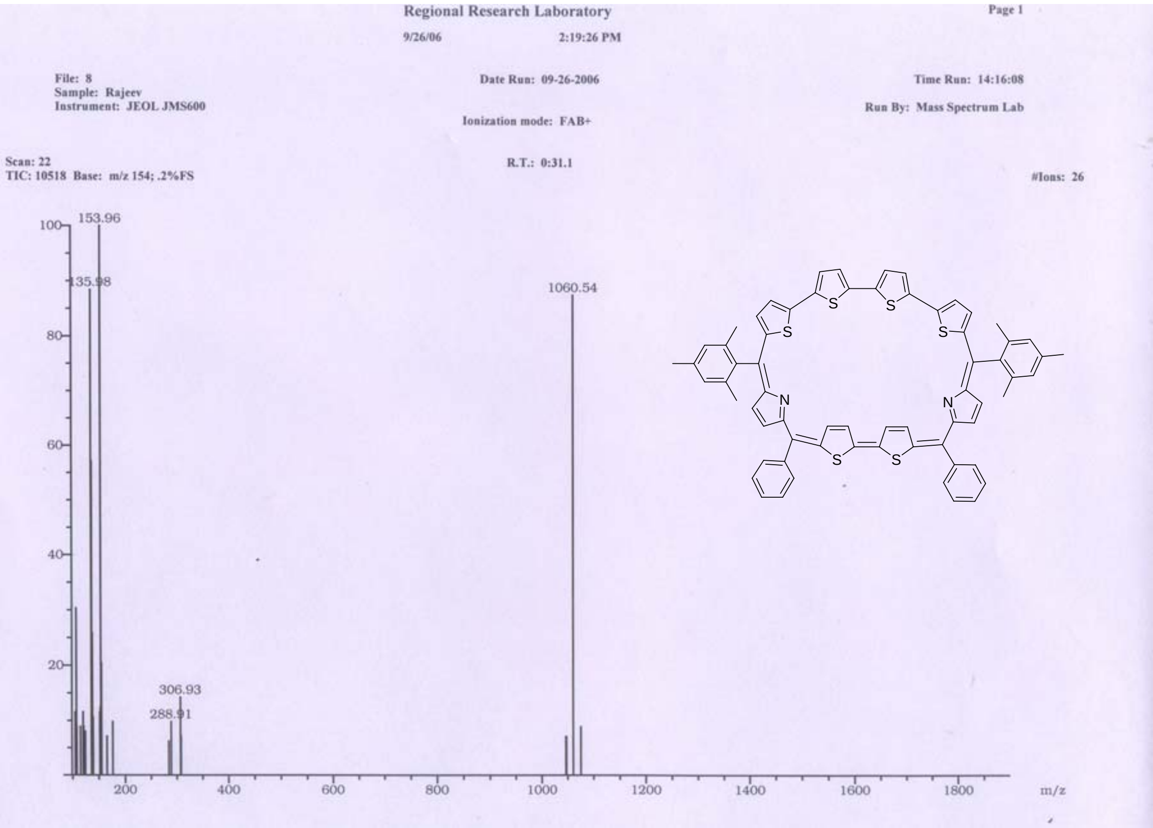
Figure 2: FAB mass spectrum of **13**



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9/26/06 2:19:26 PM

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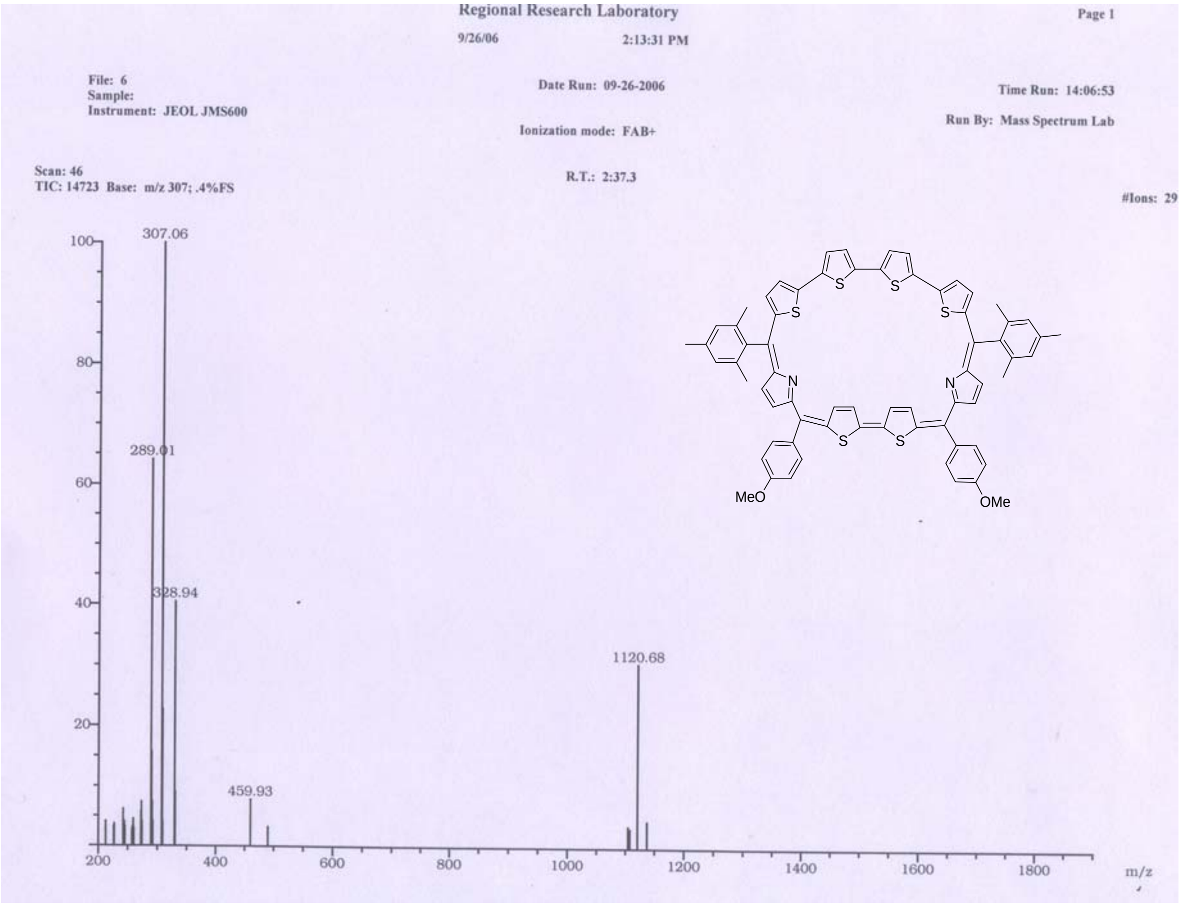
Figure 3: FAB mass spectrum of **14**



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Run By: Mass Spectrum Lab

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R.T.: 2:37.3

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Figure 4: FAB mass spectrum of **15**

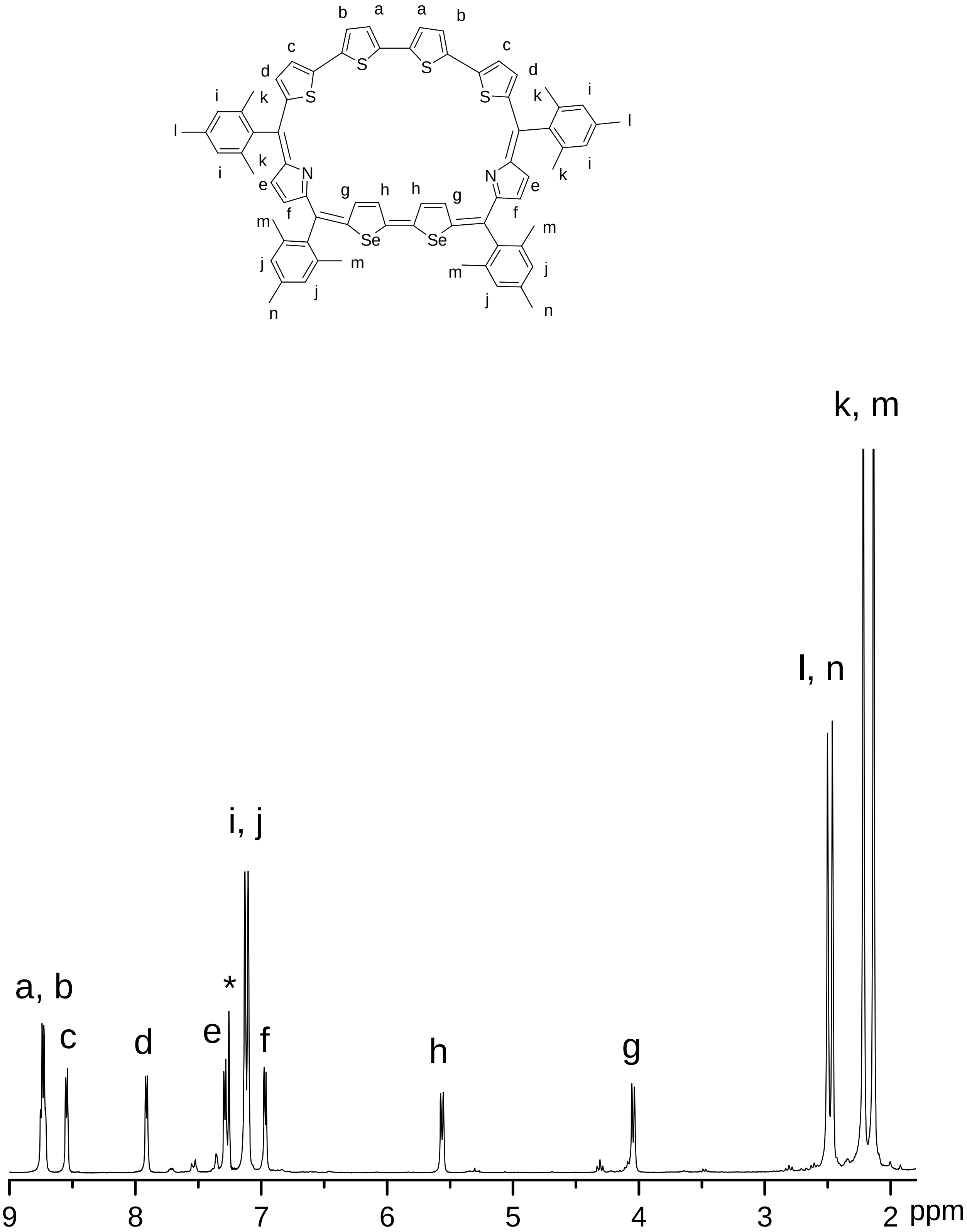

Figure 5. $^1H$ NMR spectrum of **12** at room temperature in $CDCl_3$

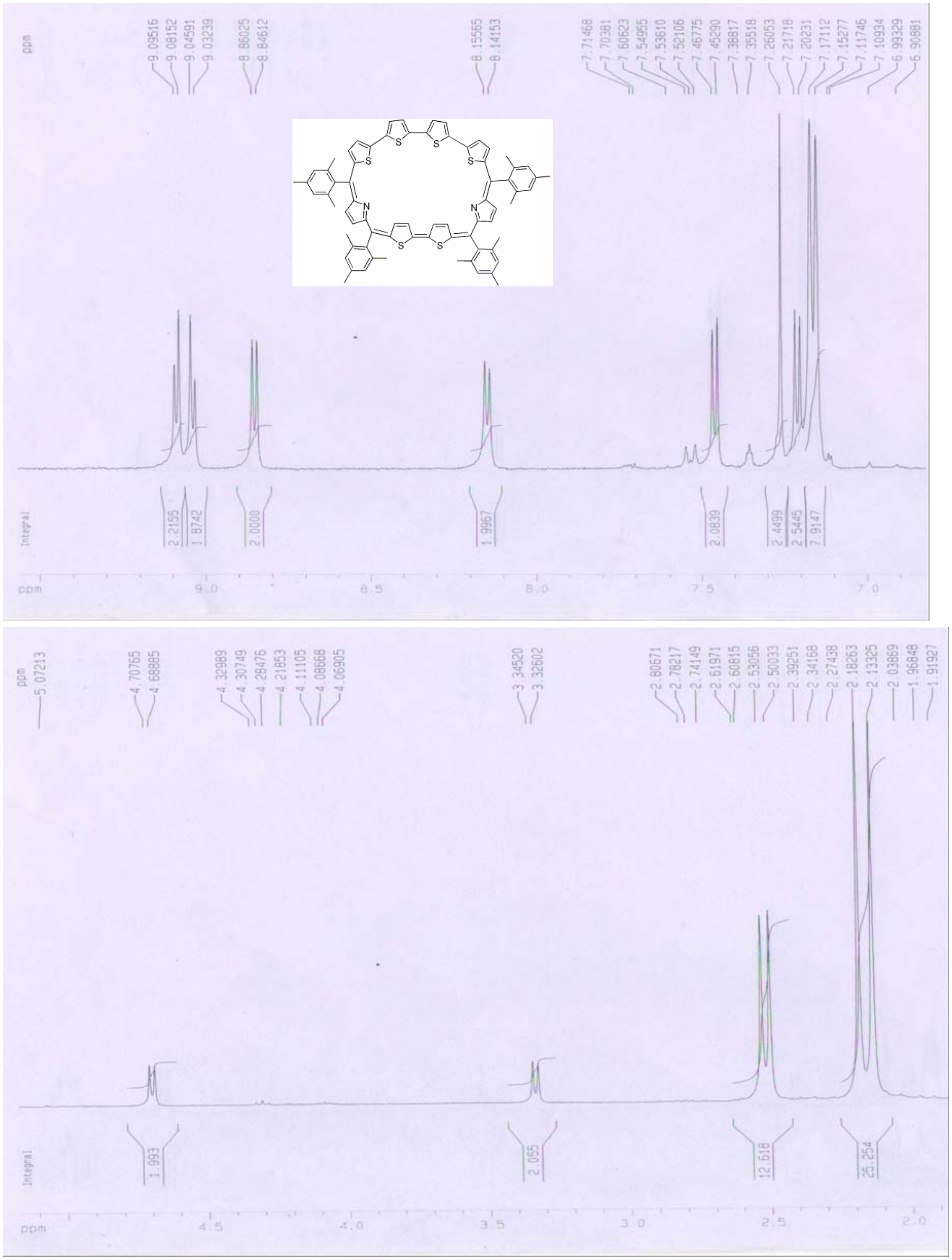

Figure 6. $^{1}$H NMR spectrum of **13** at room temperature in $CDCl_3$

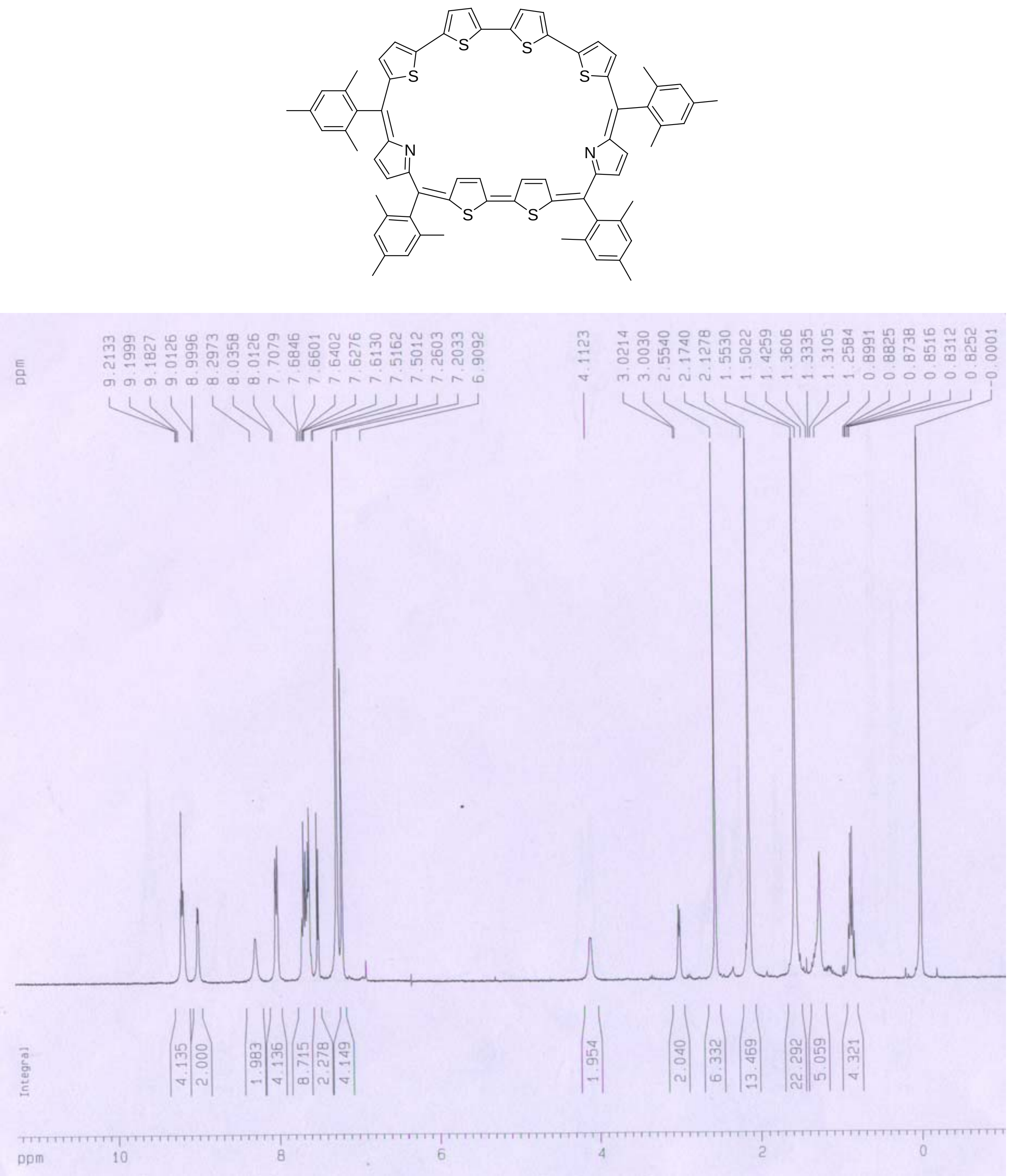

Figure 7. $^1$H NMR spectrum of **14** at room temperature in $CDCl_3$

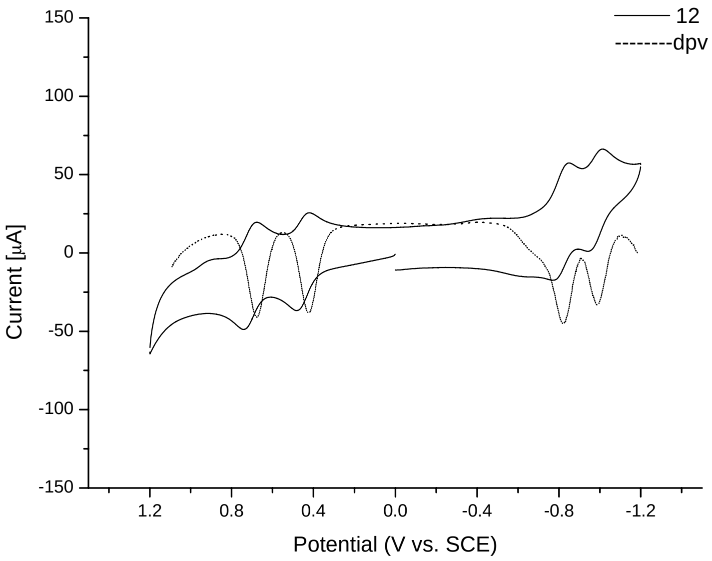

Figure 8. Cyclic voltammograms (—) and differential pulse voltammograms (---) of **12** in $CH_2Cl_2$ containing 0.1 M $TBAPF_6$, recorded at 100 mV/s scan speed.

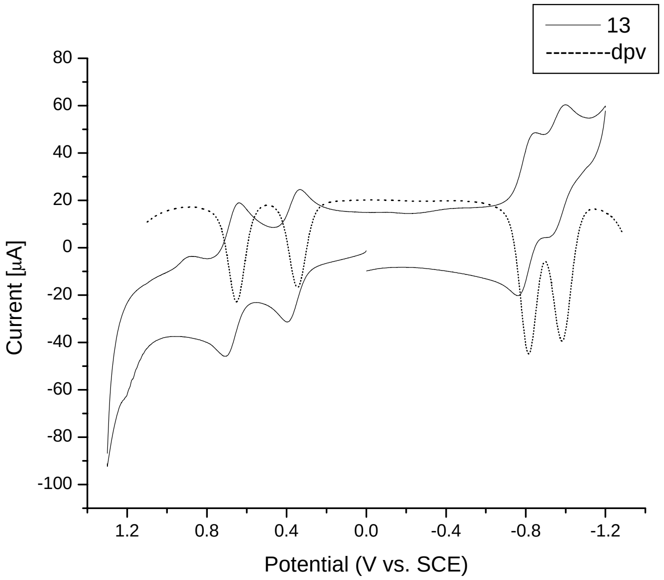

Figure 9. Cyclic voltammograms (—) and differential pulse voltammograms (---) of **13** in $CH_2Cl_2$ containing 0.1 M $TBAPF_6$, recorded at 100 mV/s scan speed.

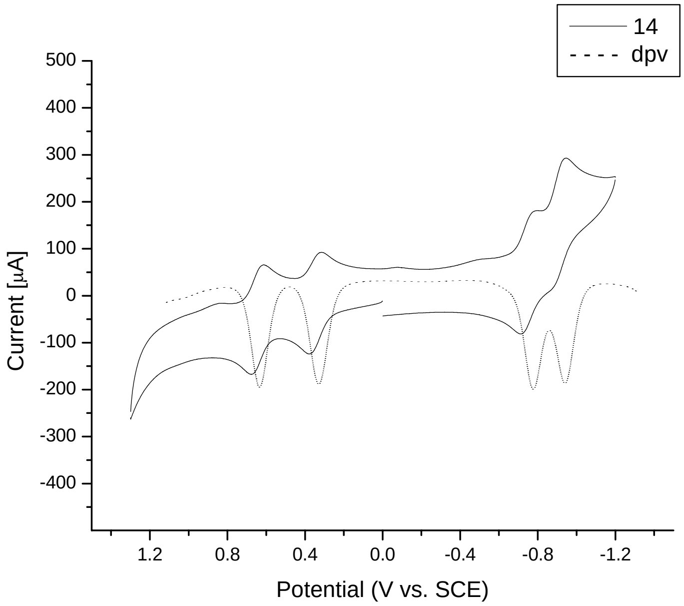

Figure 10. Cyclic voltammograms (—) and differential pulse voltammograms (---) of **14** in $CH_2Cl_2$ containing 0.1 M $TBAPF_6$, recorded at 100 mV/s scan speed.

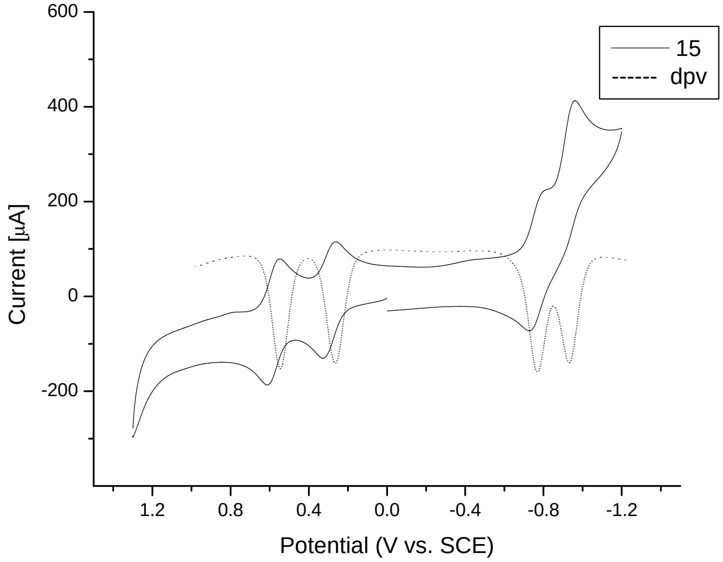

Figure 11. Cyclic voltammograms (—) and differential pulse voltammograms (---) of **15** in $CH_2Cl_2$ containing 0.1 M $TBAPF_6$, recorded at 100 mV/s scan speed.