SUPPORTING INFORMATION

Synthesis of Functionalized Thia Analogues of Phlorins and Covalently Linked Phlorin-Porphyrin Dyads

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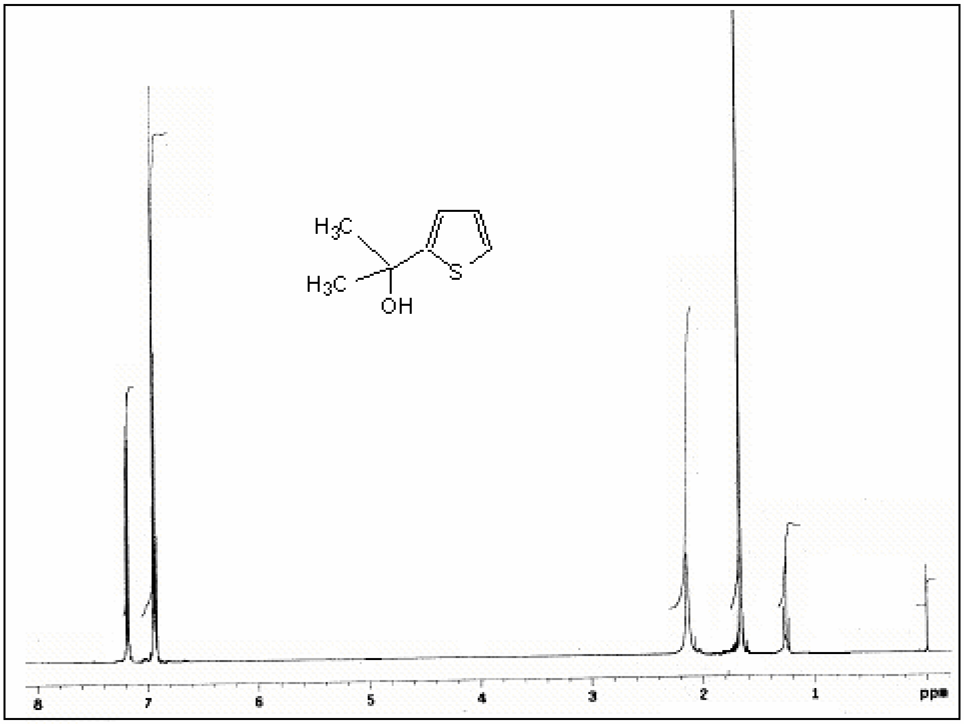
Experimental for few selected compounds:

2-{(α,α'-dimethyl)hydroxymethyl}-5-{*p*-tolylhydroxymethyl}thiophene (1). Dry, distilled ether (35 ml) was added to a 250 ml three-necked, round-bottomed flask fitted with a rubber septum and gas inlet tube, the flask was flushed with argon for 10 min. Tetramethylethylenediamine (TMEDA) (1.9 g, 2.4 ml, 16.152 mmol) and *n*-butyl lithium (12 ml of *ca*. 15% solution in hexane) were added to the stirred solution and the reaction temperature maintained at 0^{o}C in ice-bath. The 2-[α-(*p*-tolyl)-α-hydroxymethyl]-thiophene (1.5 g, 7.342 mmol) was added and the solution was stirred for 1h. An ice cold solution of dry acetone (1.0 g, 1.3 ml, 18.355 mmol) in dry THF (30 ml) was then added and stirred for additional 15 min at 0 °C. The reaction mixture was brought to room temperature and the reaction was quenched by adding an ice cold NH_4Cl solution (50ml, *ca* 1M). After standard work-up, the crude compound was subjected to silica gel column chromatography and the pure diol **1** was collected with petroleum ether/ethyl acetate (70:30). The solvent was removed in a rotary evaporator to afford **1** as brown oil (1.1 g, 57% yield). IR (KBr film, ν/cm^{-1}3394(OH), 3271 (OH). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 1.57 (s, 6H), 2.32 (s, 3H), 3.11 (br s, 2H) 5.85 (s, 1H), 6.63 (d, *J* = 3.3 Hz, 1H), 6.70 (d, *J* = 3.9 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.11, 29.11, 31.91, 53.71, 72.11, 101.97, 121.35, 123.09, 124.19, 124.81, 126.21, 129.04, 137.49, 140.32, 146.77, 154.08. ES-MS: $C_{15}H_{18}SO_2$, Calcd. av. mass 262.4, obsd. m/z 245.1 (M^{+}-17, 90%). Anal. calcd.: C, 68.67; H, 6.92; S, 12.22. Found: C, 68.48; H, 6.73; S, 12.56.

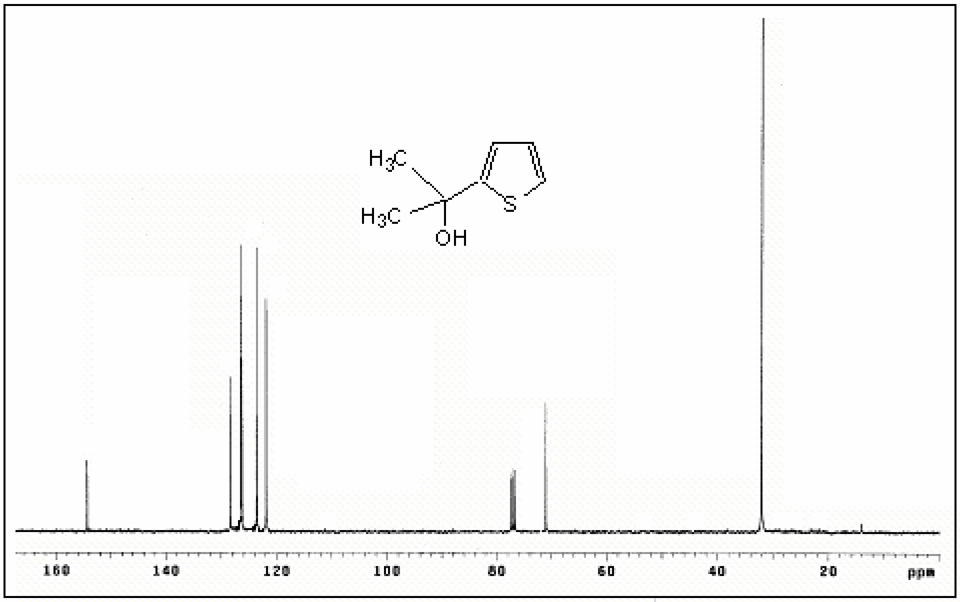
5,5'-Dimethyl-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphotrimethene (7). The thiophene diol **1** (0.4 g, 1.524 mmol), 16-thiatripyrrane **6** (0.6 g, 1.524 mmol) were condensed in 40 ml of CH_2Cl_2 under nitrogen in the presence of a catalytic amount of trifluoroacetic acid for 1h under inert atmosphere (0.1 g, 0.1 ml, 1.524 mmol). DDQ (0.3 g, 1.524 mmol) was added and stirring was continued in air for extra 1 h. The TLC analysis of crude reaction mixture showed the formation of some expanded macrocycle as reddish brown spot followed by the expected 21,23-dithiaporphotrimethene as green spot. The crude mixture was purfied by silica gel column chromatography and the desired 21,23-dithiaporphotrimethene **7** was collected as second band. The solvent was removed on rotary evaporator to afford **7** as green solid (0.2 g, 19%). M. P. >250° C. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 1.86 (s, 6H, CH_3), 2.45 (s, 9H, CH_3), 6.29 (br s, 1H, β-pyrrole), 6.49 (br s, 1H, β-pyrrole), 6.90 (br s, 1H, β-pyrrole), 7.10 (br s, 1H, β-pyrrole), 7.28 (m, 8H, Ar and β-thiophene), 7.43 (m, 4H, Ar), 7.52 (m, 4H, Ar), 11.32 (br s, 1H, NH), 12.72 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.43, 29.62, 39.06, 106.77, 121.37, 128.54, 128.77, 129.49, 131.37, 131.97, 132.55, 134.69, 137.14, 138.24, 140.34. ES-MS: $C_{43}H_{36}N_2S_2$, Calcd. av. mass, 644.8 obsd. m/z 645.2 (M^+). Anal. calcd.: C, 80.08; H, 5.63; N, 4.34; S, 9.94. Found: C, 80.28; H, 5.71; N, 4.38; S, 9.86. UV-vis λ_{max}/nm (ε/mol^{-1}dm^3 cm^{-1}): 327 (23864), 415 (32243), 686 (19368).

21,23-Dithiaporphotrimethene-ZnN$_4$ porphyrin Dyad (19)

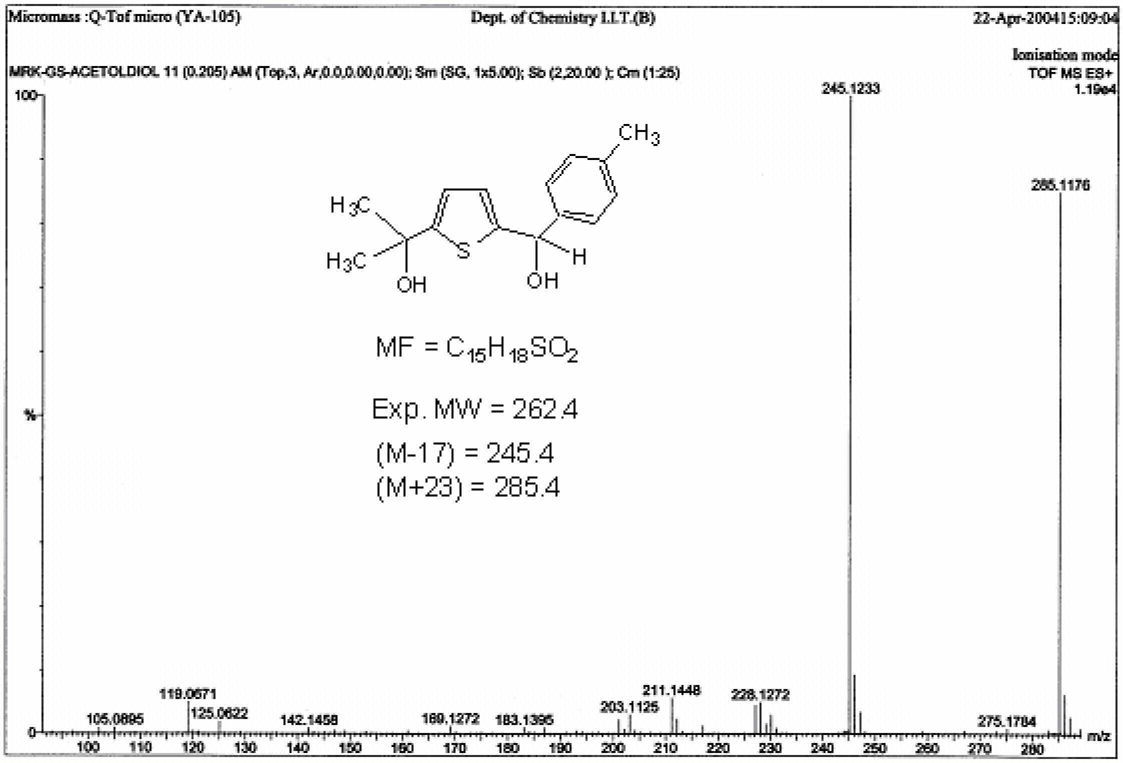
A solution of 21,23-dithiaporphotrimethene **8** (30.0 mg, 39.6 μmol) and 5,10,15-tri(mesityl)-20-(ethynylphenyl) zinc porphyrin **20** (39.0 mg, 47.5 μmol) were dissolved in dry toluene-triethylamine (5:1, 30 ml) in 50 ml round-bottomed flask and nitrogen was purged for 15 min. The reaction vessel was placed in an oil bath preheated to 50° C. To this solution, $Pd_2(dba)_3$ (5.4 mg, 5.9 μmol), $AsPh_3$ (14.3 mg, 46.8 μmol) were added and the reaction was stirred at 50 °C for 24 h. TLC analysis of the reaction mixture indicated the virtual disappearance of spots corresponding to starting materials and the appearance of a new spot corresponding to dyad. The solution was concentrated in vacuo and the resulting crude mixture was loaded on neutral alumina column packed with petroleum ether. The small amounts of porphyrin and 21,23-dithiaporphotrimethene monomers were removed first with petroleum ether/ethyl acetate (98:2) and the desired dyad **17** was collected with petroleum ether/dichloromethane (96:4). Concentration of the solution gave dyad **17** as violet solid in 35% yield (20 mg). ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 1.87 (m, 24H, CH_3), 2.47 (s, 6H, CH_3), 2.65 (s, 9H, CH_3), 6.37 (br s, 1H, β-pyrrole), 6.65 (br s, 1H, β-pyrrole), 6.73 (br s, 1H, β-pyrrole), 6.89 (m, 2H, β-pyrrole and β-thiophene), 7.17 (m, 3H, β-thiophene), 7.28-7.65 (m, 14H, Ar), 7.83 (m, 4H, Ar), 7.99 (d, *J* = 7.5 Hz, 2H, Ar), 8.25 (d, *J* = 7.2 Hz, 2H, Ar), 8.71 (s, 4H, β-pyrrole), 8.77 (m, 2H, β-pyrrole), 8.88 (br s, 2H, β-pyrrole), 11.47 (br s, 1H, NH), 13.05 (br s, 1H, NH). ES-MS: $C_{97}H_{78}N_6S_2Zn$, Calcd. av. mass, 1457.2 obsd. m/z 1457.5 (M^+). UV-vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}): 422 (598237), 513 (7224), 551 (25314), 592 (9861), 698 (18082).



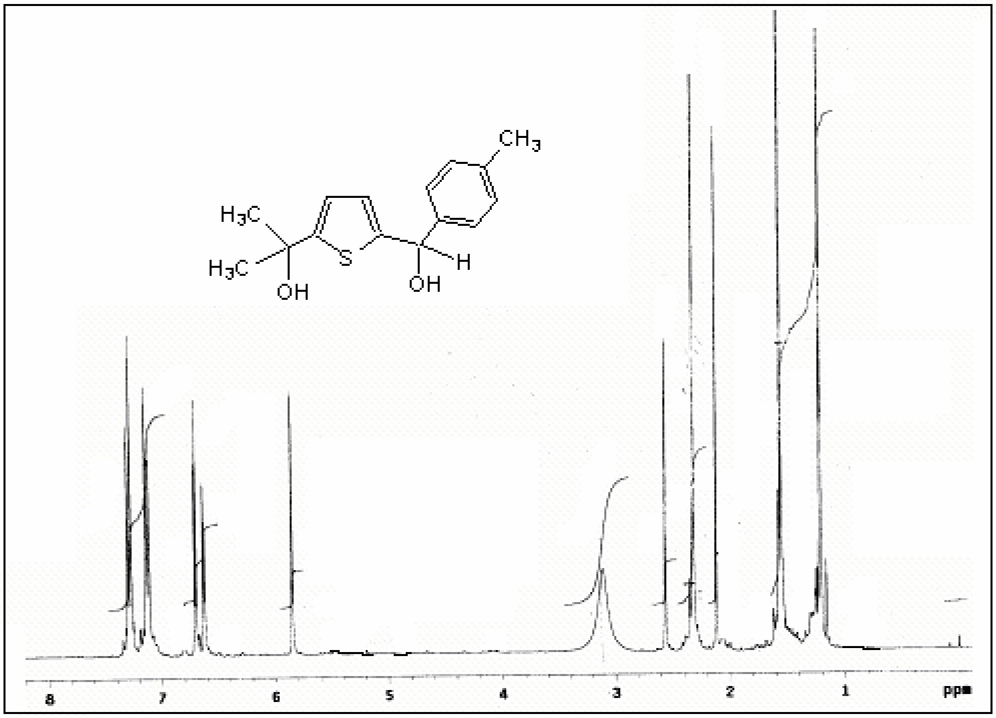
^{1}H NMR spectrum of thiophene mono-ol recorded in $CDCl_3$.



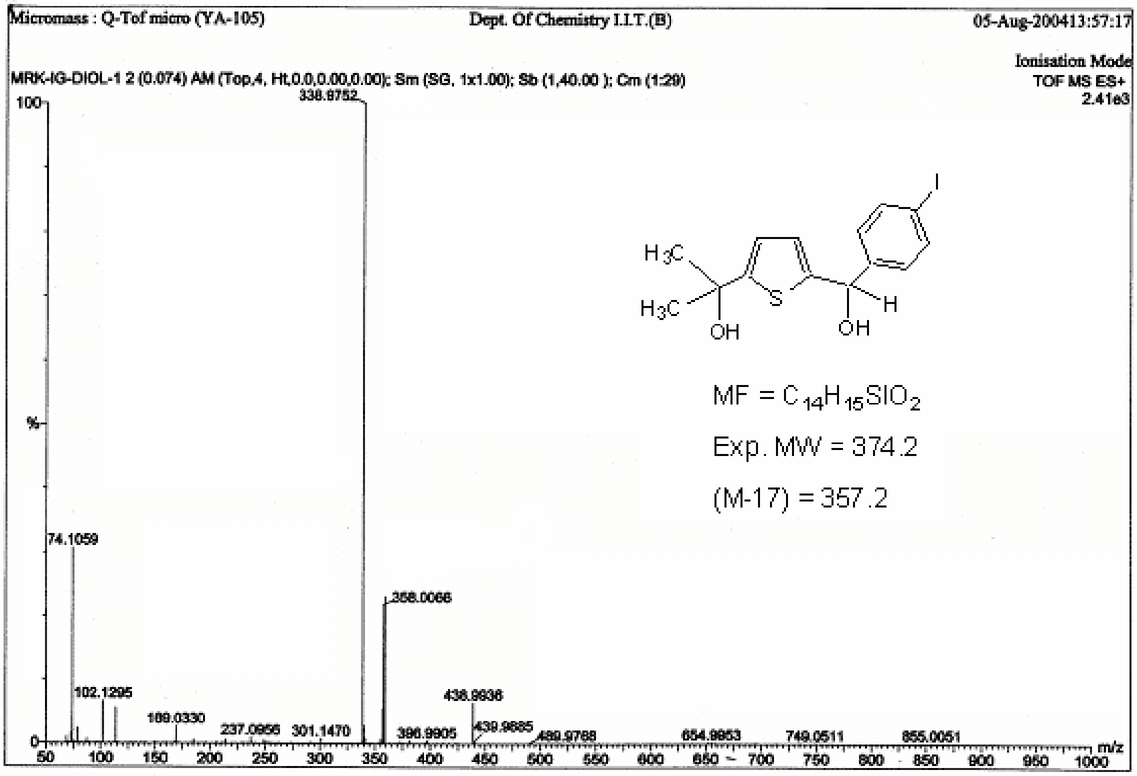
^{13}C NMR spectrum of thiophene mono-ol recorded in $CDCl_3$.



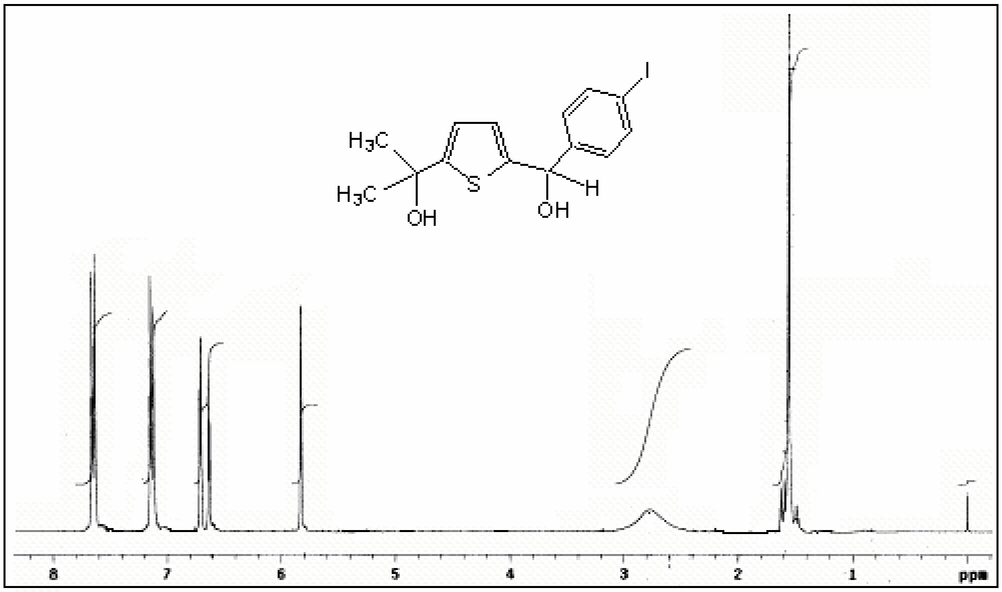
ES-MS mass spectrum of thiophene diol **1**



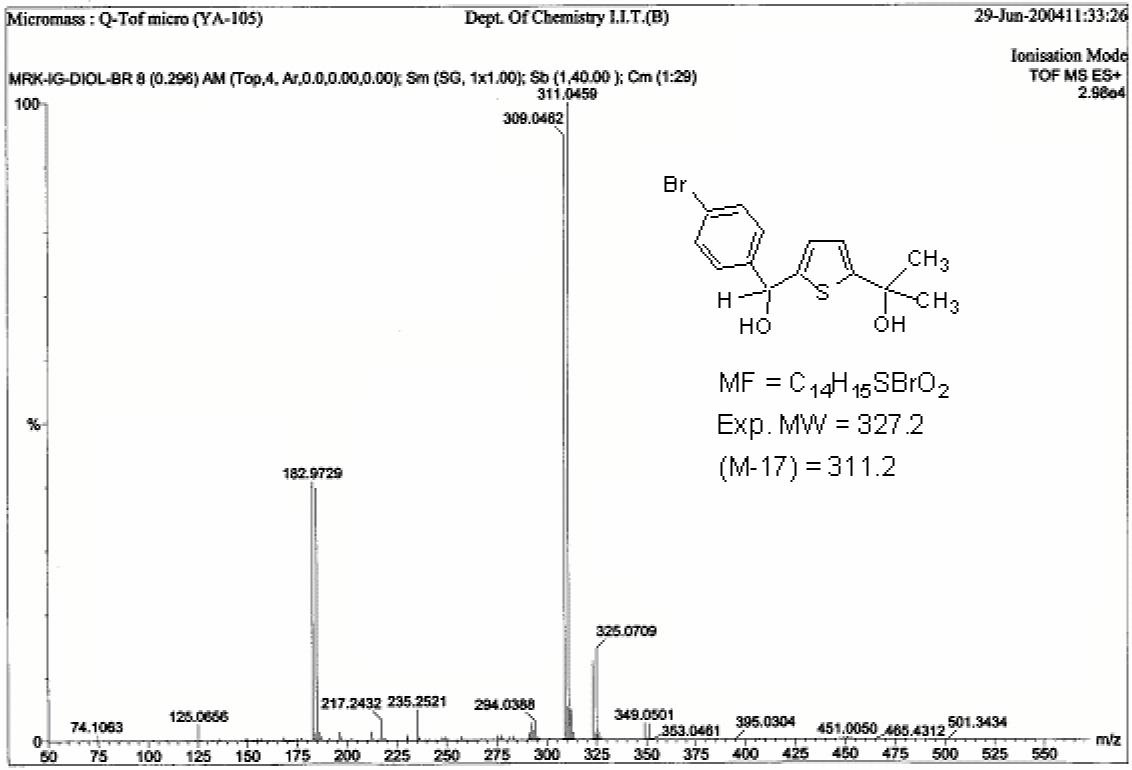
^{1}H NMR spectrum of thiophene diol **1** recorded in $CDCl_3$.



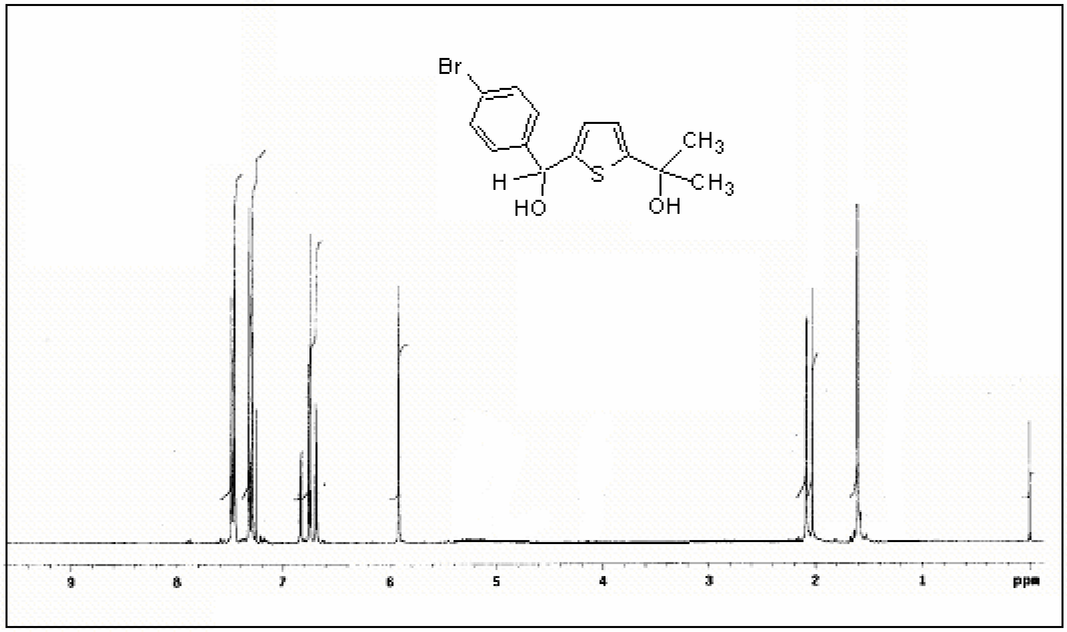
ES-MS mass spectrum of thiophene diol **2**.



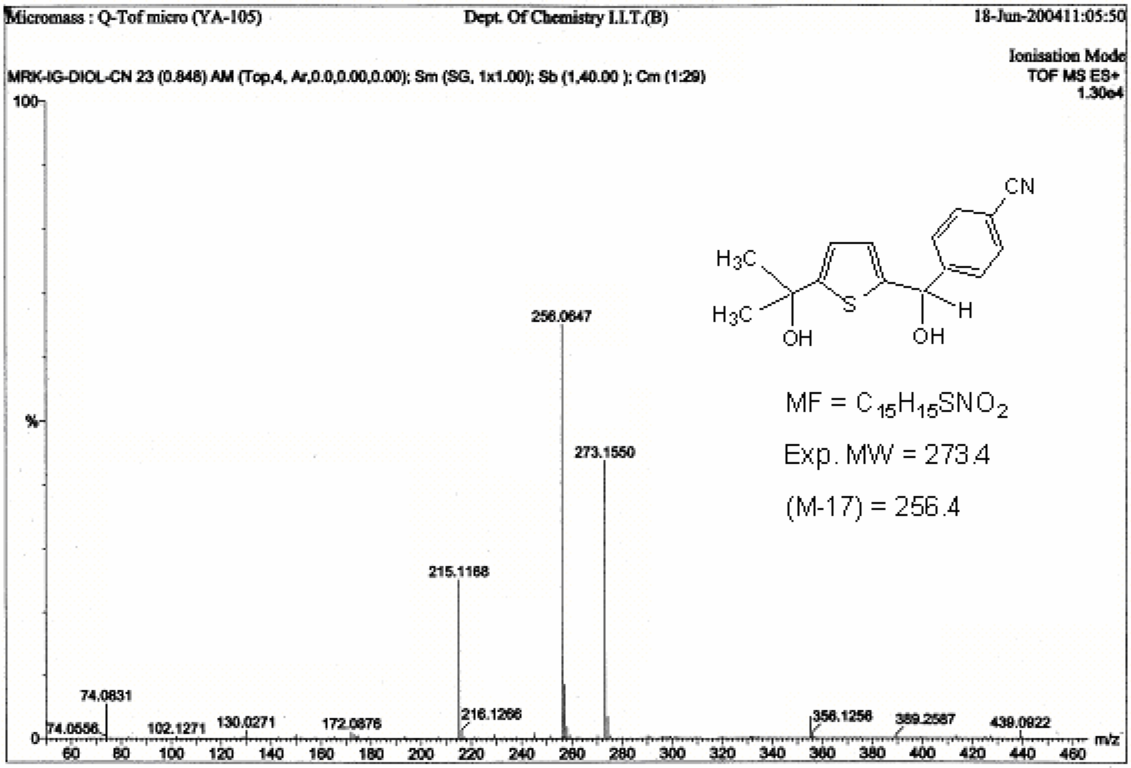
^{1}H NMR spectrum of diol **2** recorded in $CDCl_3$.



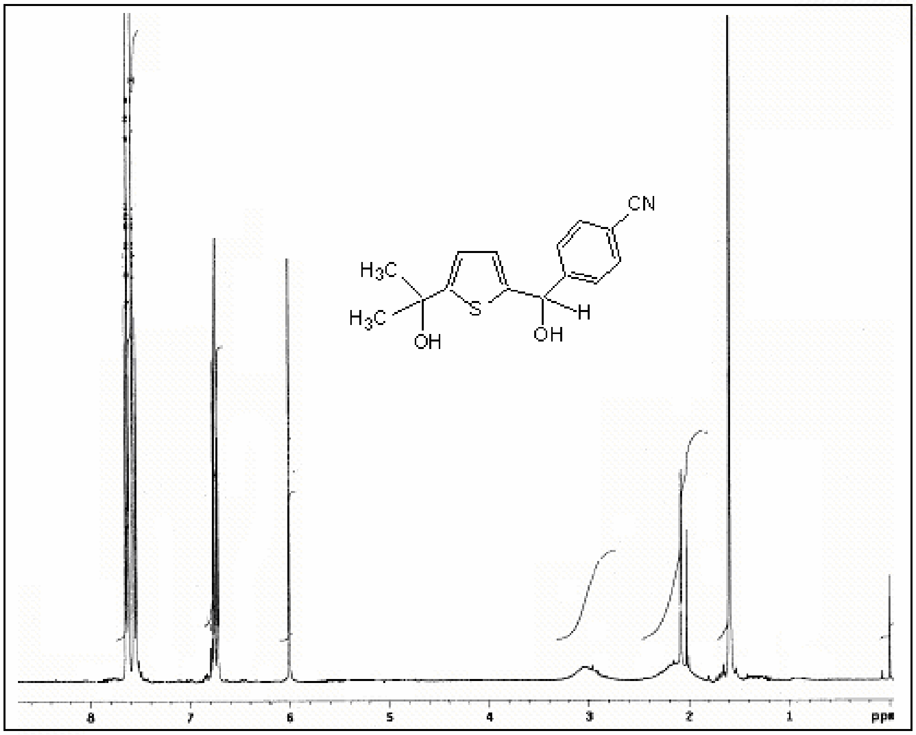
ES-MS mass spectrum of thiophene diol **3**.



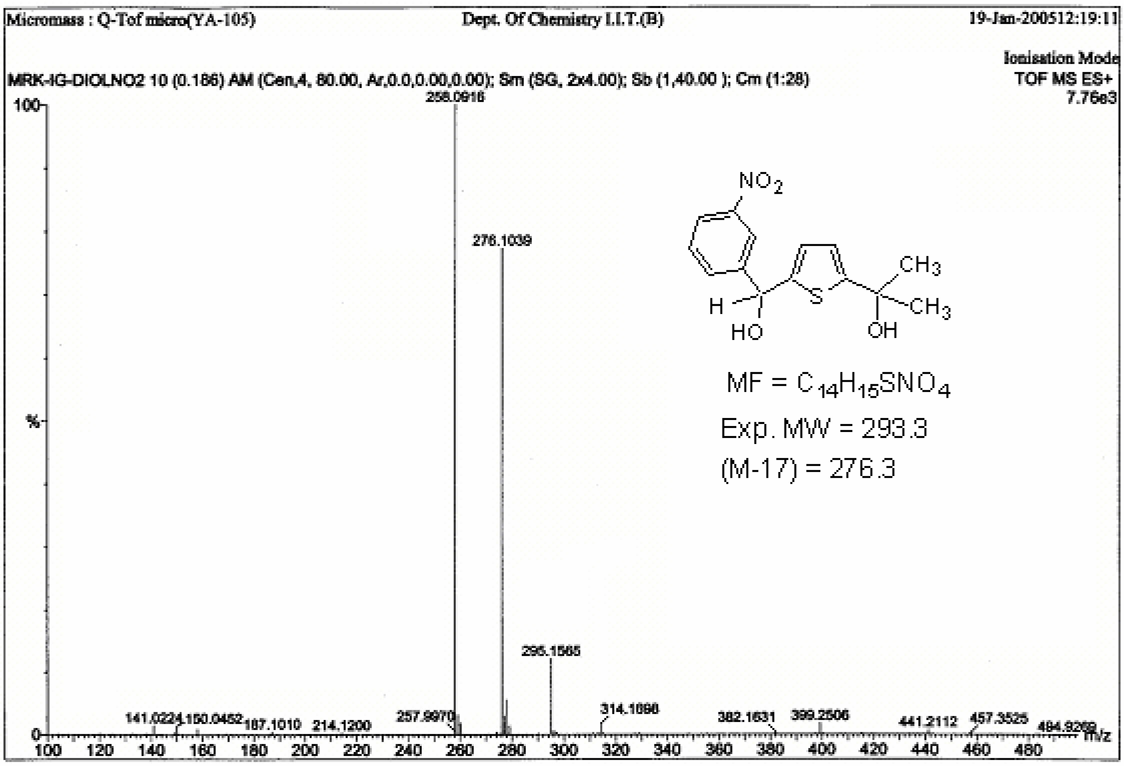
^{1}H NMR spectrum of diol **3** recorded in $CDCl_3$.



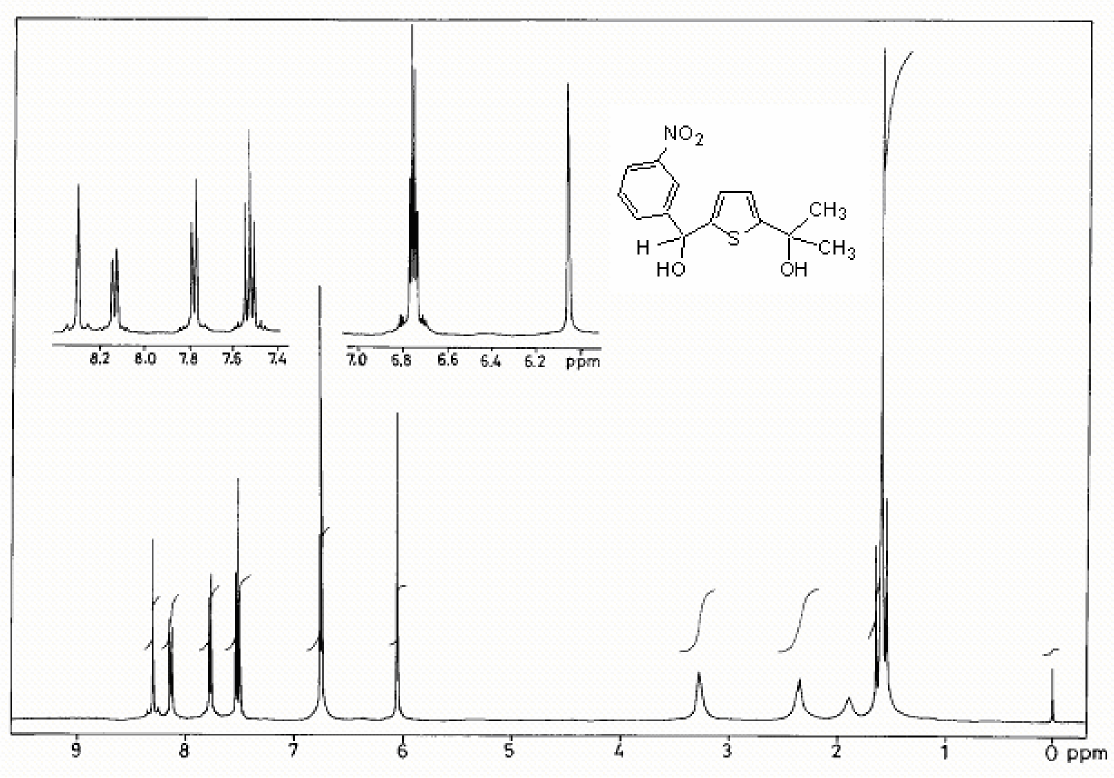
ES-MS mass spectrum of thiophene diol **4**.



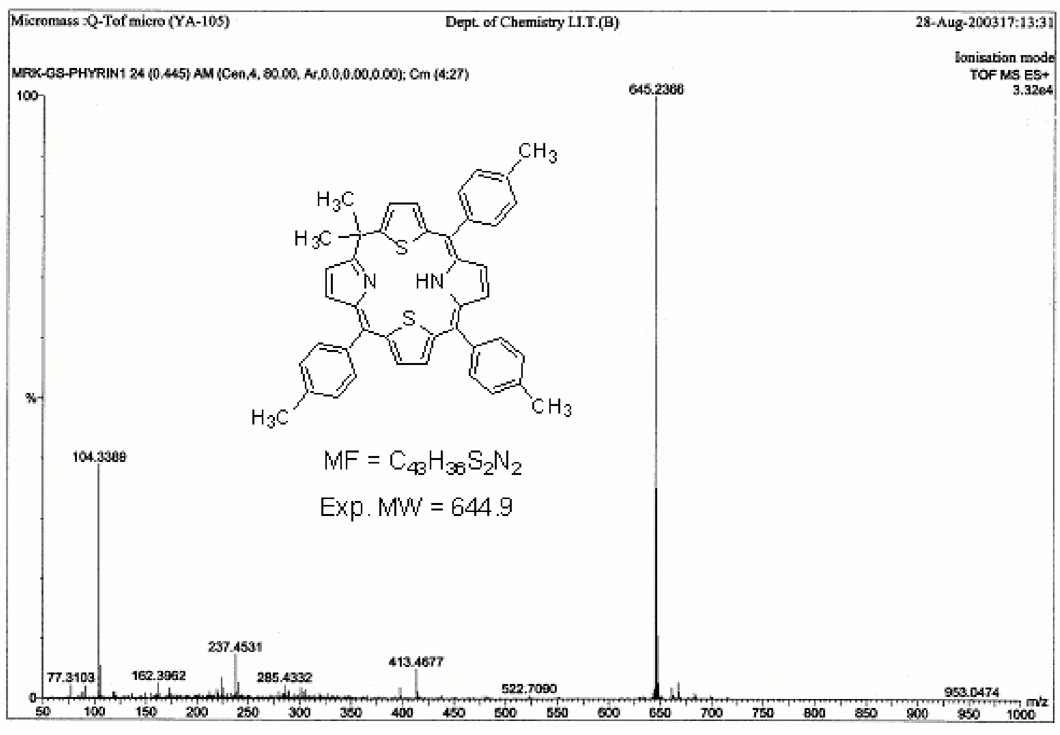
^{1}H NMR spectrum of thiophene diol **4** recorded in $CDCl_3$.



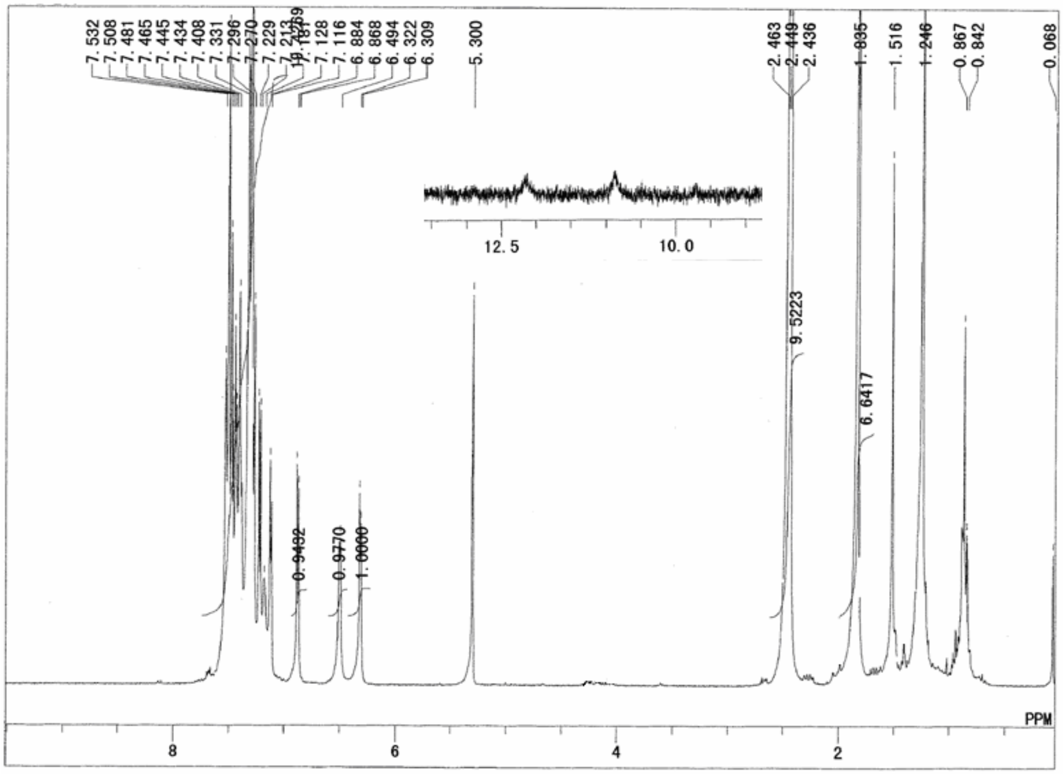
ES-MS mass spectrum of thiophene diol **5**.



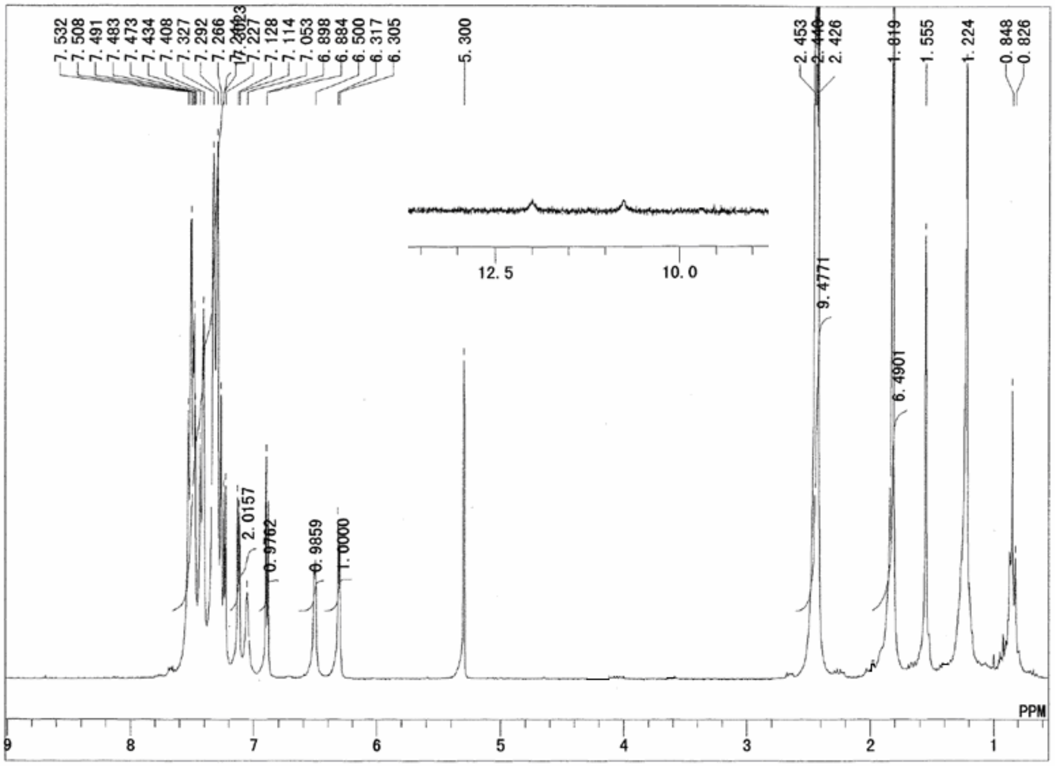
^{1}H NMR spectrum of thiophene diol **5** recorded in $CDCl_3$.



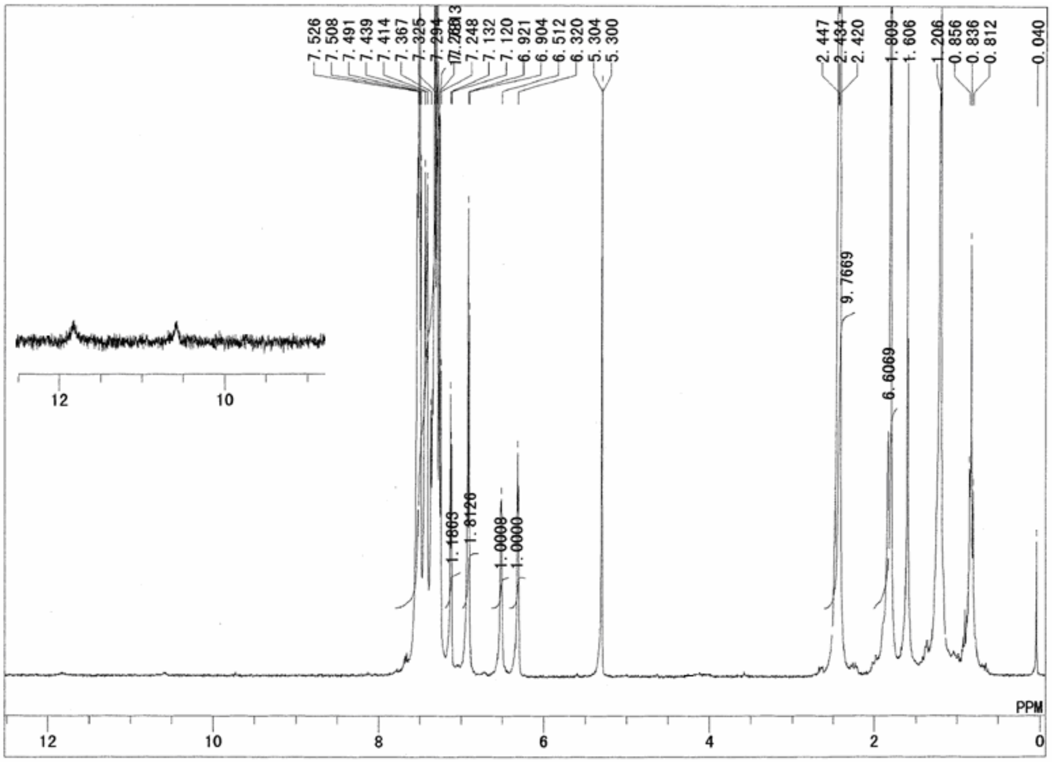
ES-MS mass spectrum of 21,23-dithiaphlorin **7**.



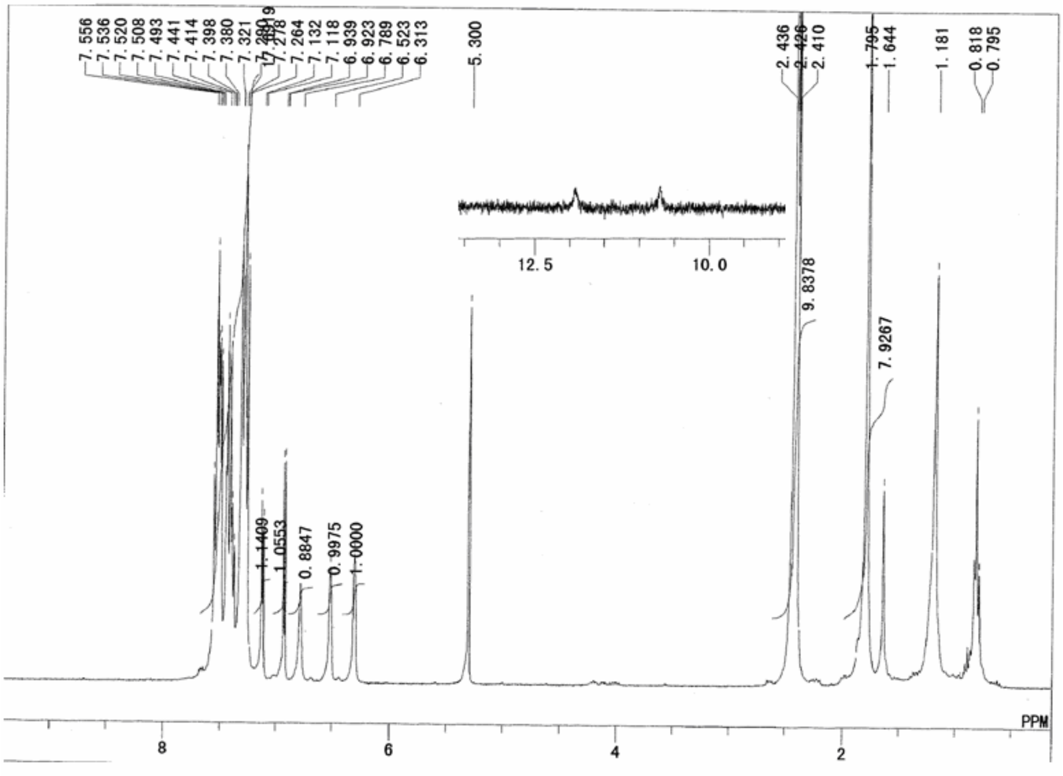
^{1}H NMR spectrum of 21,23-dithiaphlorin **7** recorded in CD_2Cl_2 at 20^o C.



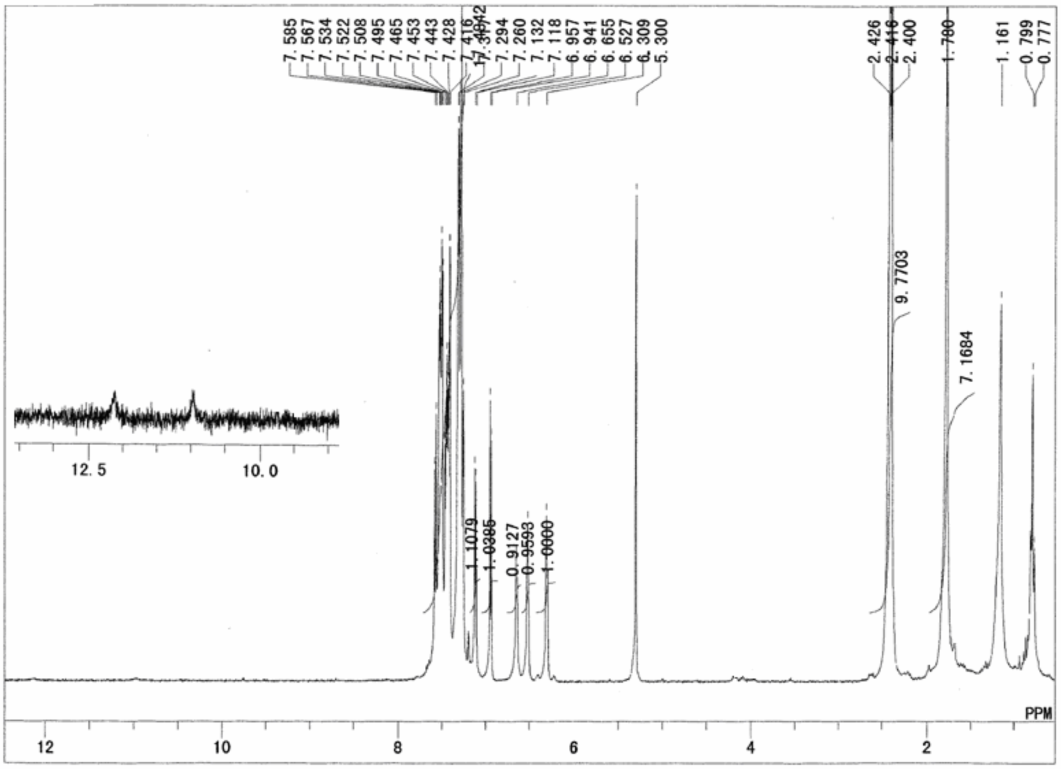
^{1}H NMR spectrum of 21,23-dithiaphlorin **7** recorded in CD_2Cl_2 at 0° C.



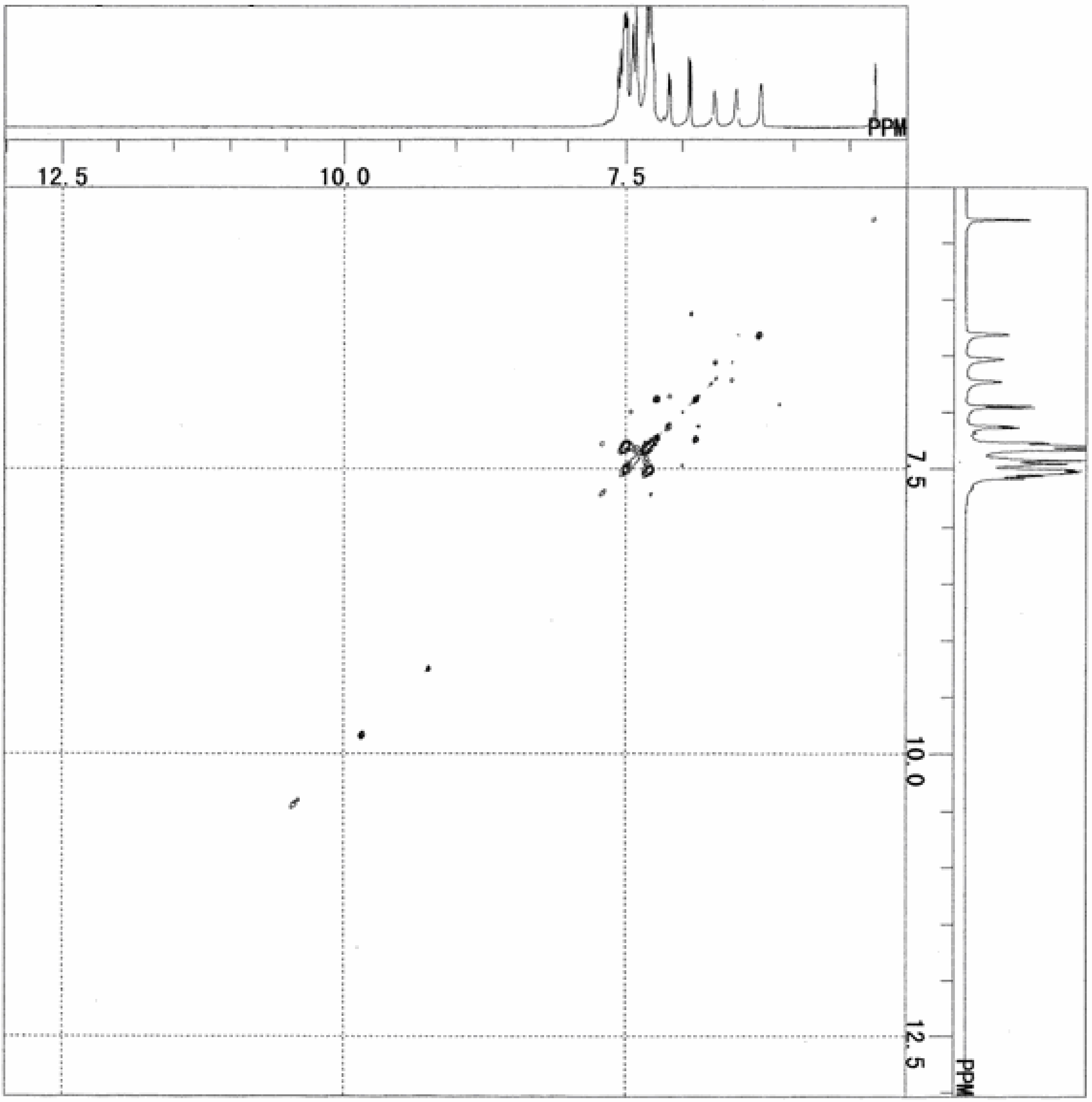
^{1}H NMR spectrum of 21,23-dithiaphlorin **7** recorded in CD_2Cl_2 at -20° C.



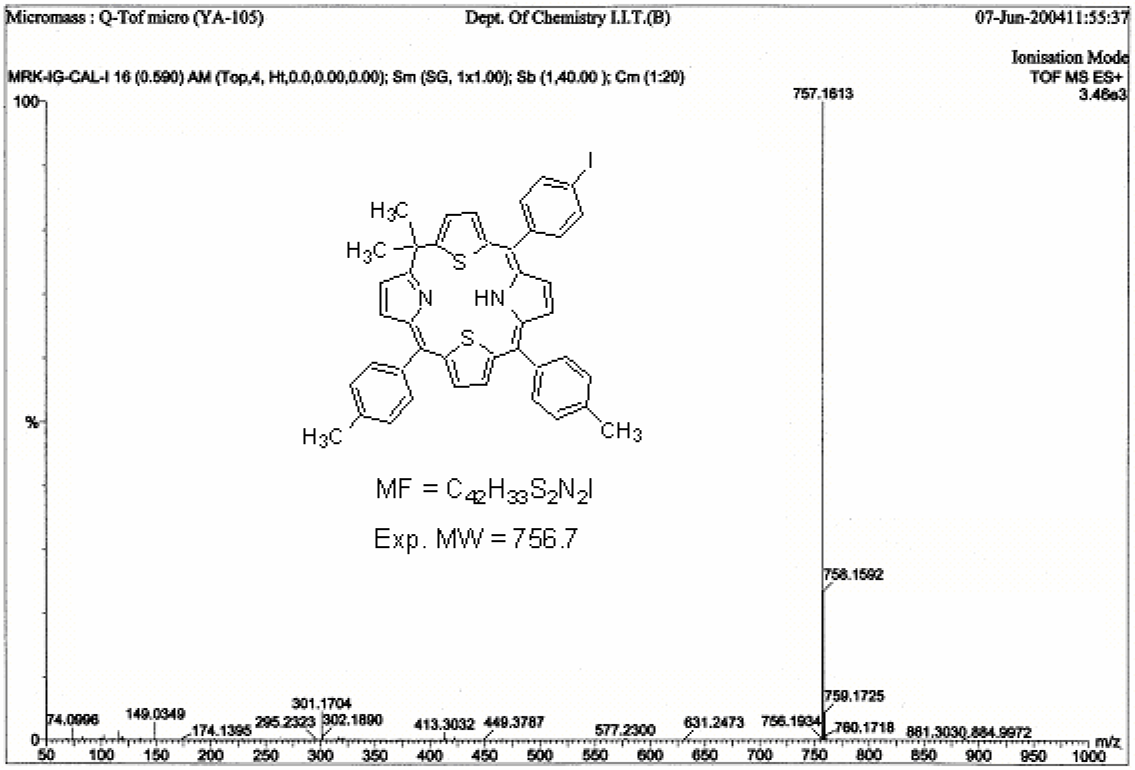
^{1}H NMR spectrum of 21,23-dithiaphlorin **7** recorded in CD_2Cl_2 at -40^o C.



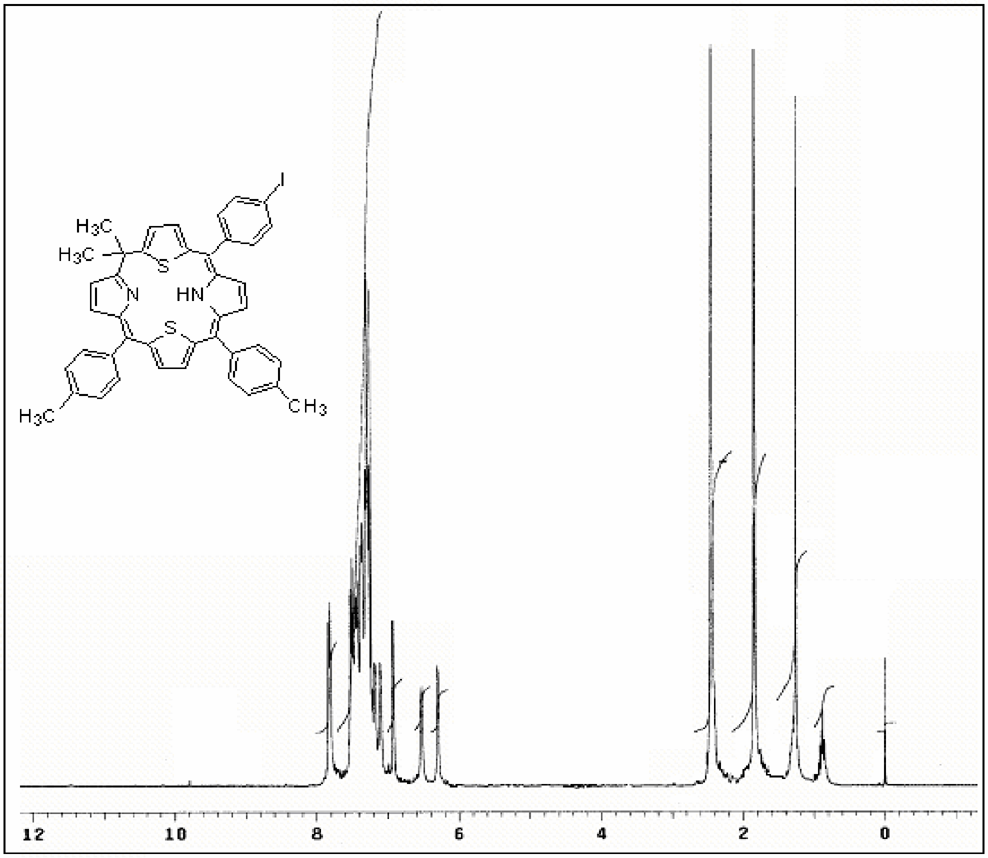
^{1}H NMR spectrum of 21,23-dithiaphlorin **7** recorded in CD_2Cl_2 at -60^o C.



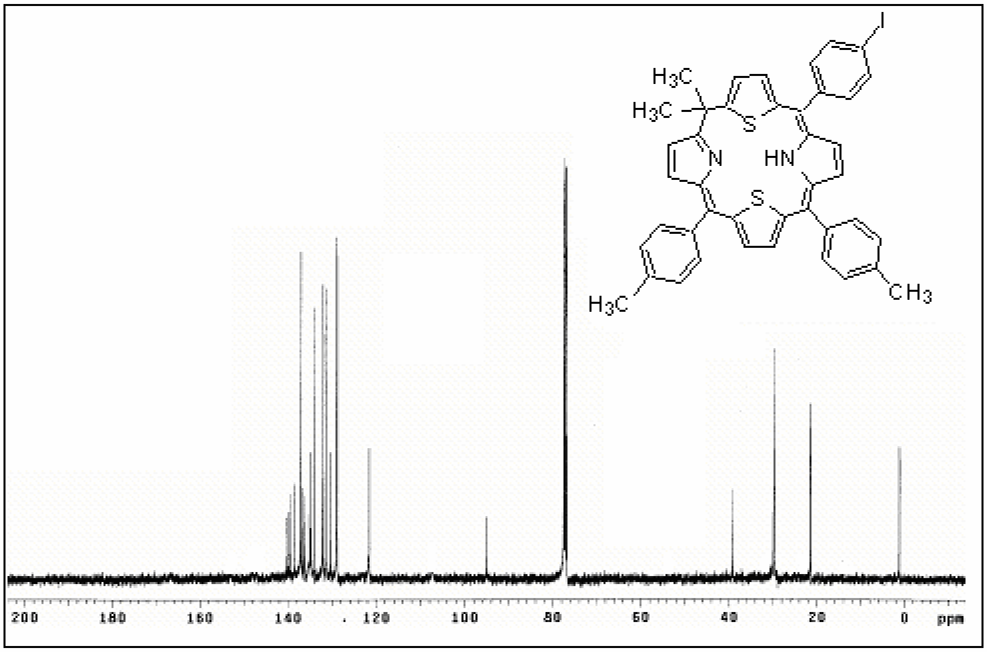
^1H-^1H COSY NMR spectrum of 21,23-dithiaphlorin **7** recorded in CD_2Cl_2 at 20° C.



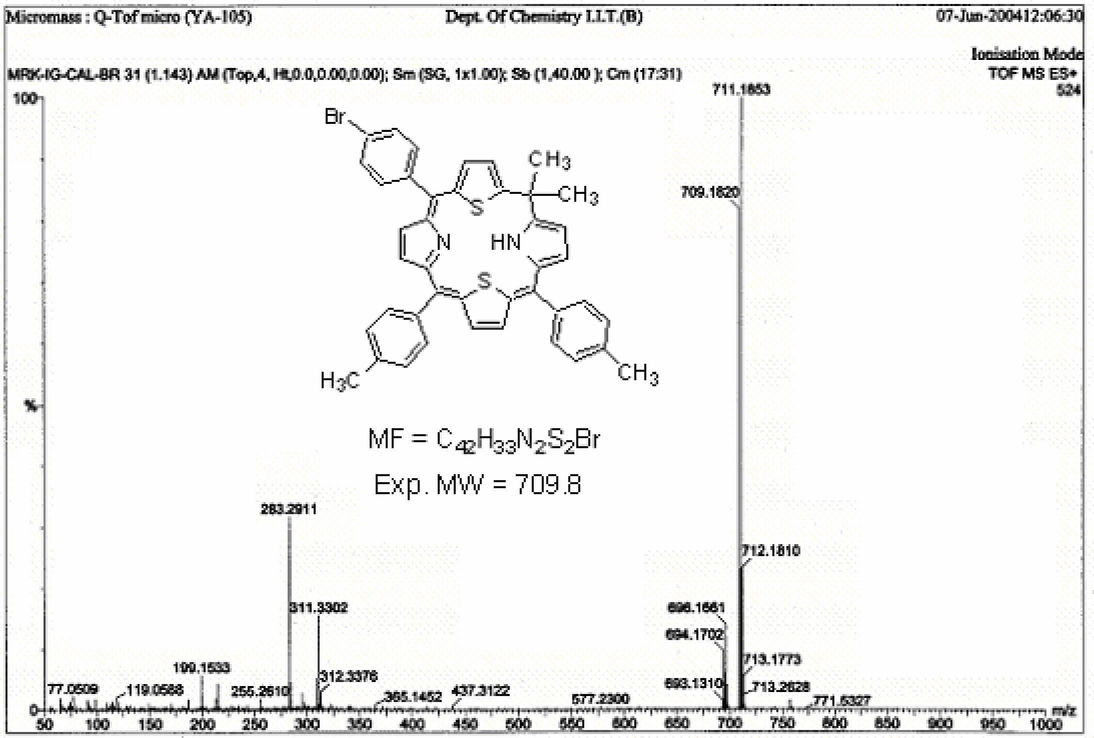
ES-MS mass spectrum of 21,23-dithiaphlorin **8**.



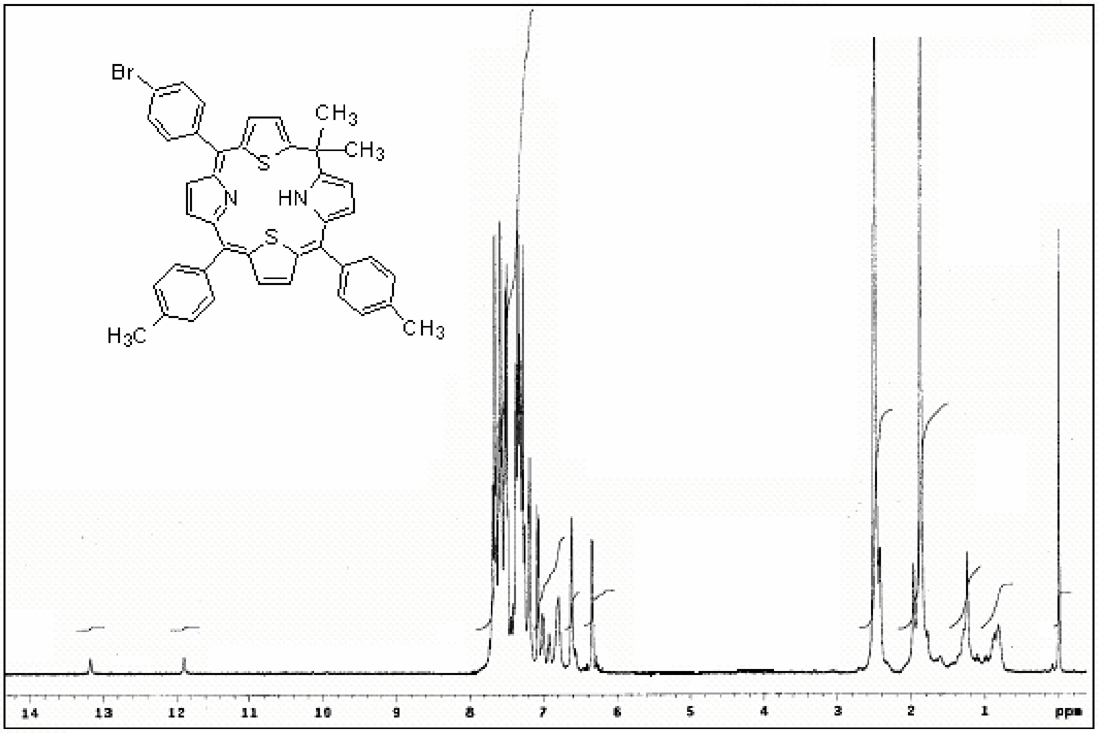
^{1}H NMR spectrum of 21,23-dithiaphlorin **8** recorded in CDCl$_3$.



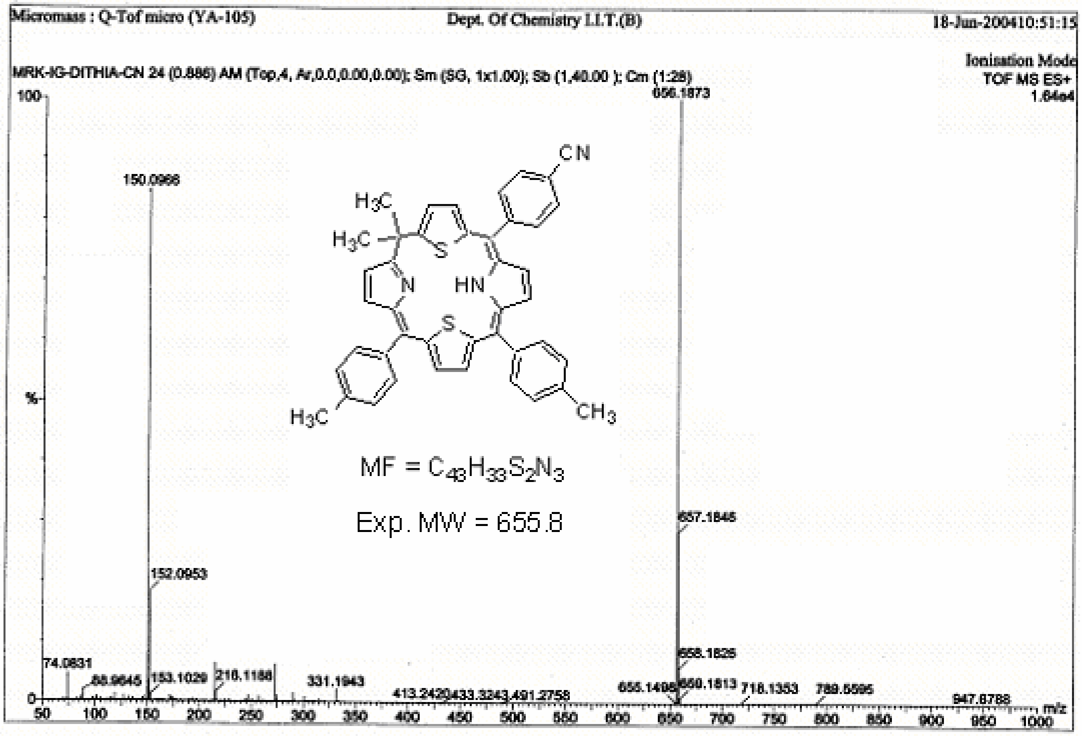
^{13}C NMR spectrum of 21,23-dithiaphlorin **8**.



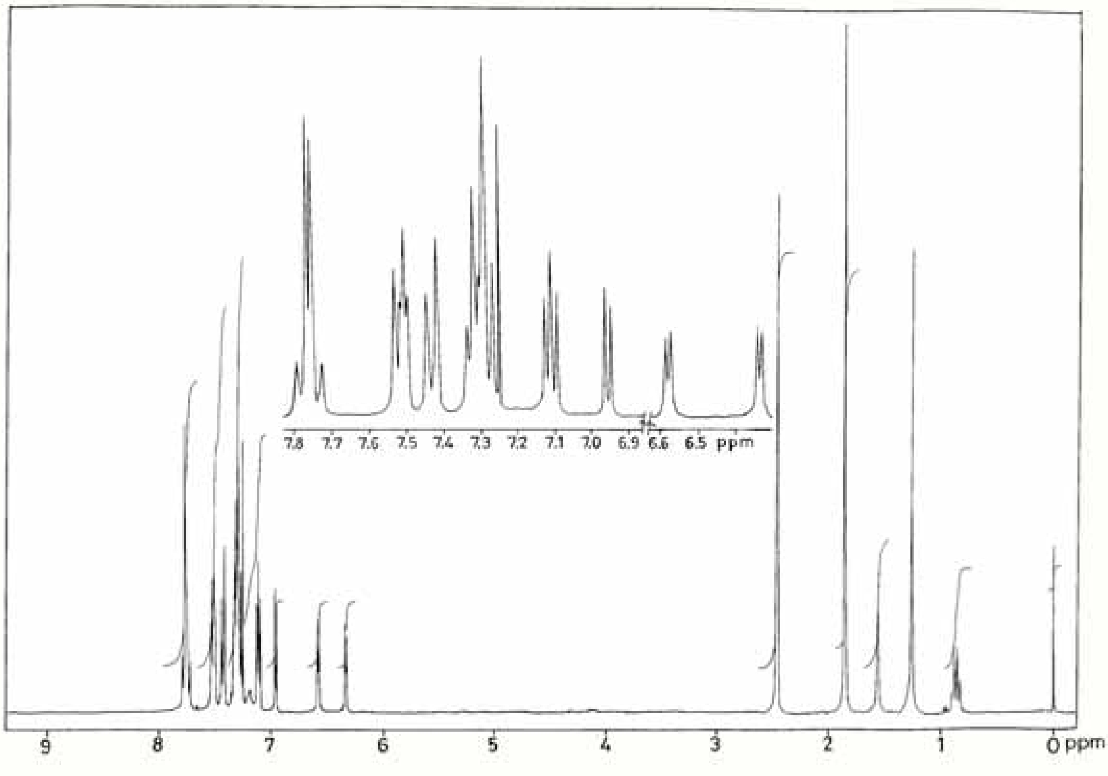
ES-MS mass spectrum of 21,23-dithiaphlorin **9**.



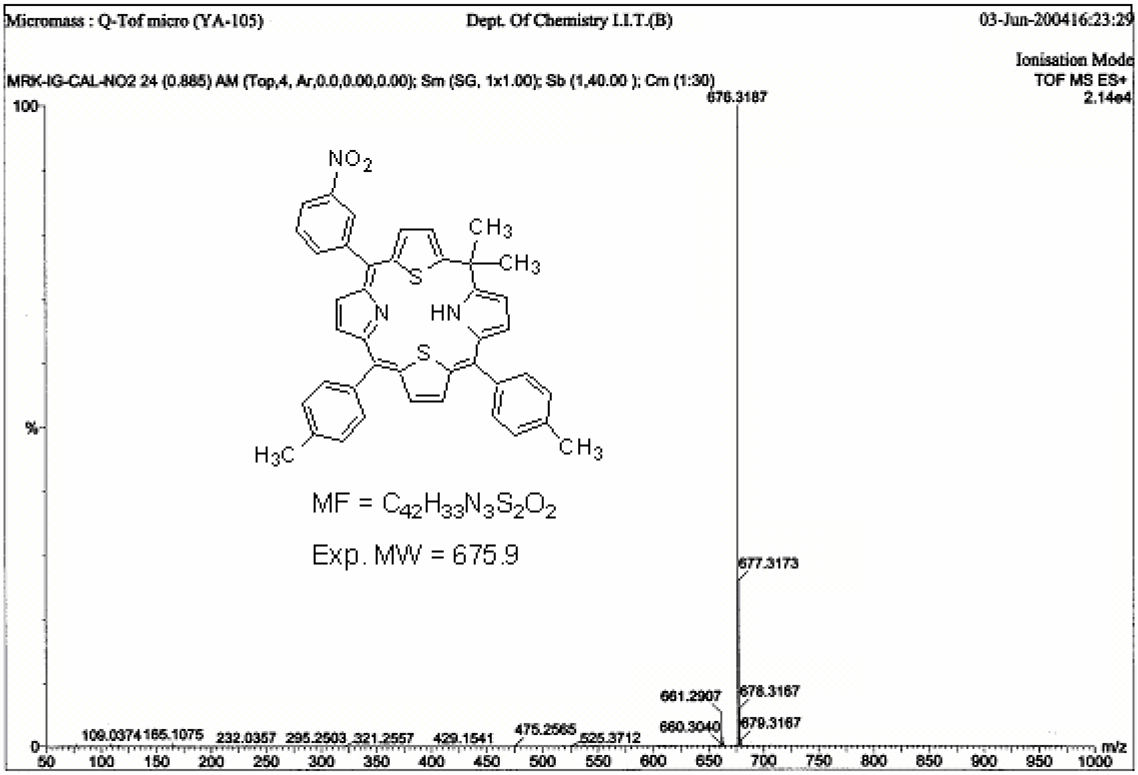
^{1}H NMR spectrum of 21,23-dithiaphlorin **9** recorded in $CDCl_3$.



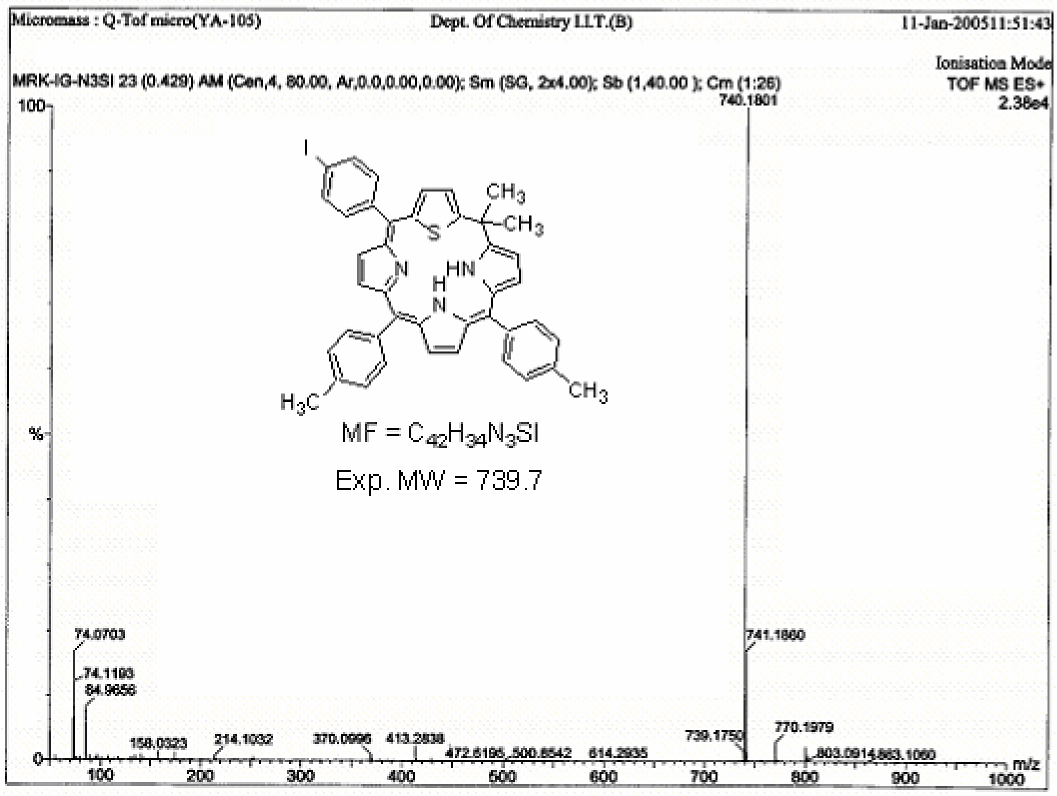
ES-MS spectrum of 21,23-dithiaphlorin **10**.



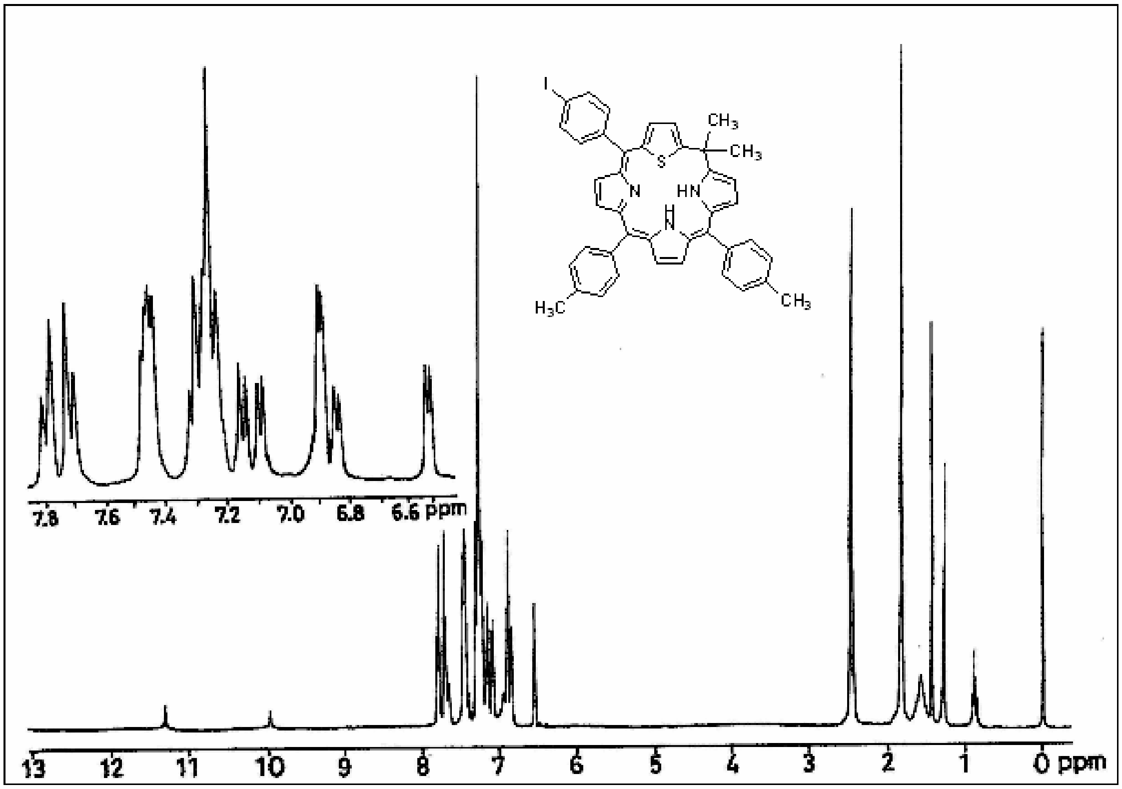
^{1}H NMR spectrum of 21,23-dithiaphlorin **10** recorded in CDCl$_3$ **.**



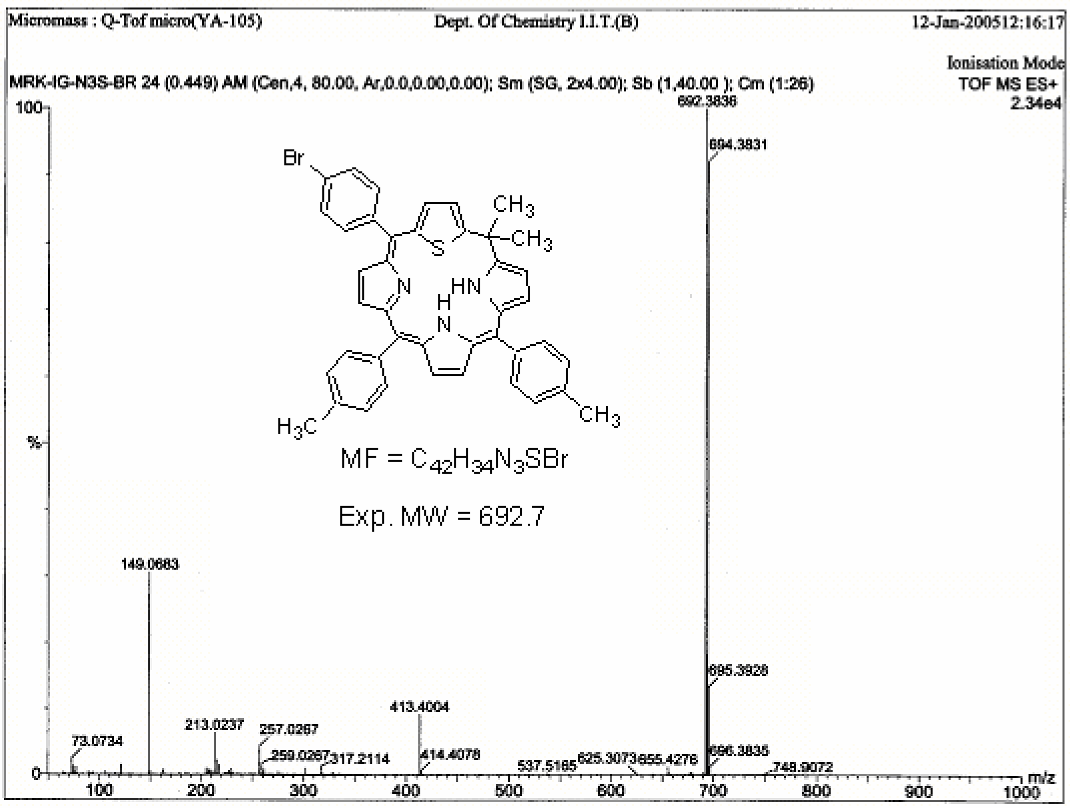
ES-MS mass spectrum of 21,23-dithiaphlorin **11**.



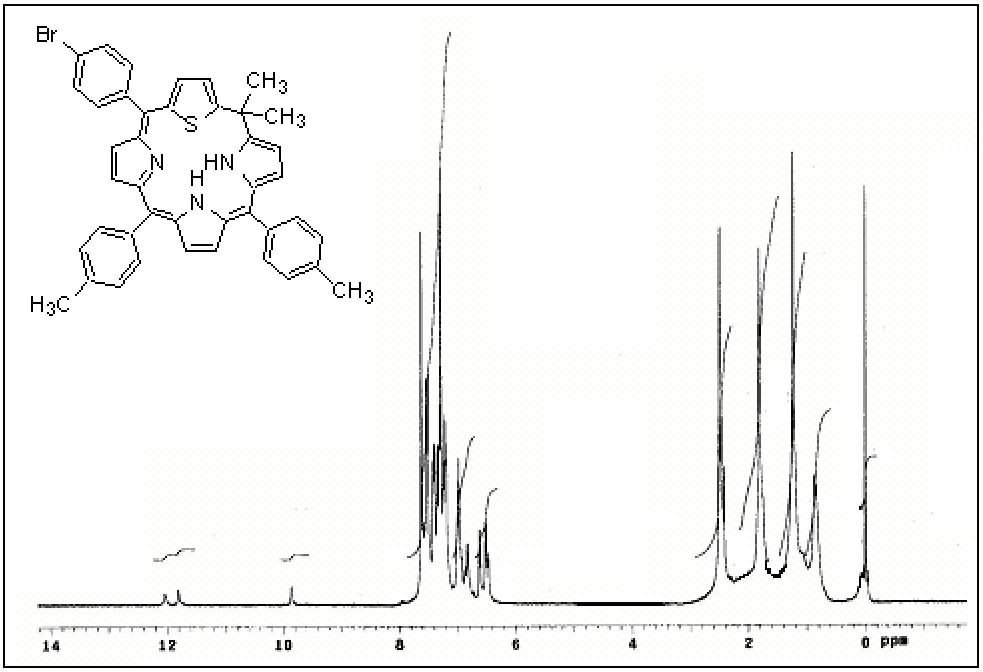
ES-MS mass spectrum of 21-monothiaphlorin **13**.



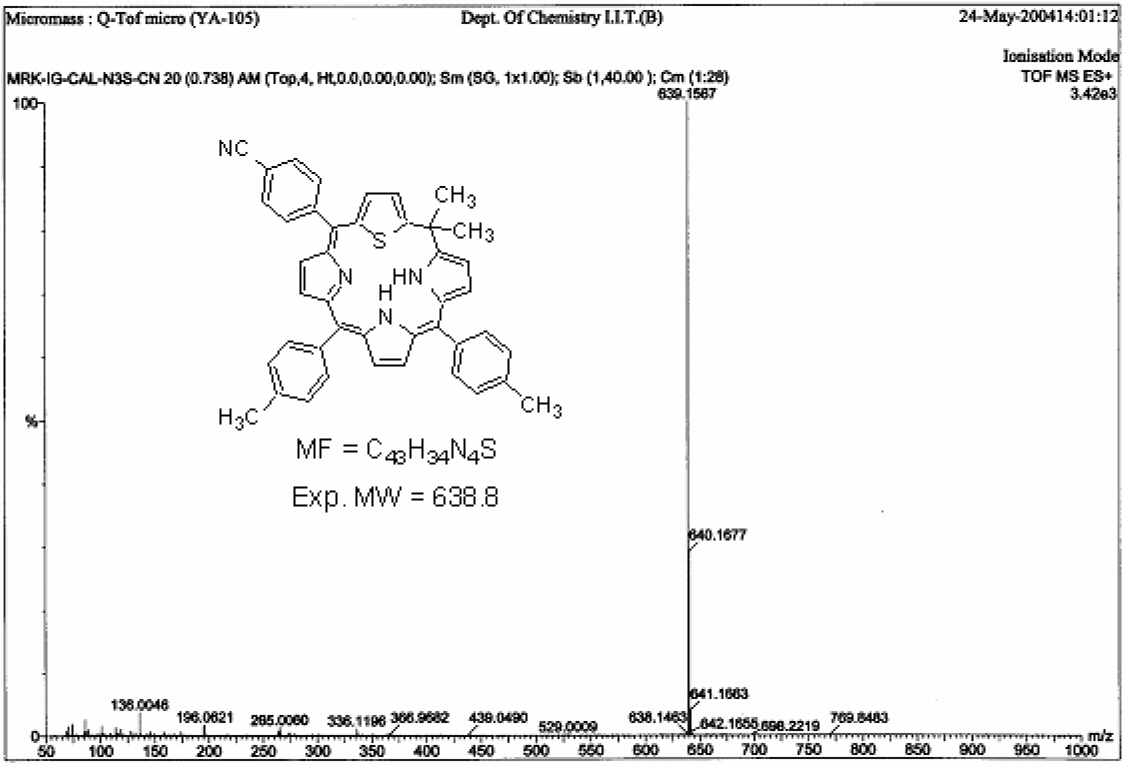
^{1}H NMR spectrum of 21-monothiaphlorin **13** recorded in CDCl$_3$.



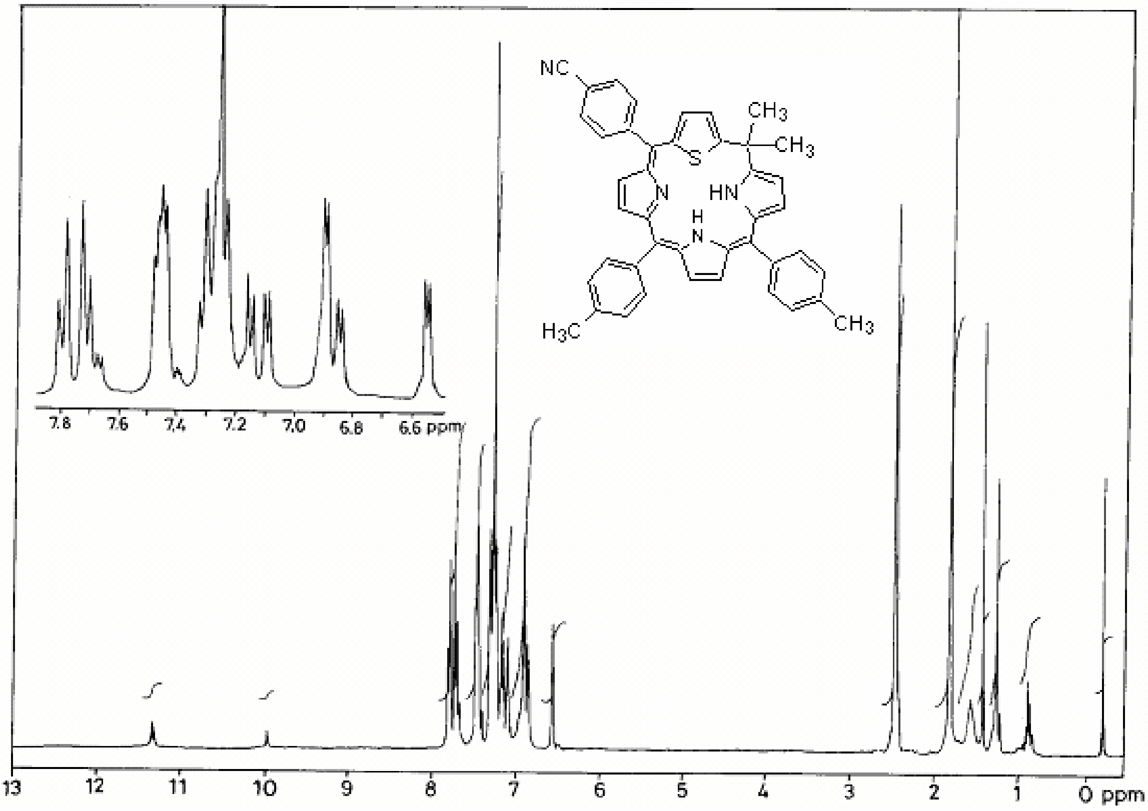
ES-MS mass spectrum of 21-monothiaphlorin **14**.



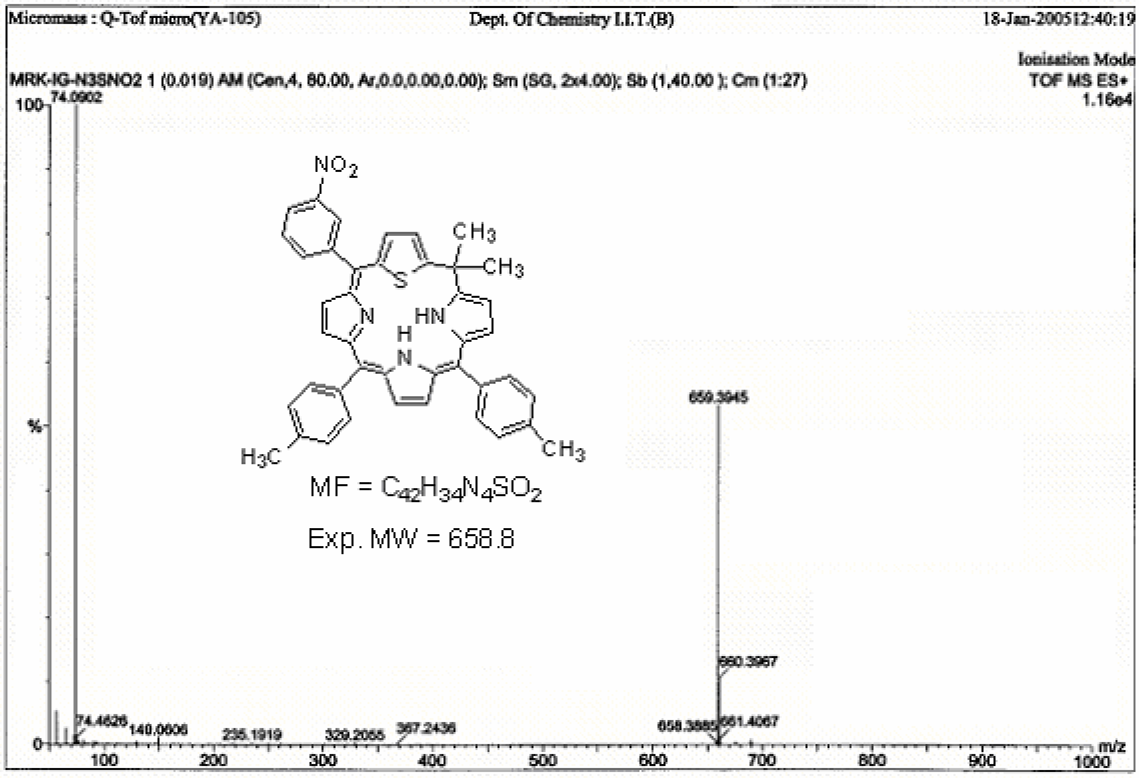
^{1}H NMR spectrum of 21-monothiaphlorin **14** recorded in CDCl$_3$.



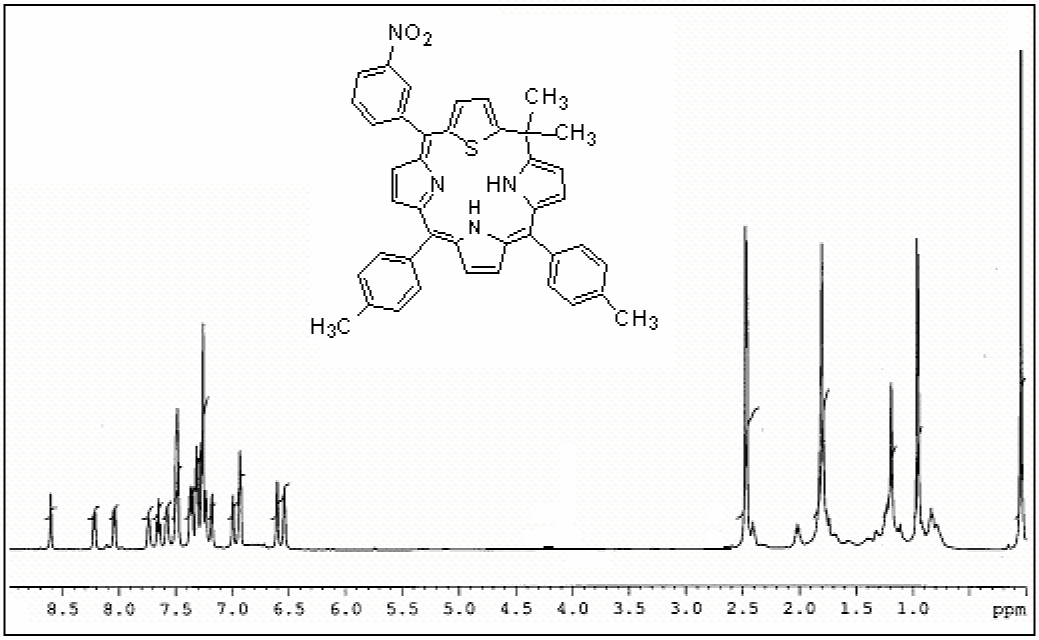
ES-MS mass spectrum of 21-monothiaphlorin **15**.



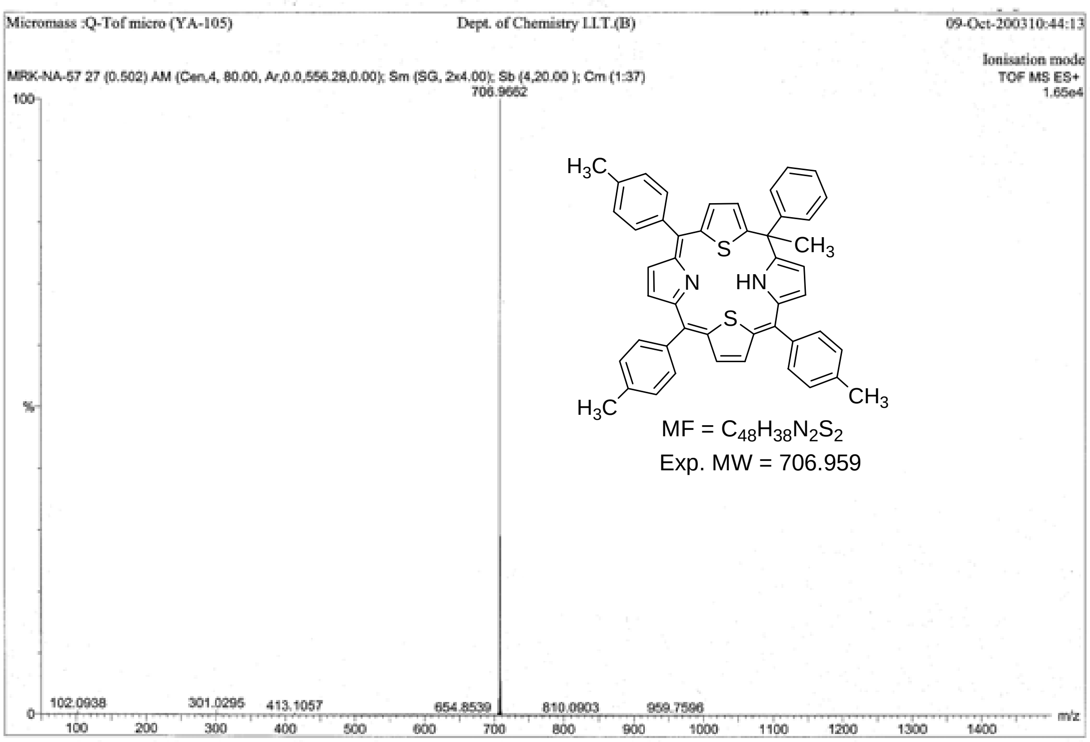
^{1}H NMR spectrum of 21-monothiaphlorin **15** recorded in $CDCl_3$.



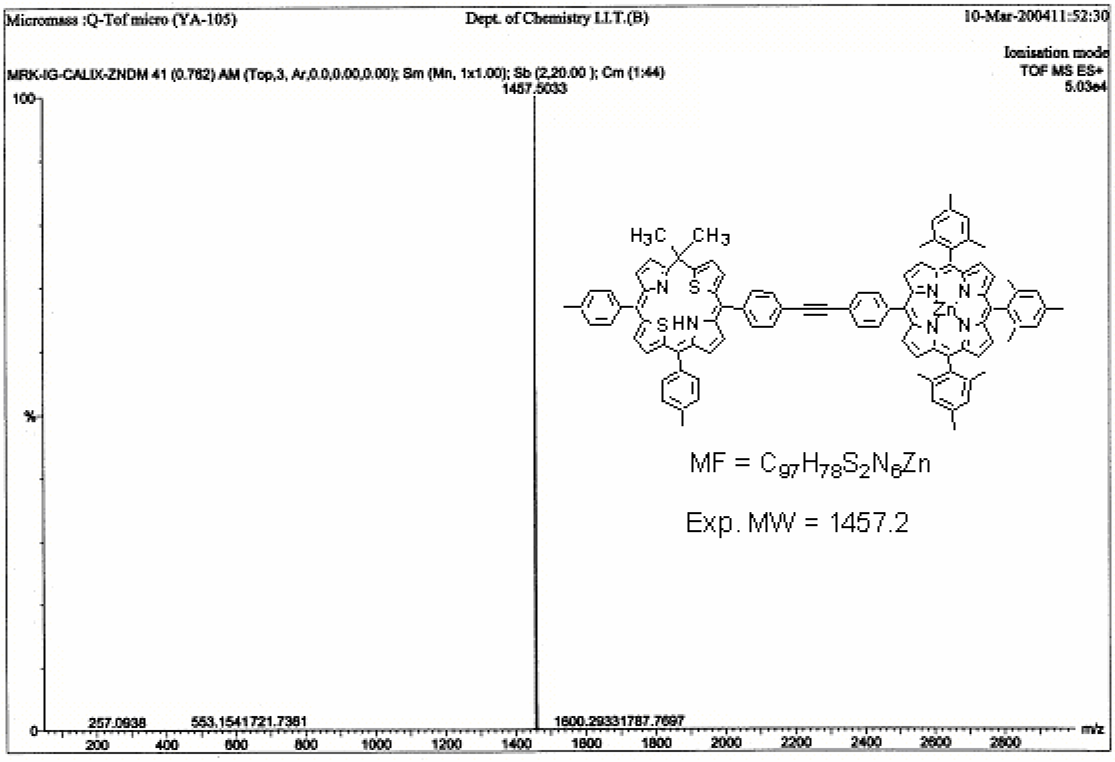
ES-MS mass spectrum of 21-monothiaphlorin **16.**



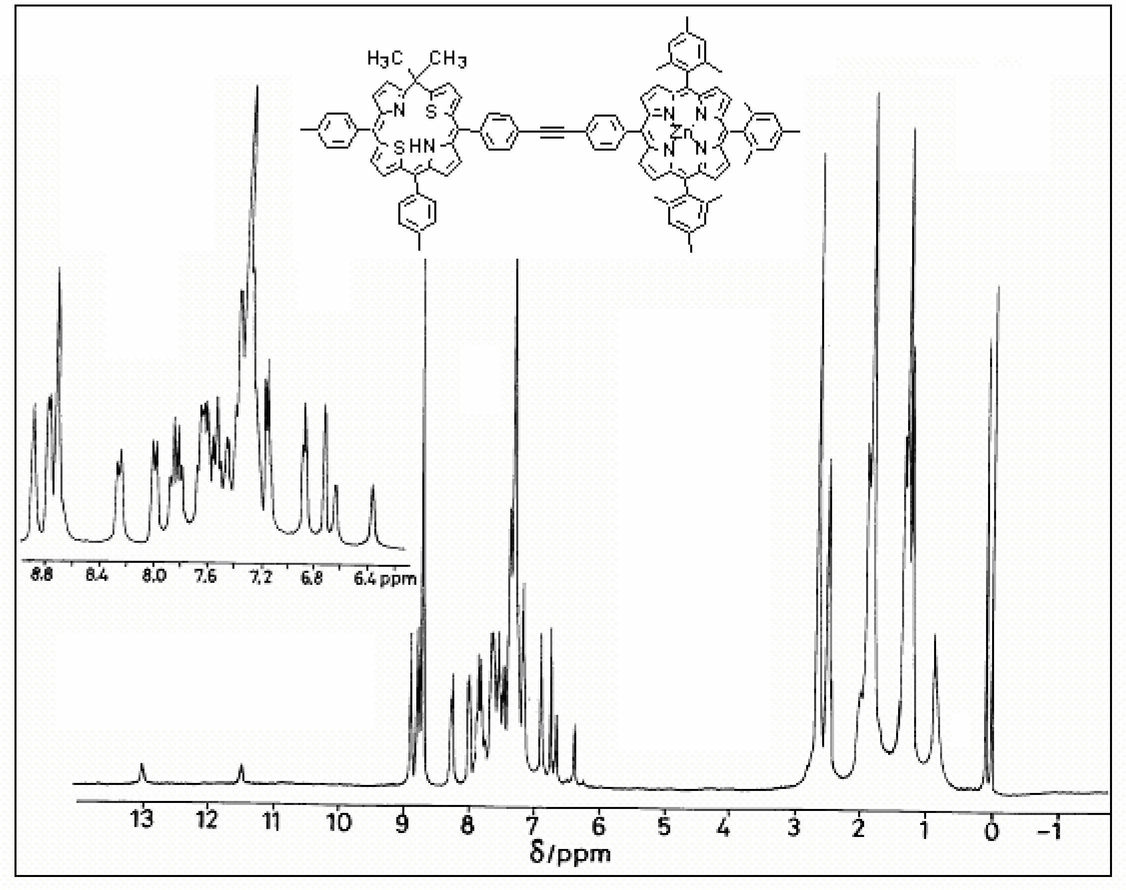
^{1}H NMR spectrum of 21-monothiaphlorin **16** recorded in $CDCl_3$.



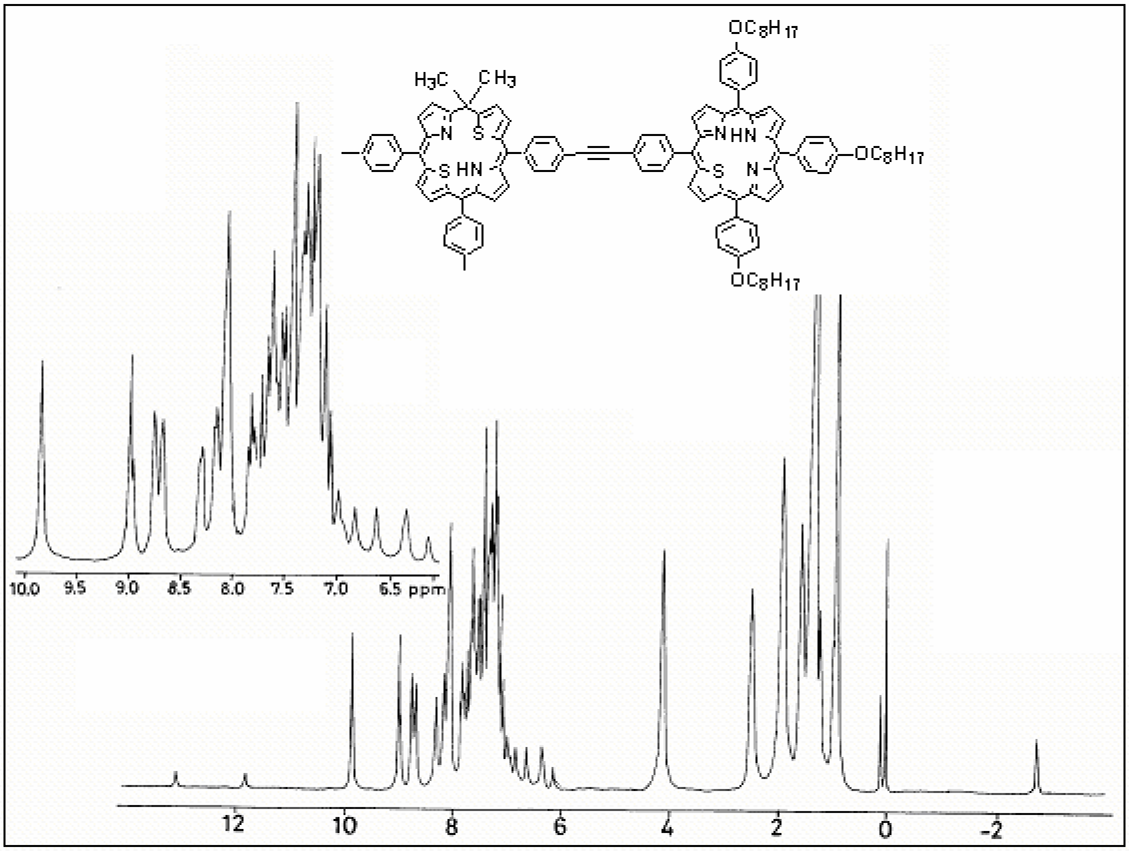
ES-MS mass spectrum of 21-monothiaphlorin **18.**



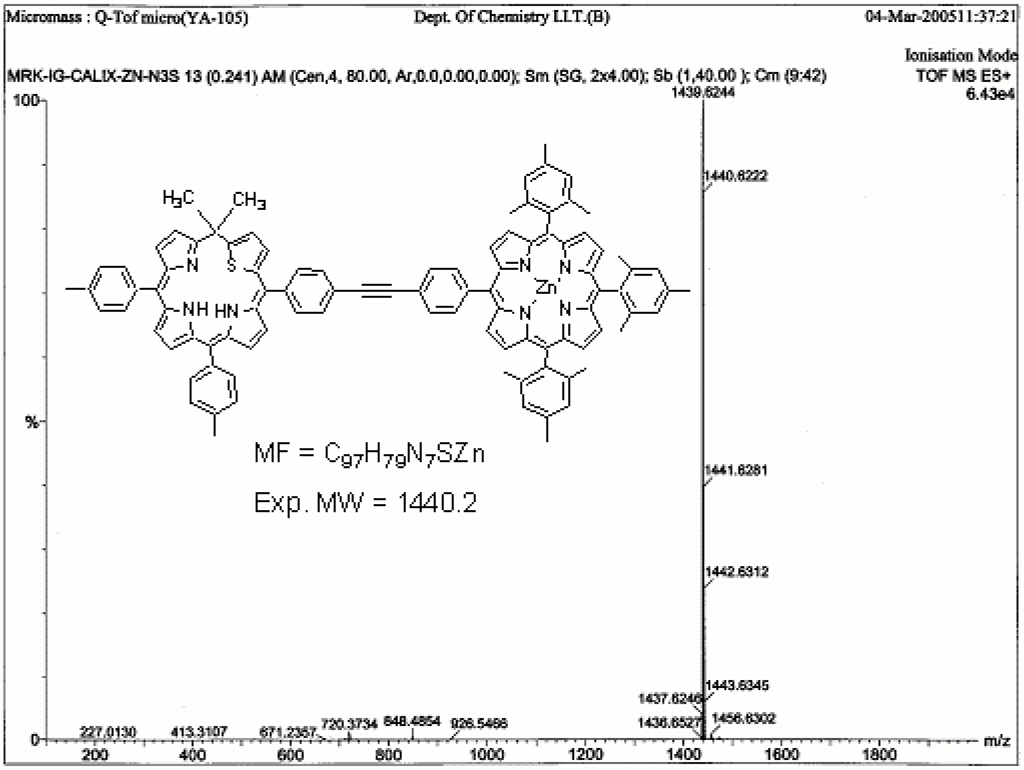
ES-MS mass spectrum of 21,23-dithiaphlorin-ZnN_4 porphyrin dyad **19**.



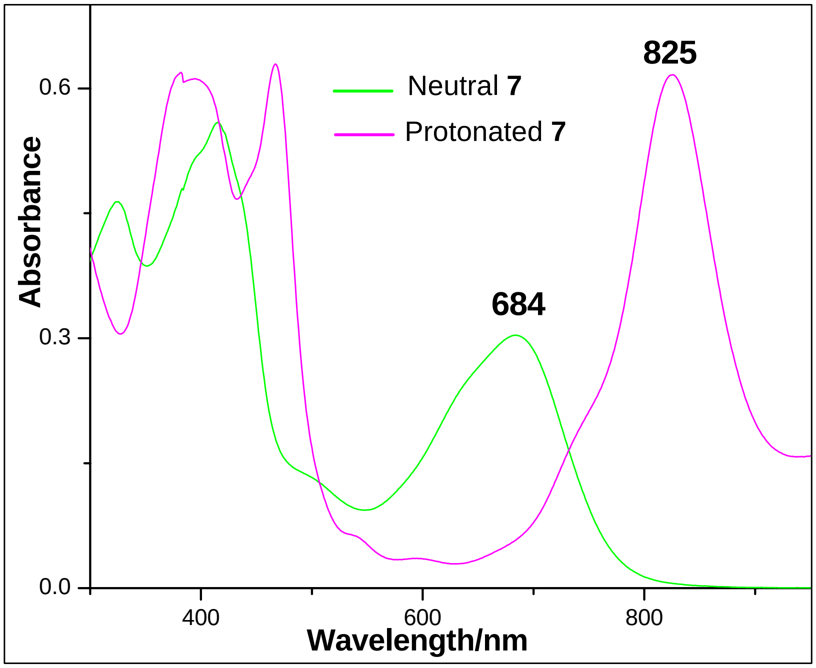
^{1}H NMR spectrum of 21,23-dithiaphlorin-ZnN$_4$ porphyrin dyad **19** recorded in CDCl$_3$.



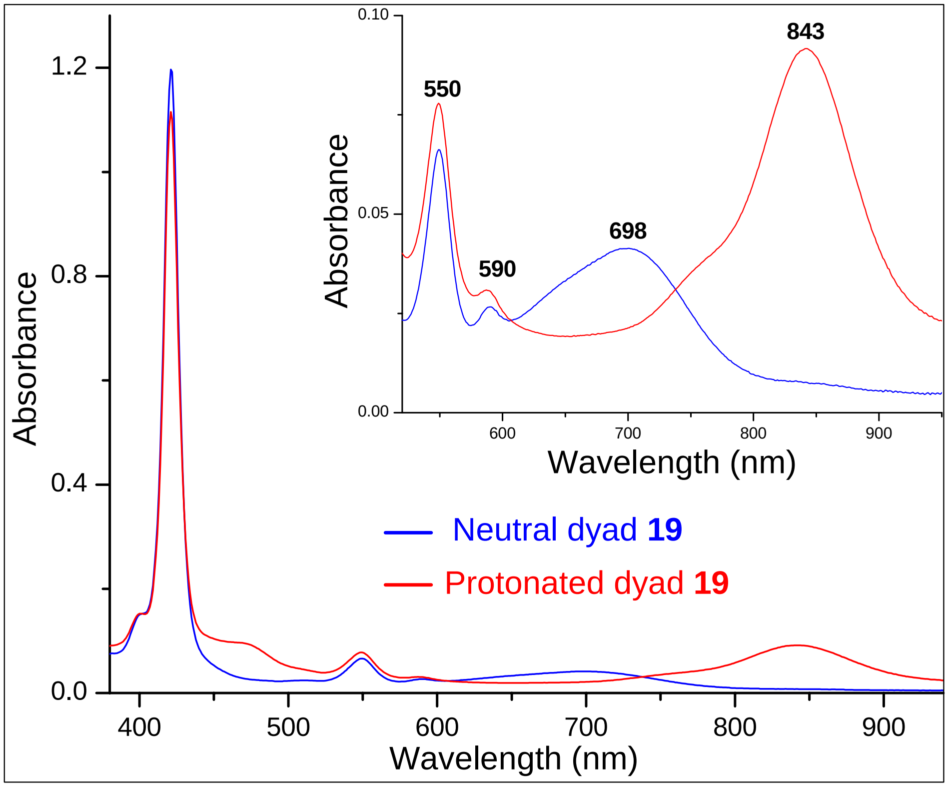
^{1}H NMR spectrum of 21,23-dithiaphlorin-N$_3$S porphyrin dyad **20** recorded in CDCl$_3$.



ES-MS mass spectrum of 21-monothiaphlorin-ZnN_4 porphyrin dyad **21**.



Absorption spectra of 21,23-dithiaphlorin **7** and its protonated form recorded in dichloromethane. The protonated 21,23-dithiaphlorin **7** was generated by the addition of dilute solution (0.2M) of trifluoroacitic acid in dichloromethane.



Absorption spectra of dyad **19** and its protonated form recorded in dichloromethane (3 mL of 1.372 x 10^{-6} M dichloromethane solution of dyad **19** was selectively protonated by addition of 4 μl of the 2 x 10^{-3} M trifluoroacetic acid). The inset shows the expansion of 520-940 nm region.

ANION BINDING STUDIES:

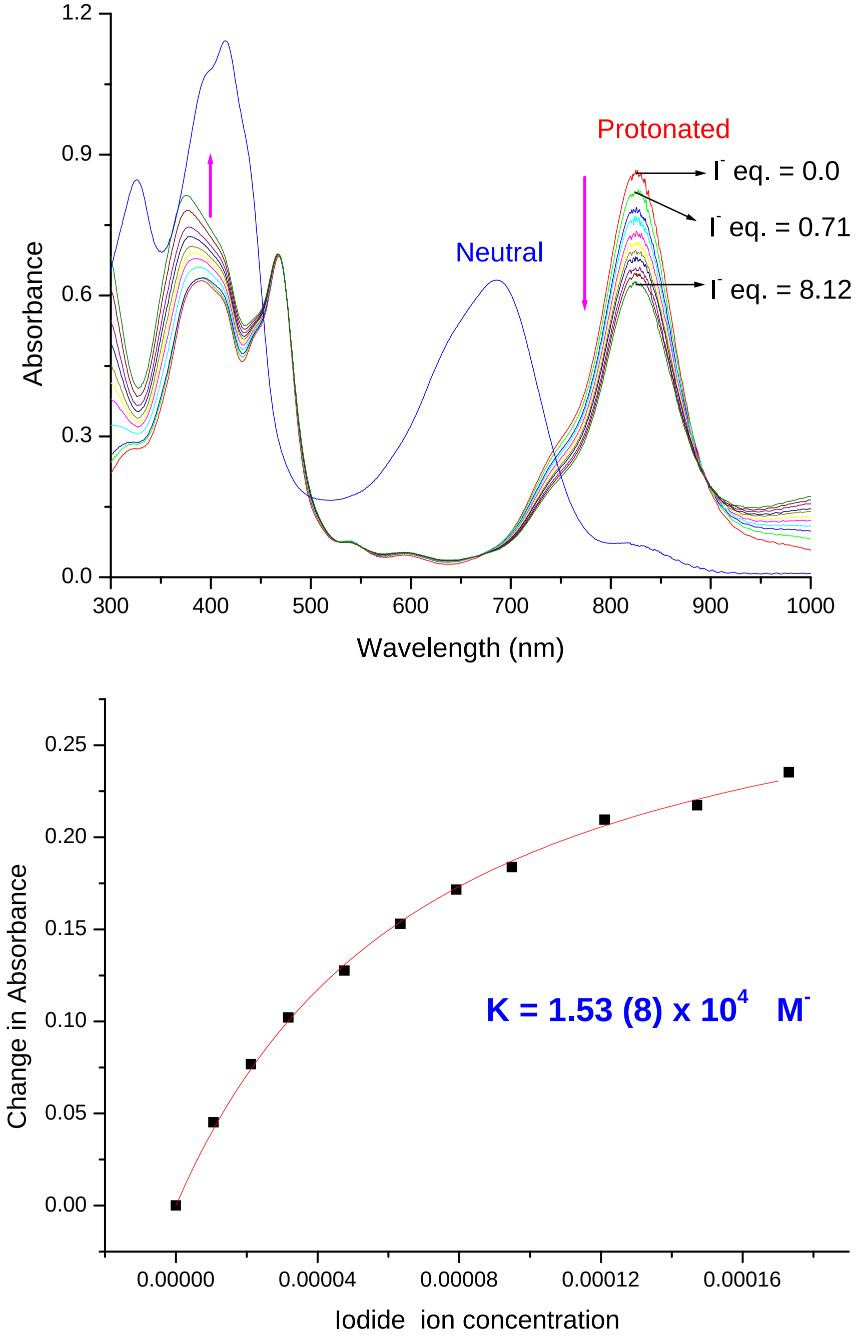
The general procedure for the UV-Vis and Fluorescence binding studies involved making sequential additions of titrant (anionic guest) using Hamilton Micro syringes to a 3 ml aliquot of the host stock solution in a spectrometric cell using dichloromethane as solvent. UV-Vis and emission spectroscopic data were then collated and combined to produce plots that showed the changes in host spectral features as a function of changes in the concentration of the guest.

Calculations of Binding Constants, *K*:

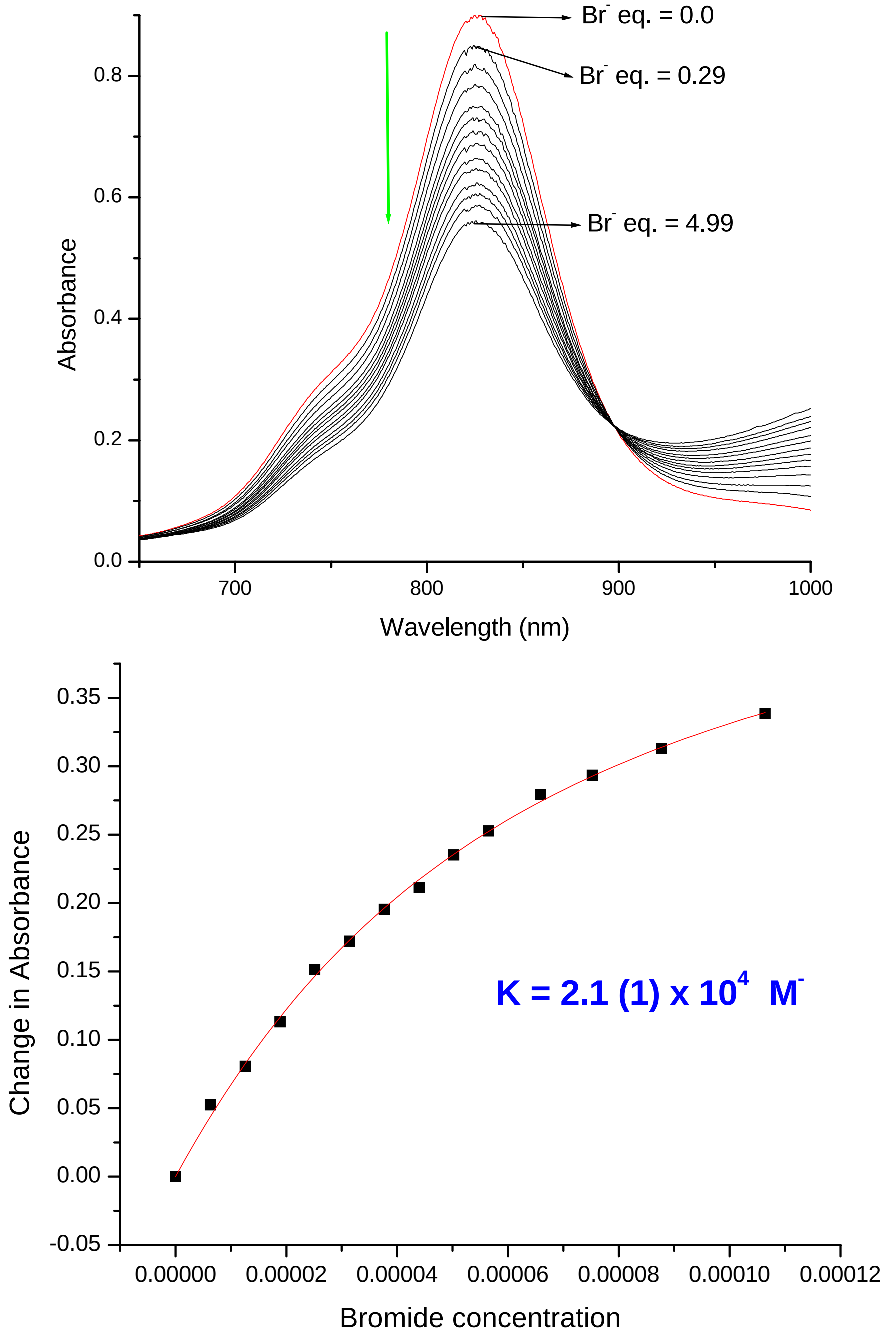
The binding constants were calculated using 1:1 anion binding model according to the following formula.* The change in absorbance, ΔA or in emission intensity ΔI, was calculated at λ value where the spectral change was maximal. The ΔA or ΔI were plotted against the concentration of the added anion guest. The data was computer fit using the Origin version 6.0 software package.

* Taken from Ref. **20** given in the article.

Representative plots and curve fits are given below:



Effect of tetrabutylammonium iodide ion titration on absorption spectra of protonated dithiaphlorin **7** in dichloromethane. The concentration of the dithiaphlorin used was 2.13 x 10^{-5} M and the concentration range of the I^- used was 1.06 x 10^{-5} M to 1.73 x 10^{-4} M. the spectra were measured at 825 nm at room temperature.



Effect of tetrabutylammonium bromide ion titration on absorption spectra of protonated dithiaphlorin **7** in dichloromethane. The concentration of the dithiaphlorin used was 2.13 x 10^{-5} M and the concentration range of the Br^- used was 6.29 x 10^{-6} M to 1.06 x 10^{-4} M. the spectra were measured at 825 nm at room temperature.

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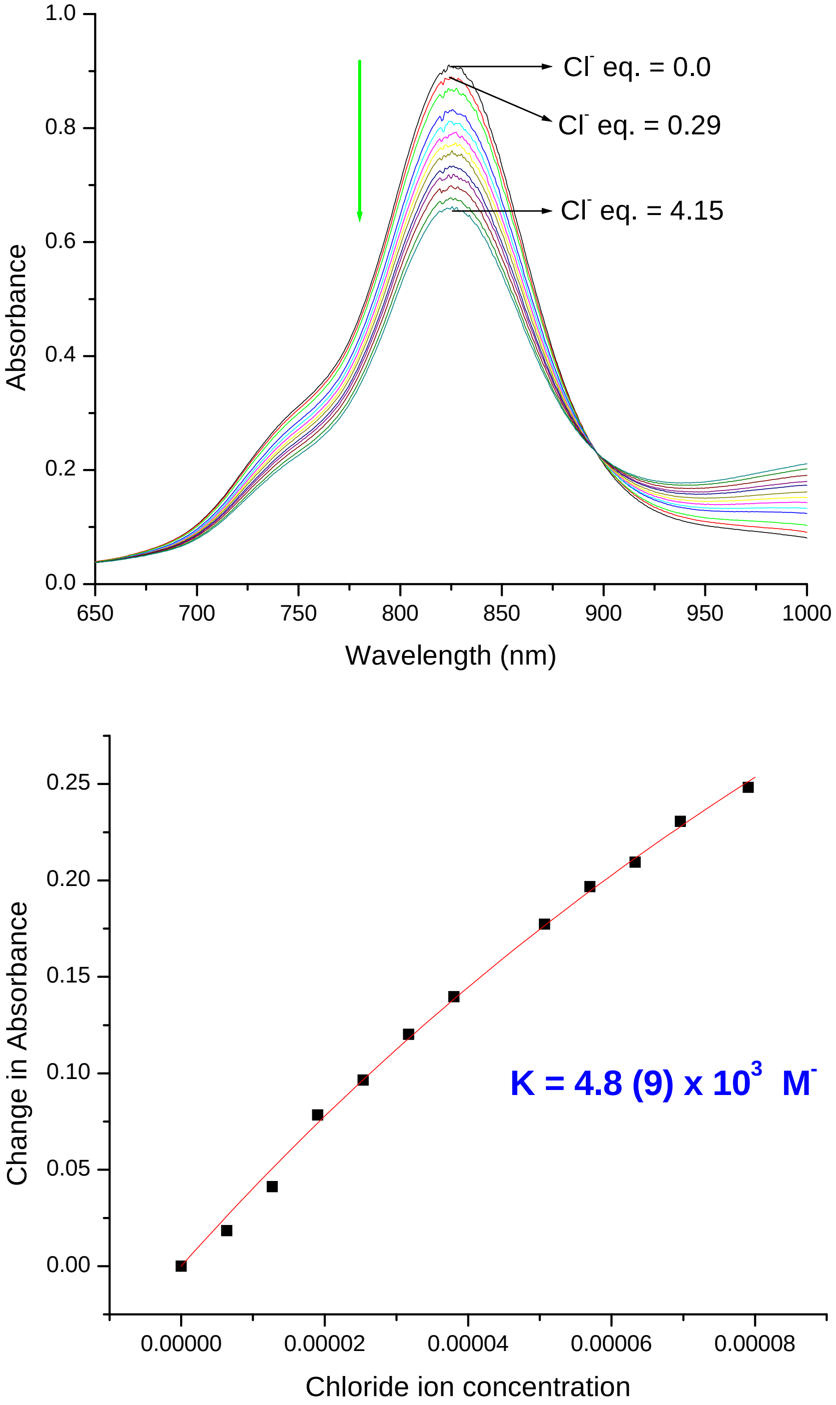
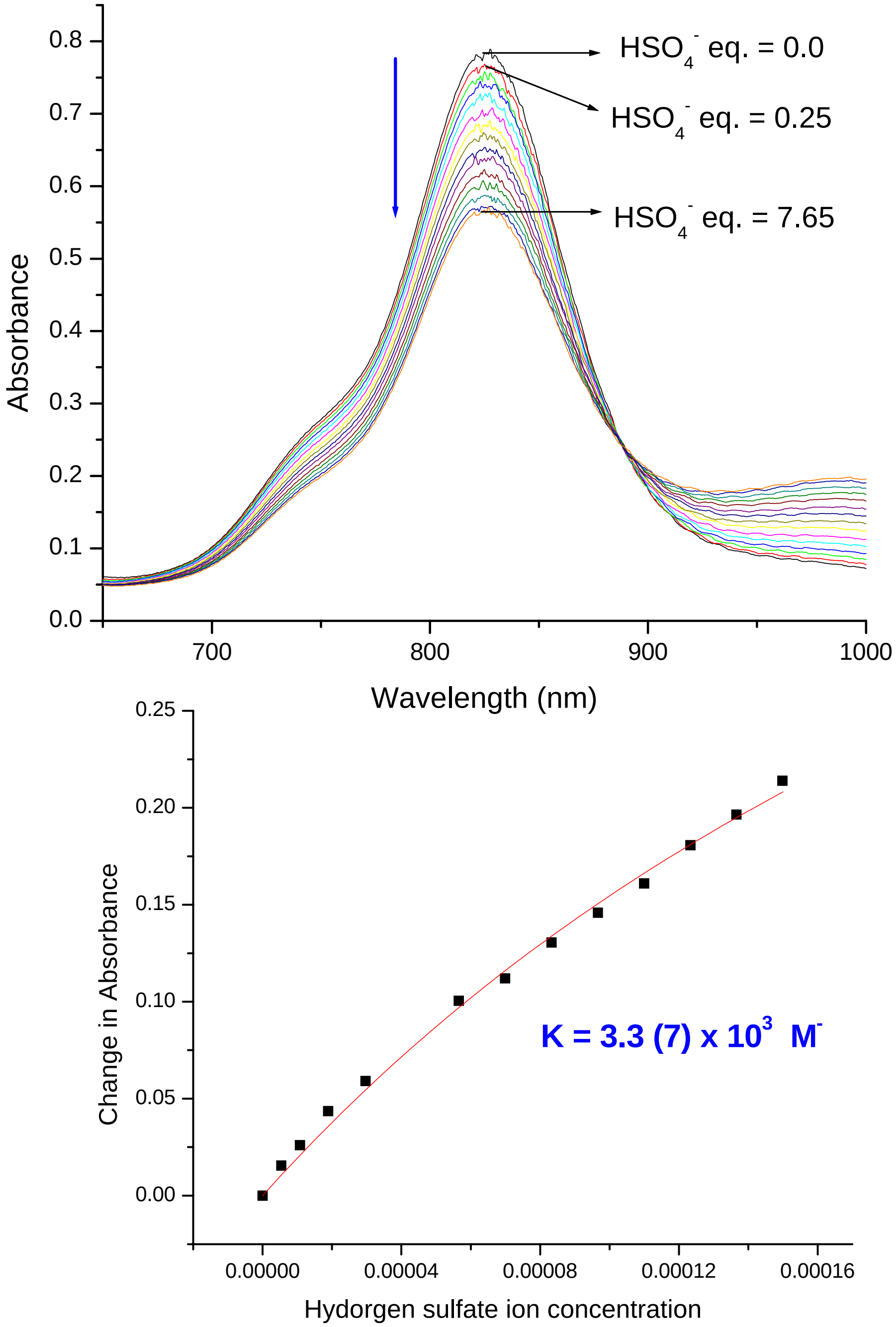
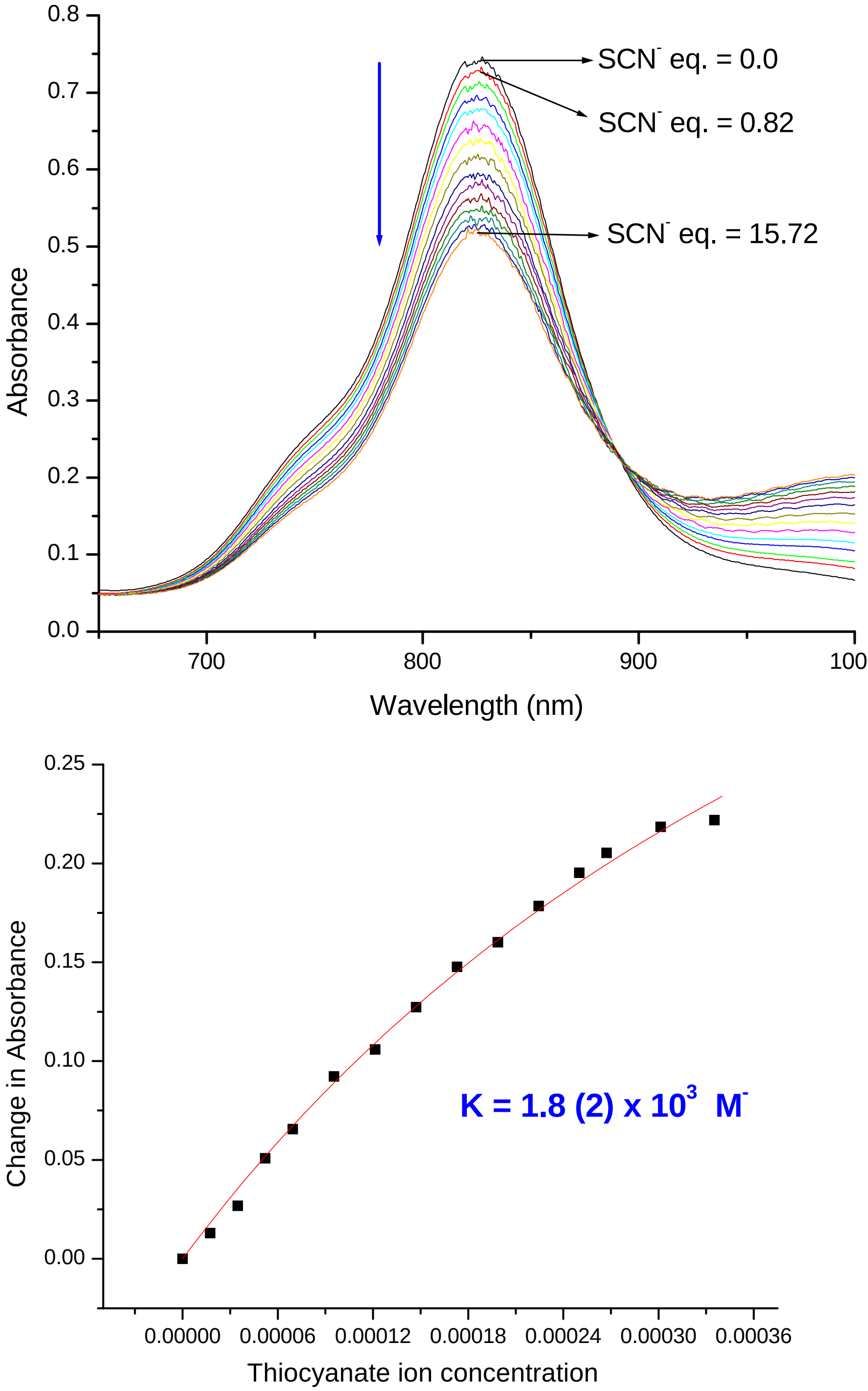


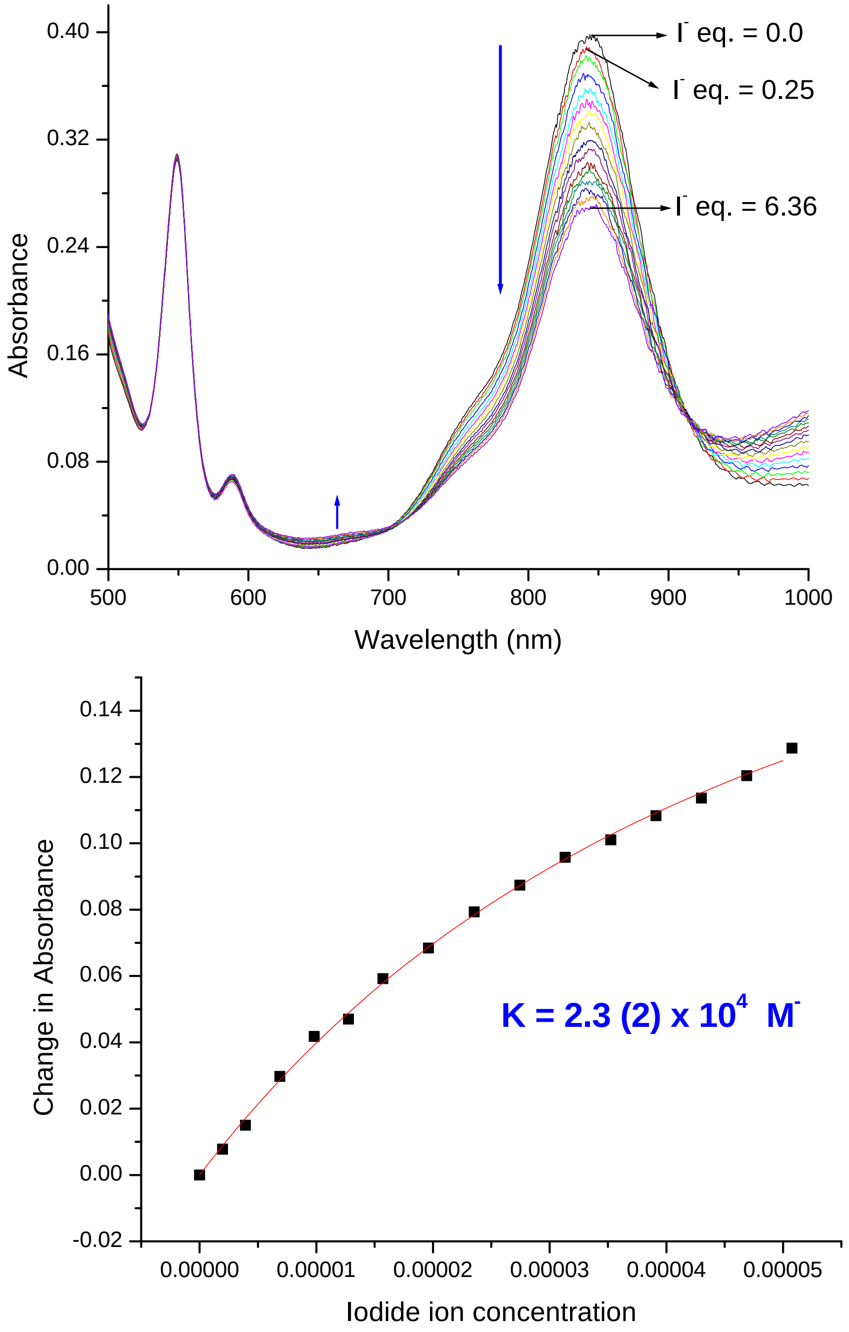
Effect of tetrabutylammonium chloride ion titration on absorption spectra of protonated dithiaphlorin **7** in dichloromethane. The concentration of the dithiaphlorin used was 2.13 x 10^{-5} M and the concentration range of the Cl^- used was 6.35 x 10^{-6} M to 8.85 x 10^{-5} M. the spectra were measured at 825 nm at room temperature..



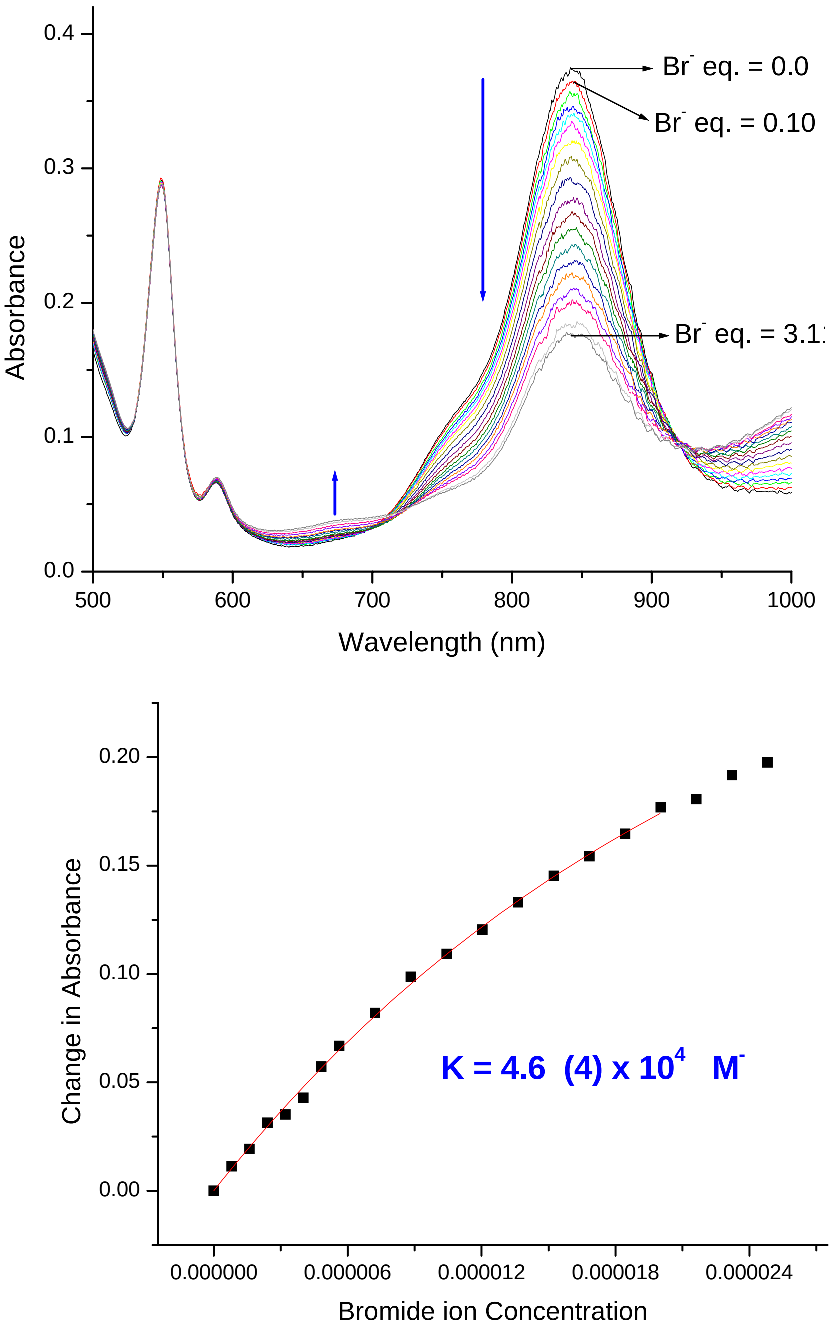
Effect of tetrabutylammonium hydrogen sulfate ion titration on absorption spectra of protonated dithiaphlorin in dichloromethane. The concentration of the dithiaphlorin used was 2.13 x 10^{-5} M and the concentration range of the HSO_4^- used was 5.39 x 10^{-6} M to 1.63 x 10^{-4} M. the spectra were measured at 825 nm at room temperature.



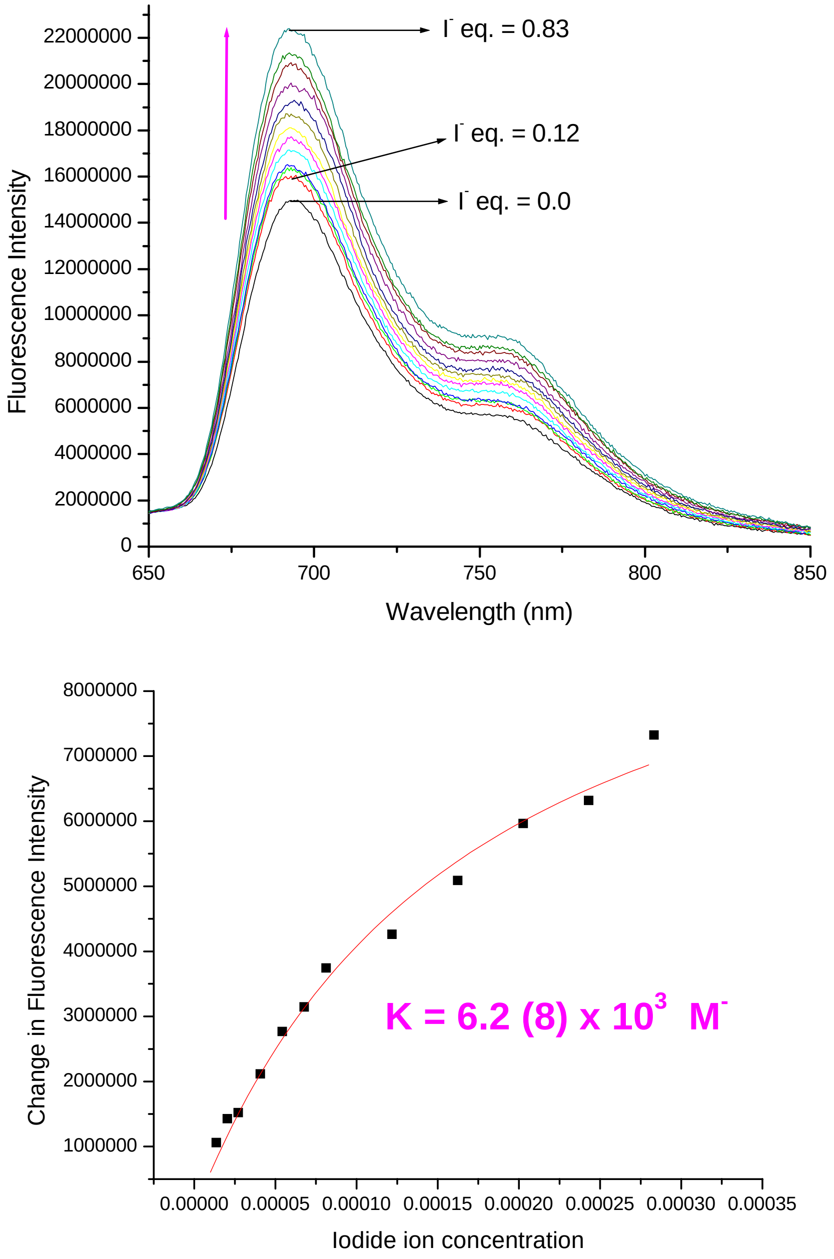
Effect of tetrabutylammonium thiocyanate ion titration on absorption spectra of protonated dithiaphlorin **7** in dichloromethane. The concentration of the dithiaphlorin used was 2.13 x 10^{-5} M and the concentration range of the SCN^{-} used was 1.74 x 10^{-5} M to 3.35 x 10^{-4} M. the spectra were measured at 825 nm at room temperature.



Effect of tetrabutylammonium iodide ion titration on absorption spectra of protonated dithiaphlorin-Zn(II)N_4 porphyrin **19** dyad in dichloromethane. The amount of TFA used was 1 μL of 2 x 10^{-3} M, (TFA concentration was 6.45 x 10^{-7} M). The concentration of the dyad **19** used was 7.98 x 10^{-6} M and the concentration range of the I^- used was 1.97 x 10^{-6} M to 5.08 x 10^{-5} M. the spectra were measured at 842 nm at room temperature.



Effect of tetrabutylammonium iodide ion titration on absorption spectra of protonated dithiaphlorin-zincN_4 porphyrin dyad **19** in dichloromethane. The amount of TFA used was 1 µL of 2 x 10^{-3} M, (TFA concentration was 6.45 x 10^{-7} M). The concentration of the dithiaphlorin used was 7.98 x 10^{-6} M and the concentration range of the Br^- used was 8.04 x 10^{-7} M to 2.48 x 10^{-5} M. the spectra were measured at 842 nm at temperature.



Effect of addition of increasing amounts of tetrabutylammonium iodide on the steady state fluorescence spectra of protonated dyad **20** (8.82 x 10^{-6} M dichloromethane solution of dyad **20** was selectively protonated by addition of 1.5 µl of the 2 x 10^{-3} M trifluoroacetic acid in dichloromethane, (TFA concentration was 9.67 x 10^{-7} M). The protonated dyad was excited at 520 nm and the concentration range of iodide salt used was 1.06 x $^{-6}$ M to 7.32 x 10^{-6} M.