Supporting Information

Ion conducting cholesterol appended pyridinium bis amide – based gel in the selective detection of Ag^+ and Cl^- ions

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1. Change in emission of 1a in $CHCl_3$ containing 0.2% DMSO.

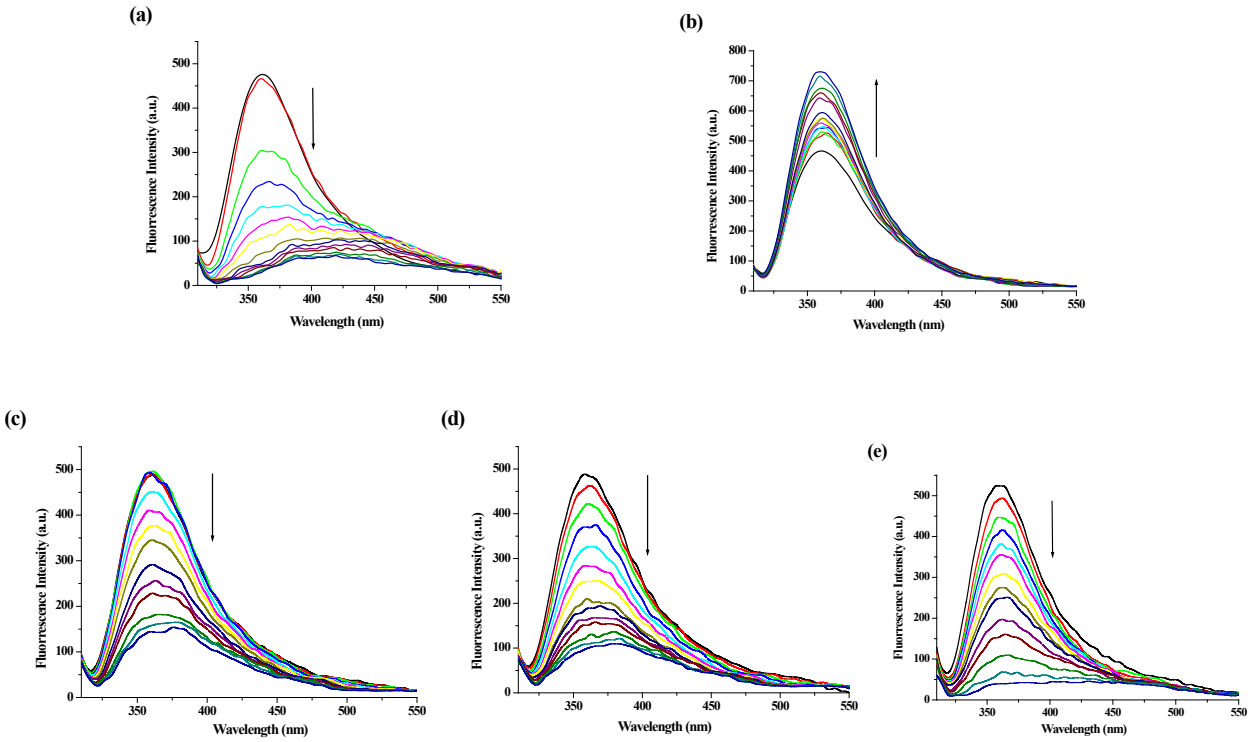


Figure 1S. Change in emission of **1a** (c = 2.25 x 10^{-5} M) upon addition of (a) F^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) OH^- in $CHCl_3$ containing 0.2% DMSO [concentration of all anions = 9.0 x 10^{-4} M].

2. Change in absorbance of 1a in $CHCl_3$ containing 0.2% DMSO

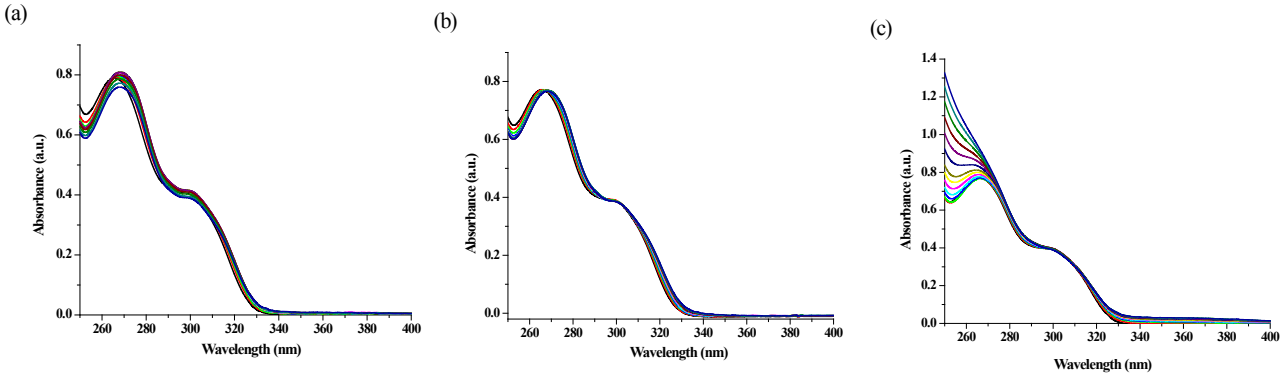


Figure 2S. Change in absorbance of **1a** (c = 2.25 x 10^{-5} M) upon addition of 6 equivalent amounts of (a) Cl^-, (b) Br^- and (c) I^- in $CHCl_3$ containing 0.2% DMSO [concentration of all anions = 9.0 x 10^{-4} M].

3. Change in absorbance of 1 in $CHCl_3$

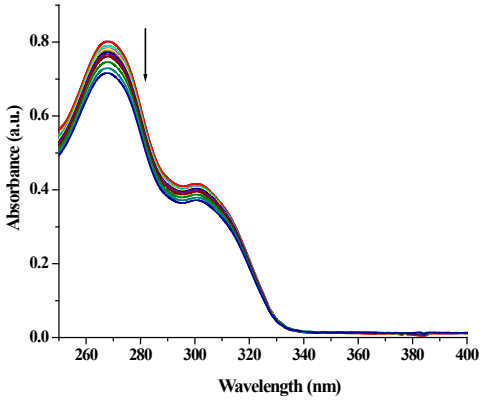


Figure 3S. Change in absorbance of **1** (c = 2.25 x 10^{-5} M) upon addition of 6 equivalent amounts of Ag^+ (c = 9.0 x 10^{-4} M) in $CHCl_3$.

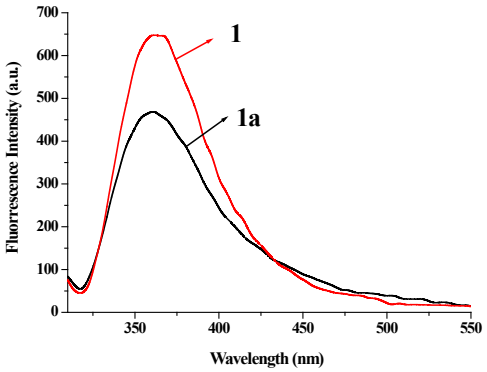


Figure 4S. Comparison of fluorescence emission spectra of **1** and **1a** (c = 2.25 x 10^{-5} M) in $CHCl_3$ containing 0.2% DMSO.

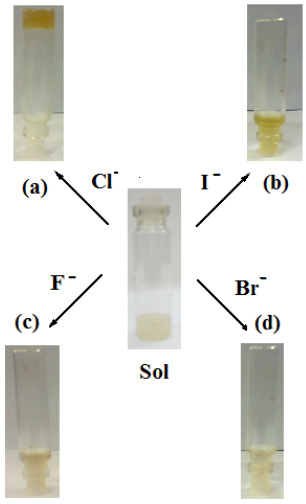


Figure 5S. Photographs showing the phase changes of **1a** (c = 8.03 $\times 10^{-3}$M) in $CHCl_3$ upon addition of 2 equiv. amounts of (a) TBACl, (b)TBAI, (c) TBAF and (d) TBABr (concentration of all halides was 2 $\times 10^{-2}$ M).

4. Binding constant curves.

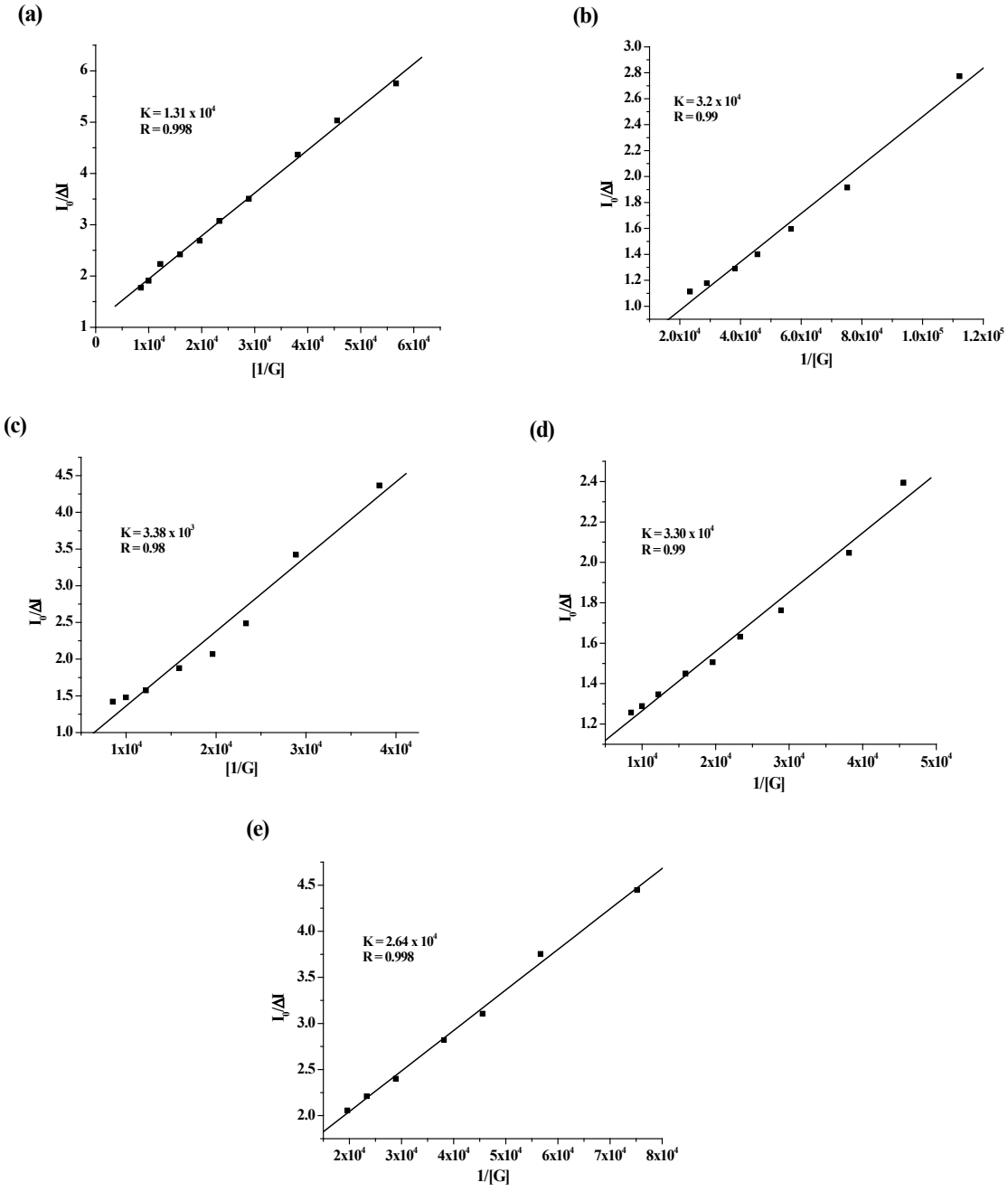


Figure 6S. Benesi–Hilderband plots for **1a** with (a) Cl^-, (b) F^-, (c) Br^-, (d) I^-, (e) OH^- ([**1a**] = 2.25 x 10^{-5} M) at 380 nm.

5. UV-VIS Job plot with Cl^- and F^-.

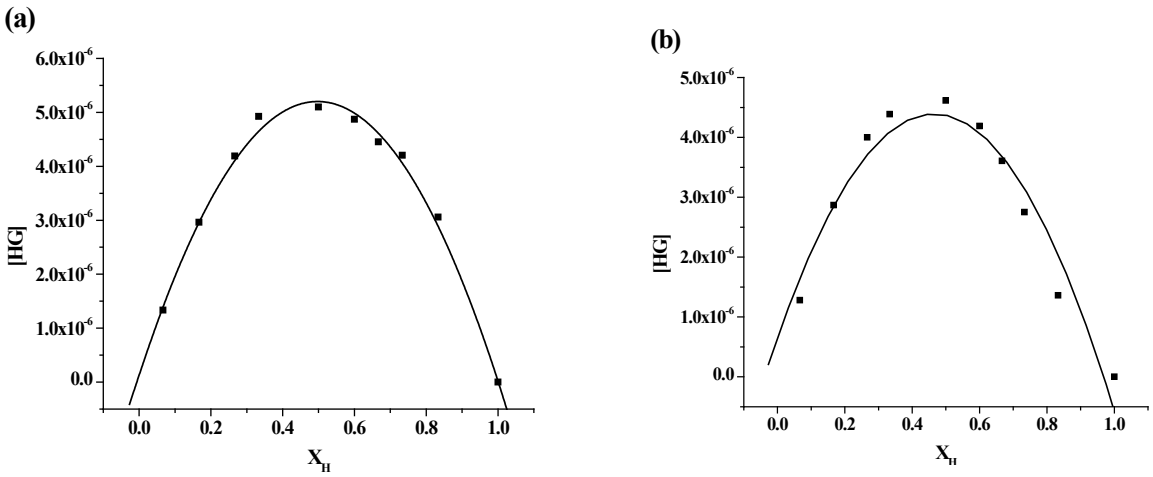


Figure 7S. Job plot of **1a** (c = 2.25 x10^{-5} M) with (a) Cl^- and (b) F^-.

6. ^{1}H NMR change with F^-.

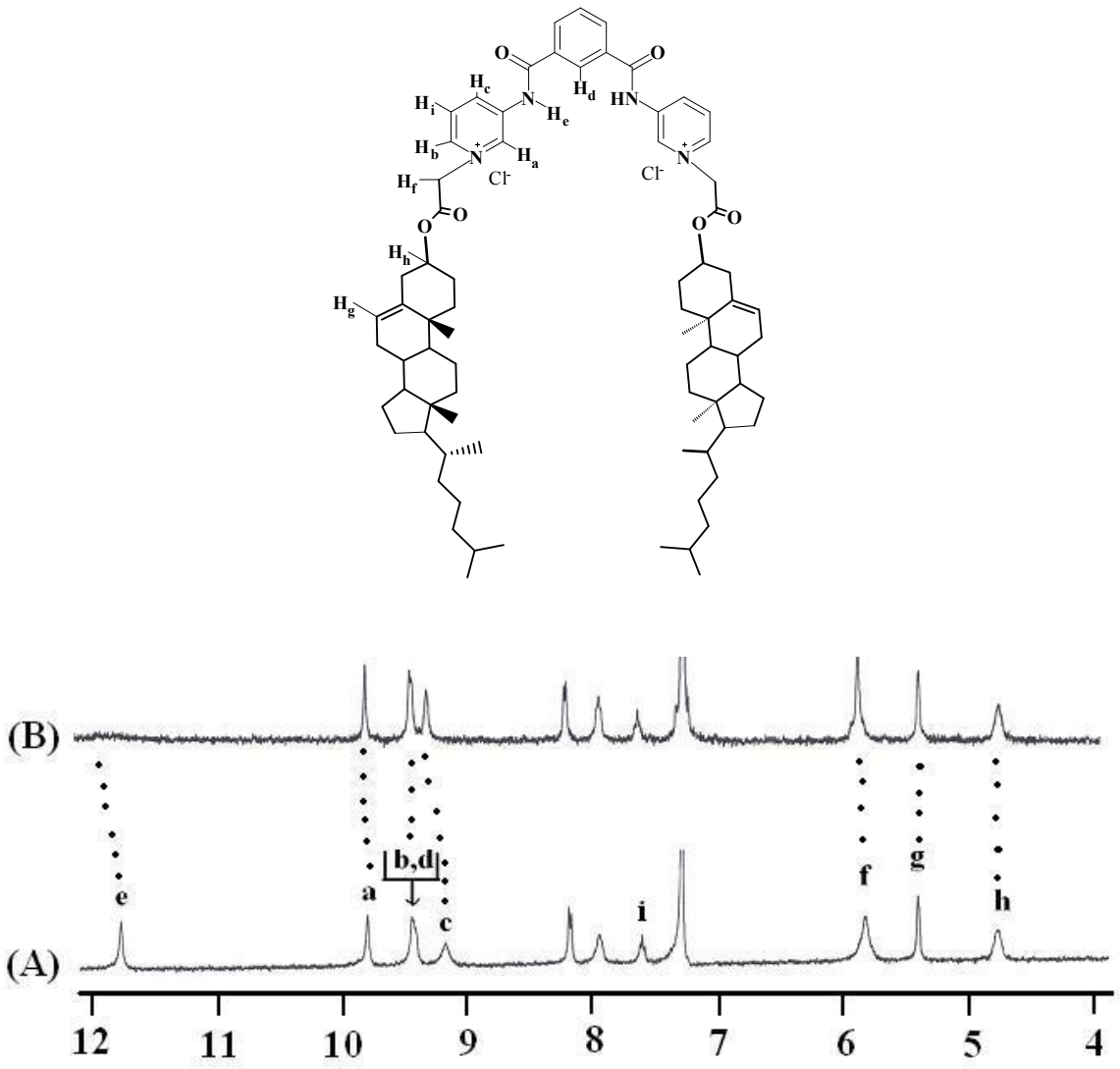


Figure 8S: Partial ^{1}H NMR (400 MHz, $CDCl_3$) of (A) compound **1** (c = 3.21 x 10^{-3} M) and (B) **1** with TBAF (1:1) [Addition of more than 1 equiv. amount of TBAF gave no sharp signal for characterization.]

7. NMR change with OH^-.

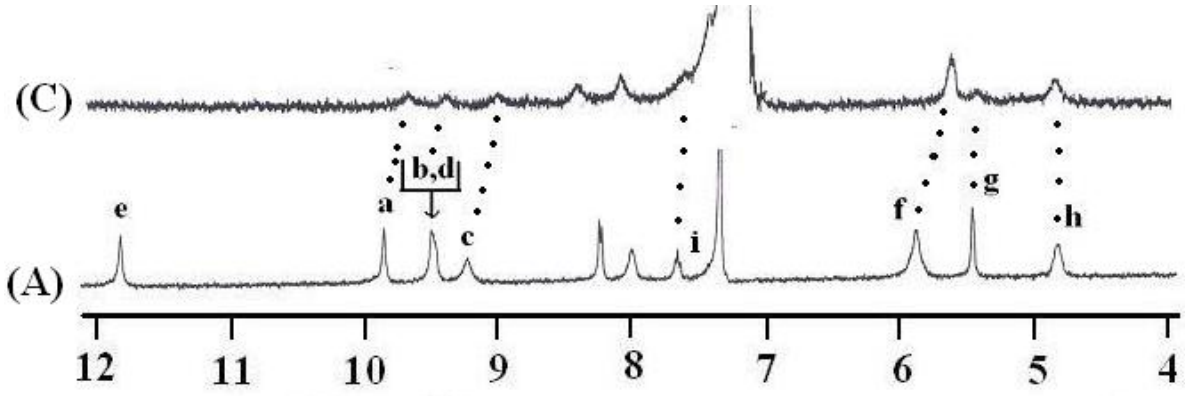


Figure 9S. Partial ^1H NMR (400 MHz, $CDCl_3$) of (A) compound **1** (c = $3.21x10^{-3}$ M) and (C) **1** with TBAOH (1:1).

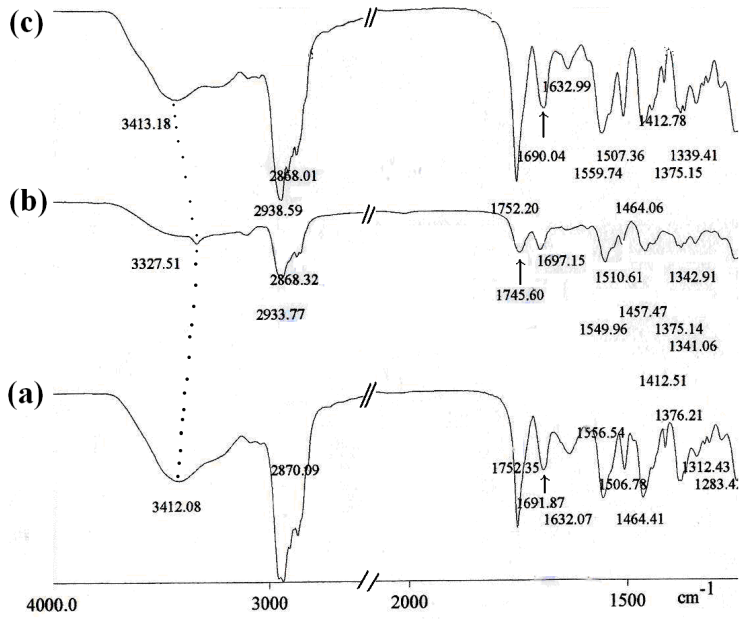


Figure 10S. Partial FTIR spectra of (a) **1** (amorphous), (b) **1** (chloroform gel) and (c) **1** with $AgClO_4$ (sol)

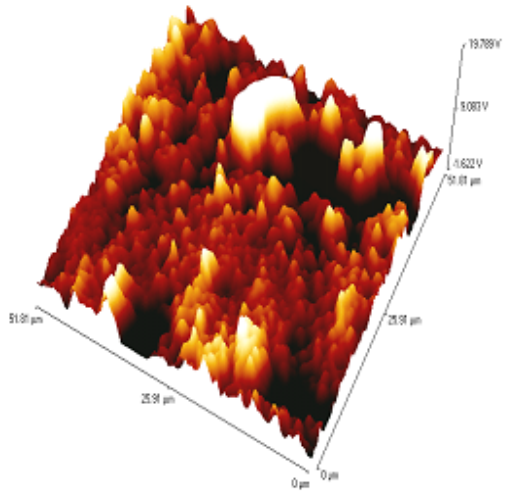


Figure 11S. AFM image in three dimension view of xerogel from $CHCl_3$ gel of **1** (scale bar: = 50 μm).

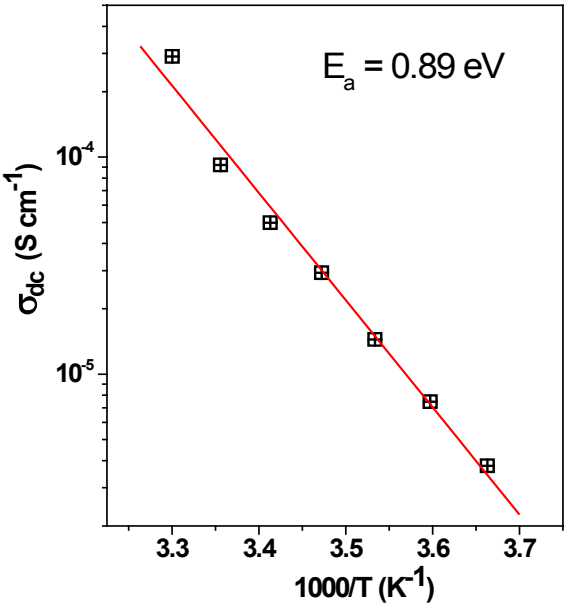


Figure 12S. Arrhenius plot of dc conductivity against the reciprocal temperature.

6. Experimental

Chloro-acetic acid 17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl ester (2)[1]

To a stirred solution of cholesterol (0.5 g, 1.29 mmol) in 20 mL dry CH_2Cl_2 was added chloroacetyl chloride (0.16 mL, 1.93 mmol) and pyridine (0.05 mL, 0.65 mmol) under nitrogenous atmosphere. The mixture was allowed to stir for 10 h at room temperature. After completion of reaction, the solvent was evaporated and the crude was extracted with $CHCl_3$ (3 × 30 mL). The organic layer was washed several times with water and separated and dried over Na_2SO_4. Evaporation of the solvent gave white solid compound. Recrystallization from petroleum ether afforded pure product 2 (0.58 g, yield 96%), mp 148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (m, 1H), 4.72 (m, 1H), 4.03 (s, 2H), 2.36 (m, 2H), 2.02–0.85 (m, 38H), 0.67 (s, 3H); FTIR (KBr, cm^{-1}): 2939, 2907, 2821, 1753, 1620, 1195.

N,N′-di-pyridin-3-yl-isophthalamide (3)[2]

The symmetrical bis amide 3 was obtained by coupling of 3-aminopyridine (1.2 g, 12.8 mmol) with isophthaloyl diacid chloride (1.3 g, 6.4 mmol) in dry CH_2Cl_2 followed by addition of triethylamine (1.4 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir for overnight. After completion of reaction, solvent was removed under vacuum. The residual mass was extracted with $CHCl_3$/CH_3OH mixture (3 x 20 mL). The organic layer was washed with $NaHCO_3$ solution (3 x 15 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residual mass was purified by column chromatography over silica gel using 4:1 chloroform: methanol as eluent to afford the desired compound 3 (730 mg, 36% yield, mp 210 ^{0}C).

^{1}H NMR (d_6-DMSO, 400 MHz): δ 10.69 (s, 2H, amide NH), 8.96 (d, 2H, *J* = 2 Hz,), 8.59 (s, 1H), 8.33 (d, 2H, *J* = 4 Hz,), 8.23-8.18 (m, 4H), 7.74 (t, 1H, *J* = 8 Hz), 7.43 (d, 1H, *J* = 8 Hz), 7.42 (d, 1H, *J* = 8 Hz); ^{13}C NMR (d_6-DMSO, 125 MHz): δ 166.2, 145.6, 142.9, 136.5, 135.5, 131.8, 129.6, 128.2, 128.0, 124.4; FTIR (KBr) ν cm^{-1} : 3418, 3054, 1676, 1613, 1585, 1556, 1481, 1429; Mass (EI): m/z 319.1 $(M+H)^+$, 225.2, 130.2.

Compound 1

Compounds 3 (0.20 g, 0.66 mmol) and 2 (0.76 g, 1.65 mmol) were taken in dry CH_3CN (30 mL) containing 1% DMF and the mixture was refluxed for 3 days. The precipitate appeared was filtered off and washed with hot CH_3CN followed by diethyl ether to have pure chloride salt 1 in 83% yield (0.68 g, mp 224 ^{0}C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ 12.42 (s, 2H), 9.84 (s, 2H), 9.29 (d, 2H, *J* = 8 Hz), 8.76 (d, 2H, *J* = 8 Hz), 8.41 (d, 2H, *J* = 8 Hz), 8.39 (s, 1H), 8.31 (t, 1H, *J* = 8 Hz), 8.18 (t, 2H, *J* = 8 Hz), 5.76 (s, 4H), 5.26 (s, 2H), 4.63 (m, 2H), 2.40 – 2.27 (m, 4H), 1.97 – 1.70 (m, 8H), 1.50 – 0.88 (m, 74H); FTIR (KBr) ν cm^{-1}: 3412, 1752, 1691; Mass (HRMS): Calcd. 1208.7946 for $(M\text{-}Cl+1)^+$ found 1208.6245 $(M\text{-}Cl+1)^+$.

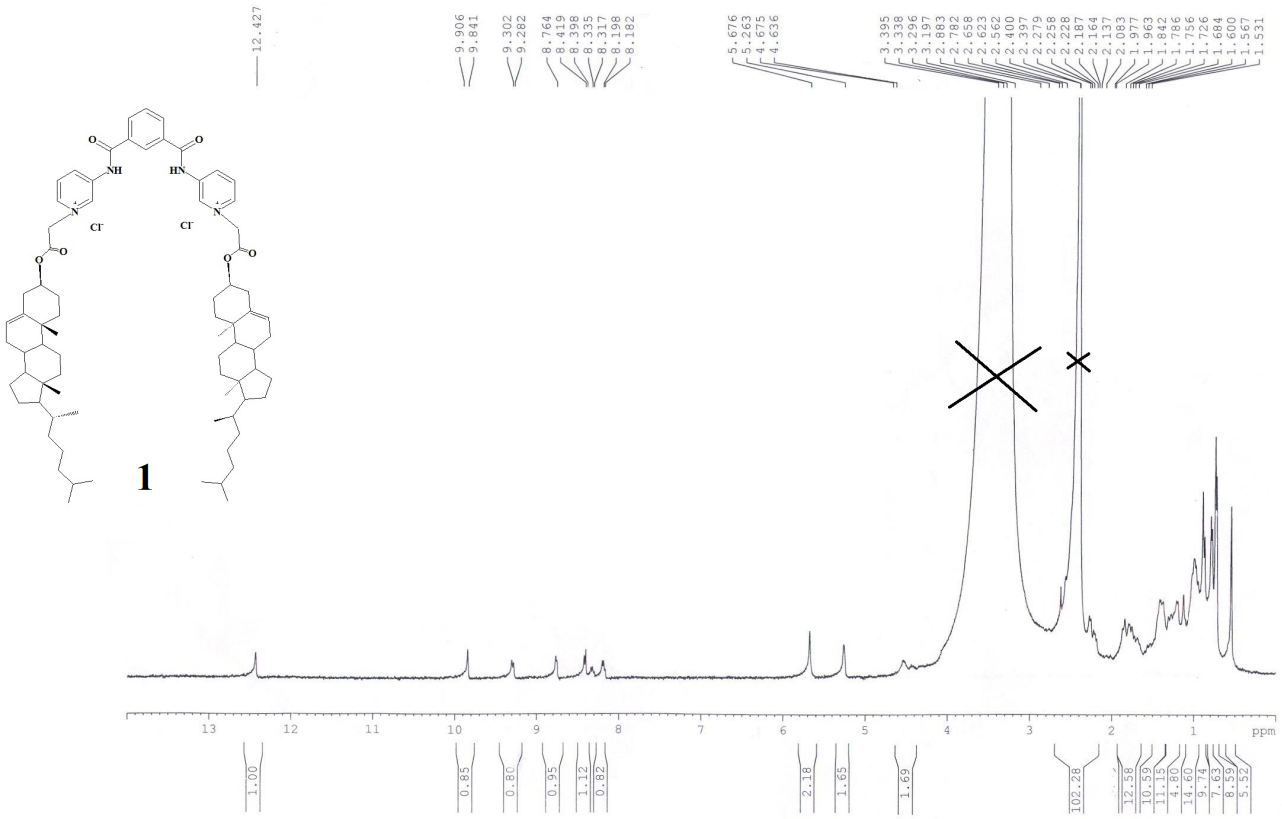
Compound 1a

The dichloride salt 1a (0.2 g, 0.16 mmol) was dissolved in MeOH (8 mL) containing 2% DMF and an aqueous solution of NH_4PF_6 (0.05 g, 0.3 mmol) was added under hot condition. After stirring the mixture for 30 min, the precipitate was filtered. Repeated crystallization of the precipitate from diethyl ether afforded pure compound 1a (0.23 g) in 96% yield, mp 196 ^{0}C.

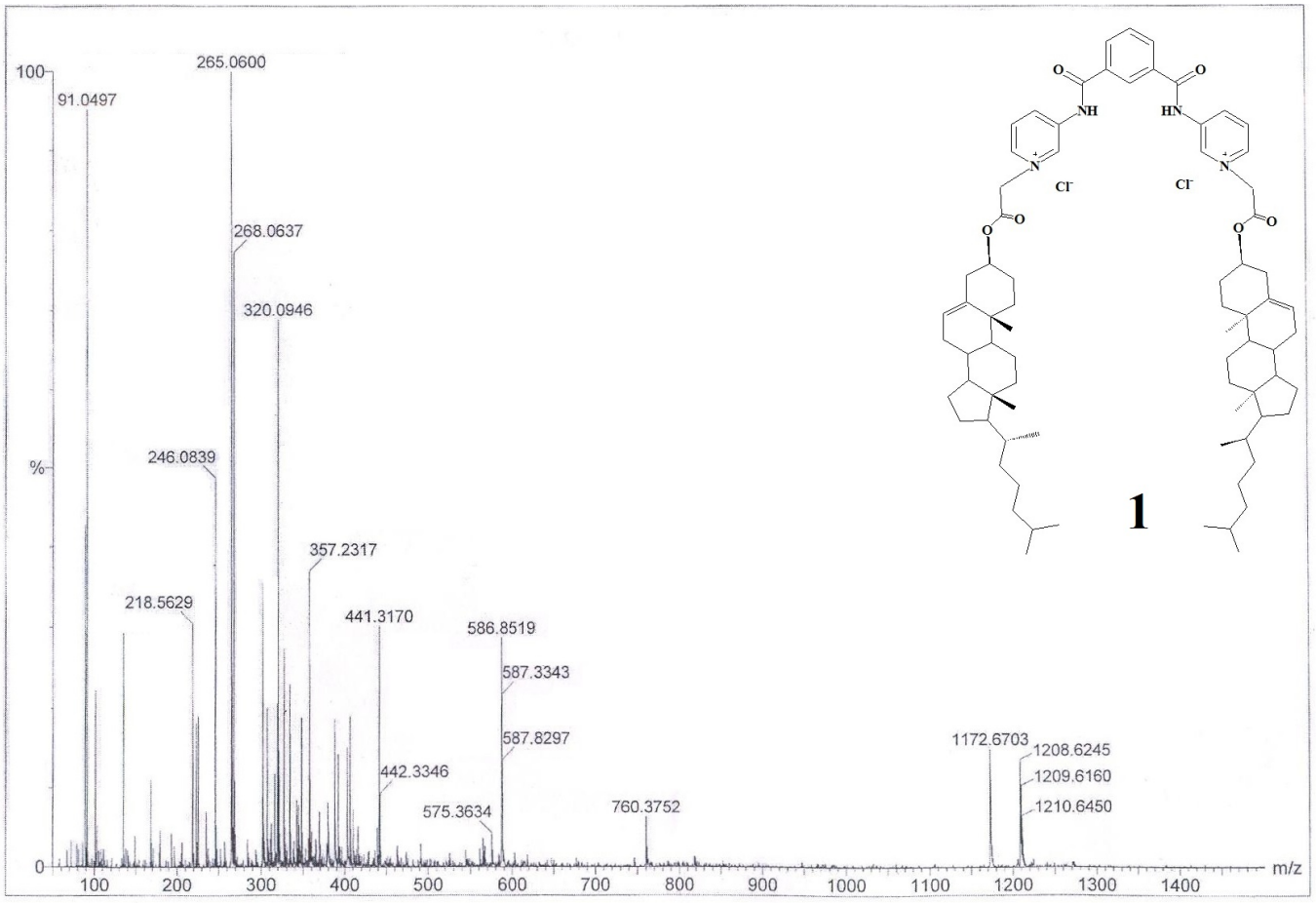
^{1}H NMR (d_6-DMSO, 400 MHz): δ 11.79 (s, 2H), 9.90 (s, 1H), 9.82 (s, 2H), 8.98 (d, 2H, *J* = 8 Hz), 8.90 (d, 2H, *J* = 8 Hz), 8.52 (d, 2H, *J* = 8 Hz), 8.45 (t, 1H, *J* = 8 Hz), 8.33 (t, 2H, *J* = 8 Hz), 5.79 (d, 4H, *J* = 8 Hz), 5.37 (s, 2H), 4.64 (m, 2H), 2.39 – 2.33 (m, 4H), 1.95 – 1.87 (m, 8H), 1.52 – 0.90 (m, 74H); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 166.3, 166.0, 141.9, 139.5, 139.4, 137.6, 136.8, 133.9, 132.4, 129.9, 128.4, 123.0, 76.5, 61.4, 56.5, 56.0, 49.8, 42.3, 37.9, 36.8, 36.5, 36.1, 35.6, 31.8, 28.2, 27.8, 27.6, 24.3, 23.6, 23.1, 22.8, 21.0, 19.4, 19.0 (one carbon in the aromatic region and two carbons in the aliphatic region are unresolved); FTIR (KBr) ν cm^{-1} : 3348, 2936, 1753, 1703; Mass (HRMS): Calcd. 1318.7977 for $(M- PF_6 +1)^+$ found 1318.6598 $M- PF_6 +1)^+$.

Procedure for measurement of ionic conductivity Measurements of frequency dependent capacitance C(ω) and conductance G(ω) of the gelatinous systemhave been done by means of the dielectric spectroscopy technique using Hioki 3532-50 LCR Hi-Tester within the frequency range of 42 Hz–5 MHz and temperature range 273-303 K, in a liquid nitrogen cryostat controlled by an Eurotherm temperature controller. The holder of the sample is a cylinder with steel electrodes separated by t = 0.5 mm. One of the electrodes has a guard ring, in order to have uniform electric field in the central portion of the gel.

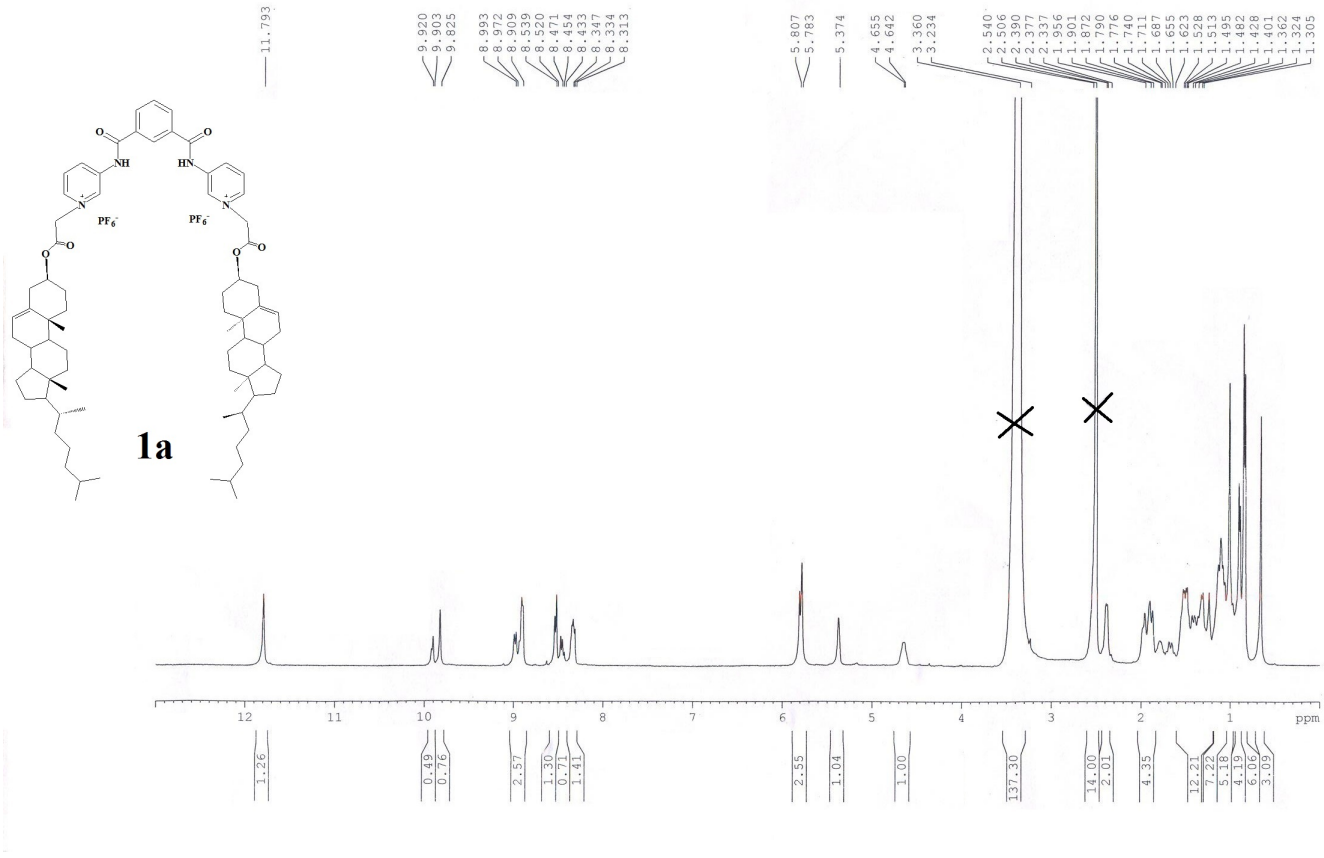
^{1}H NMR (d_6-DMSO, 400 MHz)



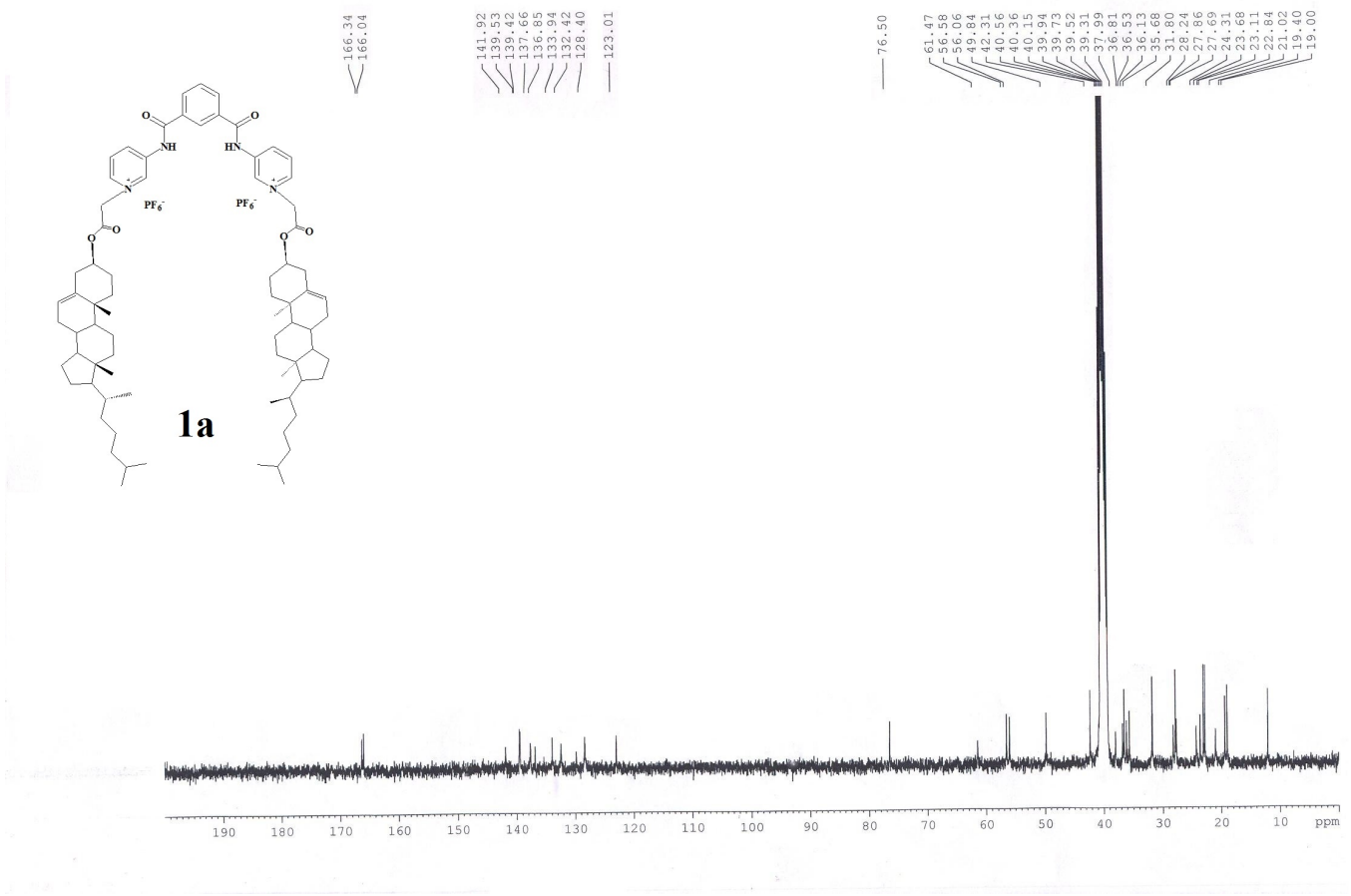
Mass



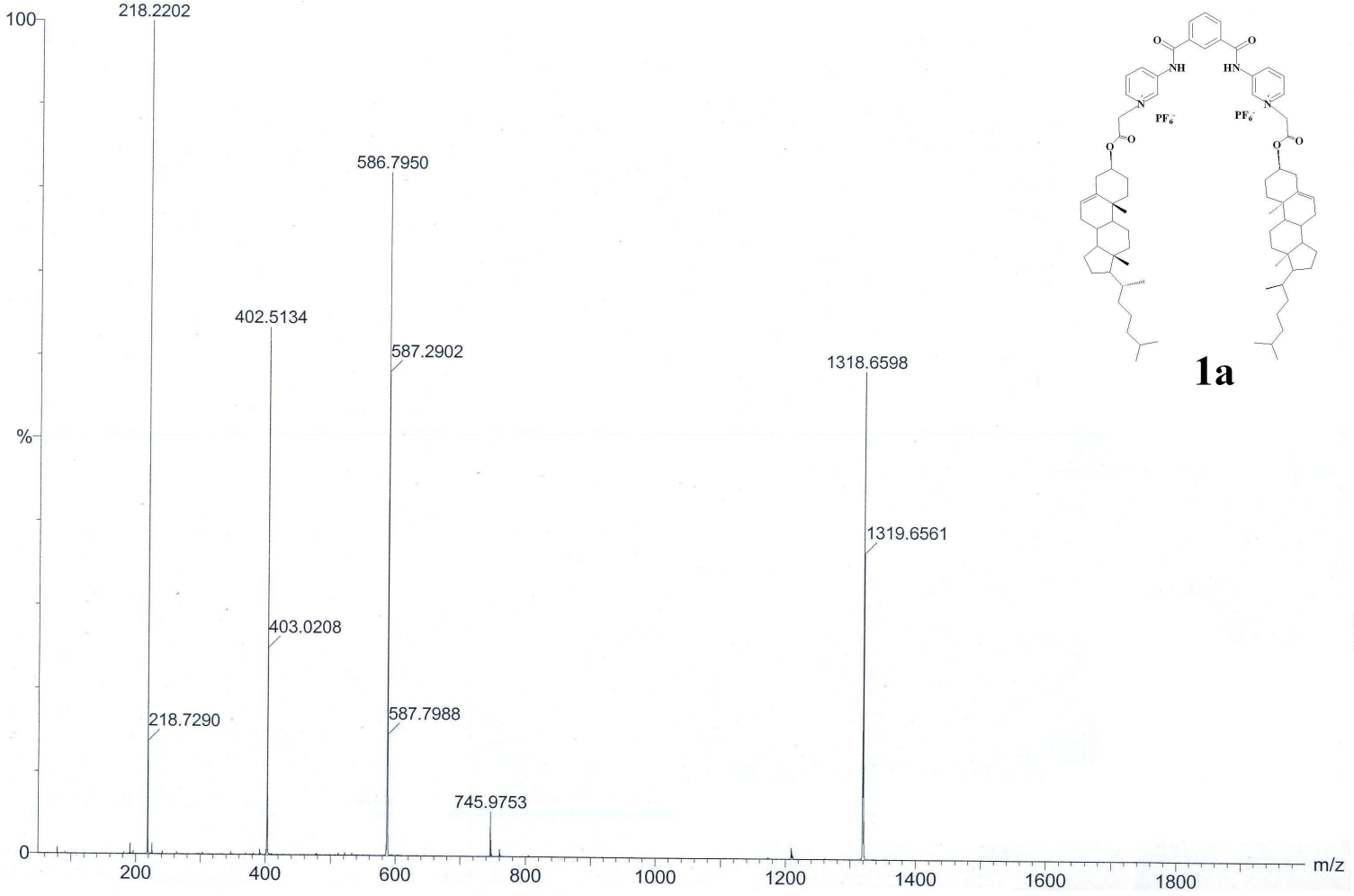
^{1}H NMR (d_6-DMSO, 400 MHz)



^{13}C NMR (d_6-DMSO, 100 MHz)



Mass



1a

References

1. K. Ghosh and D. Kar, *Org. Biomol. Chem.,* 2012, **10**, 8800

2. K. Ghosh, A. R. Sarkar and A. P. Chattopadhyay, *Eur. J. Org. Chem*., 2012, 1311;