A ferrocene imidazolium-based macrocycle as an electrochemical chemosensor for halide anions

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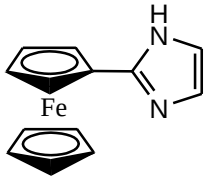
PART I: Synthesis

General Information

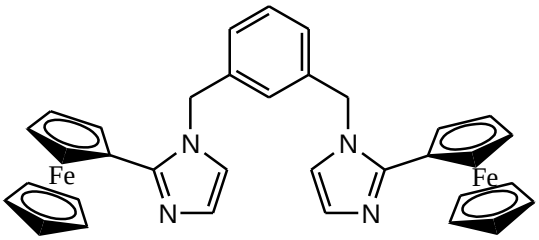
Routine NMR spectra were recorded on a Varian Mercury 300 spectrometer with ^{1}H NMR operating at 300 MHz, ^{13}C at 75.5 MHz, with NMR titrations recorded on a Varian Unity Plus 500 spectrometer with ^{1}H operating at 500 MHz Mass spectra were recorded on a Bruker micrOTOF spectrometer. Melting points were recorded on a Gallenkamp capillary melting point apparatus and are uncorrected. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H_2O was de-ionised and microfiltered using a Milli-Q ® Millipore machine. All tetrabutylammonium salts were stored in a vacuum desiccator over phosphorus pentoxide prior to use. All other solvents and commercial grade reagents were used without further purification.

2-Ferrocenyl-1H-imidazole 3.



To a solution of ferrocenylcarboxaldehyde (0.5 g, 2.33 mmol) in methanol (10 ml) was added dropwise a solution of 40% aqueous glyoxal (0.34 mL) and concentrated aqueous NH_3 (0.8 mL) was added without delay. The red solution was held at 0º C for 1 h, and was then allowed to stir for 16 h at 25º C. The solvent was removed and the resultant residue was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent to give a red solid. Yield: 0.38 g (65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (2H, *s*), 4.90 (2H, t, *J* = 1.8Hz), 4.34 (2H, t, *J* = 1.8Hz), 4.13 (5H, s) ^{13}C (75 MHz, $CDCl_3$) δ 128.8, 146.5, 76.0, 71.7, 70.2,. 68.9. MS (ESI): *m/z* calc. for $[M + H]^+$ 253.03, found 253.04.

1-(3-((2-ferrocenyl-1H-imidazol-1-yl)methyl)benzyl)-2-ferrocenyl-1H-imidazole 4.

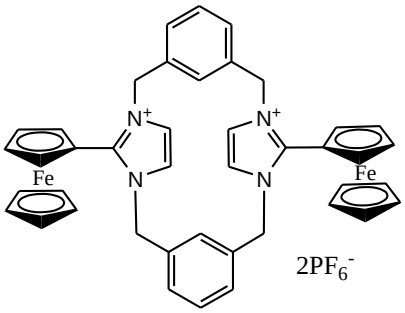


To a solution of 2-ferrocenyl-1*H*-imidazole (0.3 g, 1.2 mmol) in acetonitrile (50 ml) was added dropwise a solution of 1M NaOH (4.0 mmol) and stirred during 10 min. α,α´-Dibromo-*m*-xylene (0.157 g, 0.59 mmol) was added in one portion and the resultant mixture was stirred overnight. The solvent was removed and the resultant residue dissolved in chloroform (100 ml), which was washed with water (2 x 25 ml). The combined organic layers were dried over magnesium sulphate, filtered and dried in vacuo, the resultant residue was purified by flash chromatography on silica gel using CH_2Cl_2/EtOH 95/5 as eluent to give a red oil (0.65 g, 90 %) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (1H, *t*, *J* = 9Hz), 7.05 (2H, s) 6.96 (2H, d, *J* = 9Hz), 6.81 (2H, s), 6.77 (1H, s), 5.33 (4H, s), 4.50 (2H, t, *J* = 1.8Hz), 4.20 (2H, t, *J* = 1.8Hz), 4.06 (5H, s) ^{13}C (75 MHz, $CDCl_3$) δ 146.5, 138.2, 129.9, 128.6, 125.7, 124.0, 120.9, 74.8, 69.4, 69.2, 68.1, 49.8; MS (ESI): *m/z* calc. for $[M + H]^+$ 607.12, found 607.12.

Syn and Anti 1,1´,3,3´-bis(*m*-xylene),2,2´ferrocenyl, imidazolium bis-hexafluorophosphate $5^{2+}\cdot 2PF_6^-$ and $6^{2+}\cdot 2PF_6^-$.

To a solution of the bisimidazole **4** (0.24 g, 0.39 mmol) in acetonitrile (50 ml) was added dropwise 10 ml a solution of α,α´-Dibromo-m-xylene in acetonitrile (0.11 g, 0.39 mmol) and the resultant mixture was heated at reflux overnight. The volume of solvent was concentrated to 25 ml and then cooled to 0ºC. The resulting precipitate was collected and washed with diethylether, giving the syn and anti isomers with 82% global yield. The two isomers were isolated by flash chromatography on silica gel using CH_3CN/H_2O (saturated in KNO_3)/H_2O 14:2:1 as a eluent to give the corresponding mixture of nitrate and bromide salt which underwent anion exchange to the corresponding hexafluorophosphate salts on addition of aqueous NH_4PF_6.

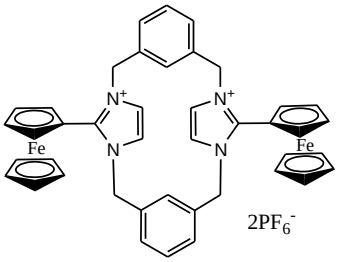
Syn 1,1´,3,3´-bis(m-xylene),2,2´ferrocenyl, imidazolium bishexafluorophosphate $5^{2+}\cdot 2PF_6^-$



$5^{2+}\cdot 2PF_6^-$ (syn)

^{1}H NMR (300 MHz, CD_3CN) δ 7.46 (10H, bs), 6.00 (4H, *d*, *J* = 12Hz), 5.59 (2H, s), 5.47 (4H, *d*, *J* = 12Hz), 4.45 (4H, t, *J* = 1.8Hz), 4.34 (10H, s), 4.16 (4H, t, *J* = 1.8Hz); ^{13}C (75 MHz, CD_3CN) δ 146.3, 136.3, 130.1, 127.6, 124.2, 119.2, 94.0, 71.9, 70.8, 70.1, 64.6, 52.3; MS (ESI): *m/z* calc. for $[M + PF_6]^+$ 855.14, found 855.14.

anti 1,1´,3,3´-bis(m-xylene),2,2´ferrocenyl, imidazolium bishexafluorophosphate $6^{2+}\cdot 2PF_6^-$



$6^{2+}\cdot 2PF_6^-$ (anti)

^{1}H NMR (300 MHz, CD_3CN) δ 7.63-7.54 (6H, m), 7.32 (4H, s), 6.08 (4H, *d*, *J* = 12Hz), 5.64 (2H, s), 5.39 (4H, *d*, *J* = 12Hz), 4.64 (4H, t, *J* = 1.8Hz), 4.46 (4H, t, *J* = 1.8Hz), 4.33 (10H, s); ^{13}C (75 MHz, CD_3CN) δ 141.4, 136.5, 130.3, 128.2, 123.8, 120.4, 95.0, 72.3, 70.8, 70.1, 64.9, 52.0; MS (ESI): *m/z* calc. for $[M + PF_6]^+$ 855.14, found 855.14.

PART II: ^{1}H-NMR Anion Binding Studies.

All ^{1}H NMR titration experiments were conducted at 293K using a Varian Unity Plus 500 MHz spectrometer. The volume of the host sample was 500 µl ($c = 1 \cdot 10^{-3}$M in CD_3CN). All anions were added as their TBA salts ($c = 2.5 \cdot 10^{-2}$M in CD_3CN). At least 13 aliquots of the TBAX solutions were added until a total of 5 equivalents of the anion had been added. Spectra were recorded after each addition, and the sample shaken thoroughly before measurement. Association constants were calculated by analysis of the resulting titration data using the WinEQNMR computer program. The various parameters were refined by non-linear least-squares analysis to achieve the best fit between observed and calculated chemical shifts. The parameters were varied until the values for the association constants converged.

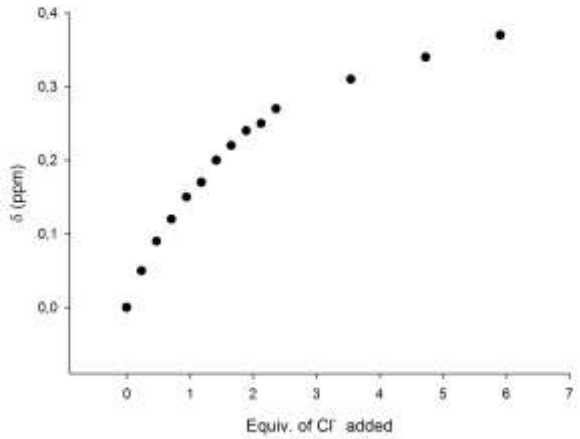


Fig SI1. ^{1}H NMR titration curves for syn $\mathbf{5}^{2+}\cdot PF_6^-$ with tetrabutylammonium chloride in CD_3CN at 295 K.

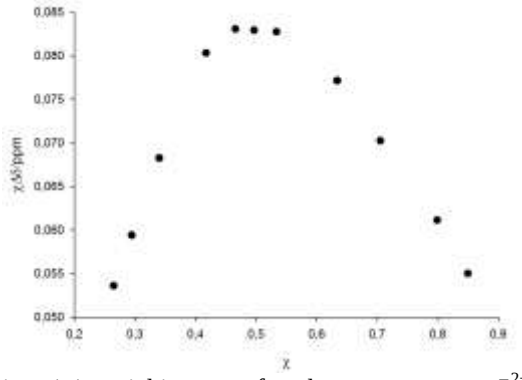


Fig SI2. Job Plot experiment indicating 1:1 stoichiometry for the receptor syn $\mathbf{5}^{2+}\cdot PF_6^-$ and chloride. The vertical axis represents the mole ratio multiplied by the shift of the imidazole protons at $\delta = 7.46$ ppm and the horizontal axis represents the mole ratio.

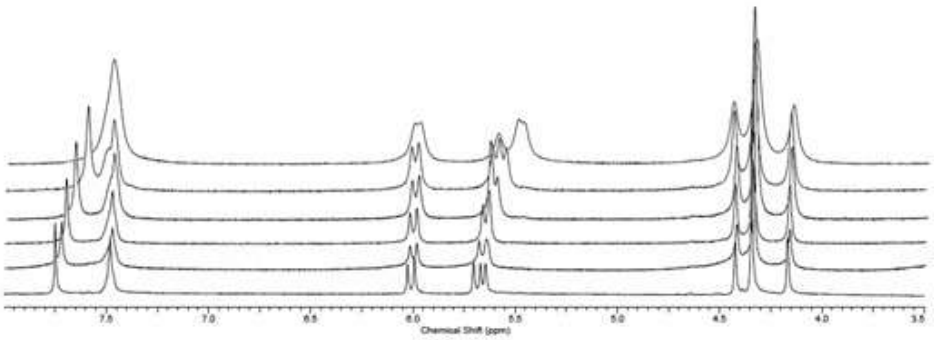


Fig SI3. Evolution of the ^{1}HNMR spectra of the syn macrocycle $\mathbf{5}^{2+}\cdot\mathbf{2PF_6}$ in CD_3CN upon addition of increasing equivalents of Br^-, from 0 (top) to 5 equiv. (bottom).

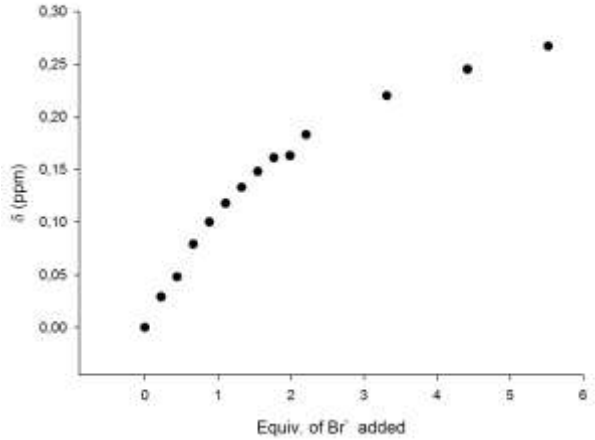


Fig SI4. ^{1}H NMR titration curves for syn $\mathbf{5}^{2+}\cdot PF_6^-$ with tetrabutylammonium bromide in CD_3CN at 295 K.

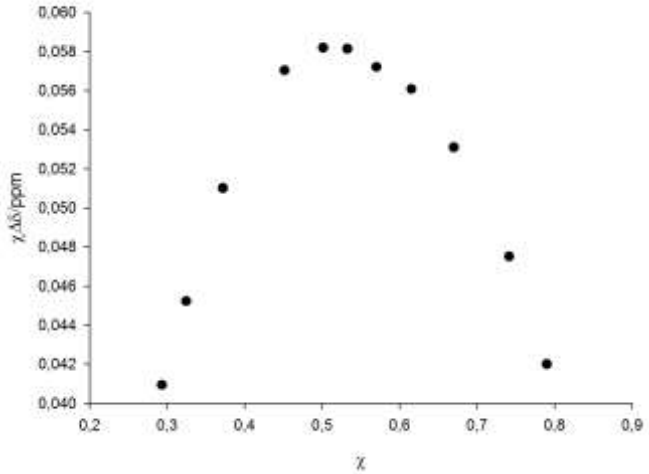


Fig SI5. Job Plot experiment indicating 1:1 stoichiometry for the receptor syn $\mathbf{5}^{2+}\cdot PF_6^-$ and bromide. The vertical axis represents the mole ratio multiplied by the shift of the imidazole protons at δ = 7.46 ppm and the horizontal axis represents the mole ratio.

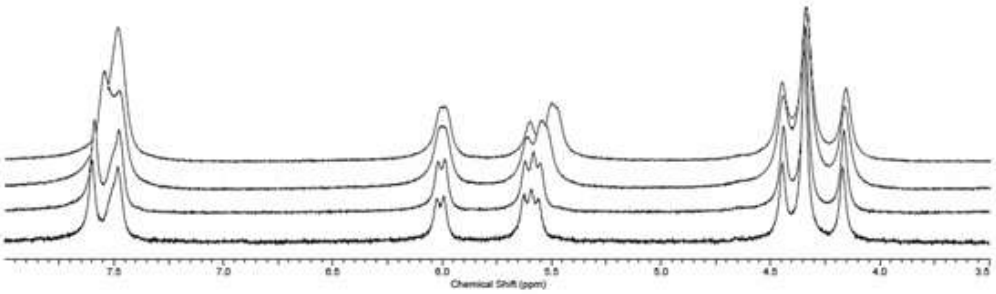


Fig SI6. Evolution of the ^{1}HNMR spectra of the syn macrocycle $\mathbf{5^{2+}\cdot 2PF_6}$ in CD_3CN upon addition of increasing equivalents of I^-, from 0 (top) to 5 equiv. (bottom).

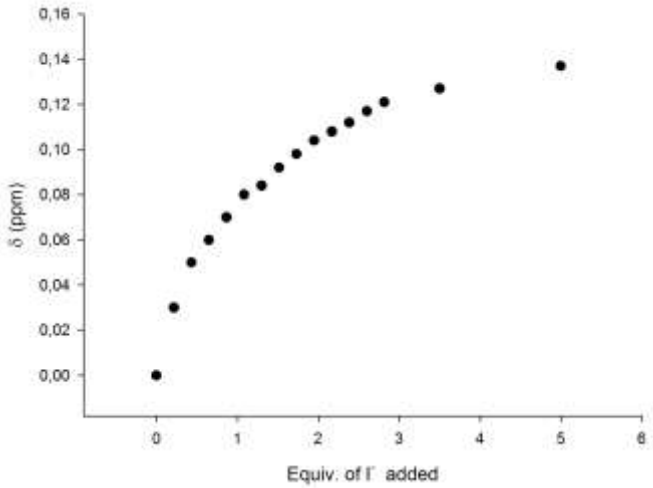


Fig. SI7. ^{1}H NMR titration curves for syn $\mathbf{5}^{2+}\cdot PF_6^-$ with tetrabutylammonium iodide in CD_3CN at 295 K.

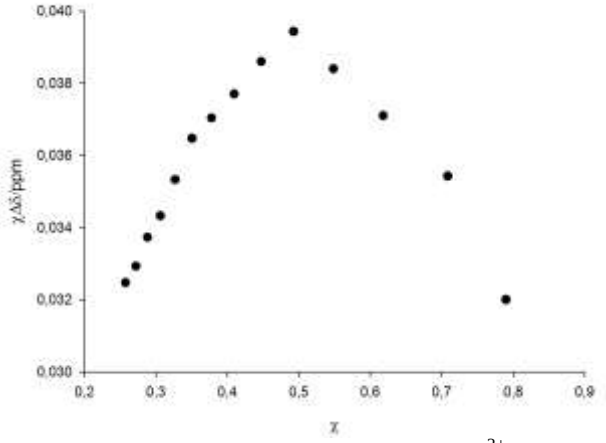


Fig SI8. Job Plot experiment indicating 1:1 stoichiometry for the receptor syn $\mathbf{5}^{2+}\cdot PF_6^-$ and iodide. The vertical axis represents the mole ratio multiplied by the shift of the imidazole protons at δ = 7.46 ppm and the horizontal axis represents the mole ratio.

PART III: Electrochemical Studies.

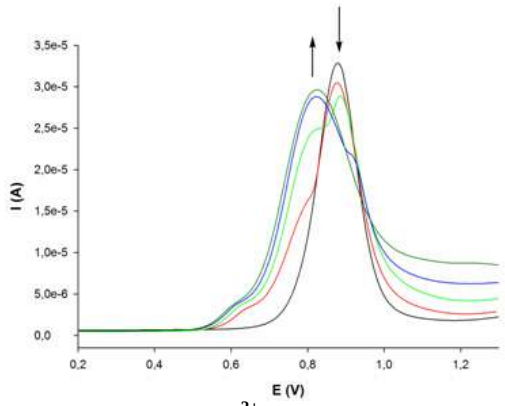


Fig SI9. Evolution of the OSWV of syn-isomer macrocycle $\mathbf{5}^{2+}\cdot\mathbf{2PF_6}^-$ (1 mM in CH_3CN), when increasing amounts of up to 1 equivalent of Cl^- anions (c = $2.5\cdot10^{-2}$ M in CH_3CN) were added, with $TBA\cdot PF_6$ as supporting electrolyte. Arrows indicates the intensities that increase or decrease during the titration.

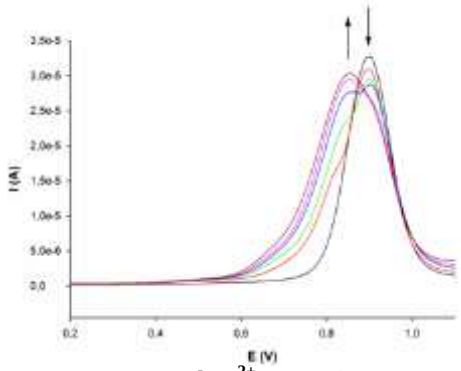


Fig SI10. Evolution of the OSWV of syn-isomer macrocycle $\mathbf{5}^{2+}\cdot\mathbf{2PF_6}^-$ (1 mM in CH_3CN), when increasing amounts of up to 1 equivalent of Br^- anions (c = $2.5\cdot10^{-2}$ M in CH_3CN) were added, with $TBA\cdot PF_6$ as supporting electrolyte. Arrows indicates the intensities that increase or decrease during the titration.

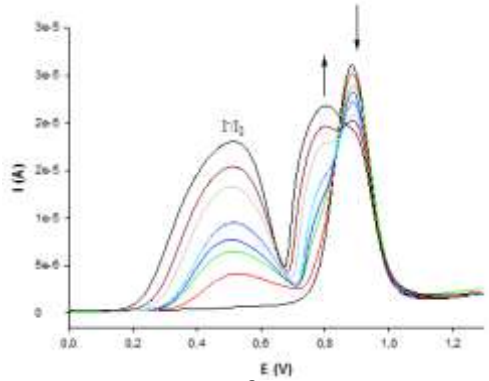


Fig SI11. Evolution of the OSWV of syn-isomer macrocycle $\mathbf{5}^{2+}\cdot\mathbf{2PF_6}^-$ (1 mM in CH_3CN), when increasing amounts of up to 1 equivalent of I^- anions (c = $2.5\cdot10^{-2}$ M in CH_3CN) were added, with $TBA\cdot PF_6$ as supporting electrolyte. Arrows indicates the intensities that increase or decrease during the titration.

PART IV: High resolution mass espectrum **8**

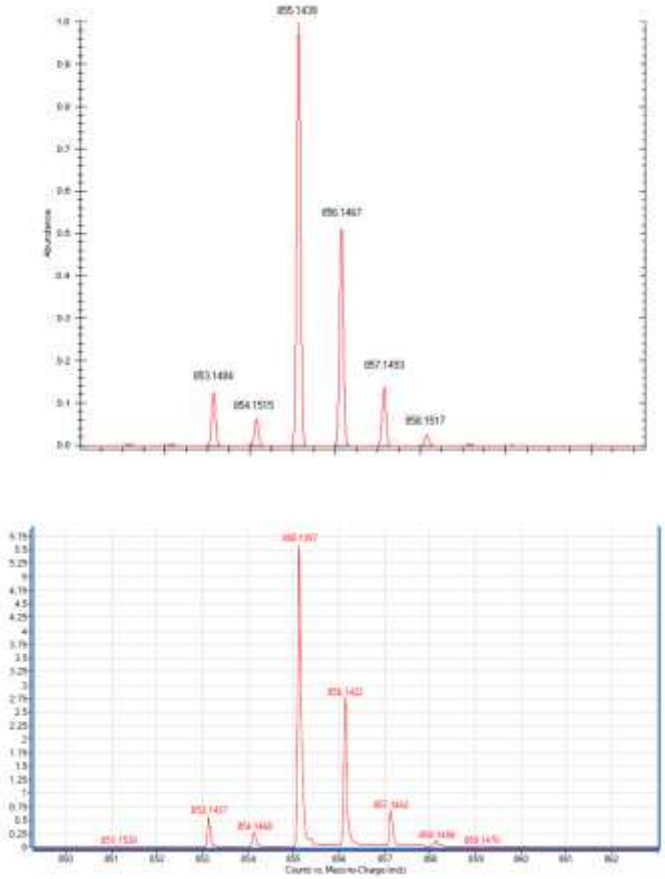


Figure SI 12. High resolution mass spectra of the macrocycle $\mathbf{5^{2+}\cdot 2PF_6^-}$ $[M^{2+}+PF_6^-]^+$ (Top) Theoretical, (Bottom) Experimental.

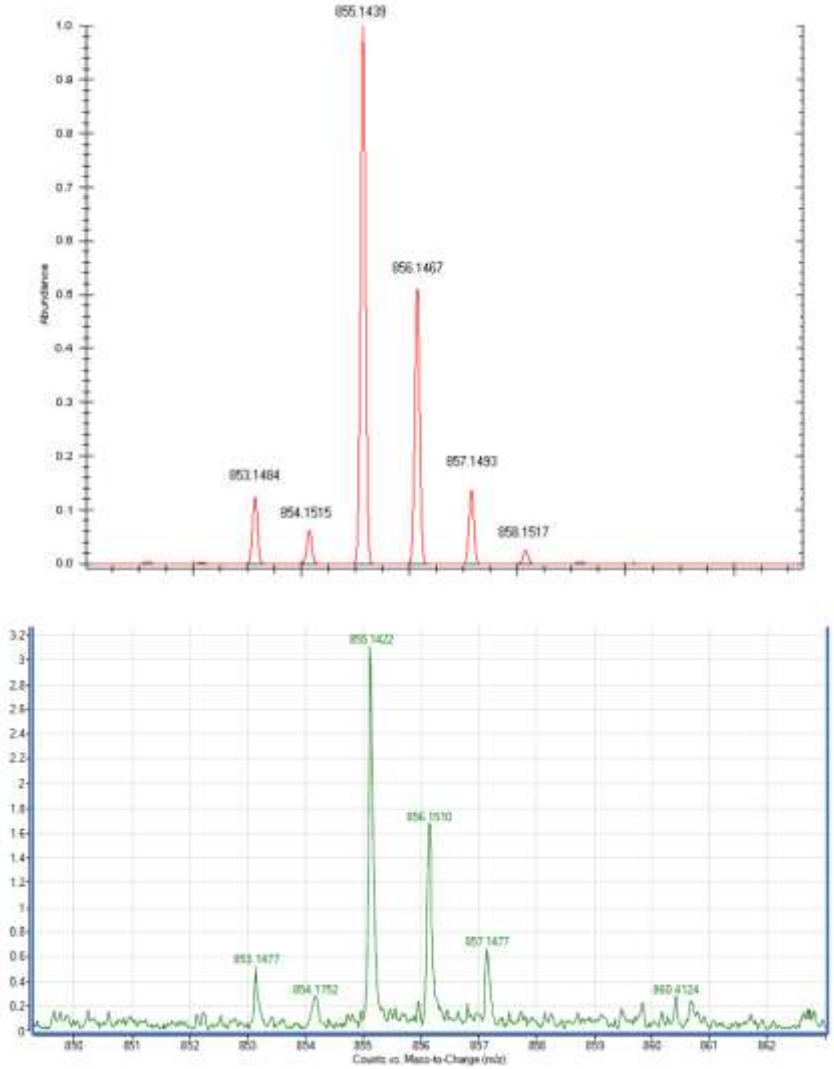


Figure SI 13. High resolution mass spectra of the macrocycle $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ $[M^{2+}+PF_6^-]^+$ (Top) Theoretical, (Bottom) Experimental.