Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

An Efficient Ruthenium Tris(bipyridine)-based Luminescent Chemosensor for Recognition of Cu(II) and Sulfide Anion in water

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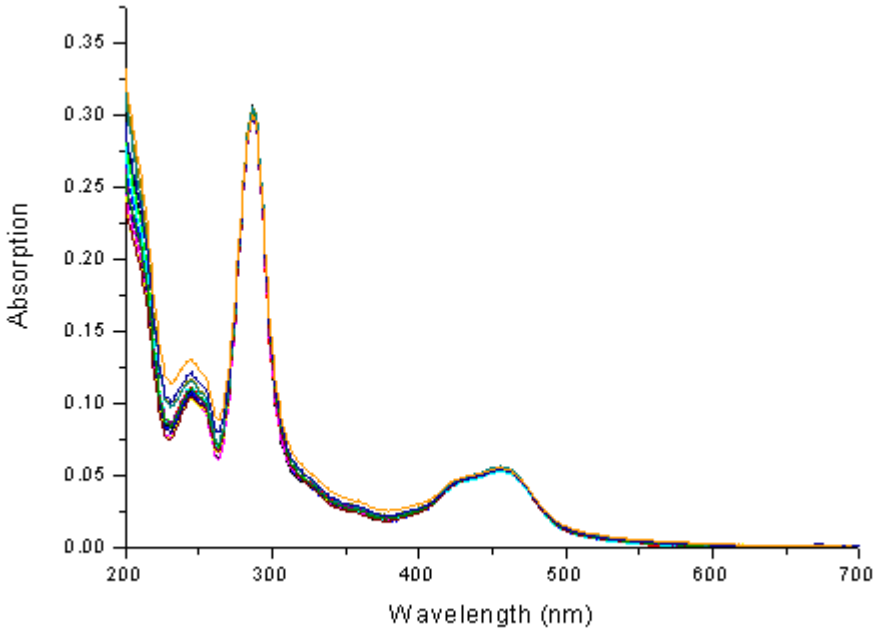

Figure S1. UV-vis spectra of Ru-Cyclen (10 μM) upon addition of various amounts of Cu^{2+} ions in 100% aqueous solutions.

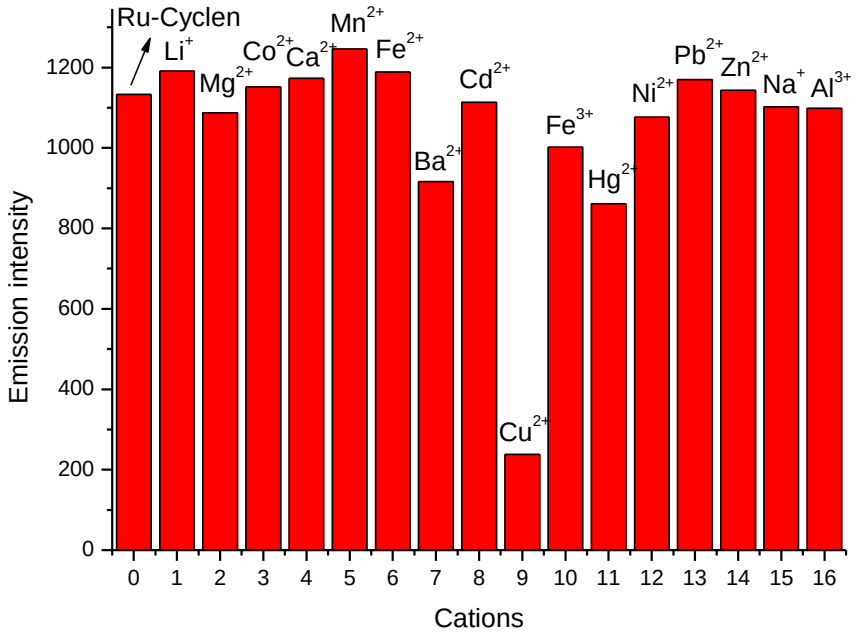

Figure S2. Luminescence response of Ru-Cyclen (10 μM) to various metal ions in 100% aqueous solutions.

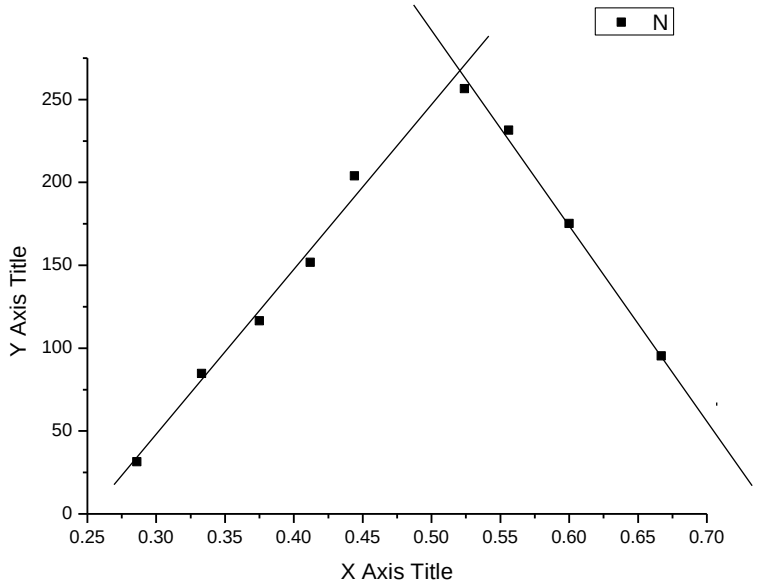

Figure S3. Job plot for determining the stoichiometry of Ru-Cyclen and Cu^{2+} in 100% aqueous solution. The total concentration of Ru-Cyclen and Cu^{2+} is 10 μM, Xcu=[Cu^{2+}]/([Cu^{2+}]+[Ru-Cyclen]).

Calculation for the binding constant by Benesi-Hildebrand method

Based on the 1:1 binding mode, the binding constant K of the complex was evaluated by the Benesi−Hildebrand (B−H) plot (eq 1). [1, 2]

$1/(F - F_{min}) = 1/\{K(F_{max} - F_{min})[Cu^{2+}]\} + 1/(F_{max} - F_{min})$ (1)

F_{min} is the luminescence intensity measured with an excess of Cu^{2+} (λ = 604 nm), F is the intensity measured in the presence of a certain concentration of Cu^{2+}, F_{max} is the intensity of free Ru-Cyclen, and K is the association constant and was obtained from a plot of $1/(F_{max} - F)$ against $1/[Cu^{2+}]$ where K is equal to the intercept/slope.

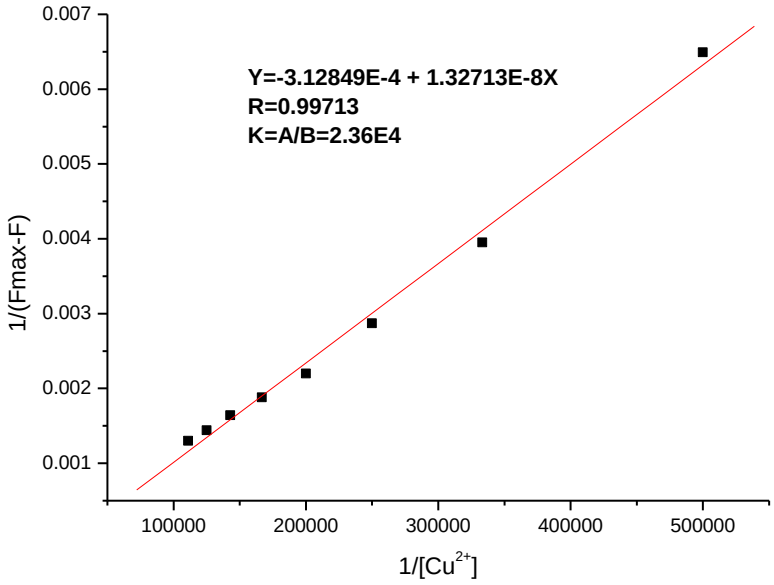

Figure S4. Benesi-Hildebrand plot of Ru-Cyclen with Cu^{2+} in 100% aqueous solutions in the linear region (0.2-0.9 equiv of Cu^{2+}) (F_{max} is the intensity of free Ru-Cyclen and F is the intensity measured in the presence of a certain concentration of Cu^{2+}).

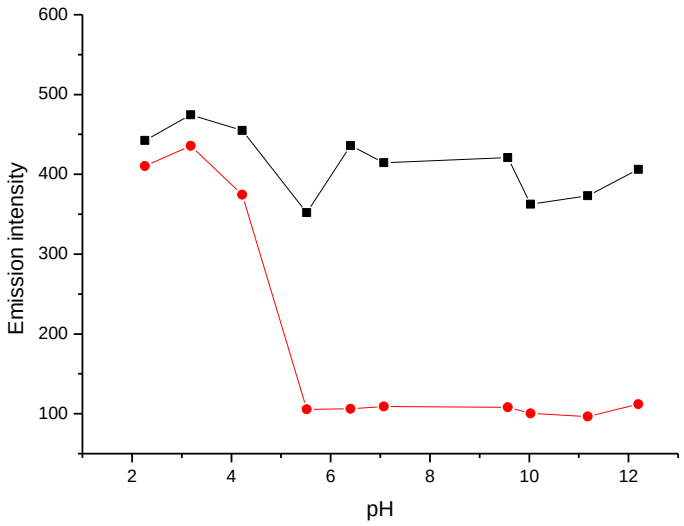

Figure S5.The luminescence response of the free Ru-Cyclen（4 μM)(black，■）and toward Cu^{2+} anion（5 μM）red，●）in varying pH values.

Calculation of detection limit

The detection limit was obtained from the luminescence titration data following the procedures of literatures.[3-5] According to the result of titrating experiment, the emission intensity data at 604 nm were normalized between the minimum intensity and the maximum intensity. A linear regression curve was then fitted to these normalized fluorescence intensity data, and the point at which this line crossed the ordinate axis was considered as the detection limit.

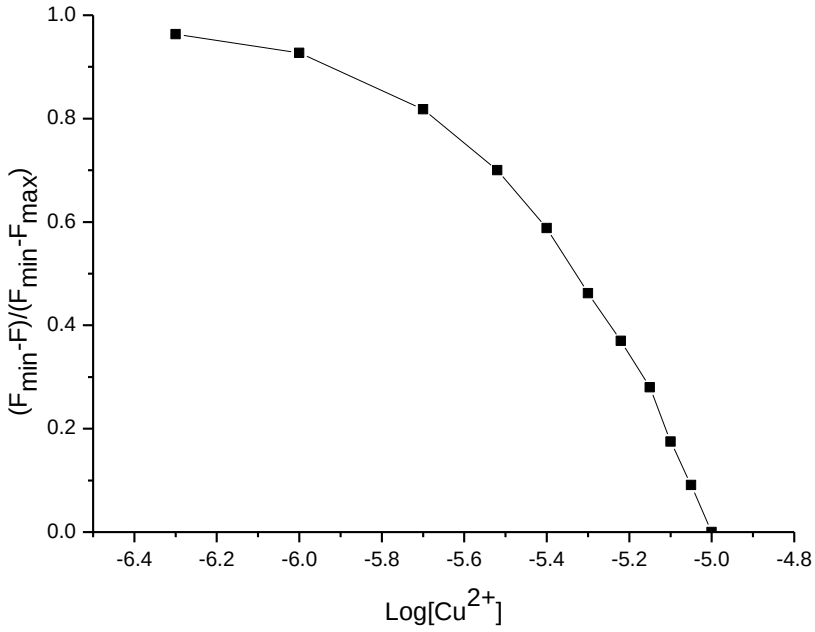

Figure S6(a). Normalized response of the luminescence signal of Ru-Cyclen (10 μM) in 100% aqueous solutions to the change of Cu^{2+} concentrations in the full region (F_{max}: maximum intensity. F_{min}: minimum intensity).

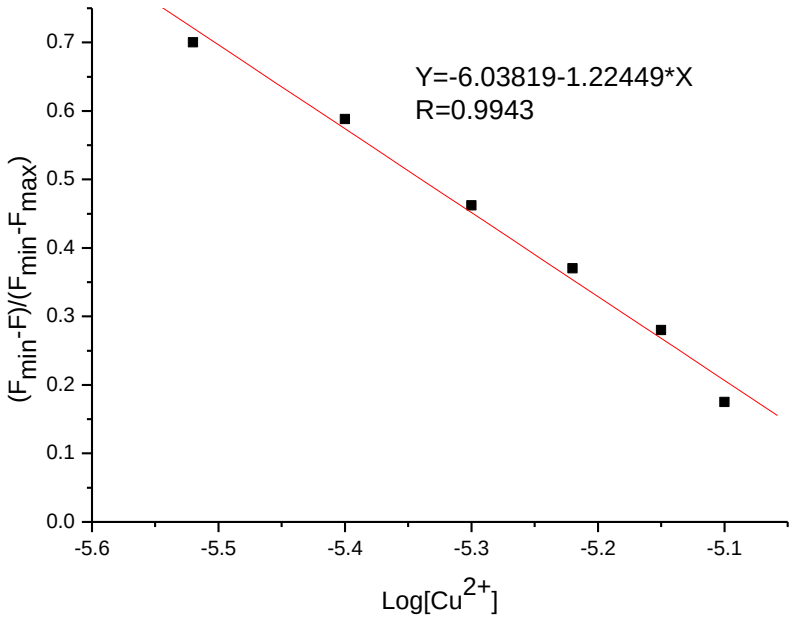

Figure S6(b). Luminescence intensity of Ru-Cyclen (10 μM) in 100% aqueous solutions at each concentration of Cu^{2+} added, normalized between the minimum fluorescence intensity and the maximum fluorescence intensity. The linear fit was drawn by taking the six points ($[Cu^{2+}]$ = 3, 4, 5, 6, 7, 8, 9 μM) of the linear region and the detection limit was determined to be 5.4×10^{-6} M.

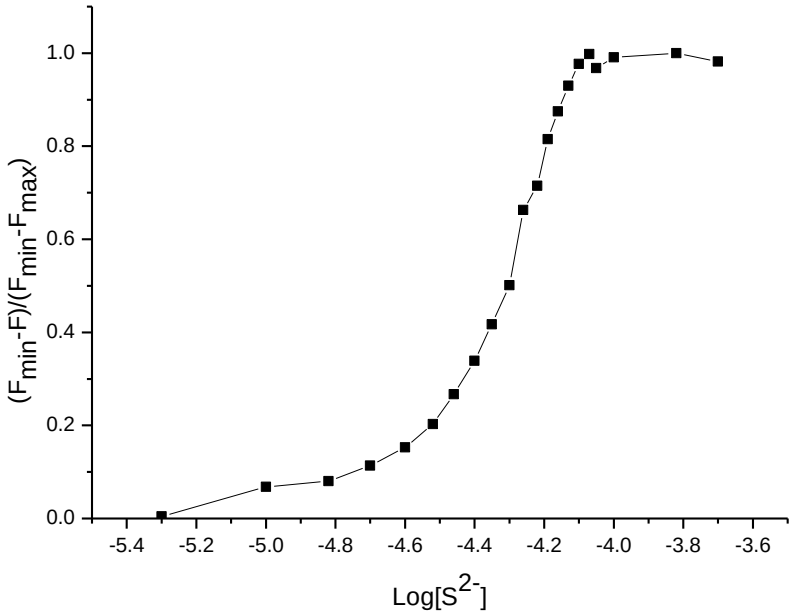

Figure S7(a). Normalized response of the luminescence signal of Ru-Cyclen-Cu system (5 μM) in 100% aqueous solutions to the change of S^{2-} concentrations in the full region (F_{max}: maximum intensity. F_{min}: minimum intensity).

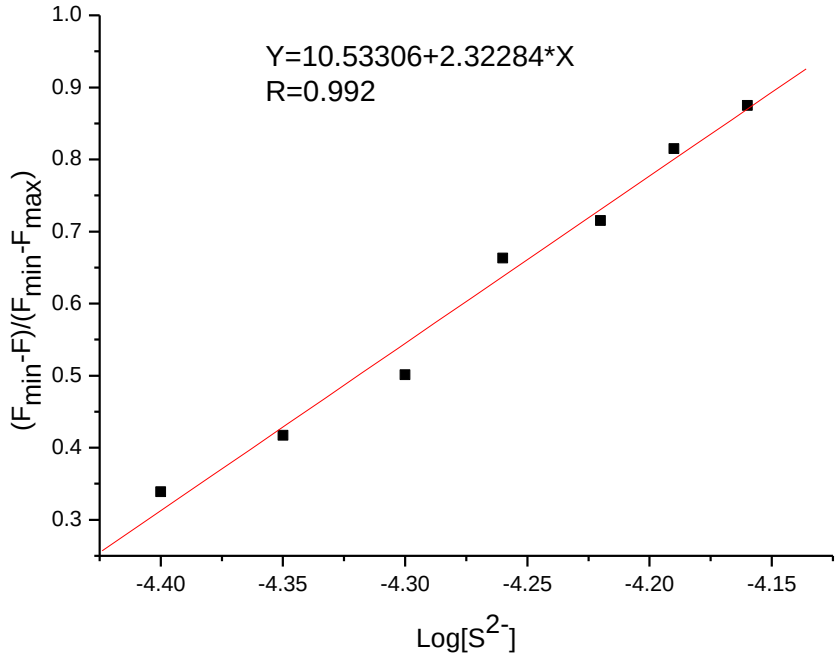

Figure S7(b). Luminescence intensity of Cu^{2+}-bound Ru-Cyclen (5 μM) in 100% aqueous solutions at each concentration of S^{2-} added, normalized between the minimum fluorescence intensity and the maximum fluorescence intensity. The linear fit was drawn by taking the seven points ([S^{2-}] = 40, 45, 50, 55, 60, 65, 70 μM) of the linear region and the detection limit was

determined to be 3.7×10^{-6} M.

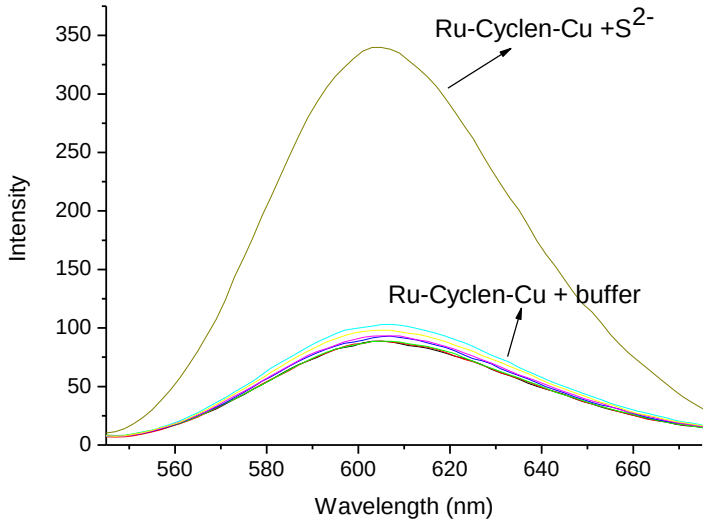

Figure S8. Changes in luminescence emission spectrum of Ru-Cyclen-Cu system with the increasing HEPES buffer solution (pH = 7.4) in water. [Ru-Cyclen-Cu] = 3 μM.

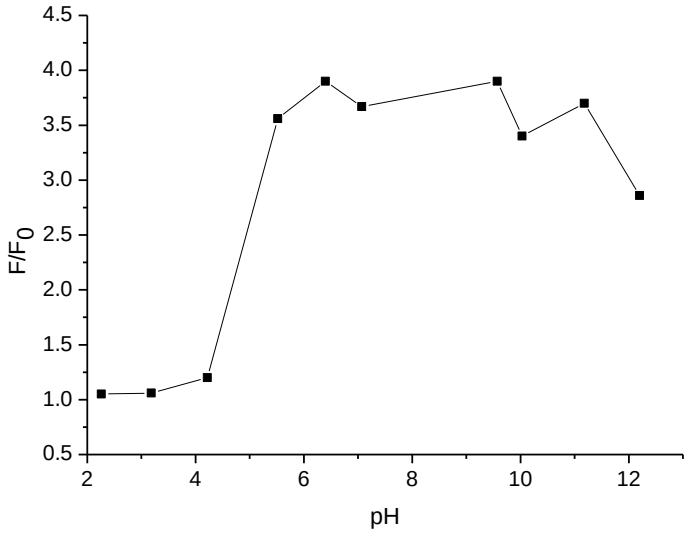

Figure S9. pH effects on the emission intensity at 605 nm of Ru-Cyclen-Cu system (4 μM) toward sulfide anions (80 μM).

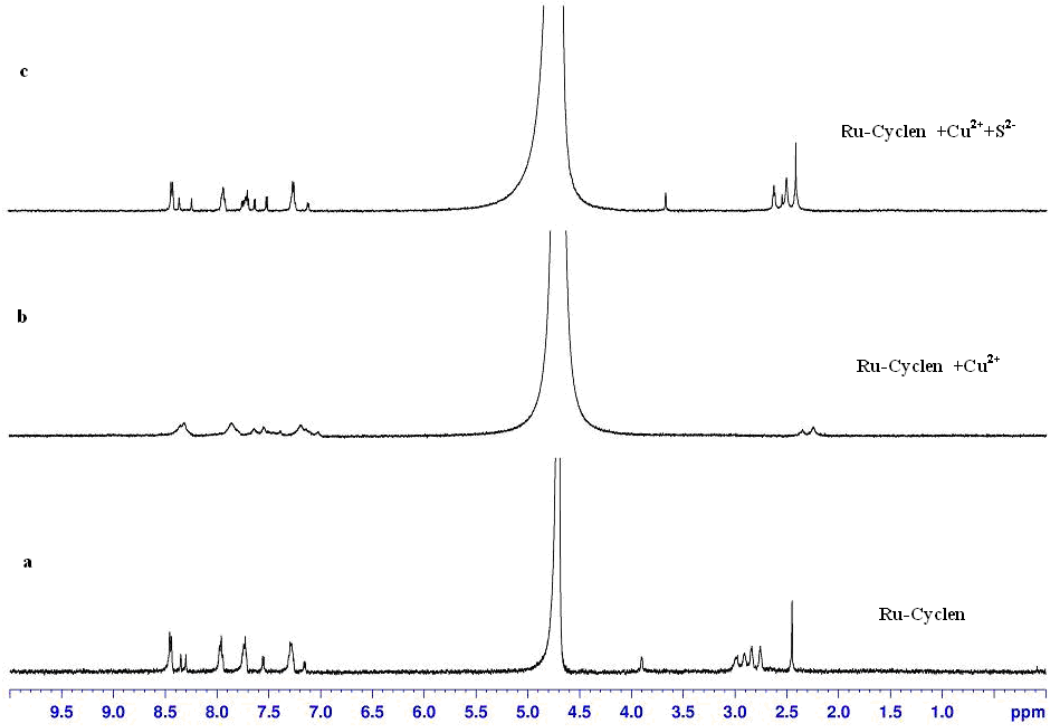

Figure S10. ^{1}H NMR (500 MHZ) spectra of complex Ru-Cyclen in D_2O. (a) Ru-Cyclen free; (b) Ru-Cyclen + Cu^{2+}; (c) Ru-Cyclen + Cu^{2+}+S^{2-}. [Ru-Cyclen] = 5 mM, [Cu^{2+}] = 5 mM, [S^{2-}] = 100 mM.

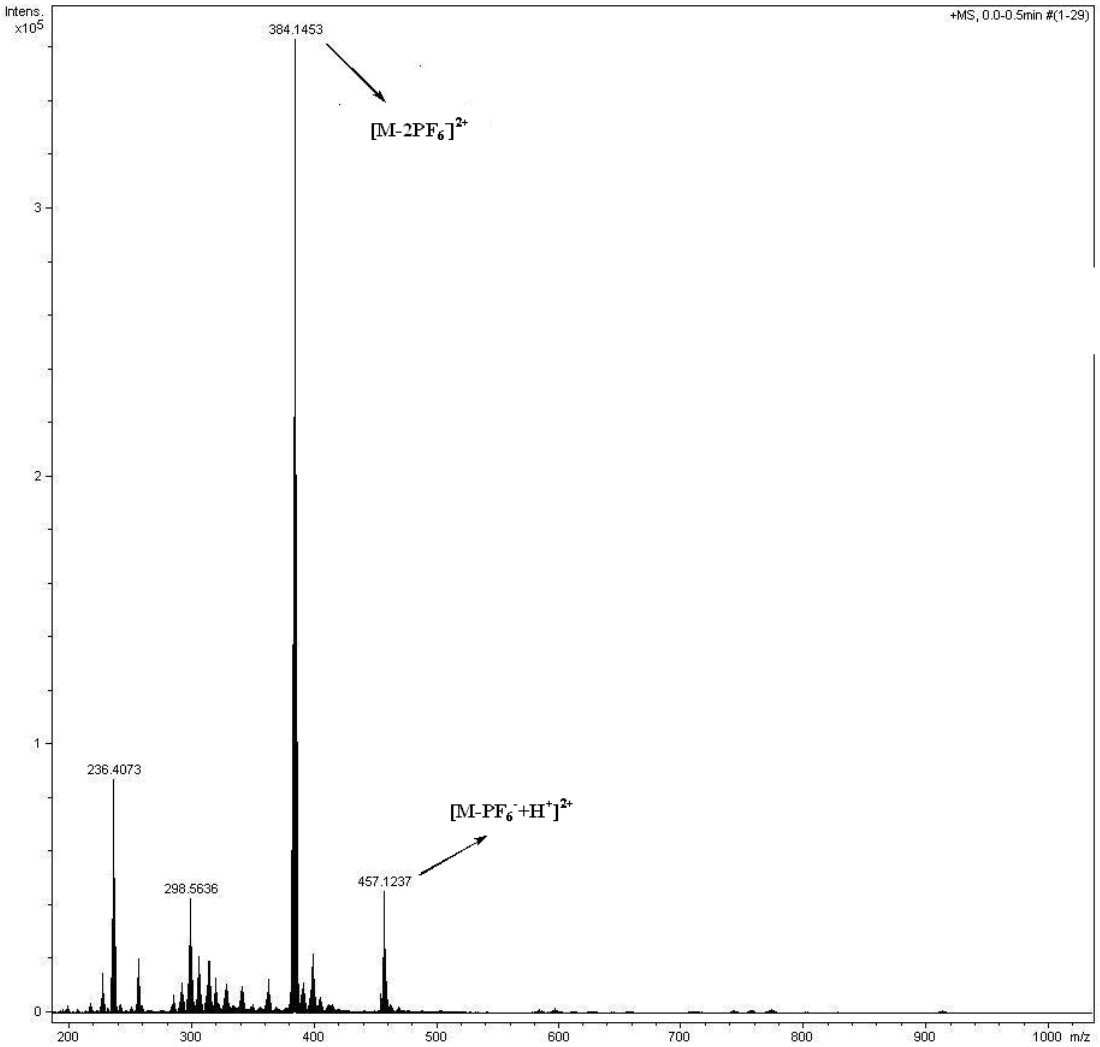

Figure S11. TOF-MS spectrum of Ru-Cyclen in water. The peaks at m/z = 384.1453 and 457.1237 correspond to $[M\text{-}2PF_6^-]^{2+}$ (calc.384.1475) and $[M\text{-}PF_6^-+H^+]^{2+}$ (calc. 457.1283)

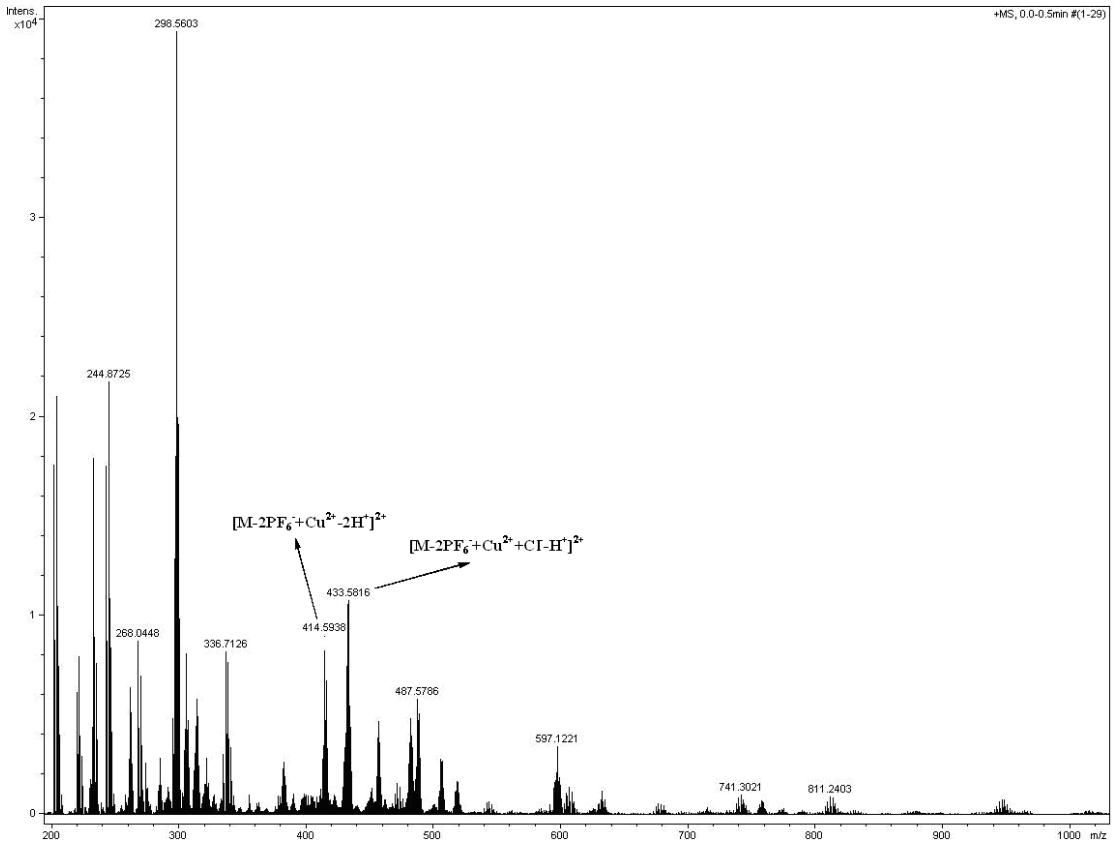

Figure S12. TOF-MS spectrum of Ru-Cyclenein water after addition of Cu^{2+}. The peaks at m/z = 414.5938 and 433.5816 correspond to $[M\text{-}2PF_6^-+Cu^{2+}\text{-}2H^+]^{2+}$ (calc.414.6044) and $[M\text{-}2PF_6^-+Cu^{2+}+Cl^-\text{-}H^+]^{2+}$ (calc. 433.5922)

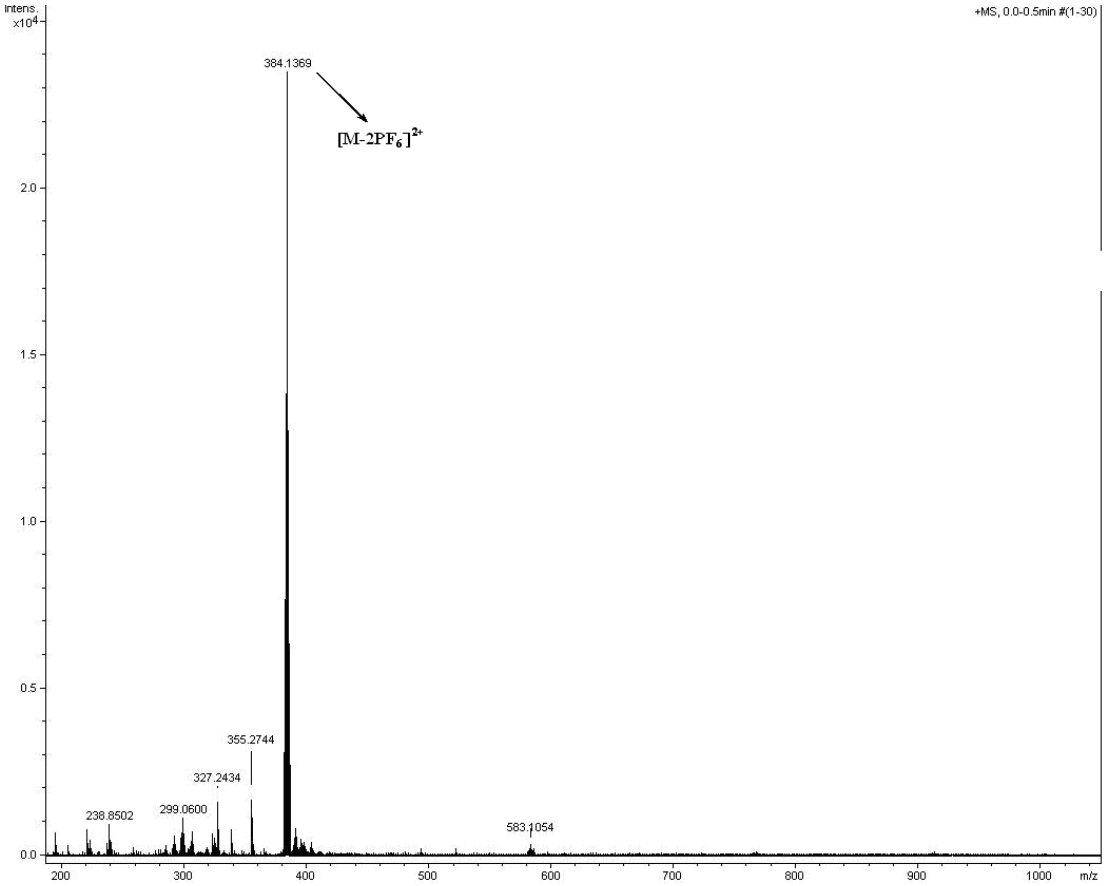

Figure S 13. TOF-MS spectrum of Ru-Cyclen in water after addition of S^{2-} followed by addition of Cu^{2+}. The peaks at m/z = 384.1369 correspond to $[M\text{-}2PF_6^-]^{2+}$.

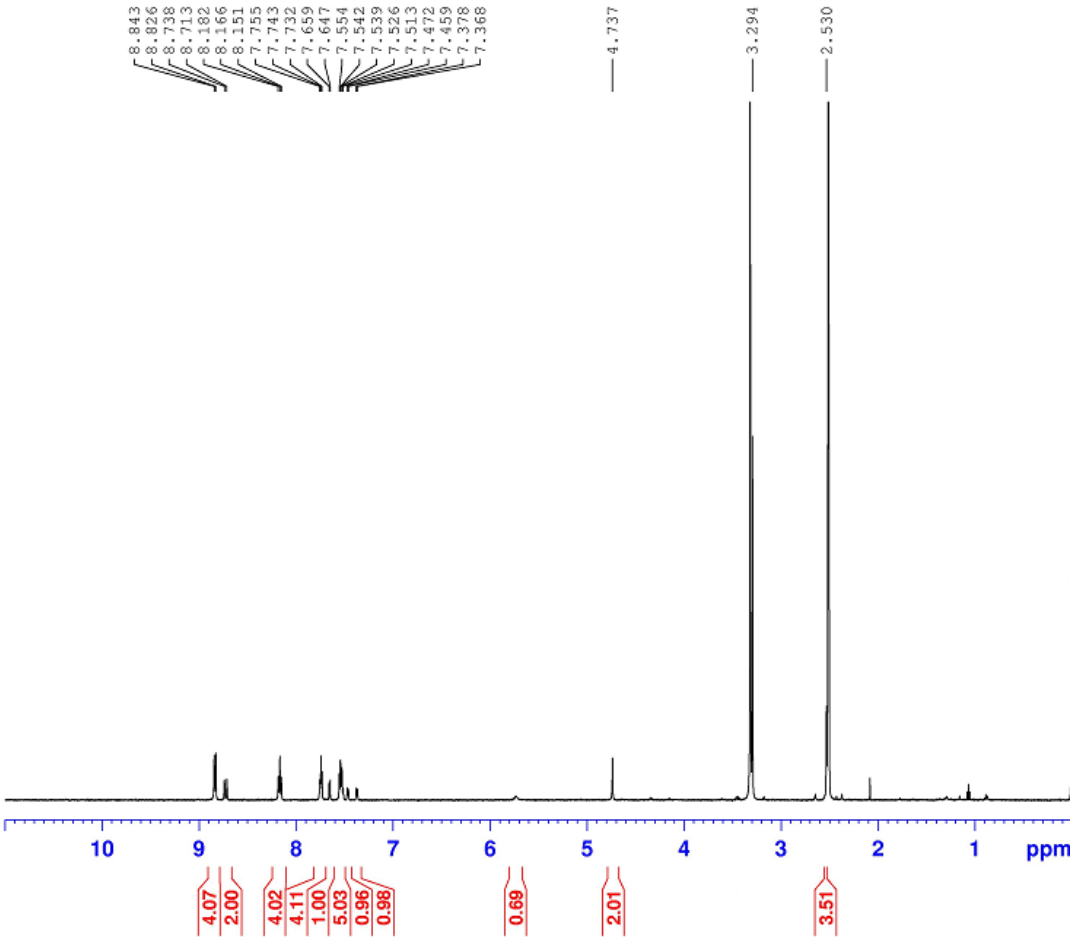

Figure S 14. ^{1}H-NMR spectrum of complex **3** in d^{6}-DMSO.

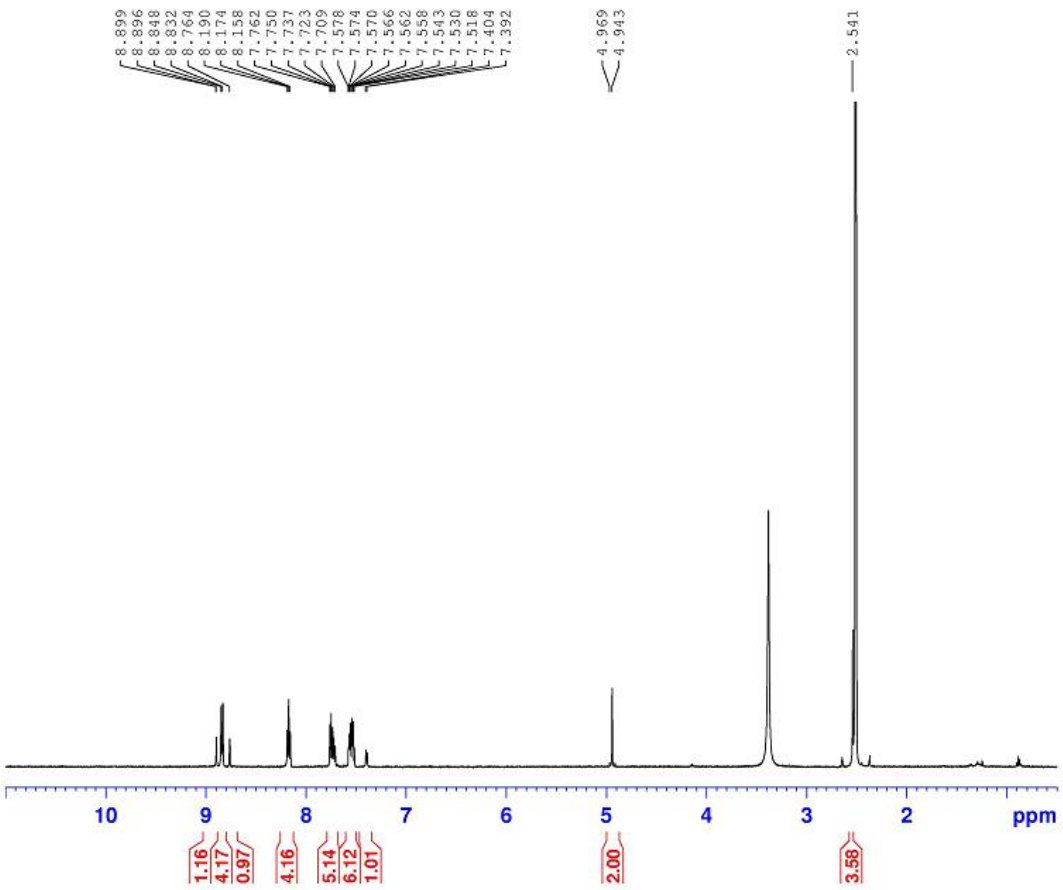

Figure S 15. ^{1}H-NMR spectrum of complex **4** in d^{6}-DMSO.

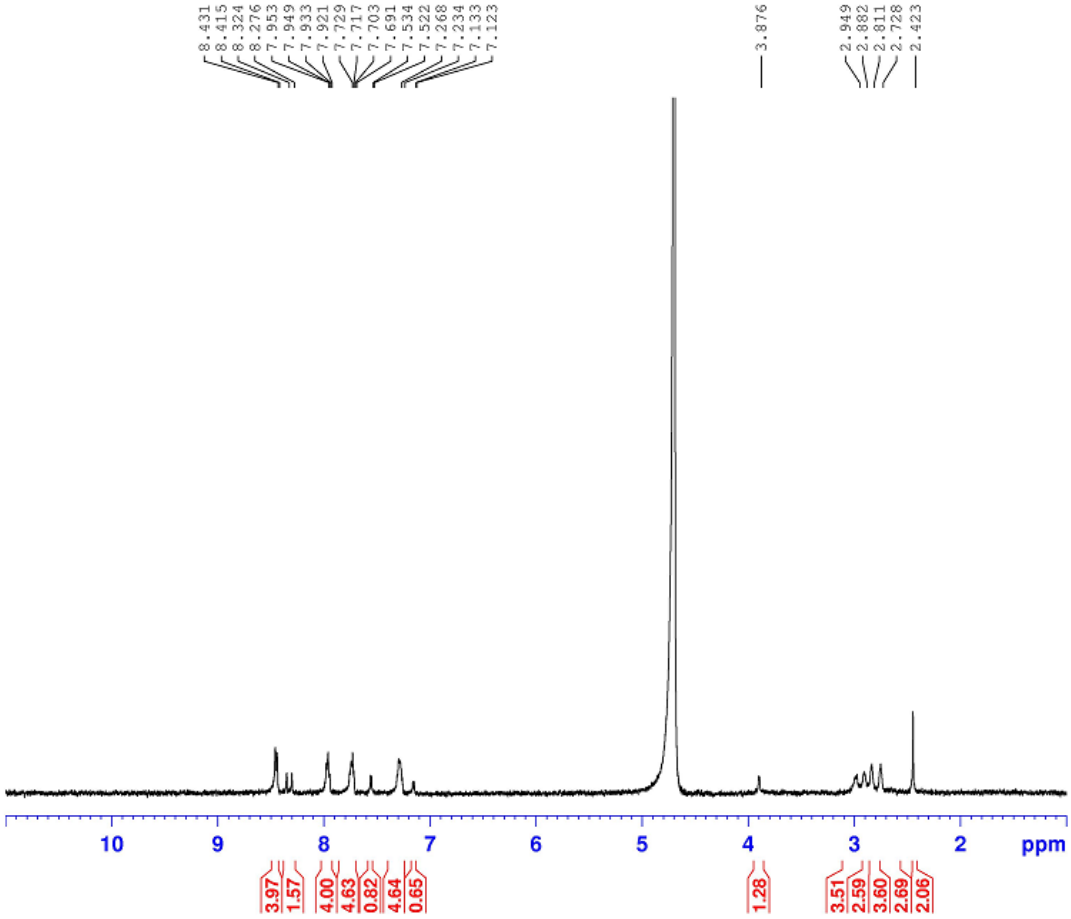

Figure S 16. ^{1}H-NMR spectrum of complex Ru-Cyclen in D_2O.

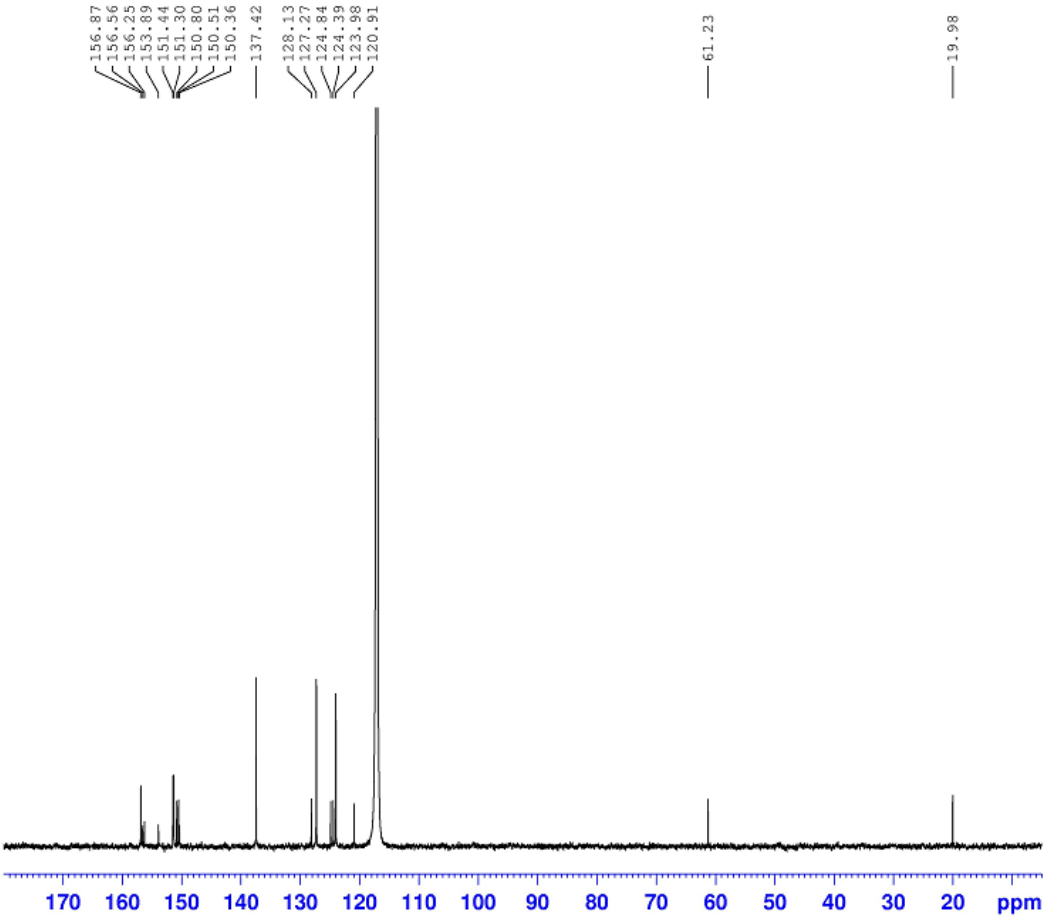

Figure S17. ^{13}C-NMR spectrum of complex **3** in CD_3CN.

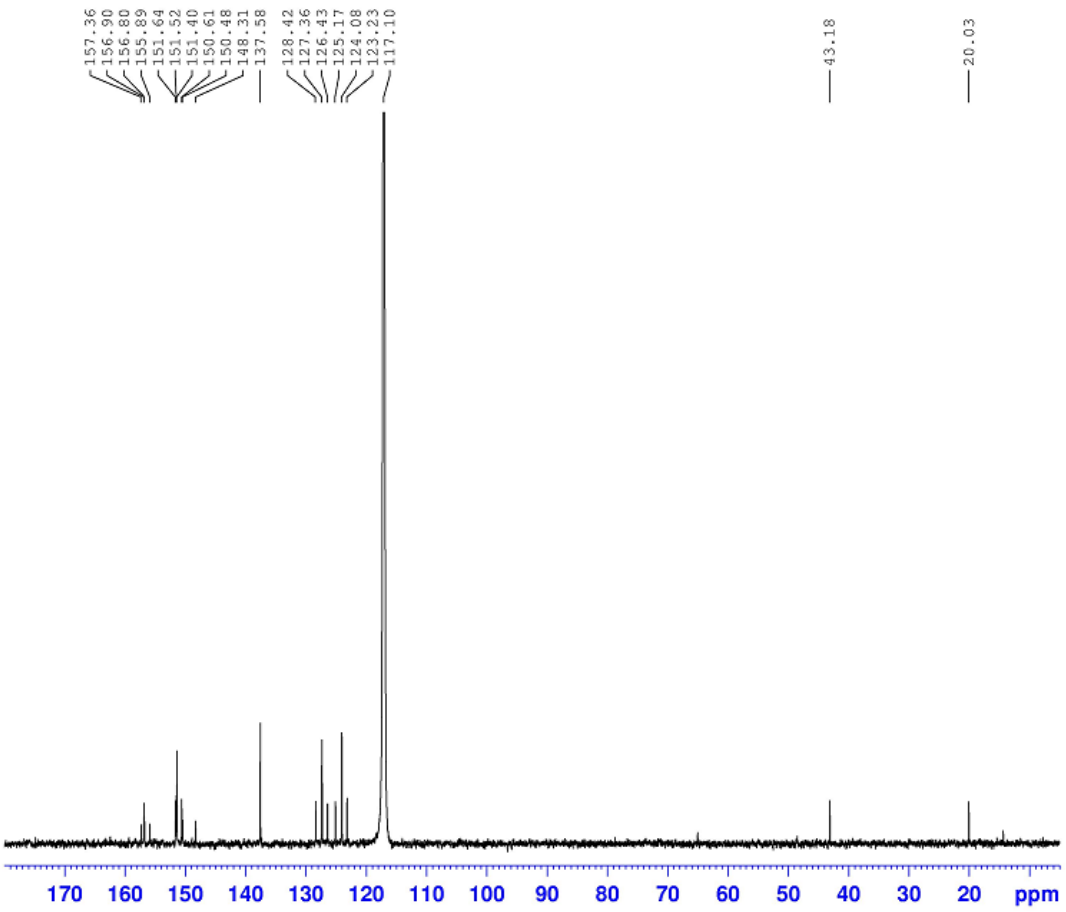

Figure S18. ^{13}C-NMR spectrum of complex **4** in CD_3CN.

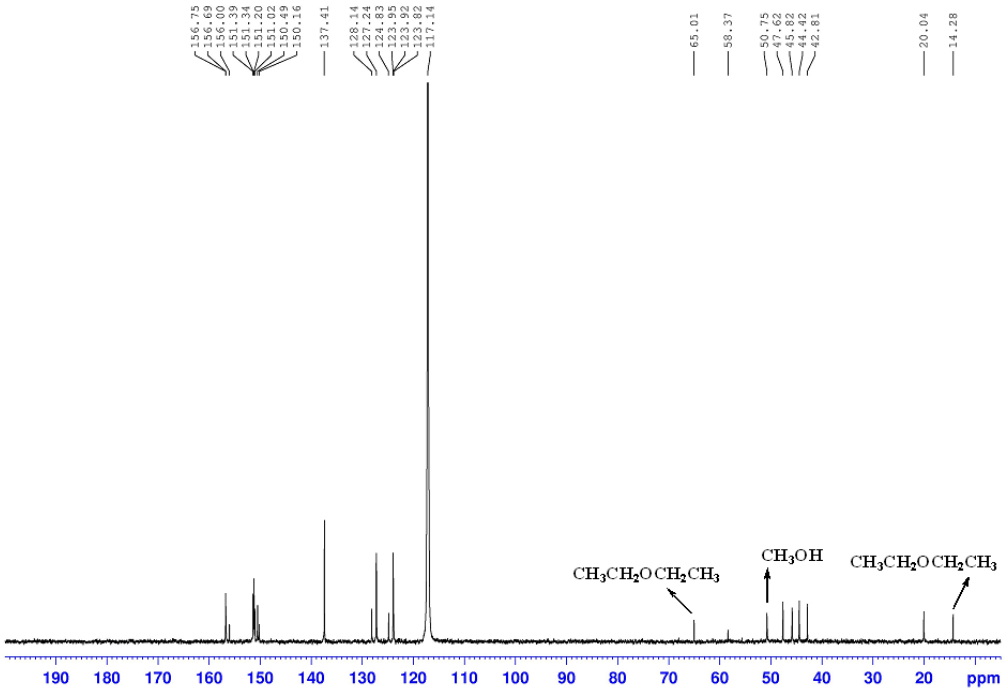

Figure S19. ^{13}C-NMR spectrum of Ru-Cyclen in CD_3CN.

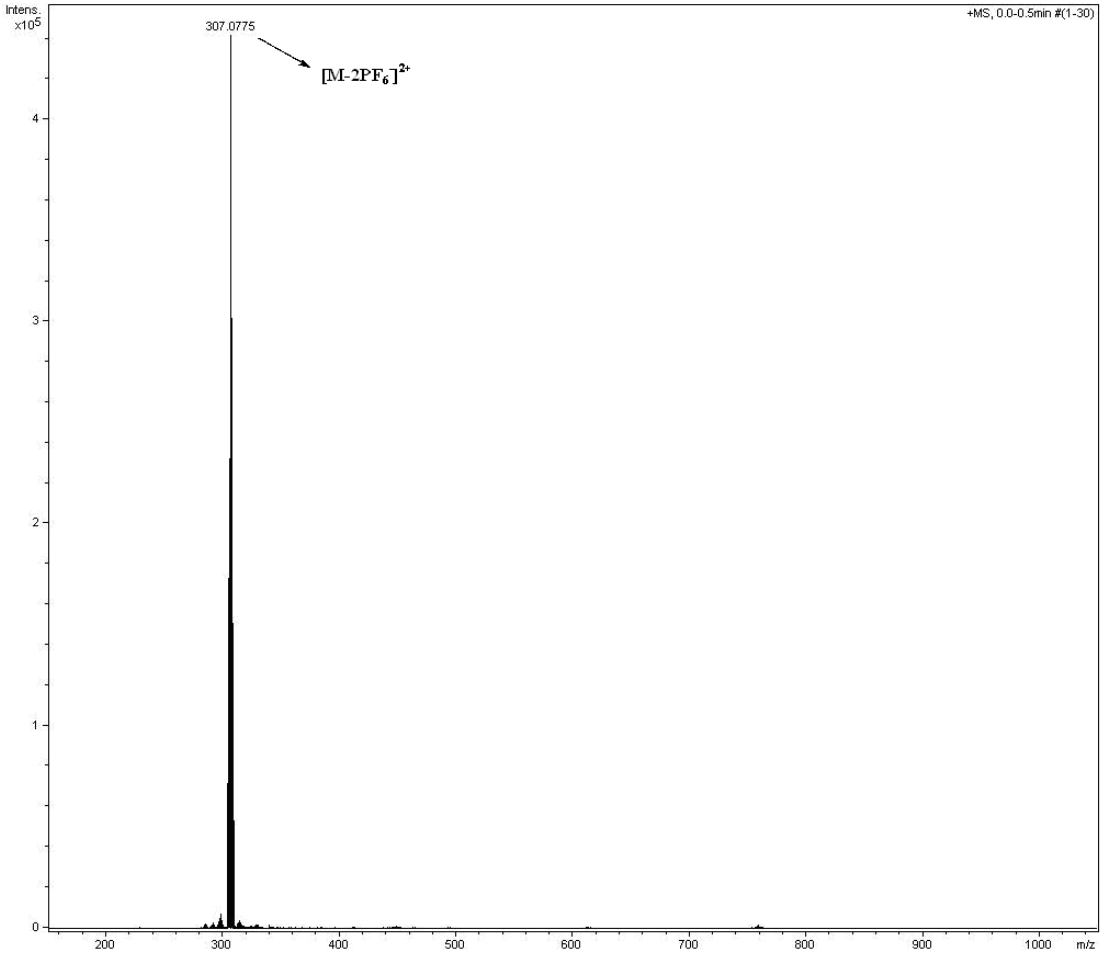

Figure S20. TOF-MS spectrum of complex **3** in CH_3CN. The peaks at m/z = 307.0775 correspond to $[M\text{-}2PF_6^-]^{2+}$ (calc.307.0683).

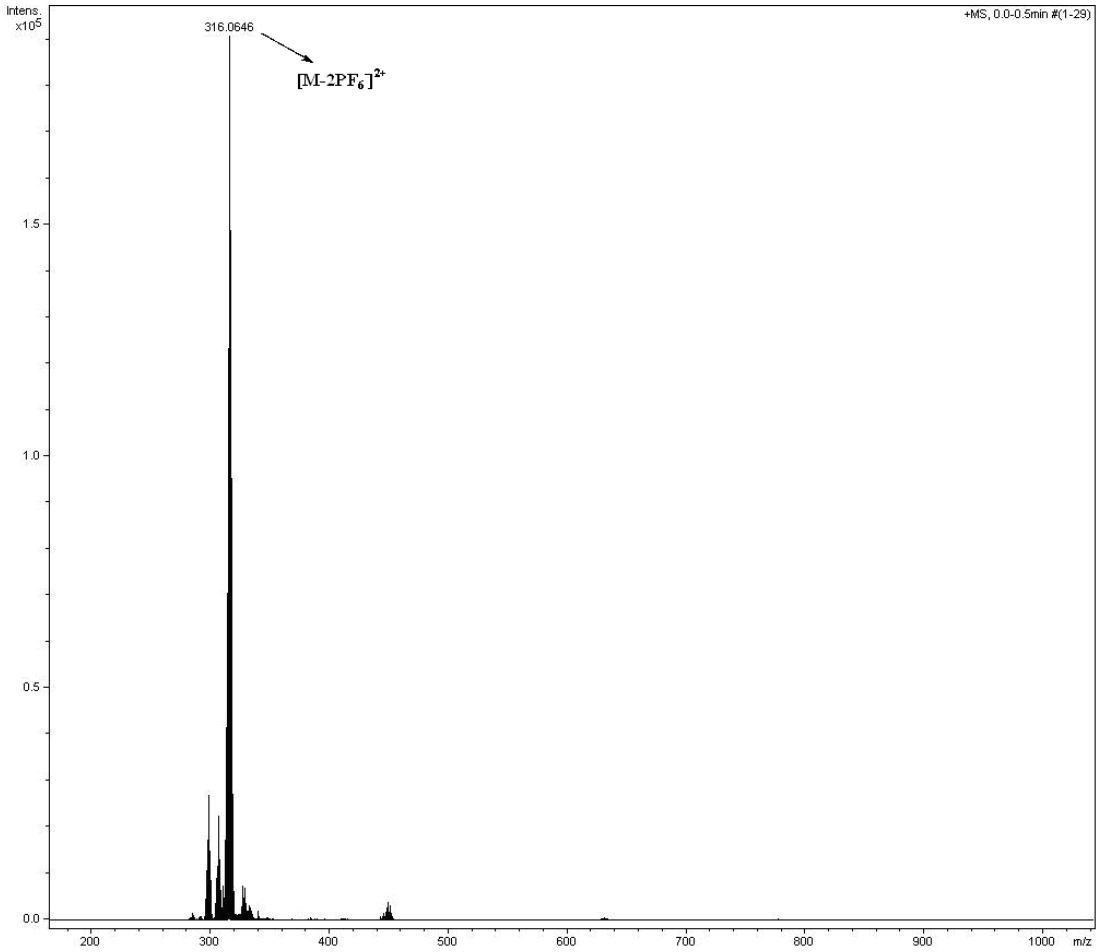

Figure S21. TOF-MS spectrum of complex **4** in CH_3CN. The peaks at m/z = 316.0646 correspond to $[M\text{-}2PF_6^-]^{2+}$ (calc.316.0572).

References

[1] I. D. Kuntz Jr, F. P. Gasparro, M. D. Johnston Jr, R. P. Taylor, *J. Am. Chem. Soc*., 1968, **90**, 4778.

[2] X. W. Cao, W. Y. Lin, L. W. He, *Organic Letters*, 2011, **13**, 4716.

[3] M. Shortreed, R. Kopelman, M. Kuhn, B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414.

[4] W. Lin, L. Yuan, L. Long, C. Guo, J. Feng, *Adv. Funct. Mater*. **2008**, *18*, 2366.

[5] A. Caballero, R. Martınez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina, and J. Veciana, *J. Am. Chem. Soc*. **2005**, *127*, 15666.