

Supporting Information (SI)

Modulation of the selectivity in anions recognition processes by complexing hydrogen- and halogen- bonding interactions

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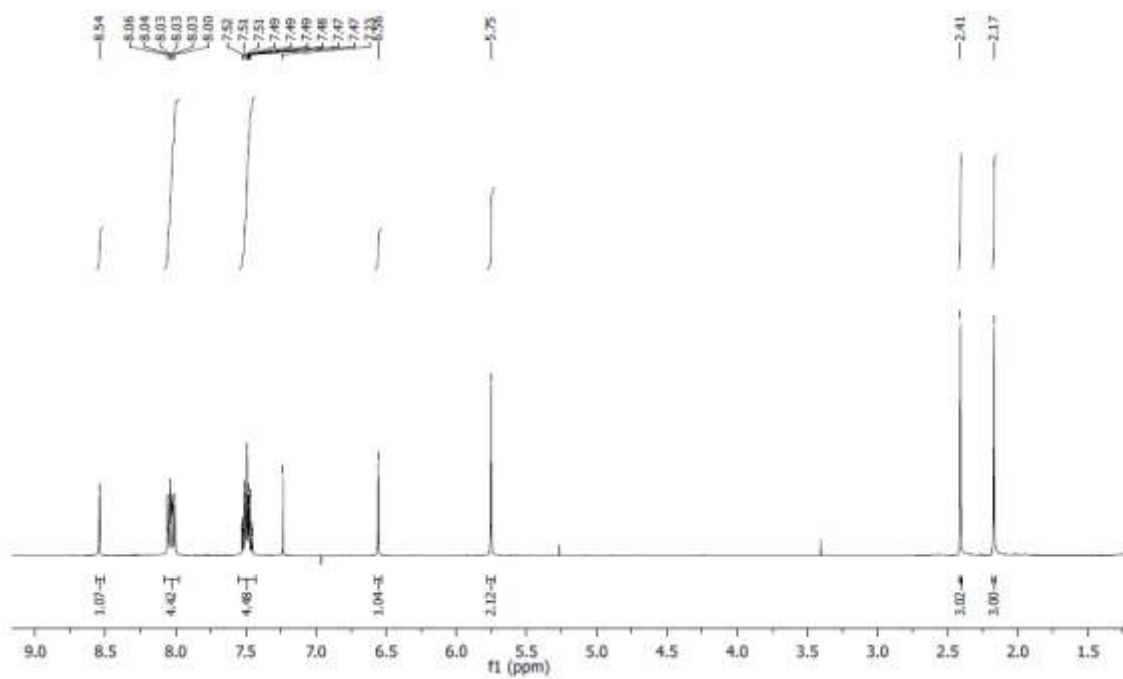
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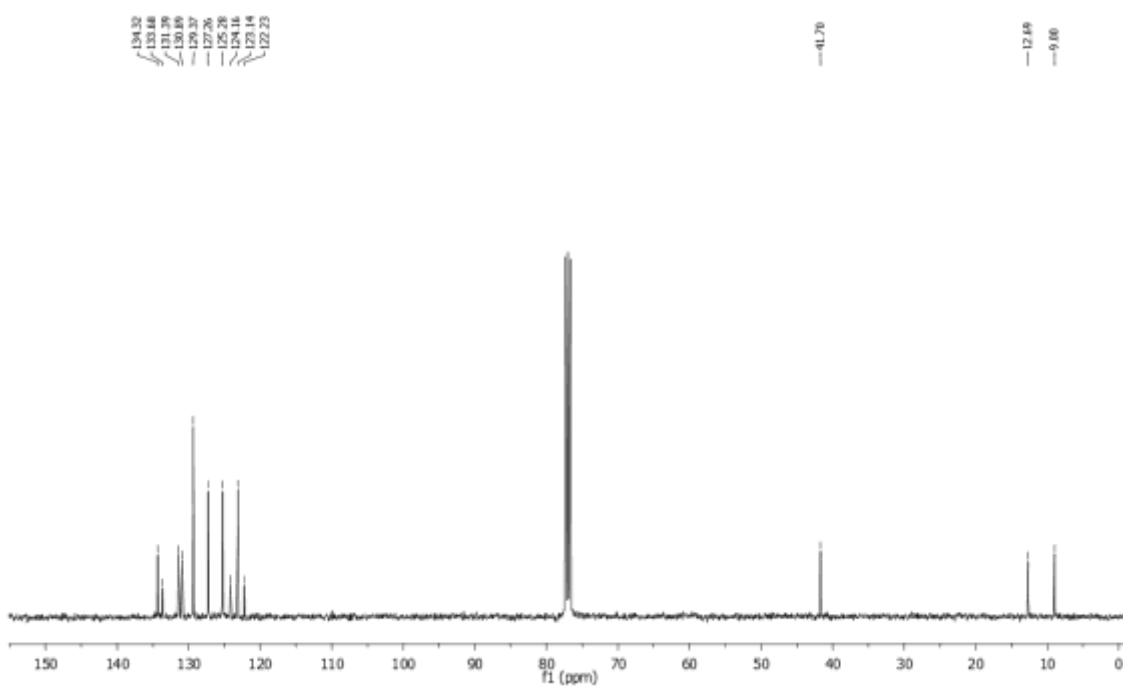
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Compound 2

^1H -NMR (CDCl_3 , 400 MHz)

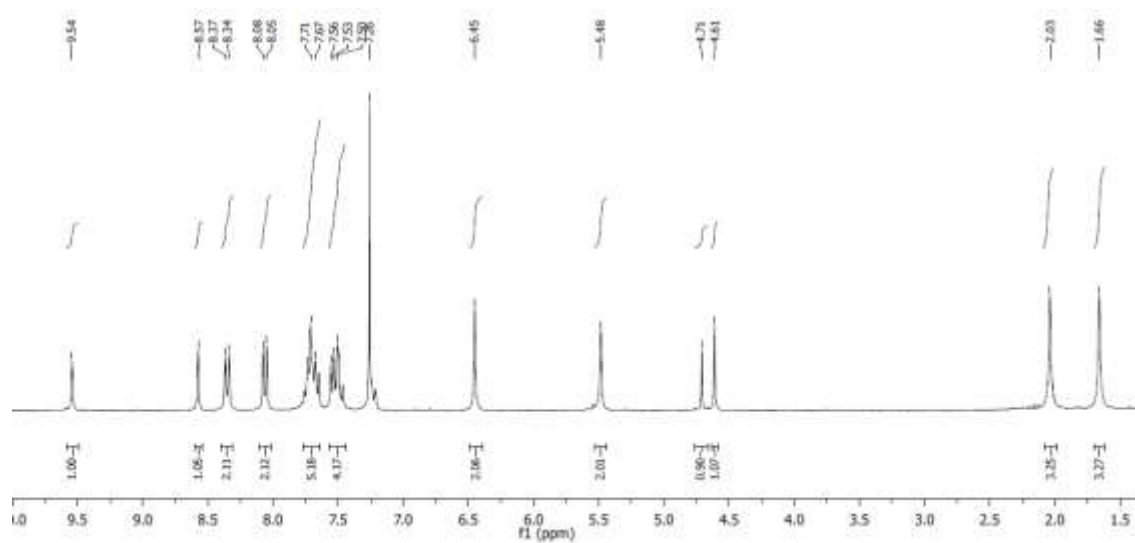


^{13}C NMR (100 MHz, CDCl_3)

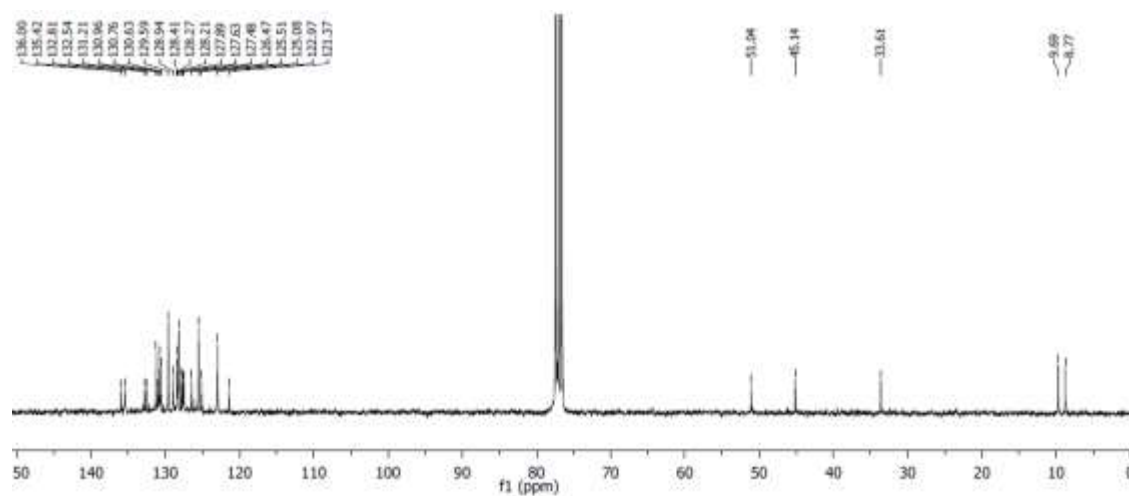


Compound 3⁺·Br⁻

¹H-NMR (CDCl₃, 400 MHz)

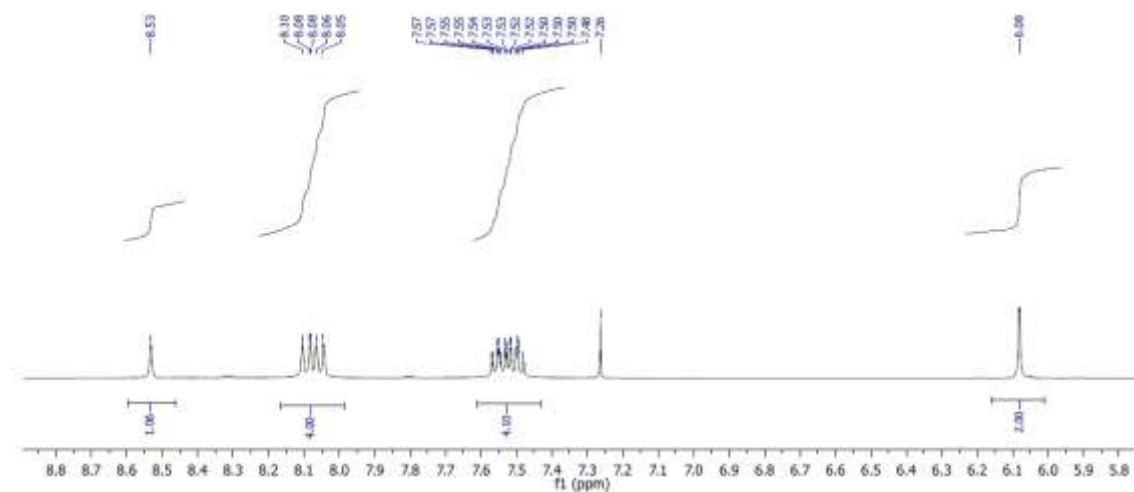
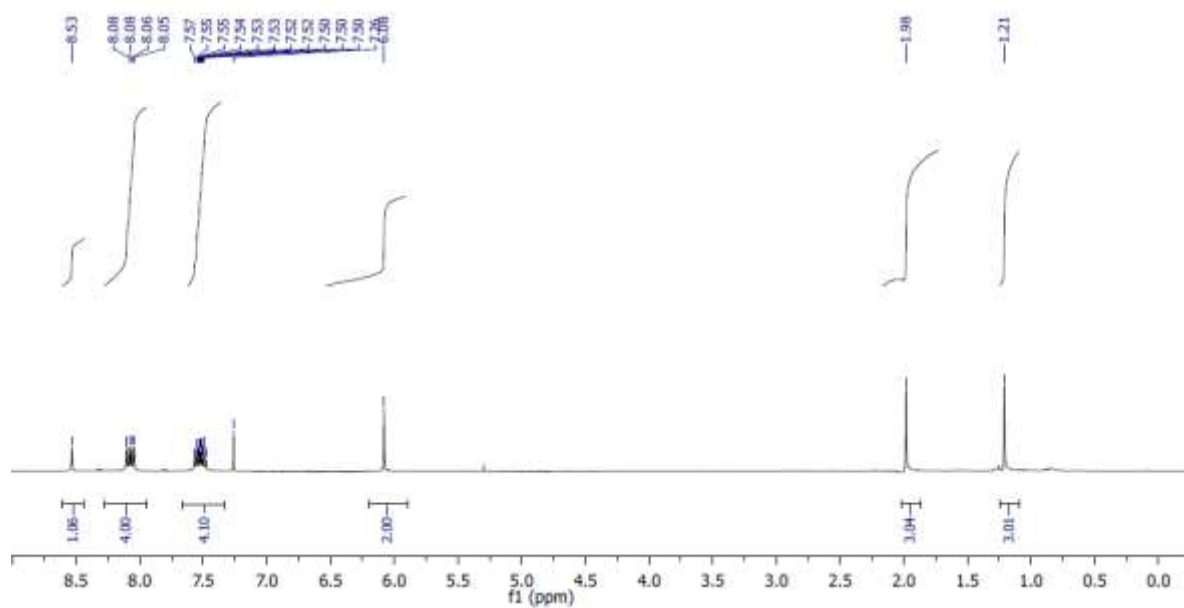


¹³C-NMR (CDCl₃, 75 MHz)

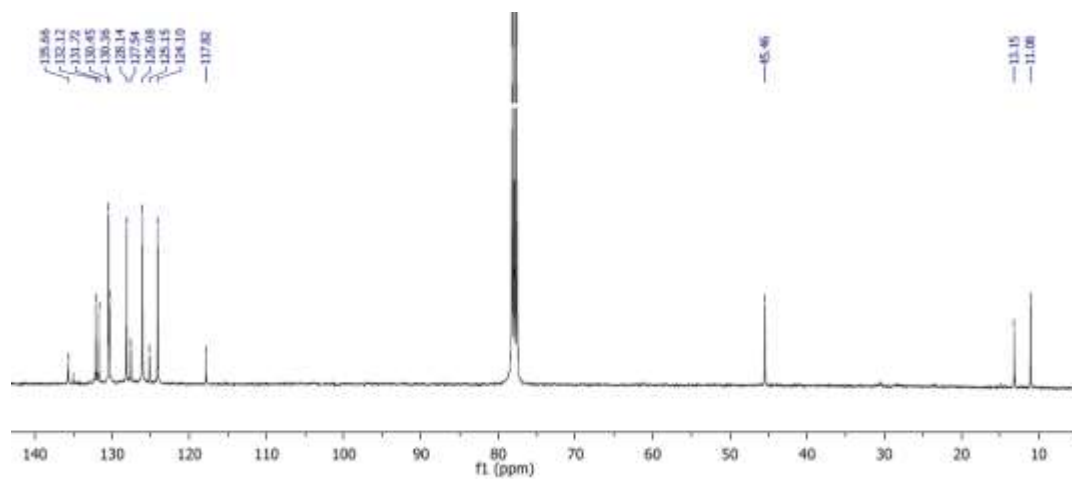


Compound 4

^1H -NMR (CDCl_3 , 400 MHz)

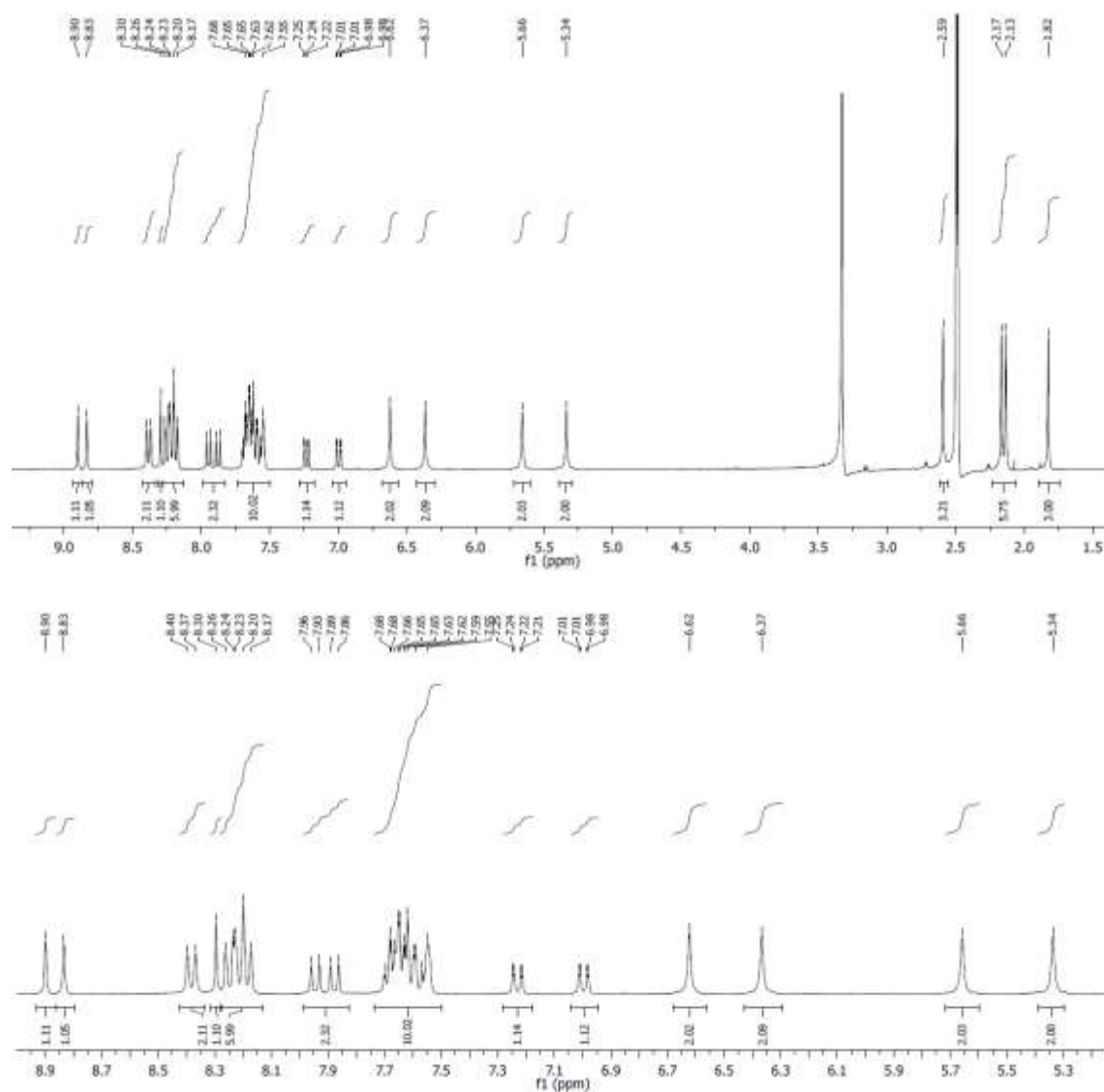


^{13}C -NMR (CDCl_3 , 100 MHz)

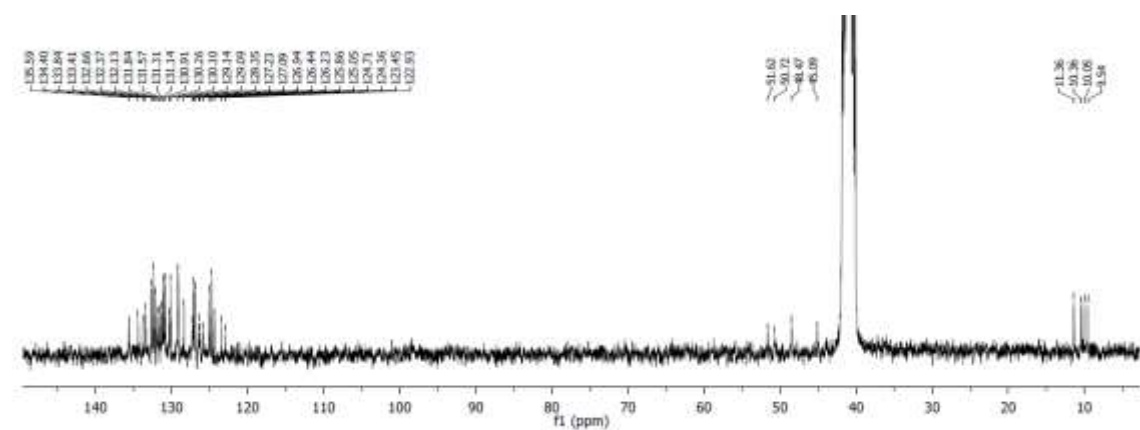


Compound $5^{2+} \cdot 2Br^-$

1H -NMR (DMSO, 400 MHz)

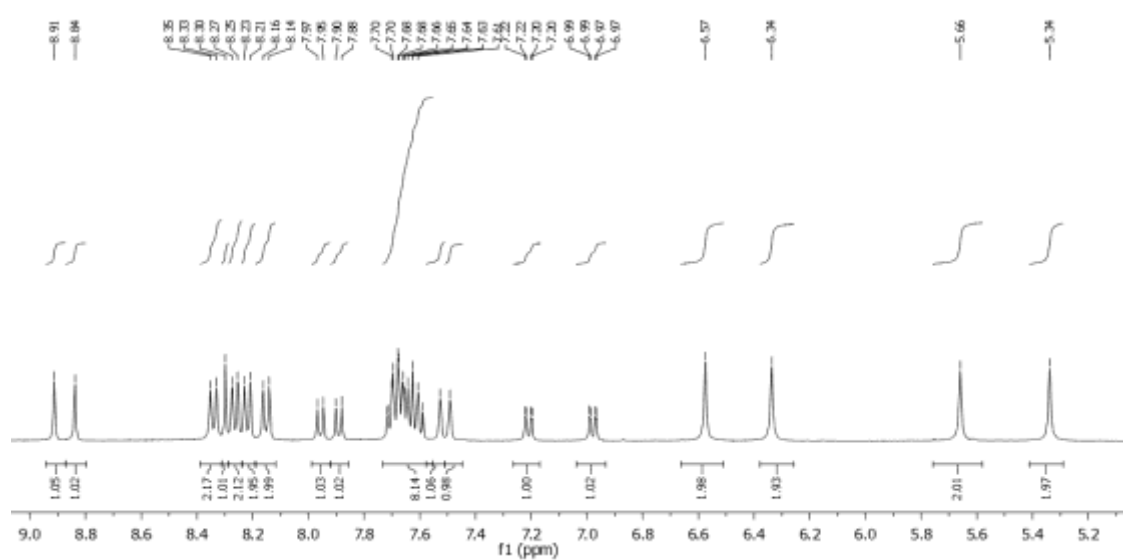
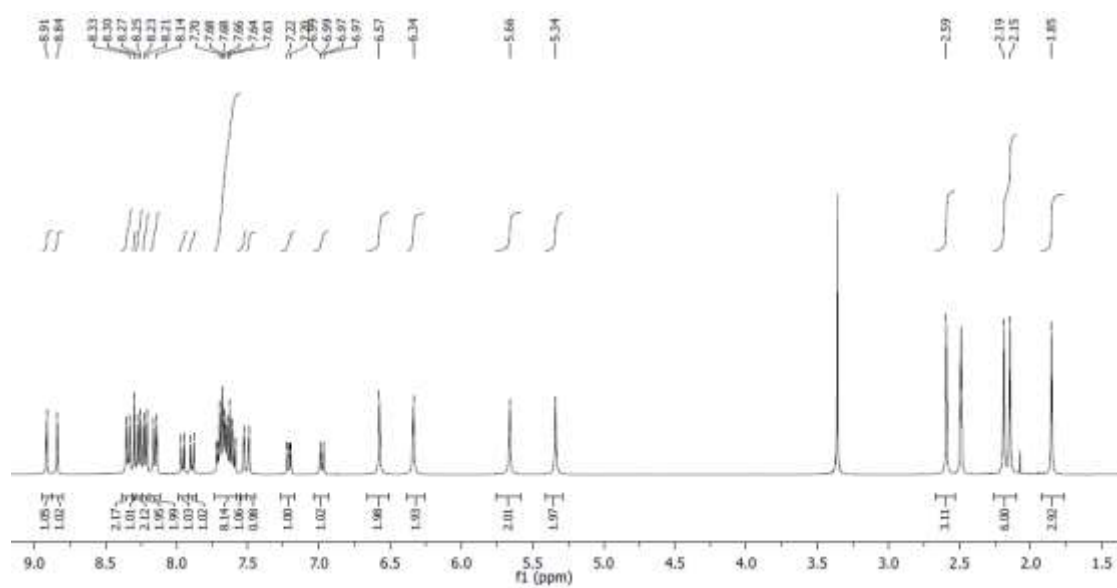


^{13}C -NMR (DMSO, 75 MHz)

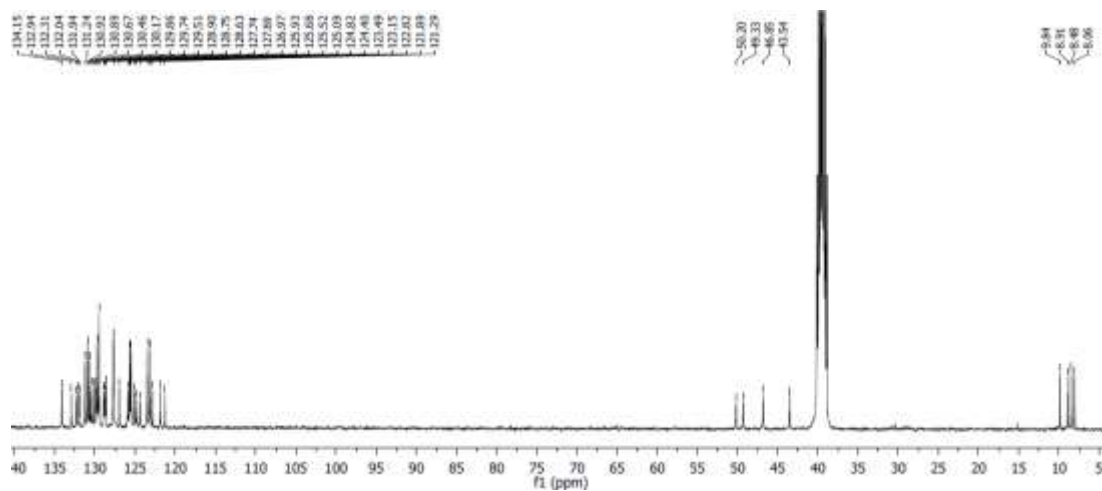


Compound $5^{2+} \cdot 2PF_6^-$

1H -NMR (DMSO, 400 MHz)



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



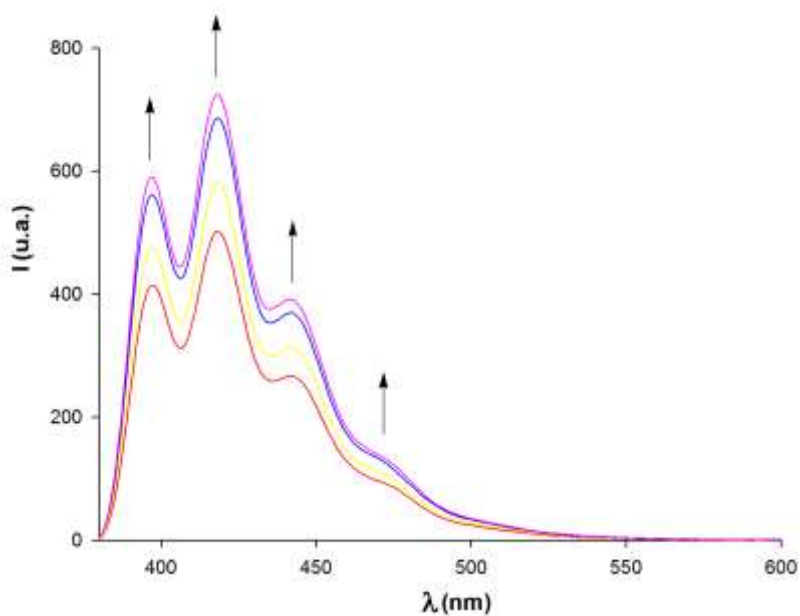


Figure S1. Changes in the fluorescence spectra of receptor $5^{2+} \cdot 2PF_6^{-}$ ($c = 1 \cdot 10^{-5}$ M in CH_3CN) upon addition of F^{-} anions from 0 to 1.8 equiv at 20 °C.

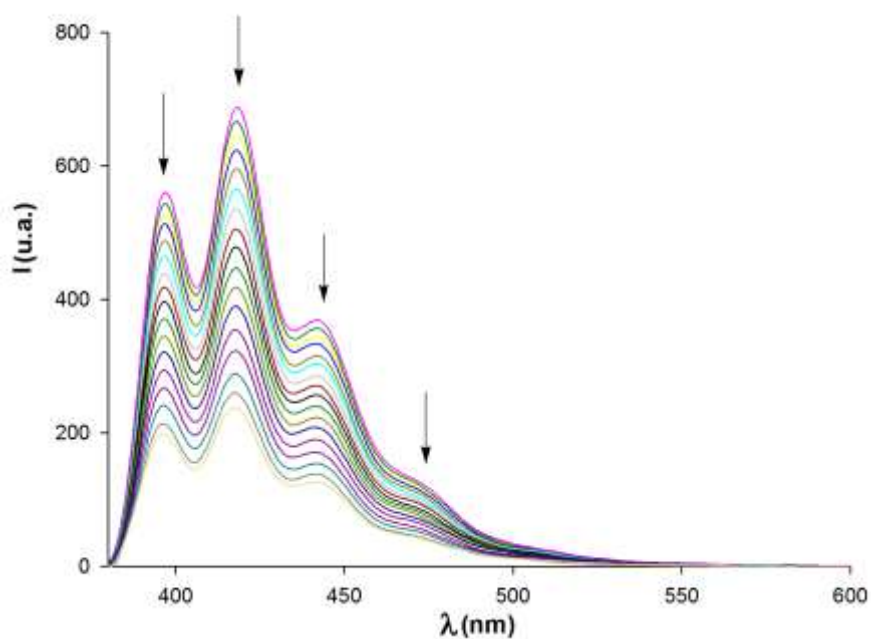


Figure S2. Changes in the fluorescence spectra of receptor $5^{2+} \cdot 2PF_6^{-}$ ($c = 1 \cdot 10^{-6}$ M in CH_3CN) upon addition of F^{-} anions from 1.8 to 5 equiv at 20 °C.

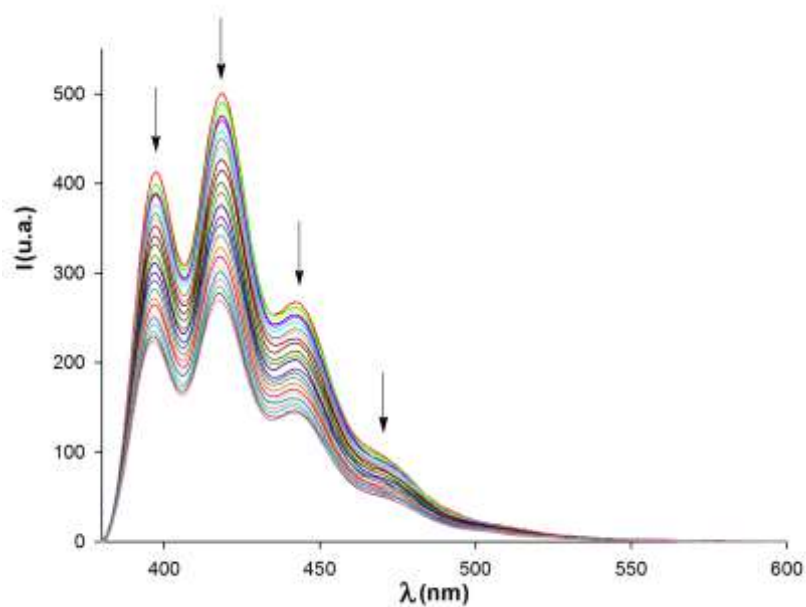


Figure S3. Changes in the fluorescence spectra of receptor $5^{2+} \cdot 2PF_6^{-}$ ($c = 1 \cdot 10^{-6}$ M in CH_3CN) upon addition of AcO^{-} anions at 20 °C.

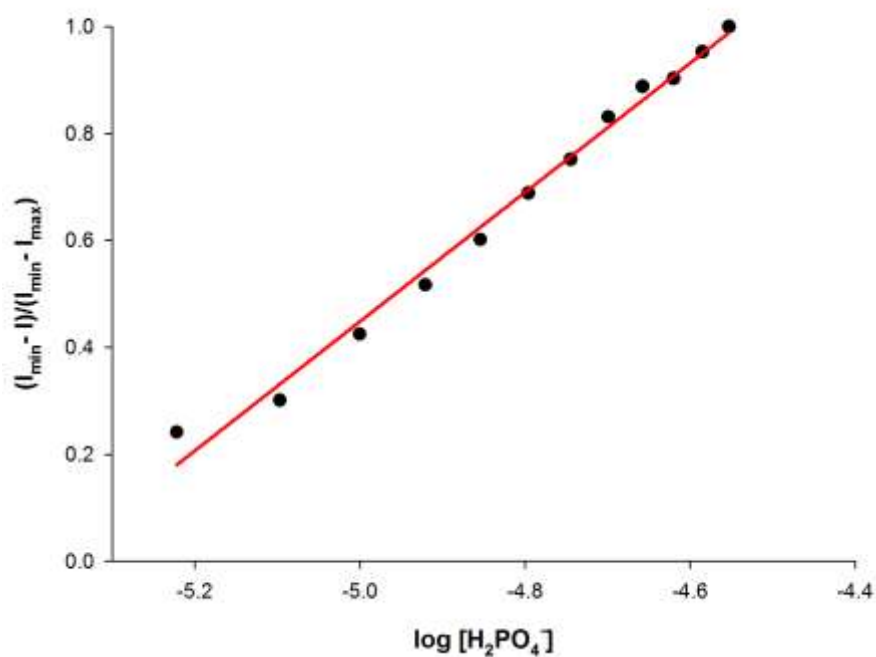


Figure S4. Fluorescence intensity of $5^{2+} \cdot 2PF_6^{-}$ (in CH_3CN) at each concentration of $H_2PO_4^{-}$ added, normalized between the minimum fluorescence intensity, found at zero equiv of $H_2PO_4^{-}$; and the maximum fluorescence intensity. The detection limit was found at $[H_2PO_4^{-}] = 3.90 \times 10^{-6}$ M.

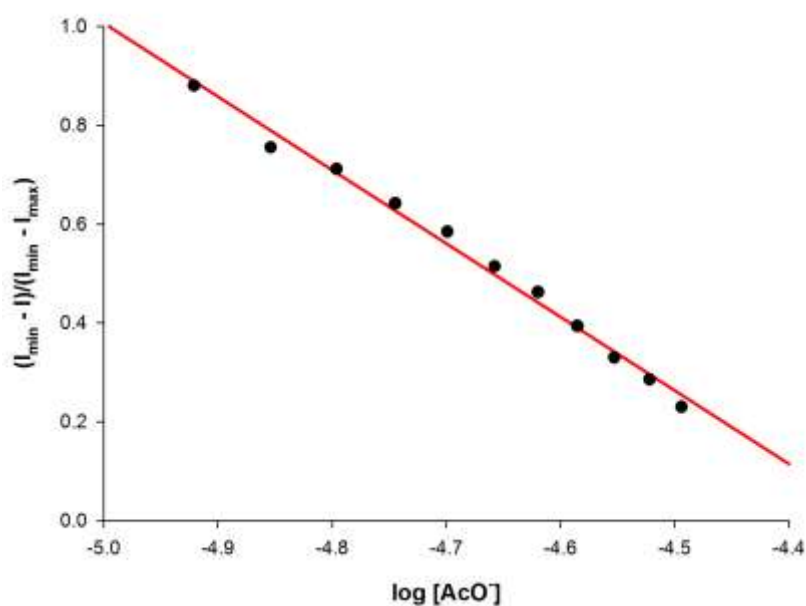


Figure S5. Fluorescence intensity of $5^{2+} \cdot 2PF_6^-$ (in CH_3CN) at each concentration of AcO^- added, normalized between the minimum fluorescence intensity, found at zero equiv of AcO^- ; and the maximum fluorescence intensity. The detection limit was found at $[AcO^-] = 4.59 \times 10^{-5} M$.

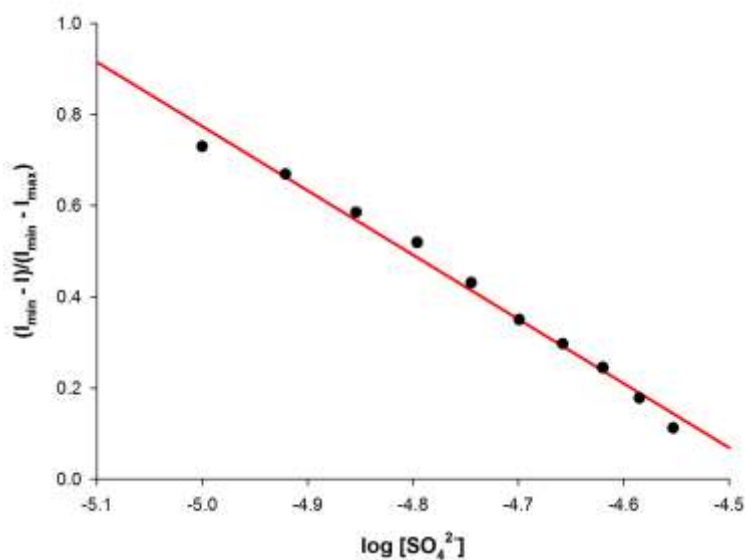


Figure S6. Fluorescence intensity of $5^{2+} \cdot 2PF_6^-$ (in CH_3CN) at each concentration of SO_4^{2-} added, normalized between the minimum fluorescence intensity, found at zero equiv of Pb^{2+} ; and the maximum fluorescence intensity. The detection limit was found at $[SO_4^{2-}] = 3.57 \times 10^{-5} M$.

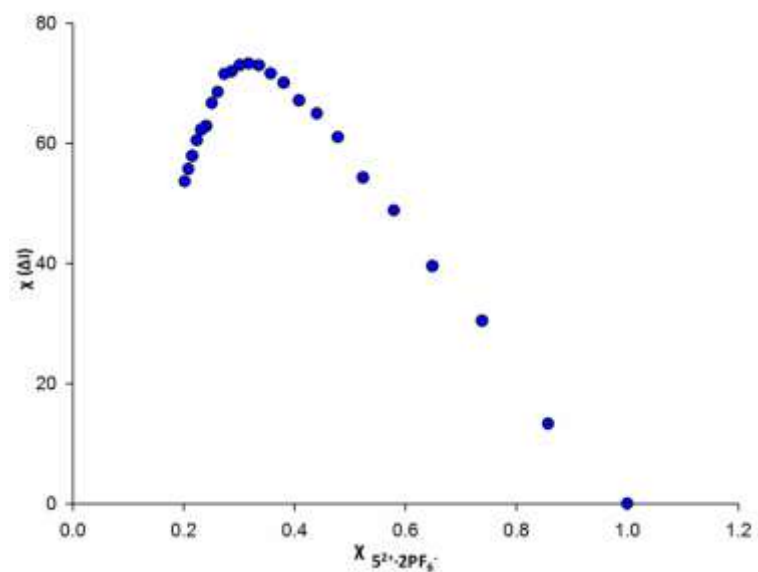


Figure S7. Job plot experiment, using the emission titration data, with a maximum at 0.33 indicating 1:2 stoichiometry for receptor $5^{2+} \cdot 2PF_6^-$ and $H_2PO_4^-$ anions.

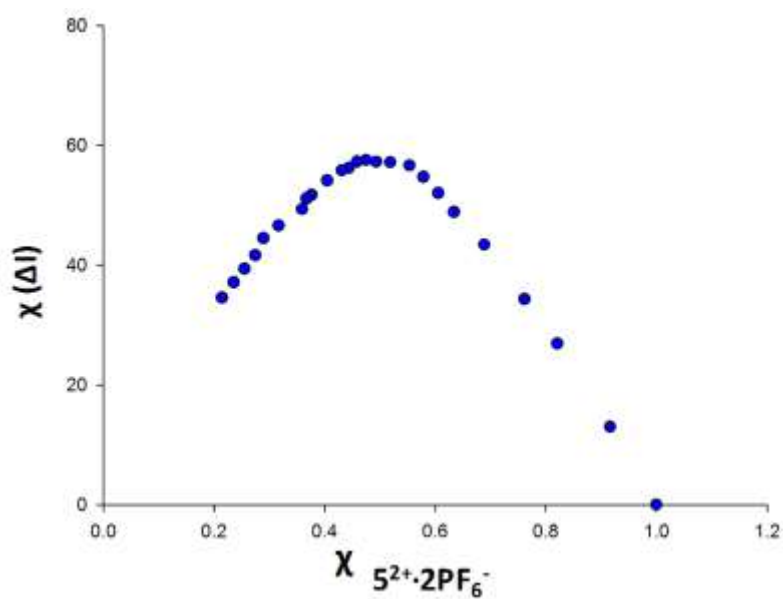


Figure S8. Job plot experiment, using the emission titration data, with a maximum at 0.5 indicating 1:1 stoichiometry for receptor $5^{2+} \cdot 2PF_6^-$ and SO_4^{2-} anions.

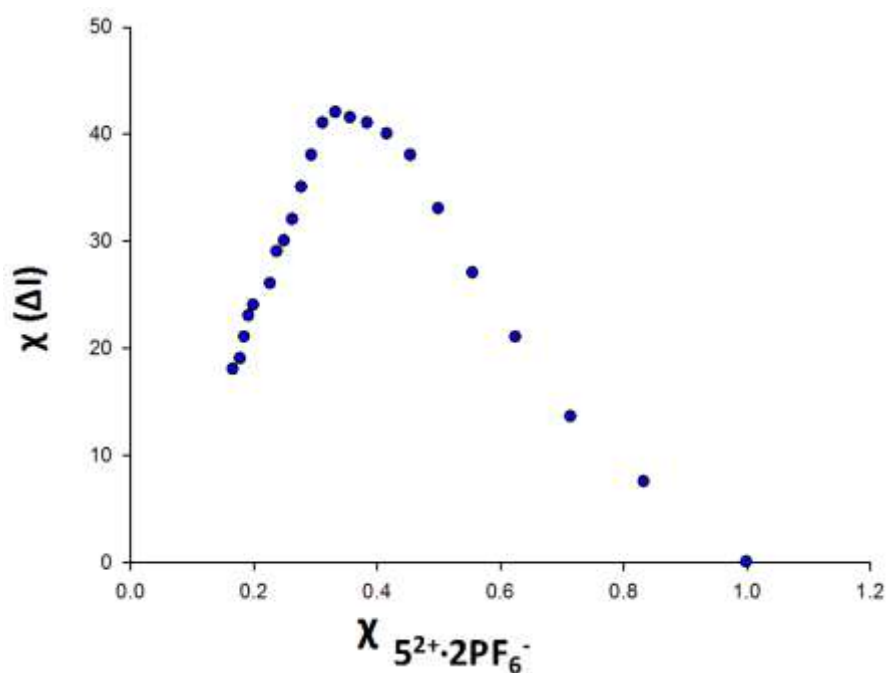


Figure S9. Job plot experiment, using the emission titration data, with a maximum at 0.33 indicating 1:2 stoichiometry for receptor $5^{2+} \cdot 2PF_6^-$ and AcO^- anions.

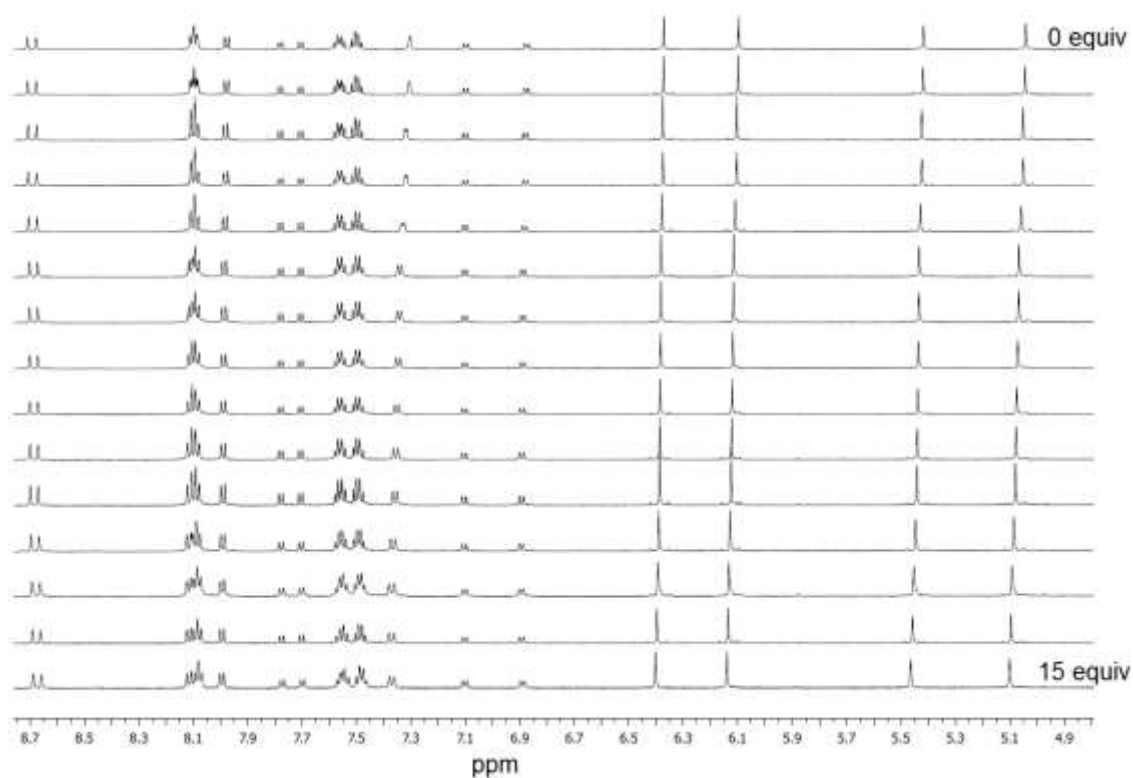


Figure S10. 1H NMR spectral changes observed in the receptor $5^{2+} \cdot 2PF_6^-$ in CD_3CN/CD_3OD (8:2, v/v) during the addition of up to 15 equivalents of SO_4^{2-} ions.

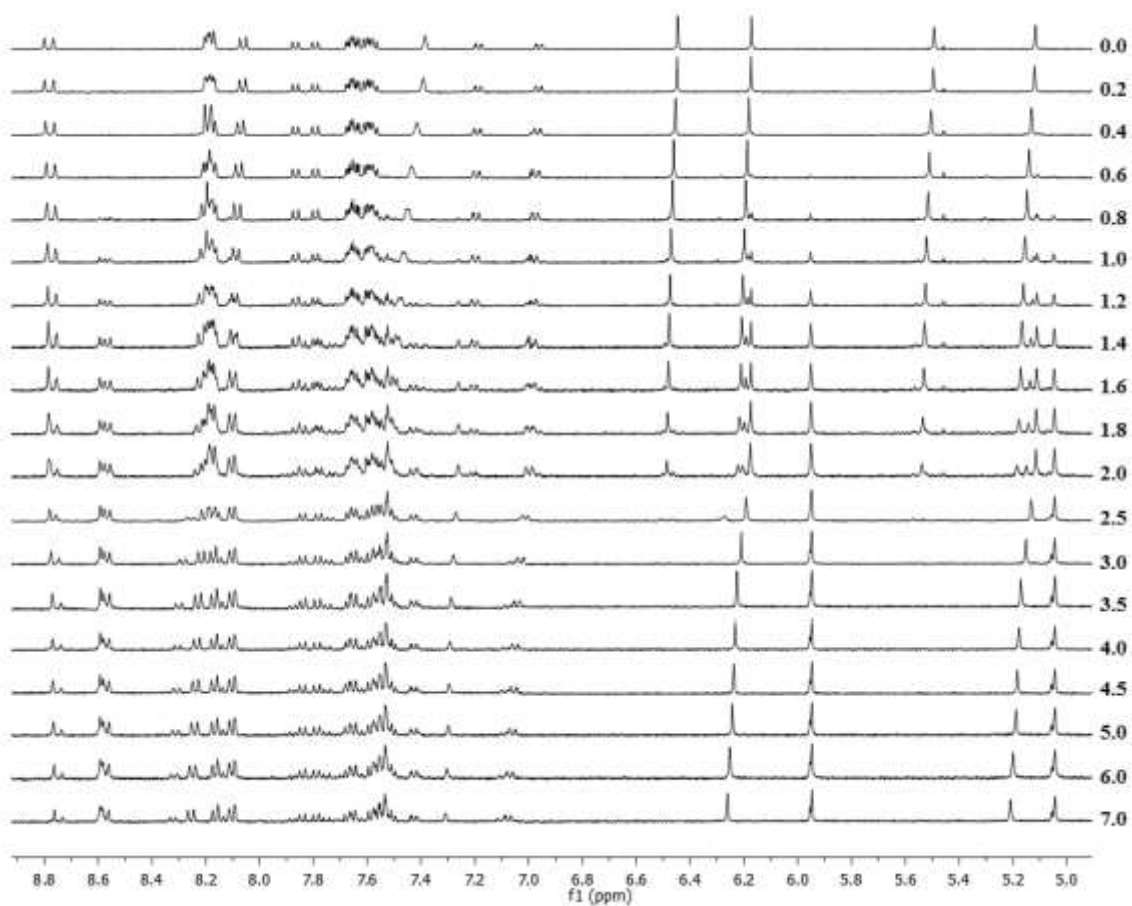


Figure S11. ^1H NMR spectral changes observed in the receptor $5^{2+} \cdot 2\text{PF}_6^-$ in $\text{CD}_3\text{CN}/\text{CD}_3\text{OD}$ (8:2, v/v) during the addition of up to 15 equivalents of $\text{HP}_2\text{O}_7^{3-}$ ions.

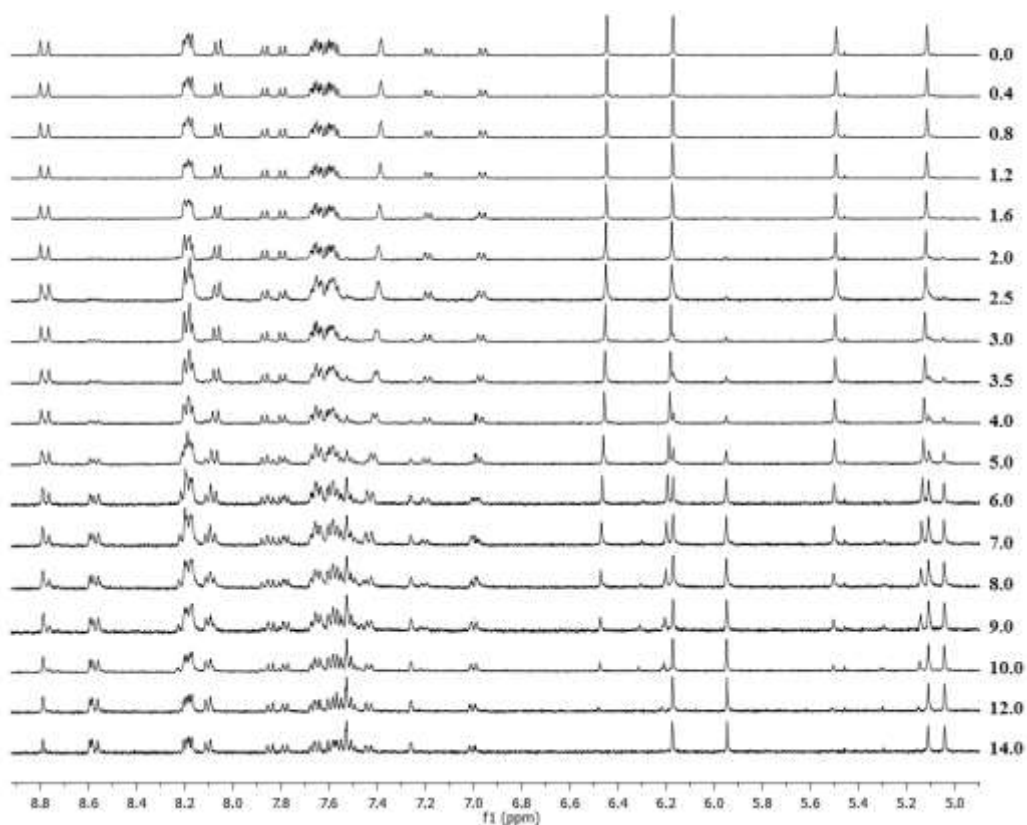


Figure S12. ^1H NMR spectral changes observed in the receptor $5^{2+}\cdot 2\text{PF}_6^-$ in $\text{CD}_3\text{CN}/\text{CD}_3\text{OD}$ (8:2, v/v) during the addition of up to 15 equivalents of F^- ions.

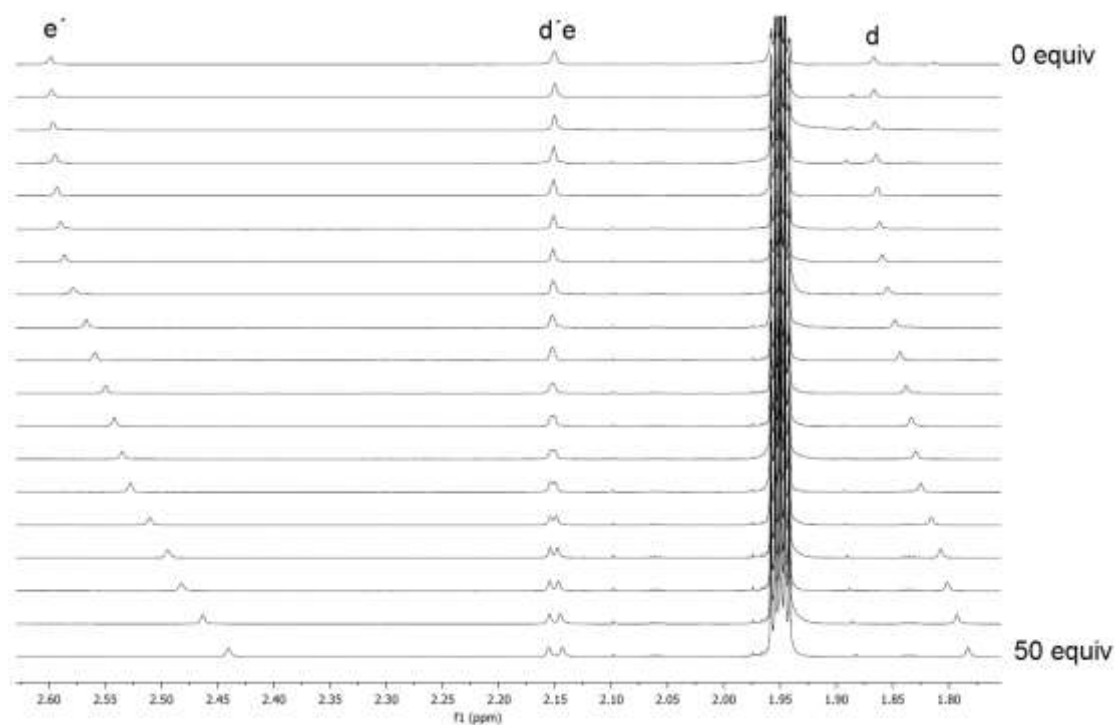


Figure S13. ^1H NMR spectral changes observed in the methyl protons of the receptor $5^{2+}\cdot 2\text{PF}_6^-$ in $\text{CD}_3\text{CN}/\text{CD}_3\text{OD}$ (8:2, v/v) during the addition of up to 50 equivalents of H_2PO_4^- ions.

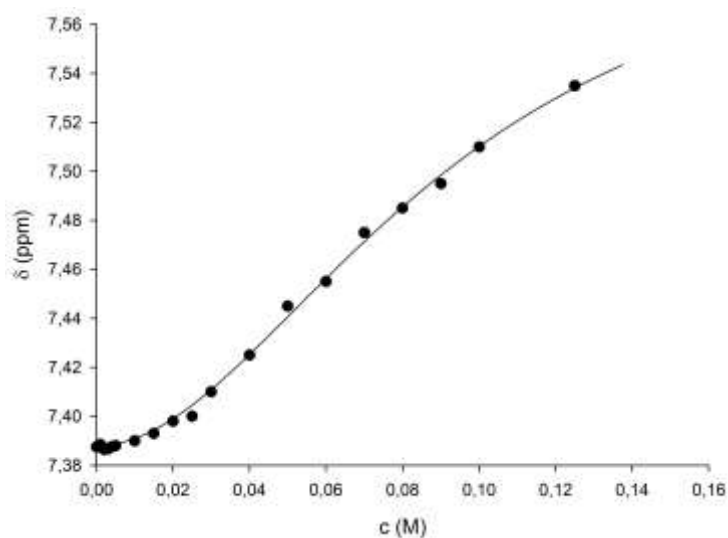


Figure S14. Changes in ^1H NMR spectra in the H_a proton of the receptor $5^{2+}\cdot 2\text{PF}_6^-$ upon addition of increasing amounts of H_2PO_4^- anions. Points represent experimental data, continuous lines represent calculate curve.

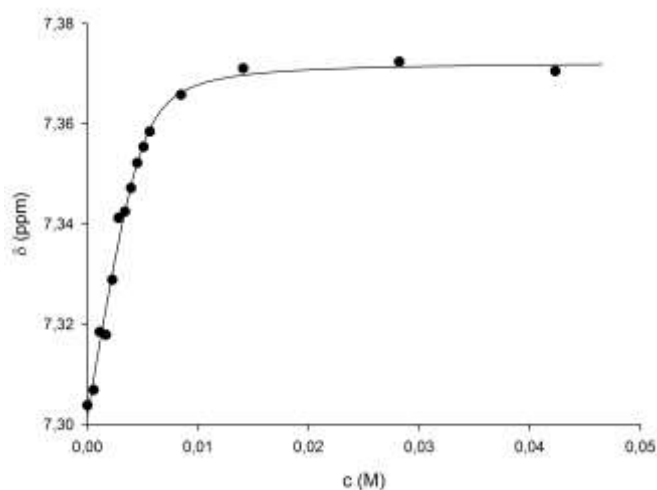


Figure S15. Changes in ^1H NMR spectra in the H_a proton of the receptor $5^{2+}\cdot 2\text{PF}_6^-$ upon addition of increasing amounts of SO_4^{2-} anions. Points represent experimental data, continuous lines represent calculate curve.

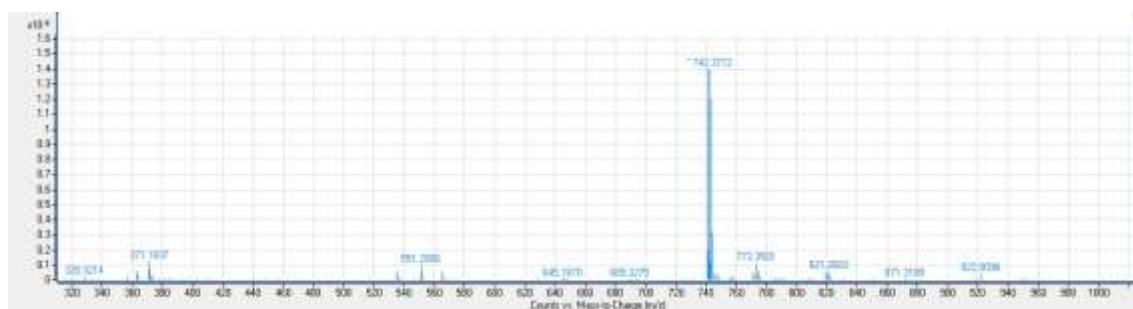


Figure S16. Mass spectrum of the solution of $5^{2+} \cdot 2PF_6^-$ in CH_3CN after the addition of 3 equivalent of $HP_2O_7^{3-}$ ions, indicating the formation of the imidazolone $6^+ \cdot PF_6^-$ $C_{52}H_{45}N_4O^+$ ($M^+ = 741.36$)