Supplementary Information

Thiacalix[4]arene Based Reconfigurable Molecular Switches: Set-Reset Memorized Sequential Device

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Contents **Page No.**

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

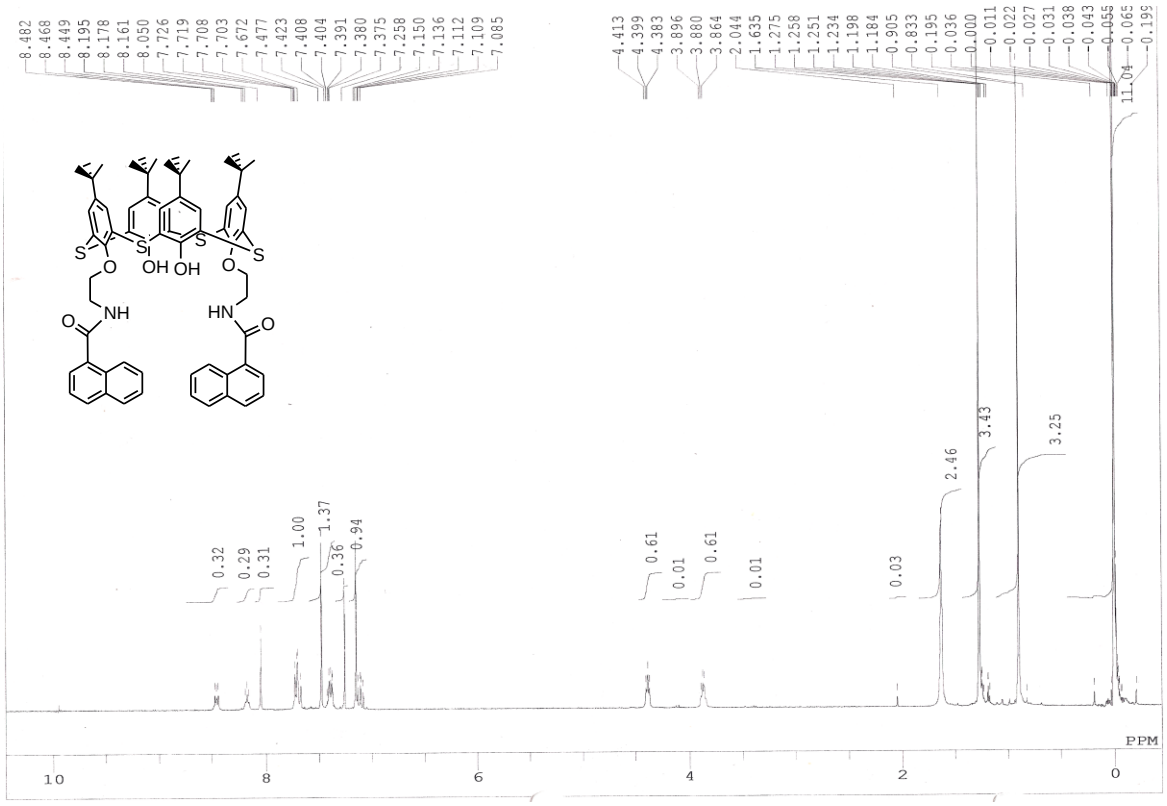

Figure S1. ^{1}H NMR spectrum of **3** in $CDCl_3$.

2. ^{13}C NMR Spectrum of **3** in $CDCl_3$.

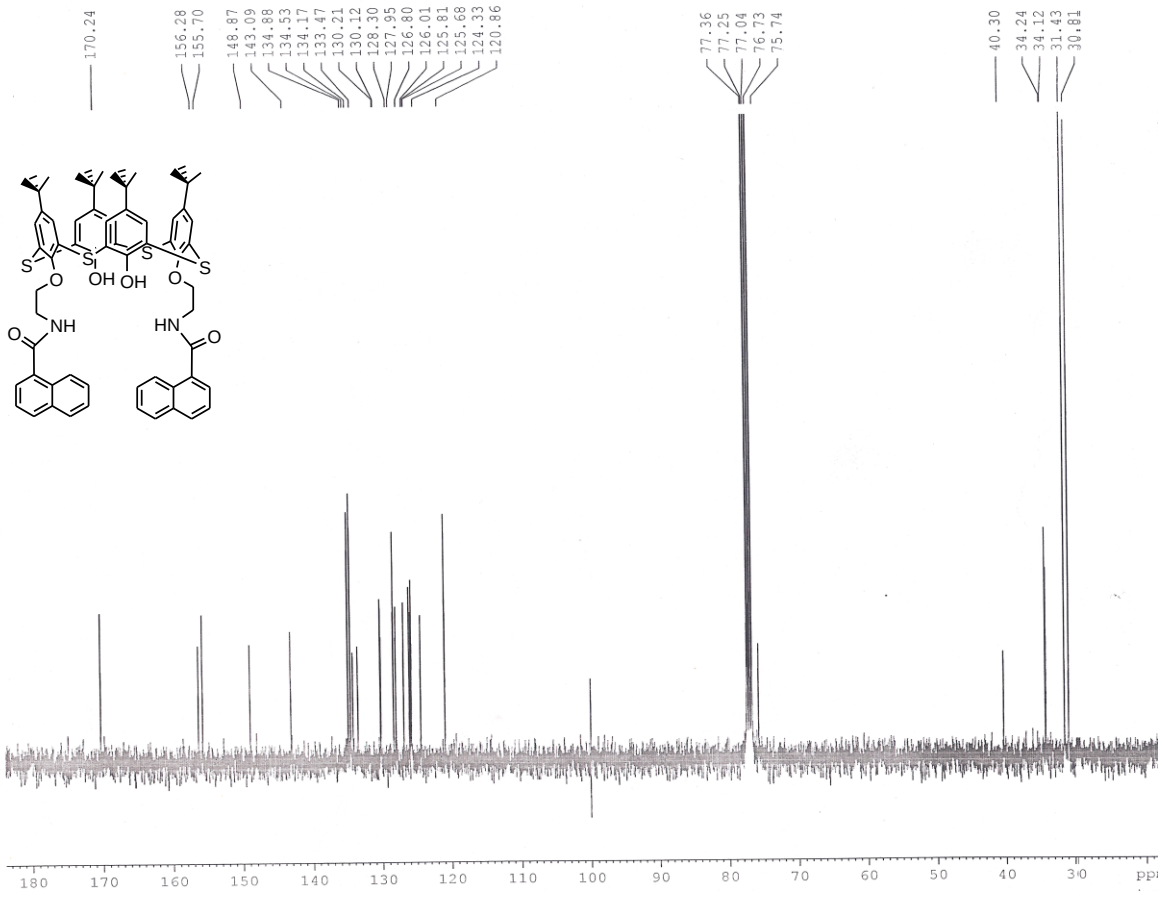

Figure S2. ^{13}C NMR spectrum of **3** in $CDCl_3$.

3. FAB mass spectrum of **3**.

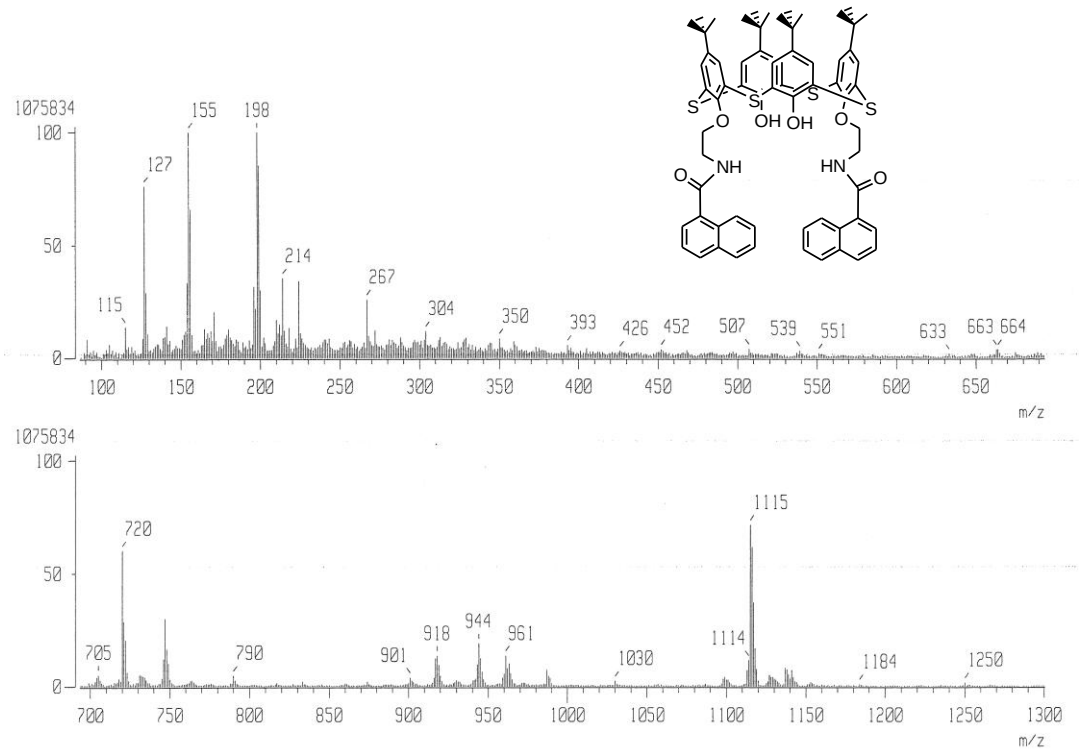

Figure S3. FAB mass spectrum of **3**.

4. ^{1}H NMR spectrum of **5** in $CDCl_3$.

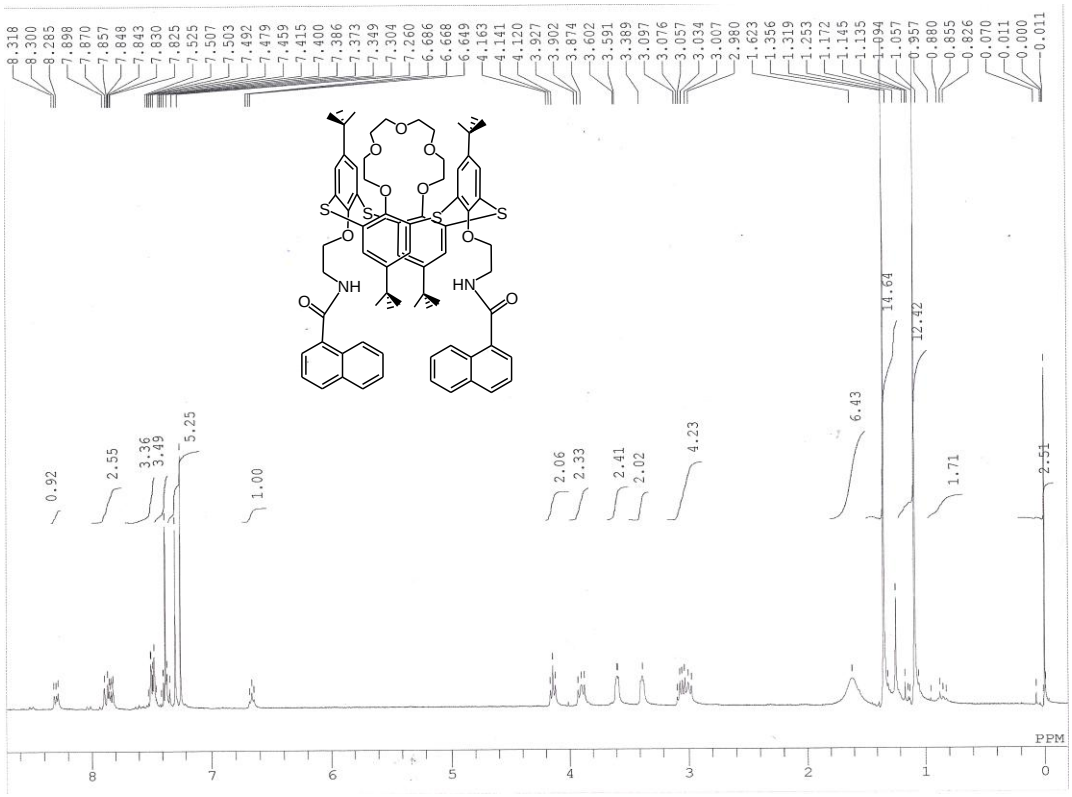

Figure S4. ^{1}H NMR spectrum of **5** in $CDCl_3$.

5. ^{13}C NMR Spectrum of **5** in $CDCl_3$.

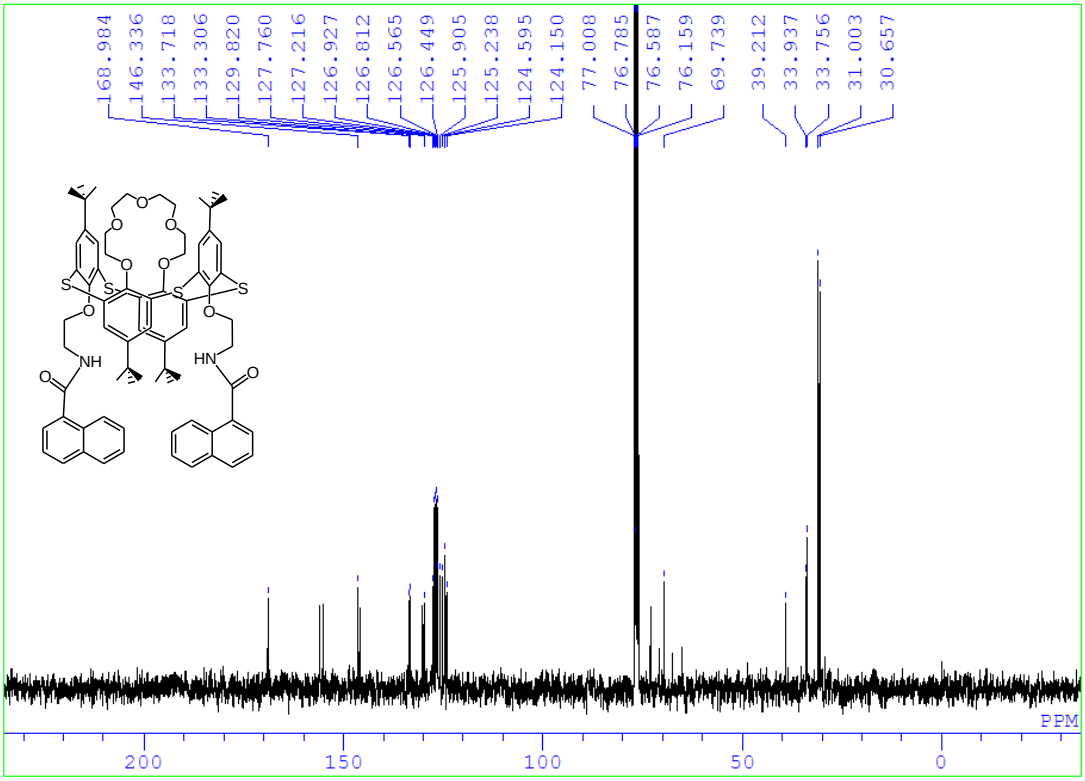

Figure S5. ^{13}C NMR spectrum of **5** in $CDCl_3$.

6. ESI mass spectrum of **5**.

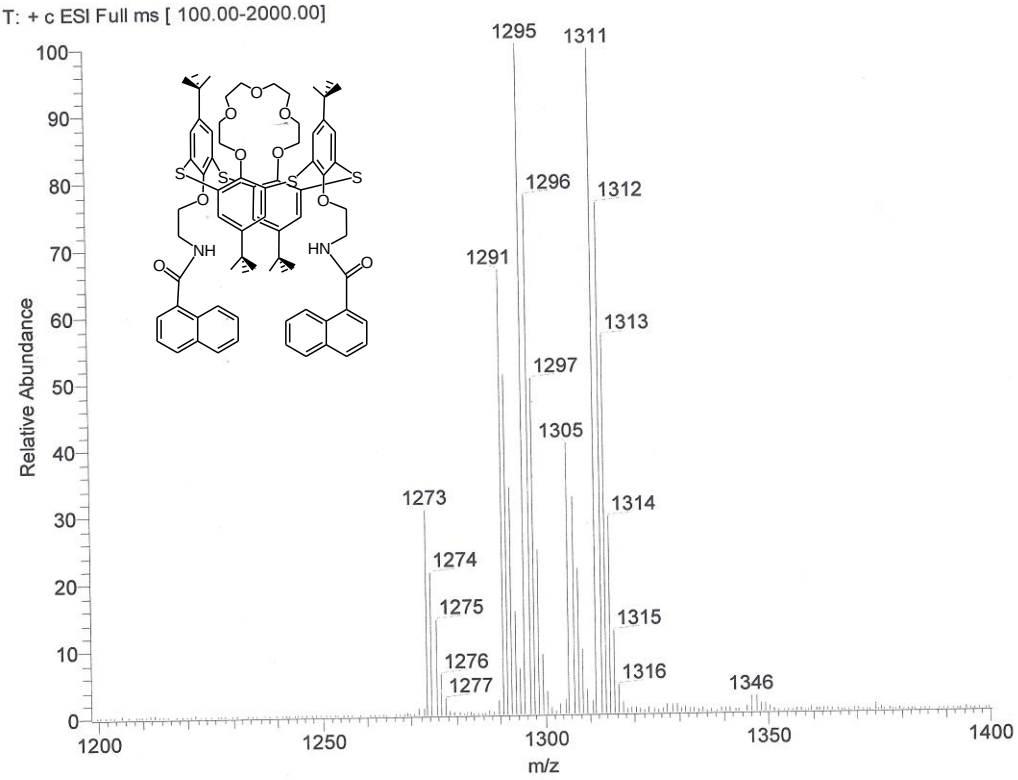

Figure S6. ESI-MS mass spectrum of **5**.

7. ^{1}H NMR spectrum of **7** in $CDCl_3$.

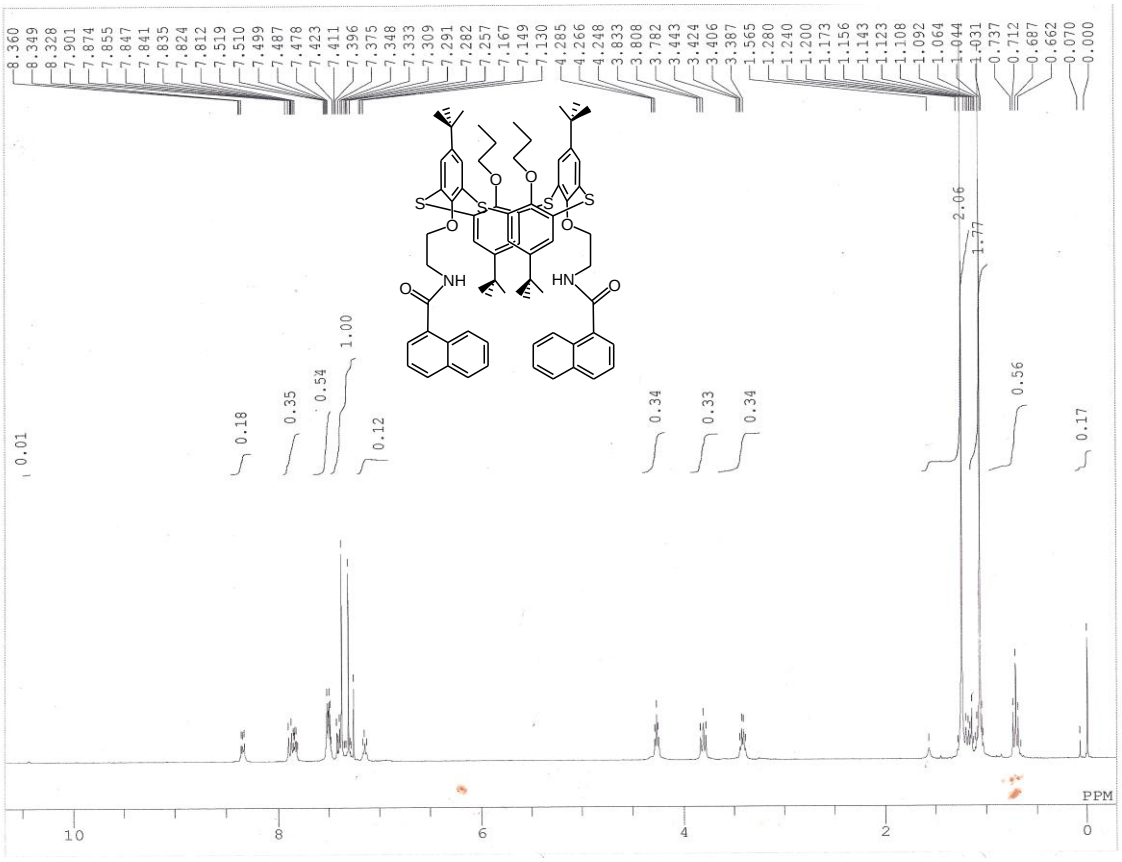

Figure S7. ^{1}H NMR spectrum of **7** in $CDCl_3$.

8. ^{13}C NMR Spectrum of **7** in $CDCl_3$.

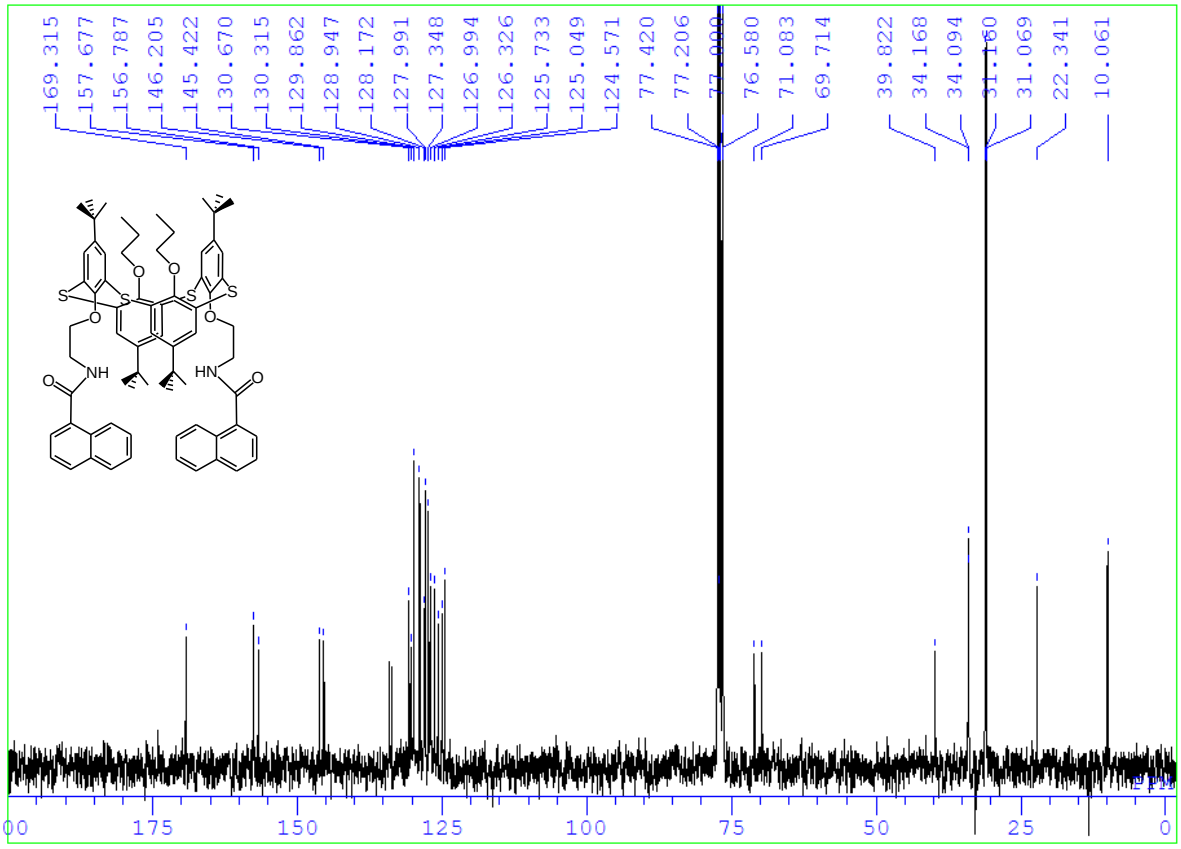

Figure S8. ^{13}C NMR spectrum of **7** in $CDCl_3$.

9. ESI-MS mass spectrum of **7**.

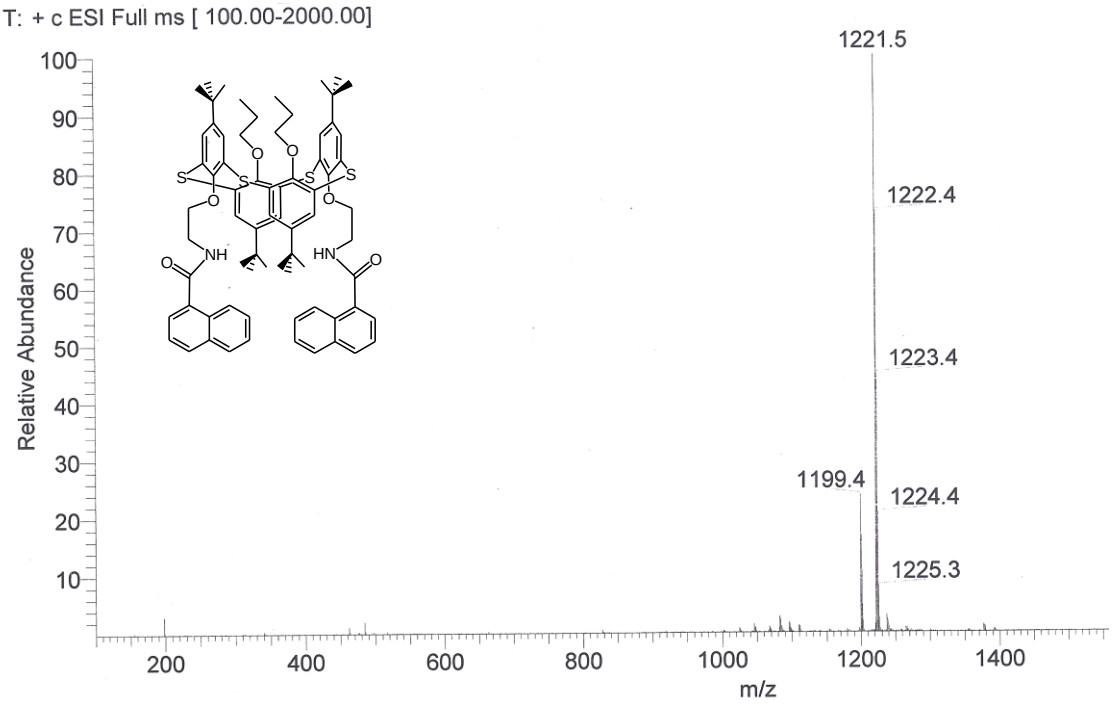

Figure S9. ESI-MS mass spectrum of **7**.

10. Absorption spectra of compound **7** (10 μM) on addition of Fe^{3+} in THF.

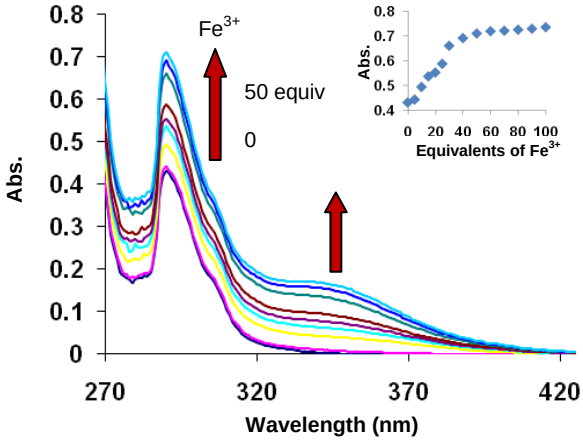

Figure S10. Absorption spectra of compound **7** (10 μM) on addition of Fe^{3+} (0 - 50 equiv) in THF.

11. Fluorescence Quantum yield.

Fluorescence quantum yield ϕ_f was determined in analytical grade THF using optically matching solutions of naphthalene ϕ_f = 0.23 in ethanol as the standard at an excitation wavelength of 275 nm and the quantum yield was calculated using following equation

$$\phi_{fs} = \phi_{fr} \times \frac{1-10^{-ArLr}}{1-10^{-AsLs}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

The quantum yield is measured at room temperature by a single excitation wavelength (338 nm for **3** coming from Xenon lamp of the spectrofluorophotometer and calculated according to the above equation. ϕ_{fs} is the radiative quantum yield of the sample, ϕ_{fr} radiative quantum yield of reference, A_s and A_r are the absorbance of the sample and the reference respectively, D_s and D_r the respective areas of emission for sample and reference respectively. L_s and L_r are the lengths of the absorption cells respectively. N_s and N_r are the index of refraction of the sample and reference solutions (pure solvents were assumed respectively).

Table 2. Quantum yields of receptors **3**, **5**, **7** and their cation and anion complexes.

Receptors and complexes	Quantum yield
3	0.159
$3.Fe^{3+}$	0.447
$3.F^-$	0.330
$3.Fe^{3+}.F^-$	0.152
5	0.134
$5.Fe^{3+}$	0.011
$5.Hg^{2+}$	0.263
$5.K^+$	0.220
$5.F^-$	0.271
$5.Fe^{3+}.Hg^{2+}$	0.11
$5.Fe^{3+}.K^+$	0.044
$5.Fe^{3+}.F^-$	0.072
7	0.067
$7.Fe^{3+}$	0.007
$7.Hg^{2+}$	0.227
$7.F^-$	0.294
$7.Fe^{3+}.Hg^{2+}$	0.139
$7.Fe^{3+}.F^-$	0.088

12. Proposed π-Interactions between two naphthalene moieties upon addition of Fe^{3+} ion.

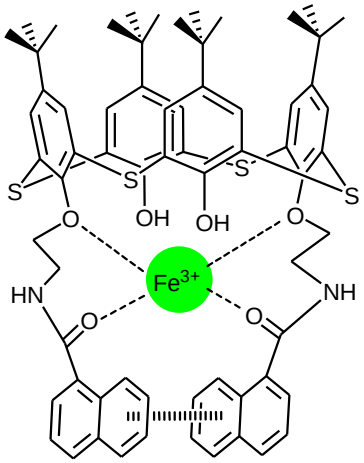

Figure S11. Proposed π-Interactions between two naphthalene moieties upon addition of Fe^{3+} ion.

13. Fluorescence emission spectra of receptor **7** (10 μM) upon addition of Fe^{3+} in THF.

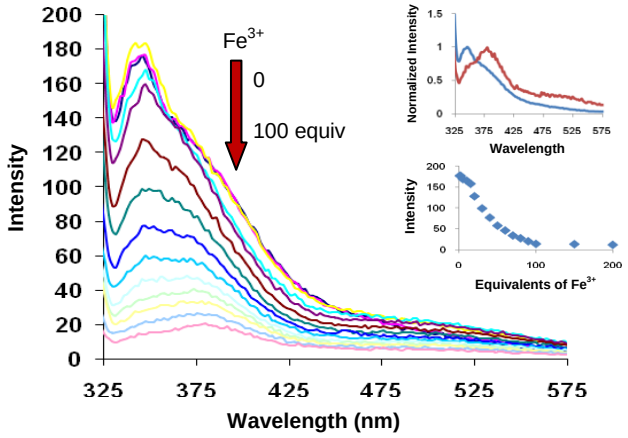

Figure S12. Fluorescence emission spectra of receptor **7** (10 μM) upon various addition of Fe^{3+} (0-100 equiv) in THF.

14. Pictorial representation of binding modes of compound **5** and **7** upon addition of Fe^{3+} ion.

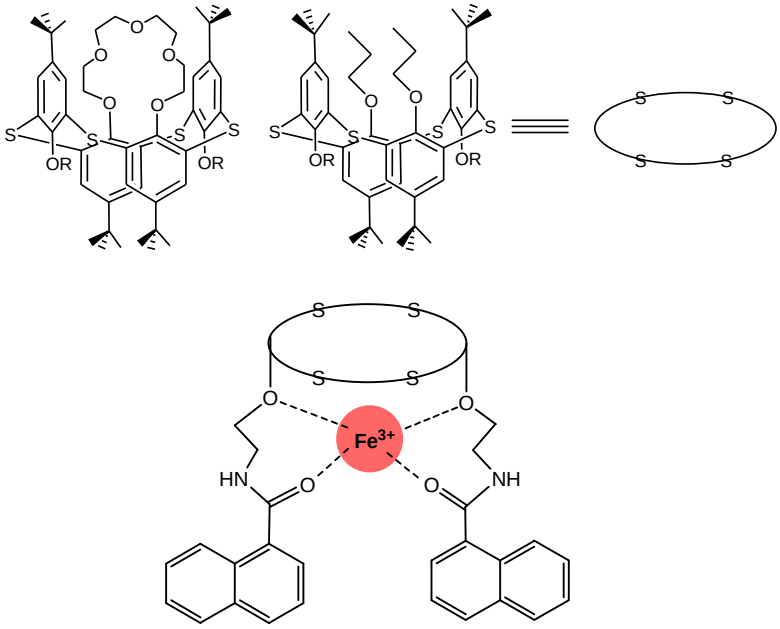

Figure S13. Pictorial representation of binding modes of compound **5** and **7** upon addition of Fe^{3+} ion.

15. Fluorescence emission spectra of receptor **7** (10 μM) upon addition of Hg^{2+} in THF.

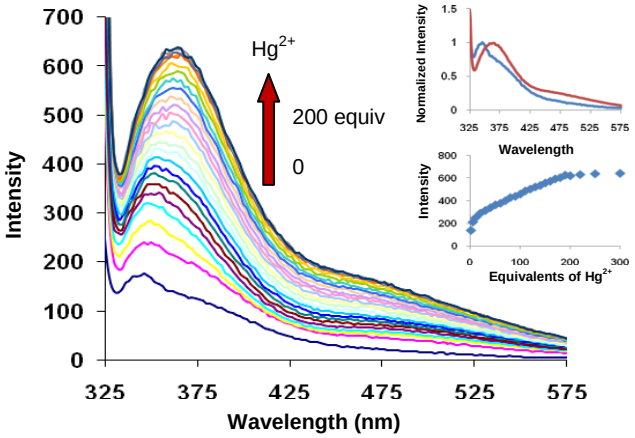

Figure S14. Fluorescence emission spectra of receptor **7** (10 μM) upon various addition of Hg^{2+} (0-200 equiv) in THF.

16. ^{1}H NMR of compound **5** + Hg^{2+} (5 equiv) ions in $CDCl_3$ + CD_3CN (8:2, v/v).

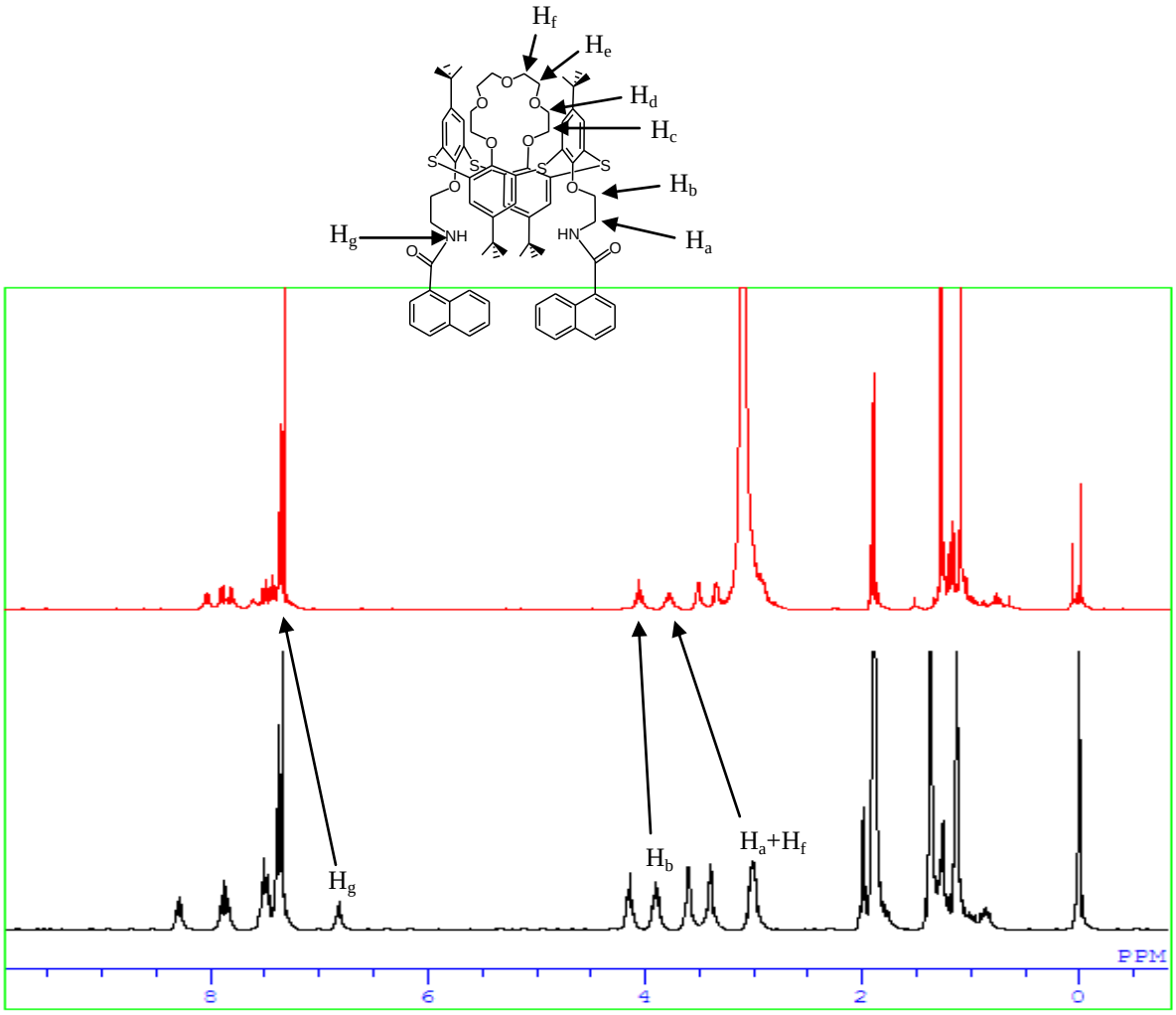

Figure S15. ^{1}H NMR of compound **5** + Hg^{2+} (5 equiv) ions in $CDCl_3$ + CD_3CN (8:2, v/v).

17. ^{1}H NMR of compound **5** + K^+ (5 equiv) ions in $CDCl_3$ + CD_3CN (8:2, v/v).

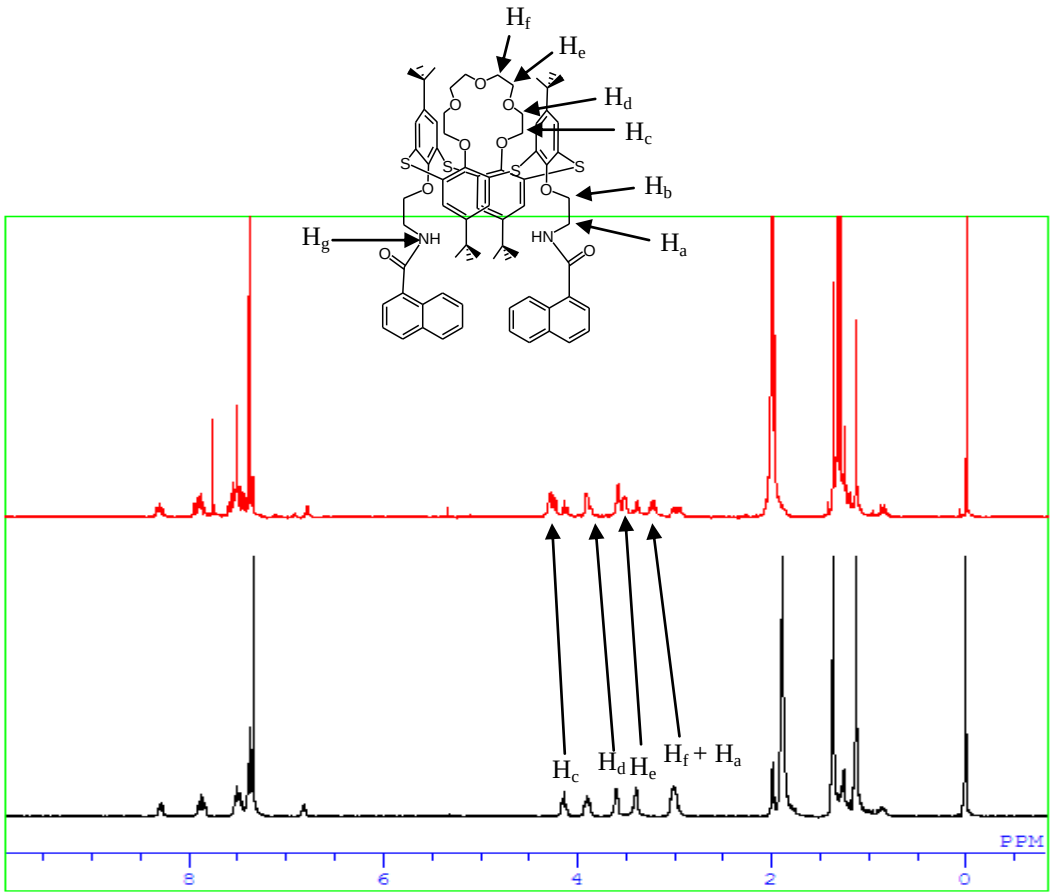

Figure S16. ^{1}H NMR of compound **5** + K^+ (5 equiv) ions in $CDCl_3$ + CD_3CN (8:2, v/v).

18. Job plot of compounds **3, 5** and **7** with Fe^{3+} / Hg^{2+} / F^- in THF.

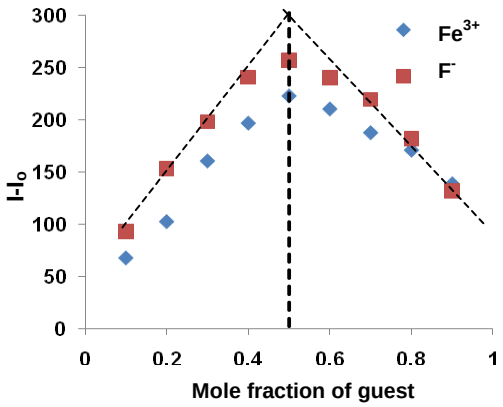

Figure S17. Job's plot of **3** with Fe^{3+} and F^- in THF. (Guest = Fe^{3+} or F^-).

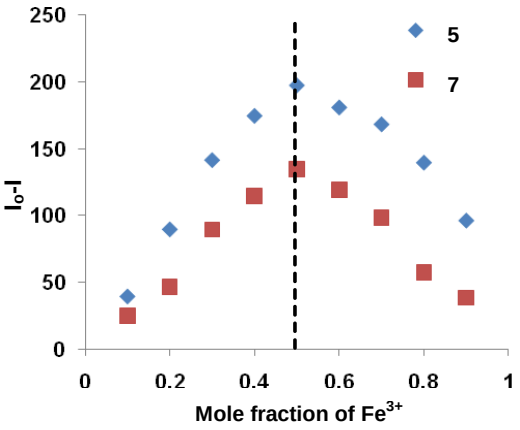

Figure S18. Job's plot of **5** and **7** with Fe^{3+} in THF.

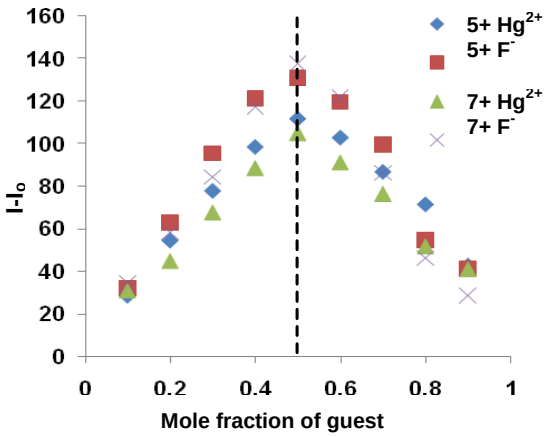

Figure S19. Job's plot of **5** and **7** with Hg^{2+} and F^- in THF. (Guest = Hg^{2+} or F^-).

19. Fluorescence emission spectra of receptor **7** (10 μM) upon addition of F^- in THF.

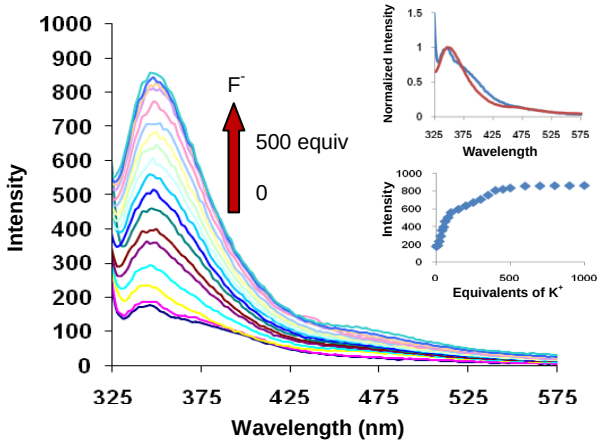

Figure S20. Fluorescence emission spectra of receptor **7** (10 μM) upon various addition of F^- (0-500 equiv) in THF.

20. ^{1}H NMR of compound **3** with F^- ions (1.0 equiv) in $CDCl_3$.

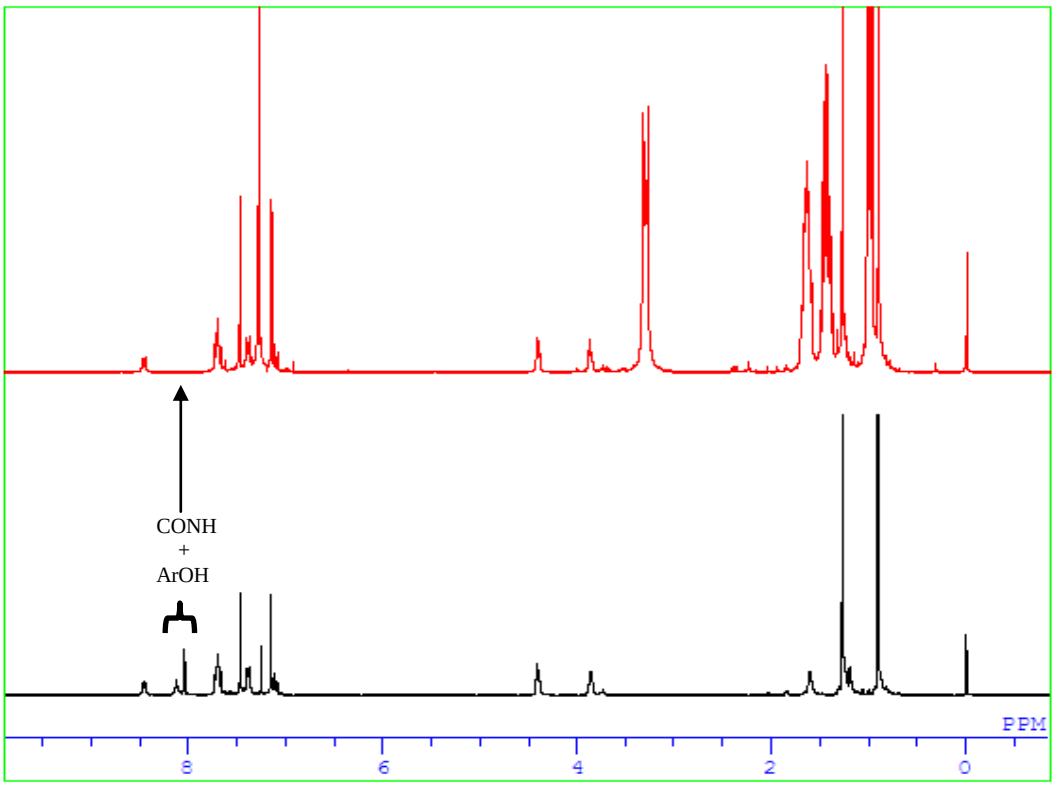

Figure S21. ^{1}H NMR of compound **3** with F^- ions (1.0 equiv) in $CDCl_3$.

21. ^{1}H NMR of compound **5** with F^- ions (1.0 equiv) in $CDCl_3$.

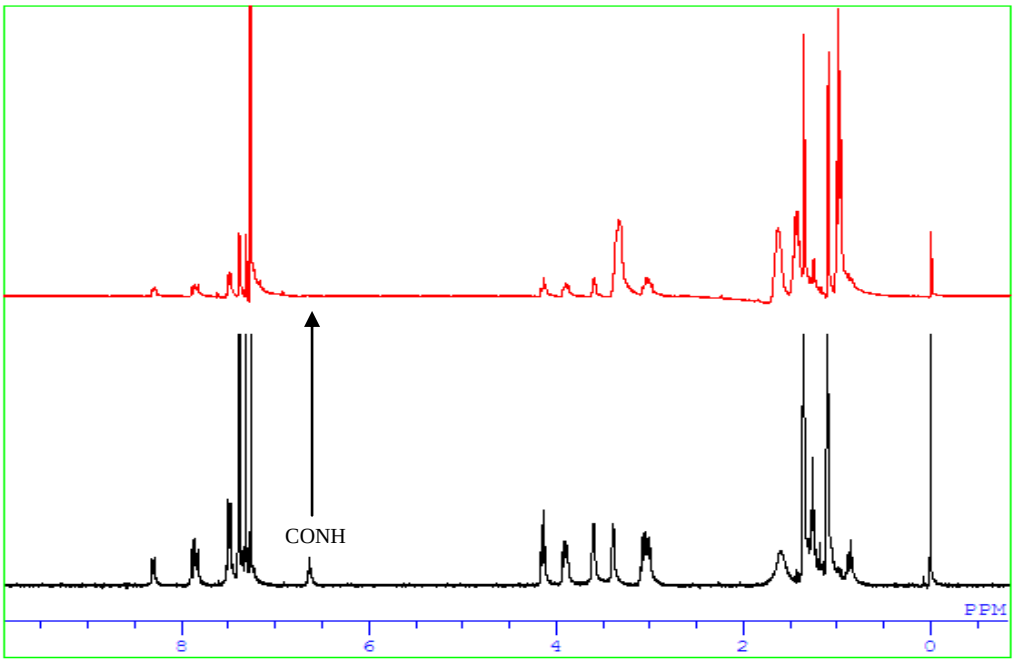

Figure S22. ^{1}H NMR of compound **5** with F^- ions (1.0 equiv) in $CDCl_3$.

22. Selectivity of compounds **3, 5** and **7** towards F^- ions over other anions.

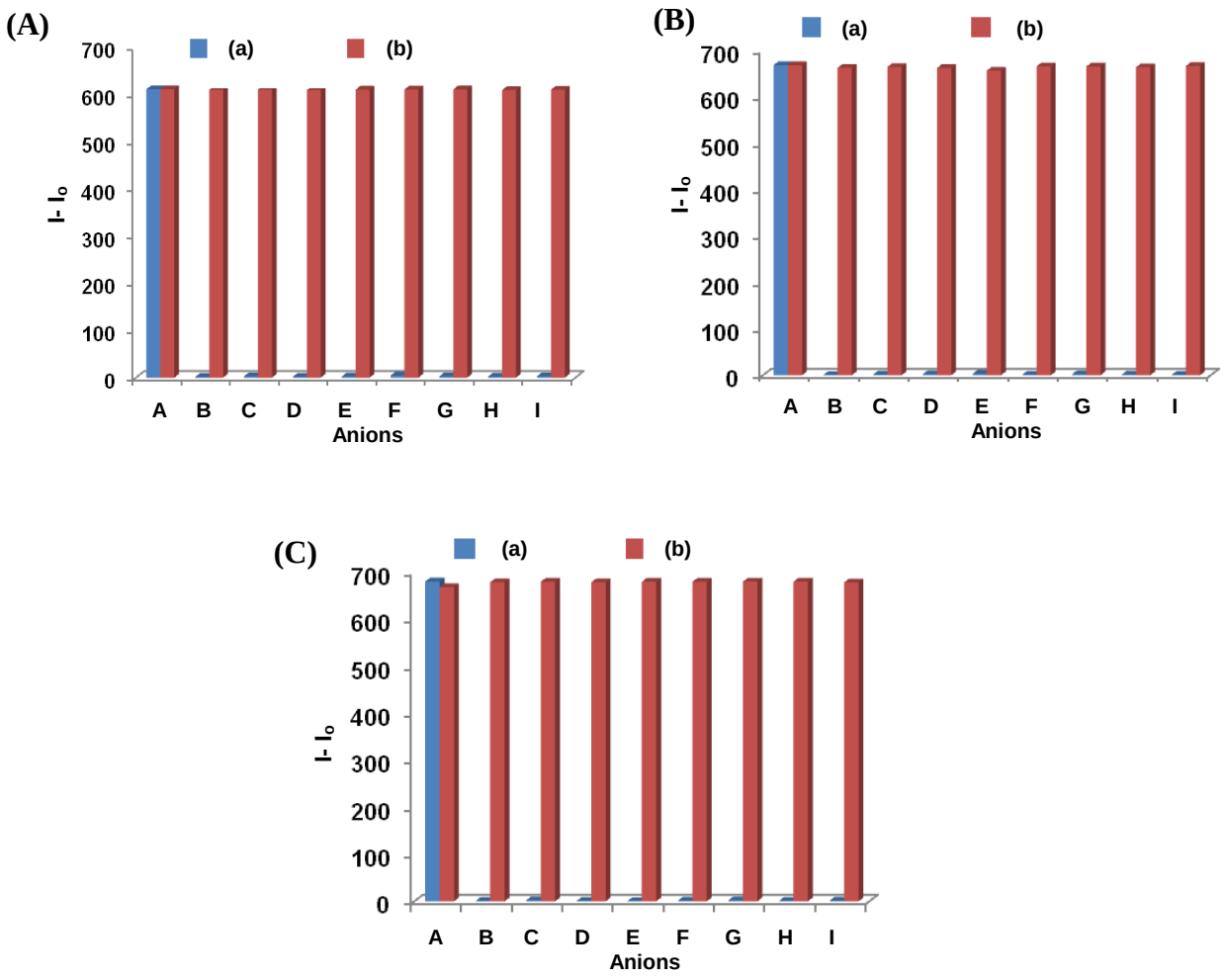

Figure S23. (a) Selectivity of (A) **3**, (B) **5**, (C) **7** (10 µM, each) toward F^- ions (500 equiv) upon addition of different anions and (b) Competitive selectivity of (A) **3**, (B) **5**, (C) **7** (10 µM, each) towards F^- ions (500 equiv) in the presence of different anions in THF. A = F^-, B = Cl^-, C = Br^-, D = I^-, E = OAc^-, F = CN^-, G = HSO_4^-, H = NO_3^-, I = $H_2PO_4^-$.

23. Fluorescence emission spectra of receptor **3**.Fe^{3+}.F^- upon addition of Fe^{3+} in THF.

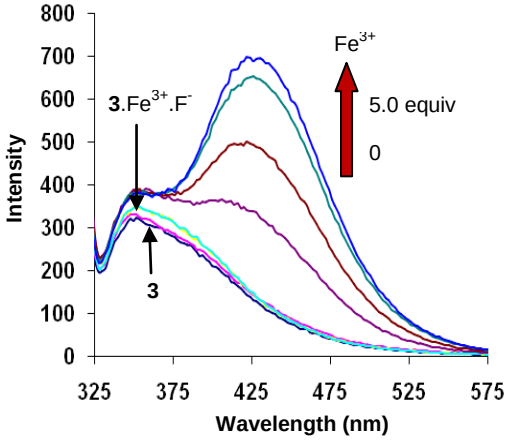

Figure S24. Fluorescence emission spectra of **3**.Fe^{3+} .F^- upon various addition of Fe^{3+} (0-5.0 equiv) in THF.

24. Fluorescence emission spectra of receptor **7.Fe**$^{3+}$ upon addition of Hg^{2+} in THF.

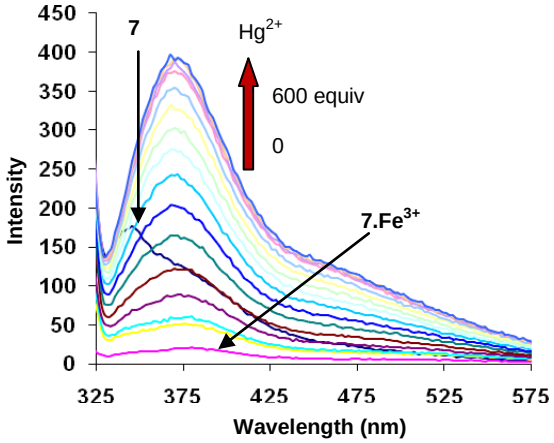

Figure S25. Fluorescence emission spectra of receptor **7.Fe**$^{3+}$ upon various addition of Hg^{2+} (0-600 equiv) in THF.

25. The "On-Off" switchable process and allosteric behaviour with Fe^{3+} and Hg^{2+} ions.

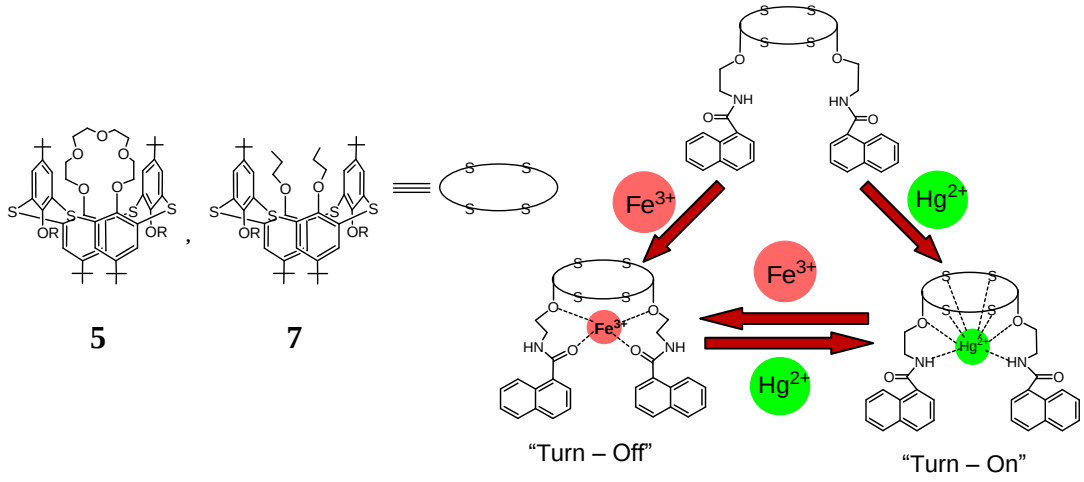

Figure S26. The compounds **5** and **7** showing "On-Off" switchable process with negative allosteric behaviour with Fe^{3+} and Hg^{2+} ions.

26. Fluorescence emission spectra of **5.Fe^{3+}.Hg^{2+}** and **7.Fe^{3+}.Hg^{2+}** upon addition of Fe^{3+} ions.

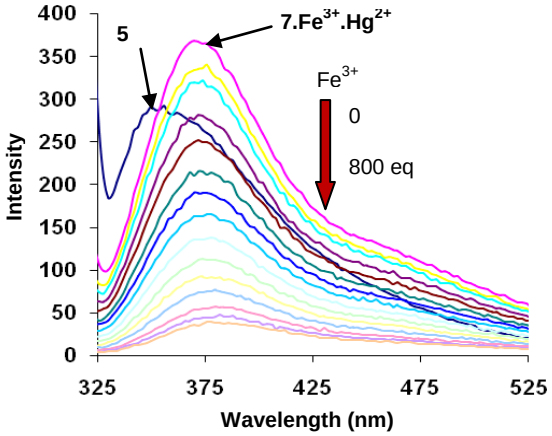

Figure S27. Fluorescence emission spectra of **5.Fe^{3+}.Hg^{2+}** upon various addition of Fe^{3+} (0-800 equiv) in THF.

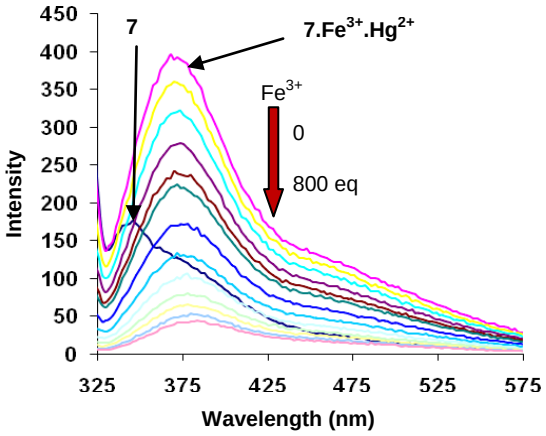

Figure S28. Fluorescence emission spectra of **7.Fe^{3+}.Hg^{2+}** upon various addition of Fe^{3+} (0-800 equiv) in THF.

27. The "On-Off" switchable process and allosteric behaviour of compound **5** with Fe^{3+} and K^{+} ions.

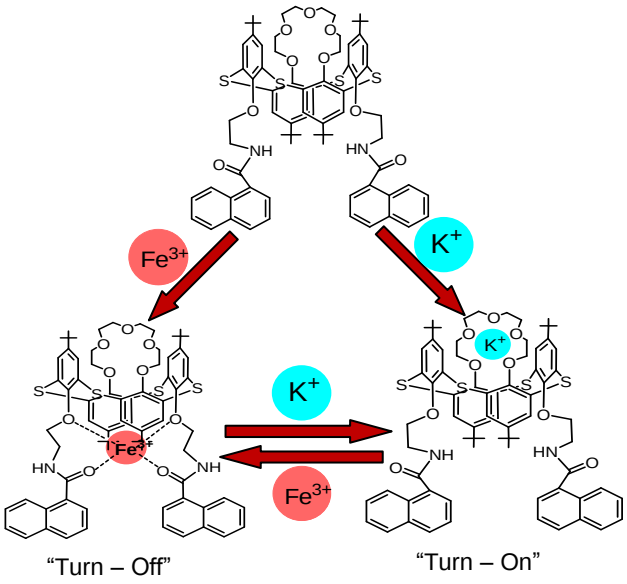

Figure S29. The compound **5** showing "On-Off" switchable process with negative allosteric behaviour with Fe^{3+} and K^{+} ions.

28. Fluorescence emission spectra of receptor **7.Fe^{3+}** complex upon addition of F^- in THF.

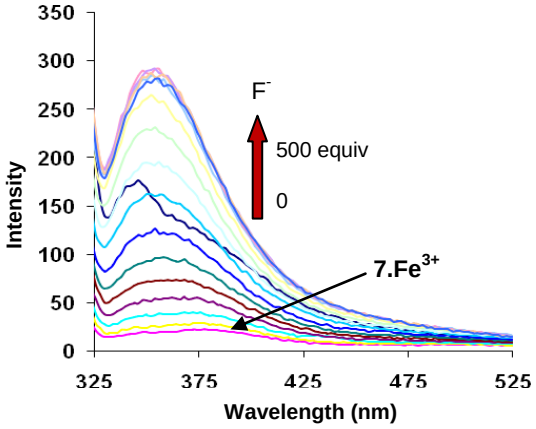

Figure S30. Fluorescence emission spectra of receptor **7.Fe^{3+}** complex upon various addition of F^- (0-500 equiv) in THF.

29. Fluorescence emission spectra of **5.Fe^{3+}.F^{-}** complex and **7.Fe^{3+}.F^{-}** complex upon addition of Fe^{3+} ions.

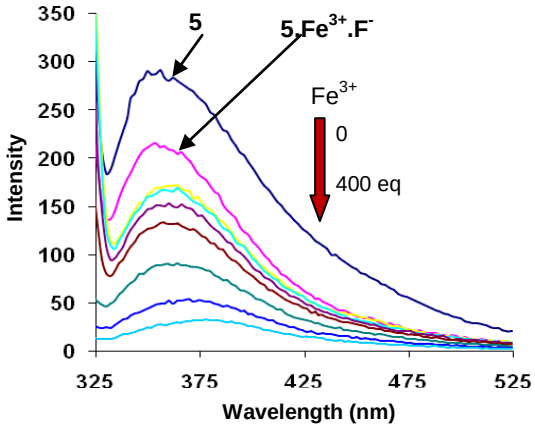

Figure S31. Fluorescence emission spectra of **5.Fe^{3+}.F^{-}** complex upon various addition of Fe^{3+} (0-400 equiv) in THF.

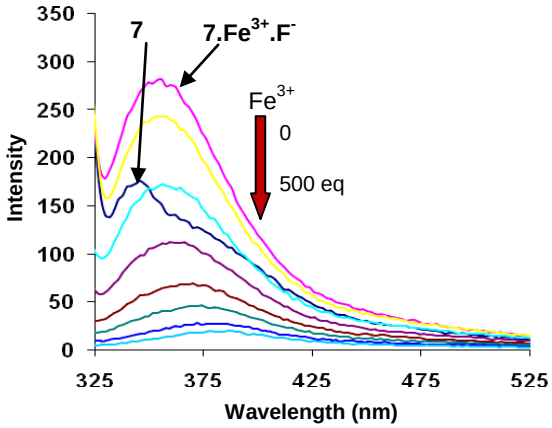

Figure S32. Fluorescence emission spectra of **7.Fe^{3+}.F^{-}** complex upon addition of Fe^{3+} (0-500 equiv) in THF.