Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Manuscript title: **Positive and negative allosteric effects of thiacalix[4]arene-based receptors having urea and crown–ether moieties**

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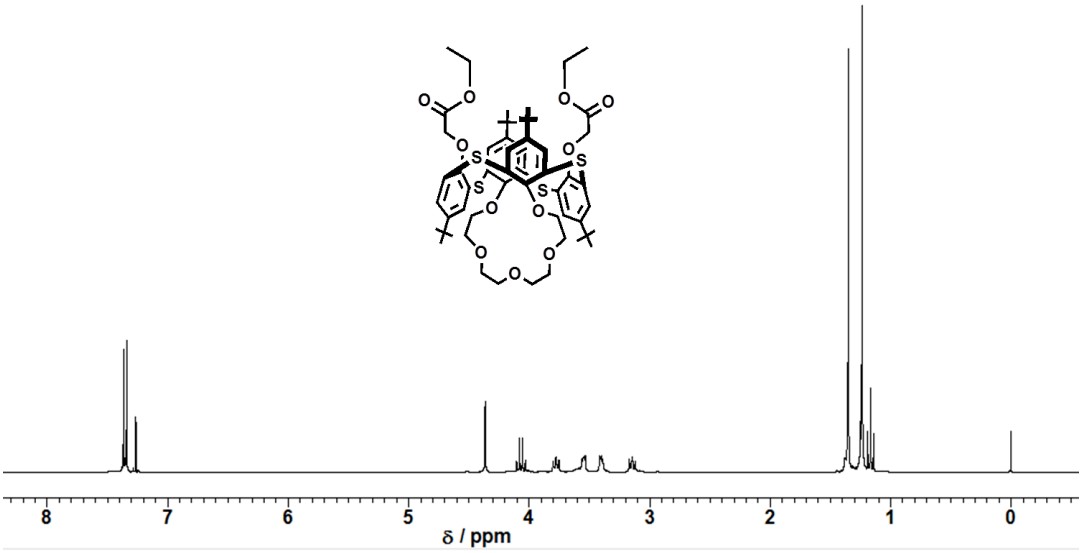

Figure S1. ^{1}H–NMR spectra of **2** (300 MHz, $CDCl_3$, 293 K).

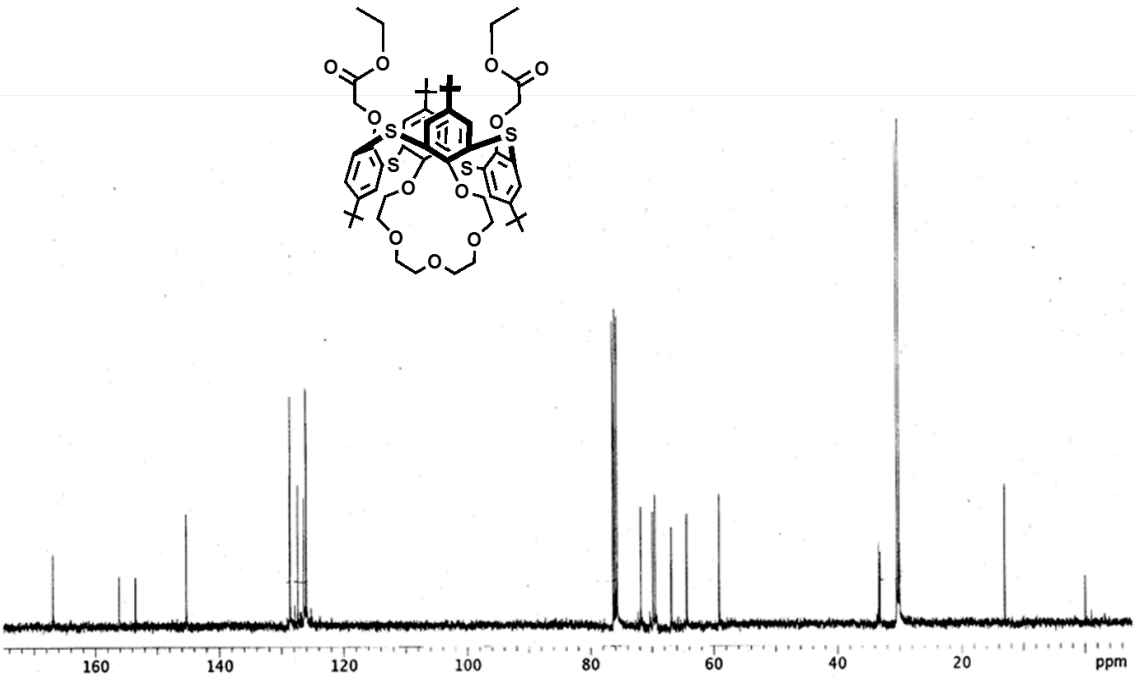

Figure S2. ^{13}C–NMR spectra of **2** (75 MHz, $CDCl_3$, 293 K).

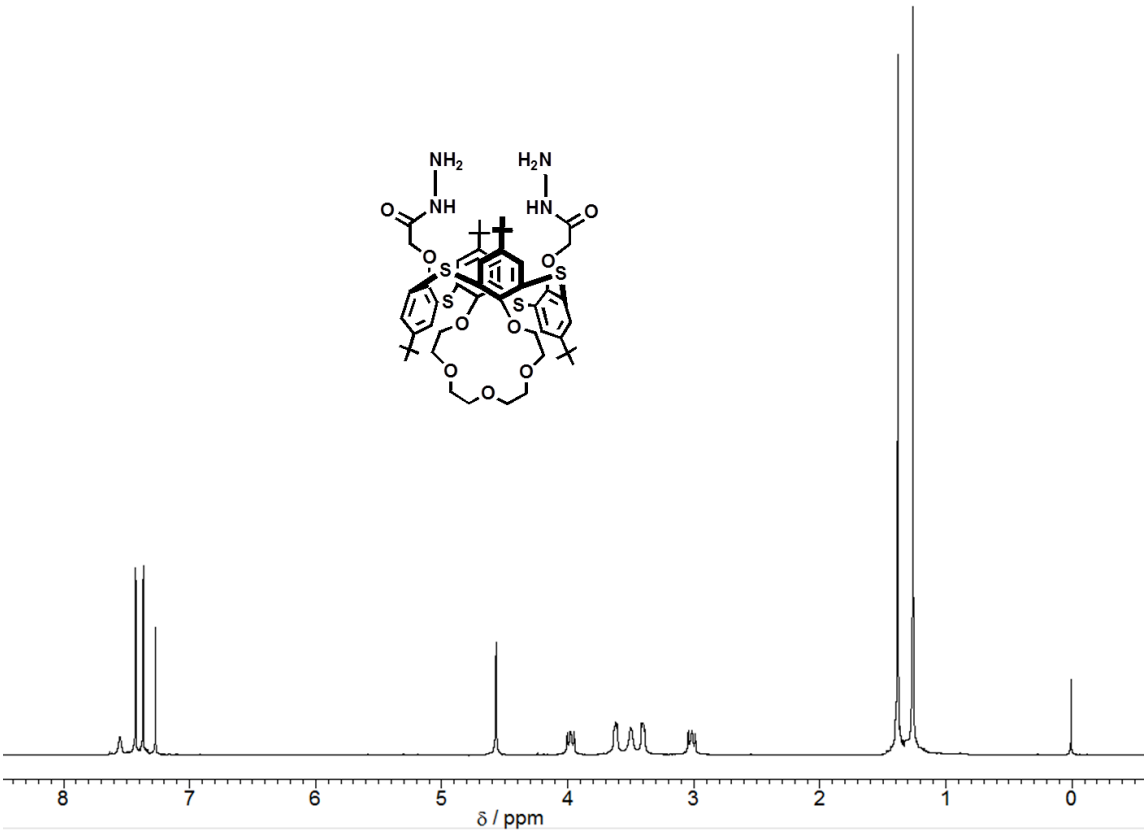

Figure S3. ^{1}H–NMR spectra of **3** (300 MHz, $CDCl_3$, 293 K).

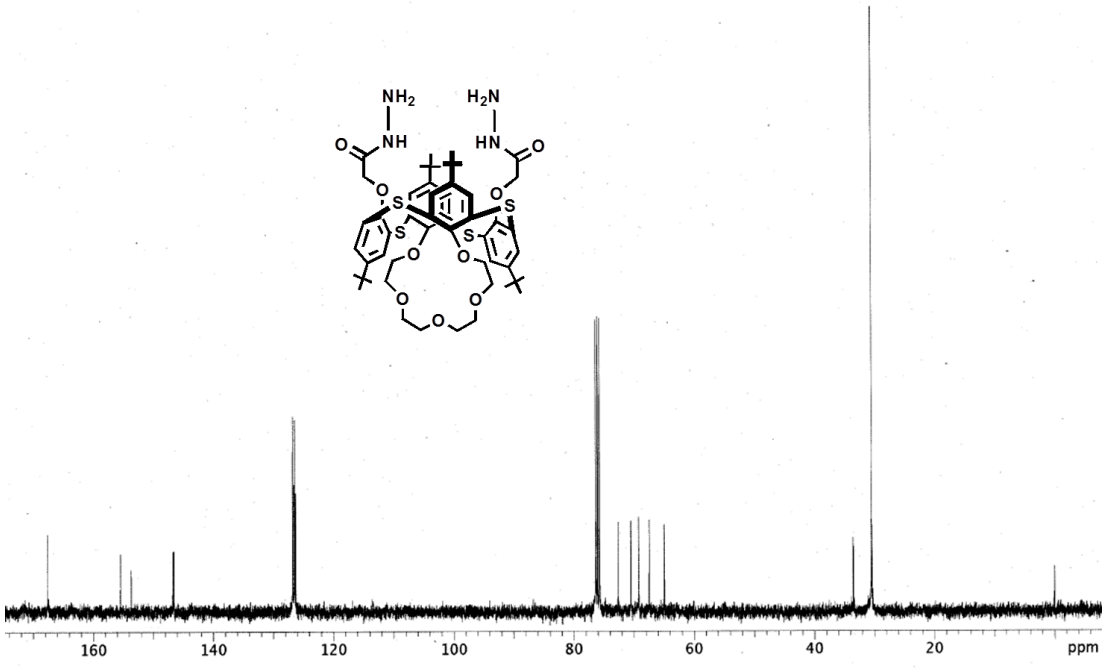

Figure S4. ^{13}C–NMR spectra of **3** (75 MHz, $CDCl_3$, 293 K).

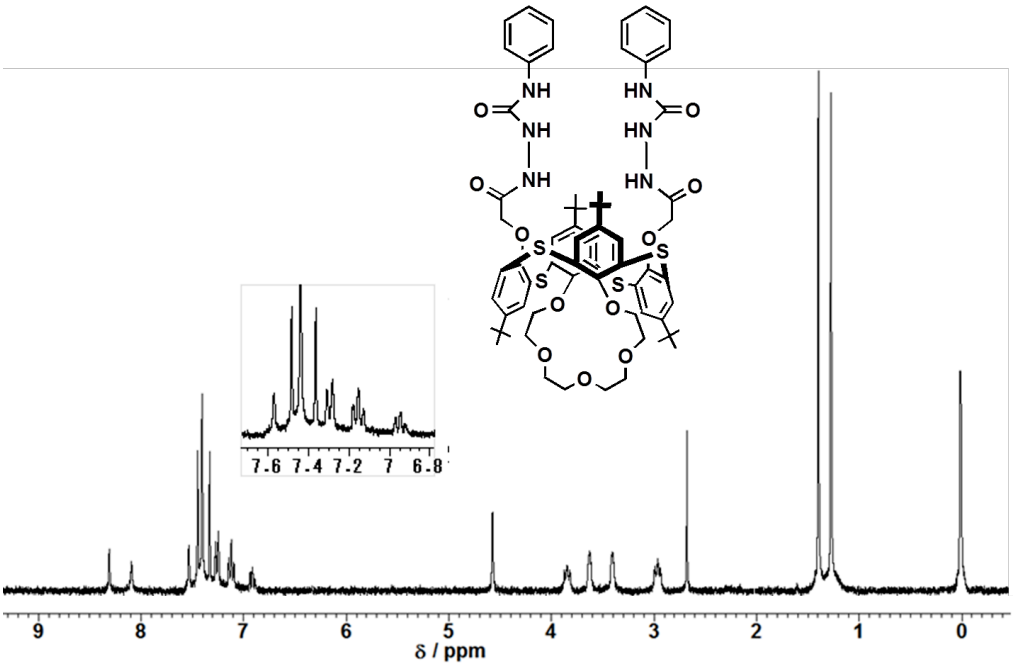

Figure S5. ^{1}H–NMR spectra of $\mathbf{4_a}$ (300 MHz, $CDCl_3$–DMSO, 293 K).

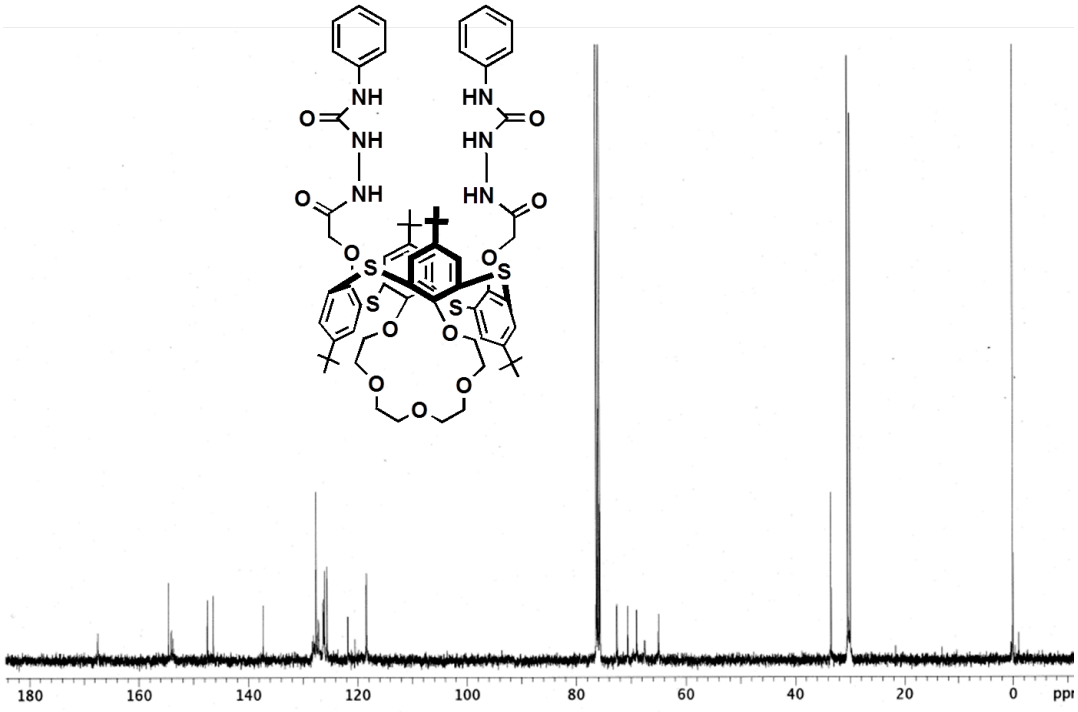

Figure S6. ^{13}C–NMR spectra of $\mathbf{4_a}$ (75 MHz, $CDCl_3$–DMSO, 293 K).

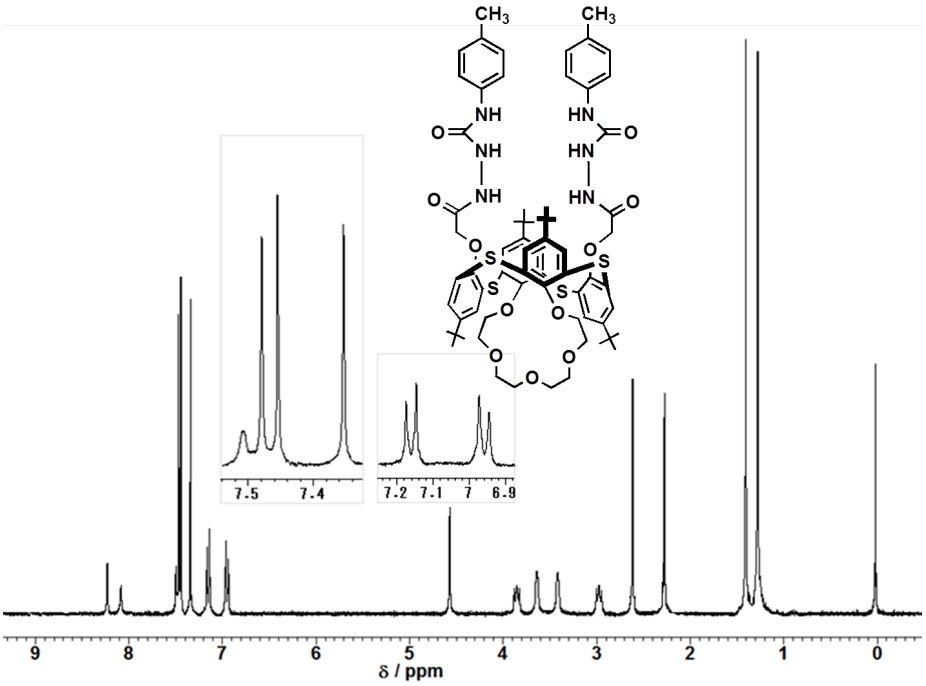

Figure S7. ^{1}H–NMR spectra of $\mathbf{4_b}$ (300 MHz, $CDCl_3$–DMSO, 293 K).

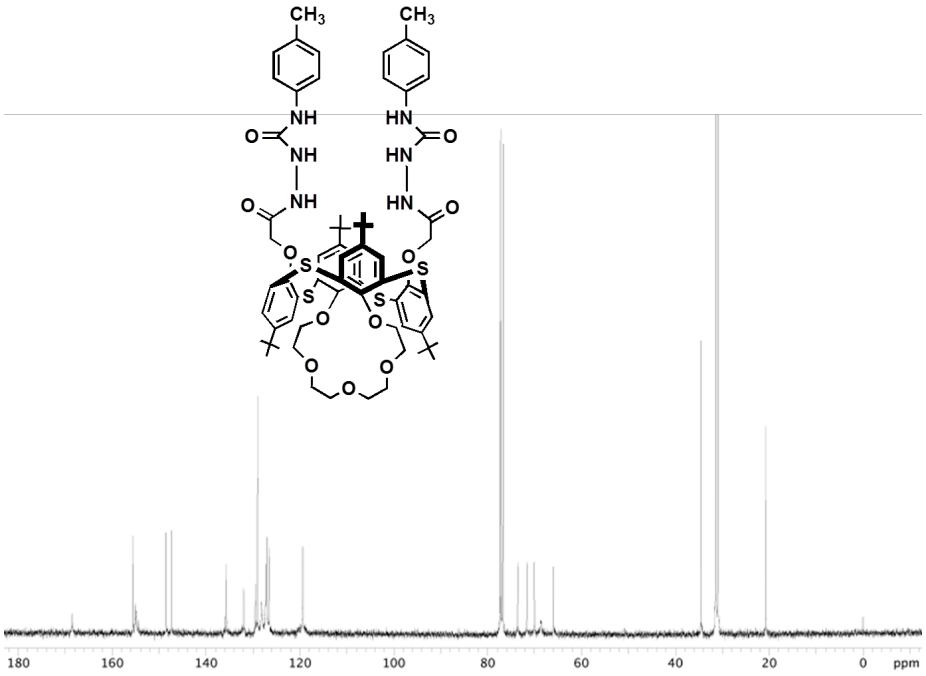

Figure S8. ^{13}C–NMR spectra of $\mathbf{4_b}$ (75 MHz, $CDCl_3$–DMSO, 293 K).

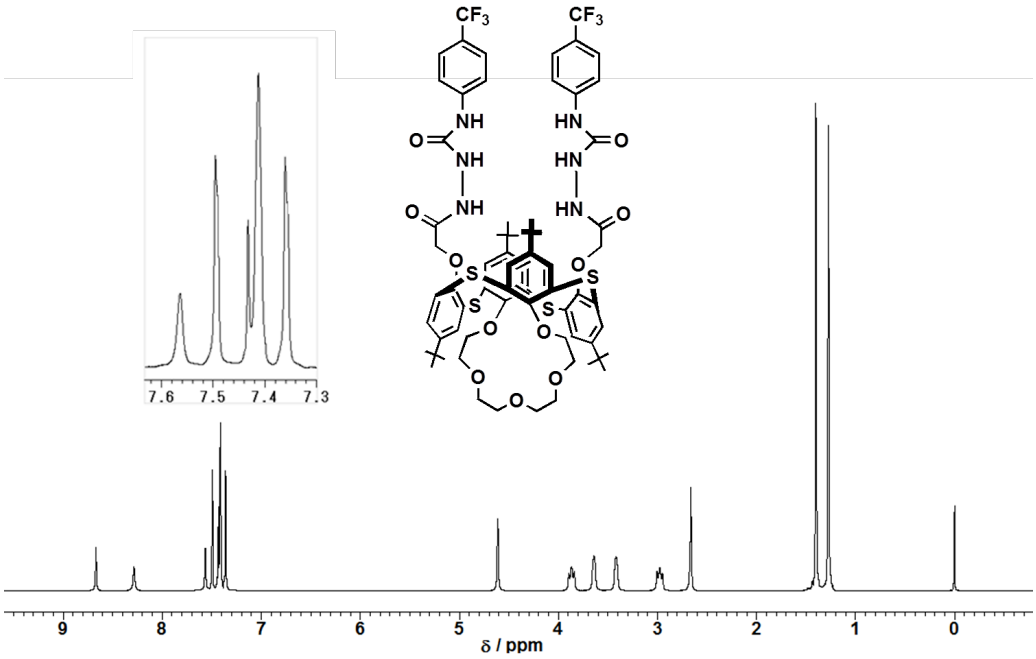

Figure S9. ^{1}H–NMR spectra of **4$_c$** (300 MHz, $CDCl_3$–DMSO, 293 K).

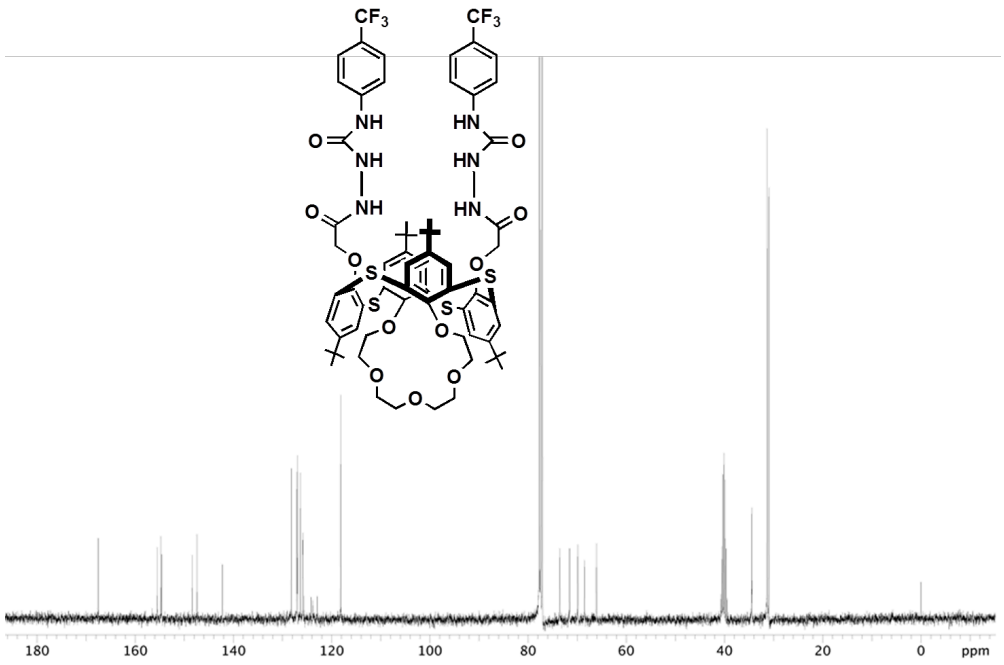

Figure S10. ^{13}C–NMR spectra of **4$_c$** (100 MHz, $CDCl_3$–DMSO, 293 K).

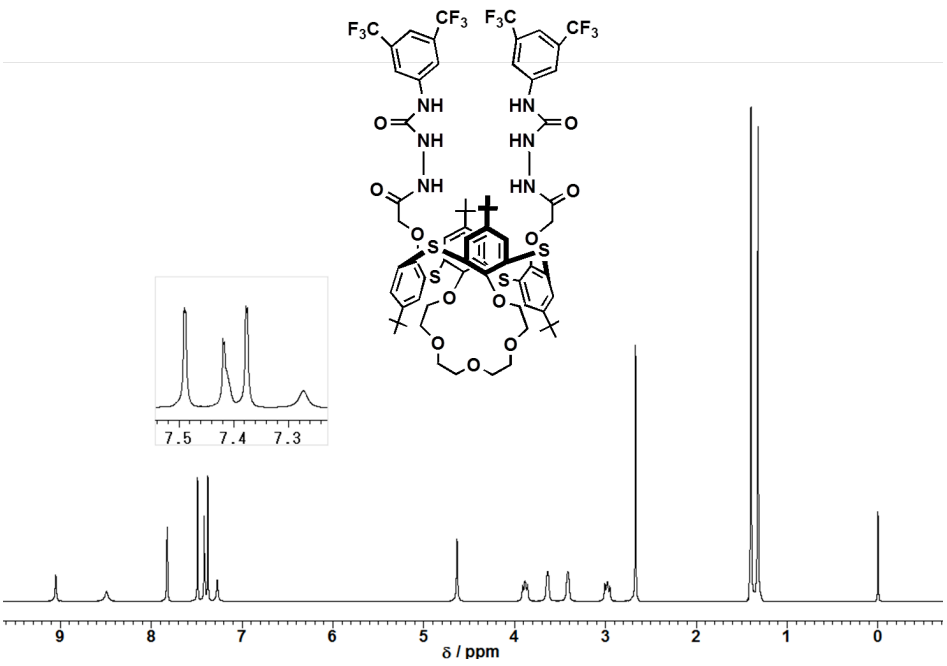

Figure S11. ^{1}H–NMR spectra of **4$_{d}$** (300 MHz, $CDCl_3$–DMSO, 293 K).

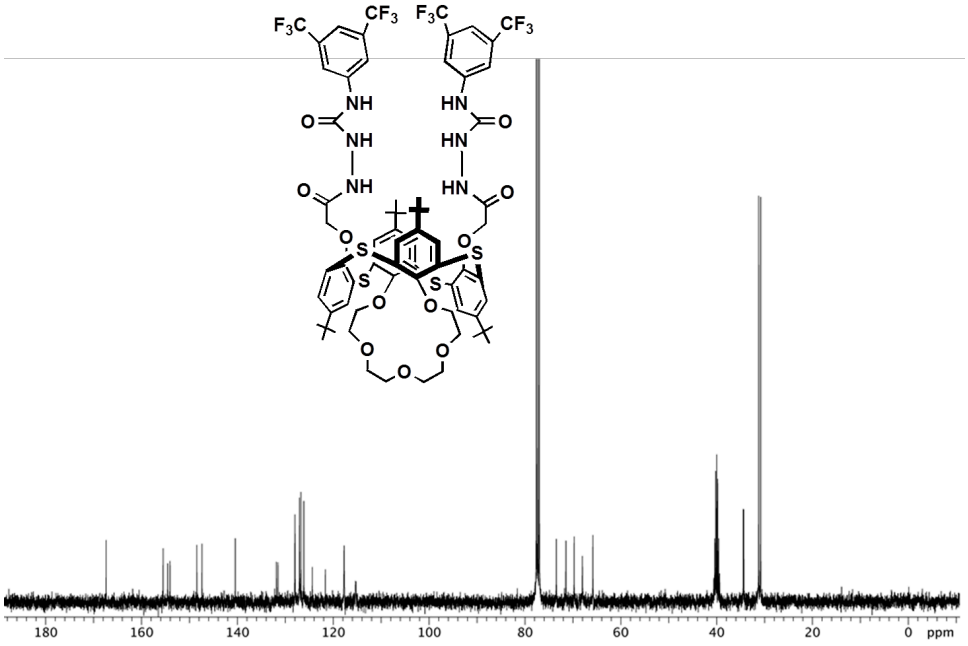

Figure S12. ^{13}C–NMR spectra of **4$_{d}$** (100 MHz, $CDCl_3$–DMSO, 293 K).

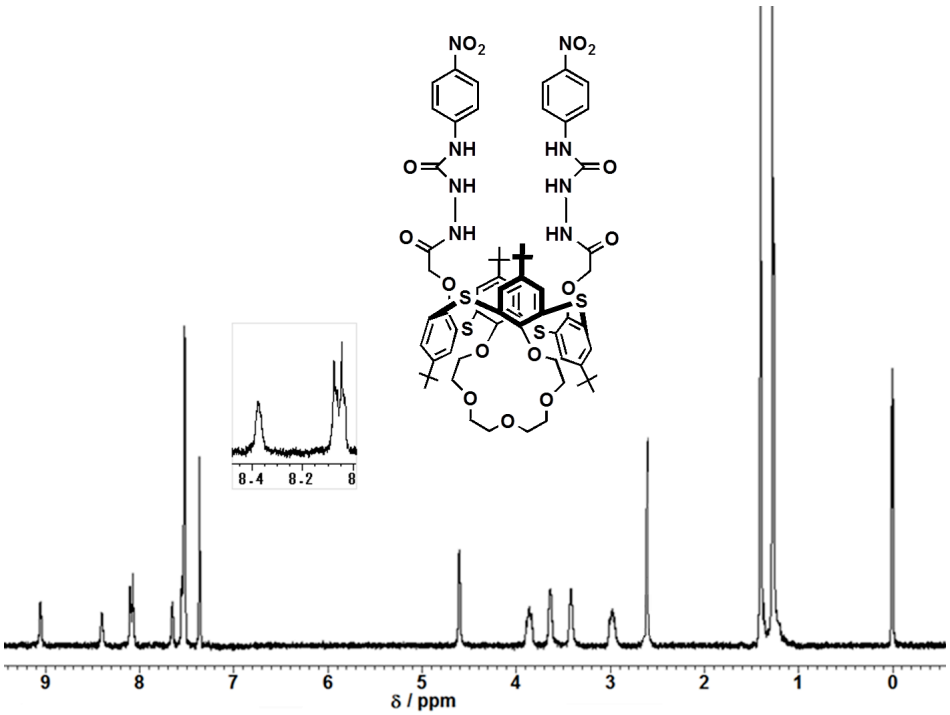

Figure S13. ^{1}H–NMR spectra of **4**$_{e}$ (300 MHz, $CDCl_3$–DMSO, 293 K).

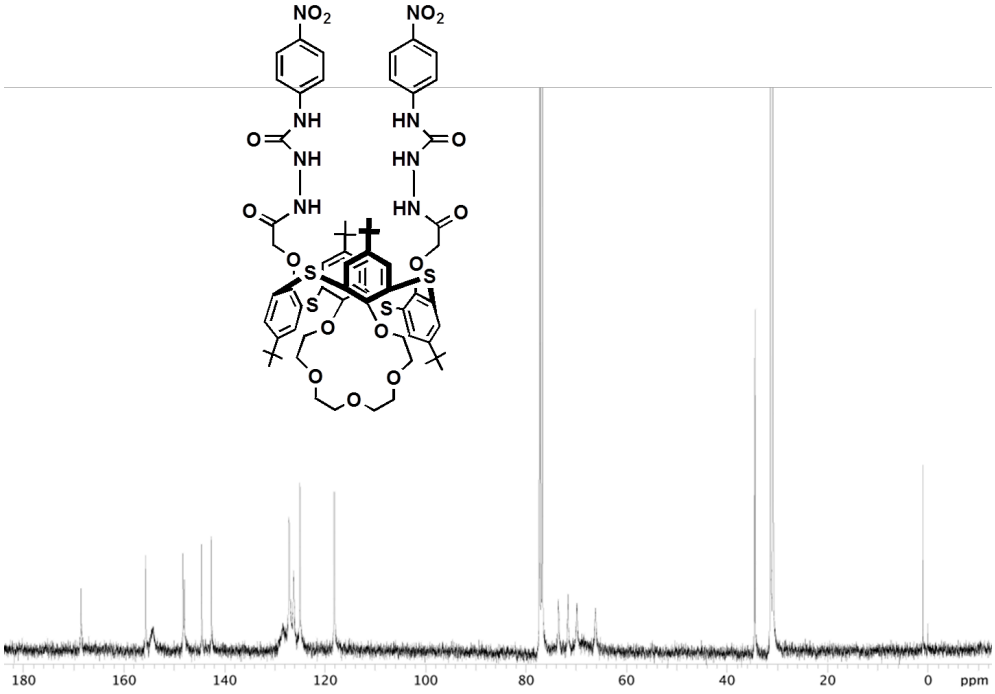

Figure S14. ^{13}C–NMR spectra of **4**$_{e}$ (100 MHz, $CDCl_3$–DMSO, 293 K).

X–ray crystal structure of receptor 4_b

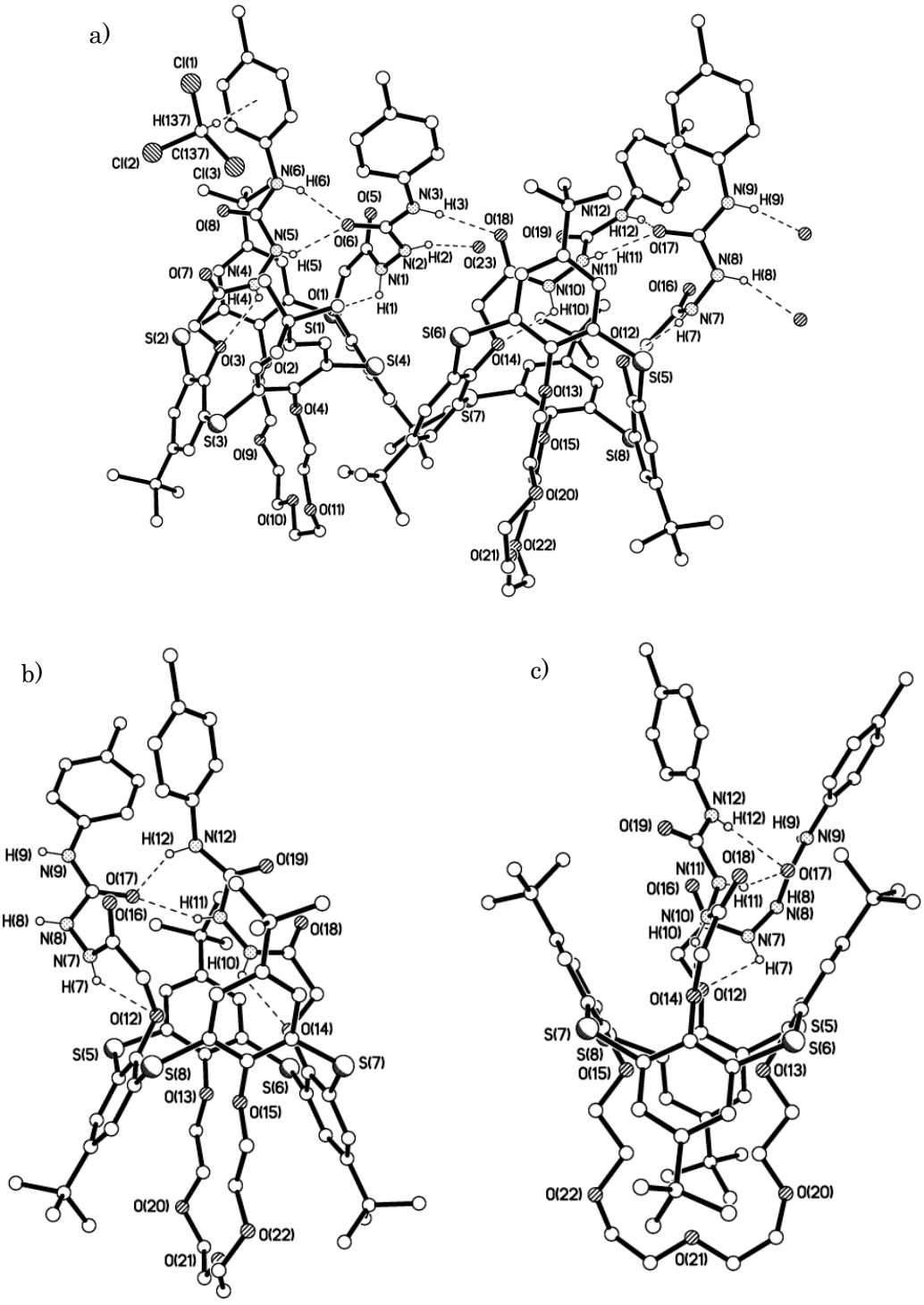

Figure S15. a) X–ray crystal structure of the asymmetric unit of receptor 4_b. H–bonds shown as dashed lines. b) & c) One of two similar molecules in the asymmetric unit is shown in two orientations rotated by approx. 90°. H atoms not involved in H-bonding, minor disorder components, and solvent of crystallization are omitted for clarity.

X–ray crystal structure of receptor 4_e

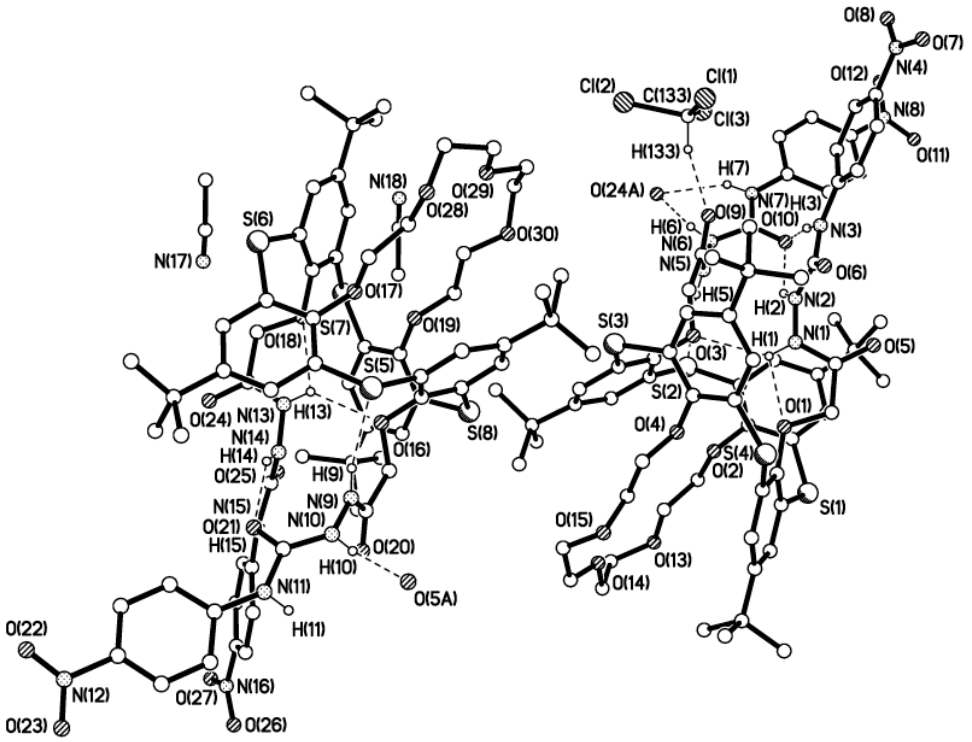

Figure S16. X–ray crystal structure of the asymmetric unit of receptor $\mathbf{4_e}$. H–bonds shown as dashed lines. H atoms not involved in H-bonding, minor disorder components, and solvent of crystallization are omitted for clarity.

Experimental Section

Selective absorption behaviours of receptors $\mathbf{4_{a\sim e}}$ ***to various anions.*** The UV–vis titration experiments of $\mathbf{4_{a\sim e}}$ were investigated by addition of anions (100 μL) (7.5 mM in CH_3CN solution) to 3 mL of $\mathbf{4_{a\sim e}}$ solution (2.5 μM in $CDCl_3$–DMSO, 10:1, v/v), respectively. The excitation wavelength was 343 nm.

K^+ titration of receptor $\mathbf{4_e}$ ***solution determined by absorption.*** The UV-vis titration experiment of $\mathbf{4_e}$ was investigated by adding increasing concentrations of KSO_3CF_3 (50 μL) (3.8 mM in CH_3CN solution) to 3 mL of $\mathbf{4_e}$ solution (2.5 μM in $CDCl_3$–DMSO, 10:1, v/v) in a cuvette. The spectra were recorded immediately after mixing. The excitation wavelength was 343 nm.

Selective absorption behaviours of receptor $\mathbf{4_e \bullet K^+}$ ***to various anions.*** The fluorescent response of $\mathbf{L \bullet K^+}$ to different anions was investigated by addition of KSO_3CF_3 (50 μL) (4.5 mM in CH_3CN) to 3 mL of $\mathbf{4_e}$ solution (2.5 μM in $CDCl_3$–DMSO, 10:1, v/v) in a cuvette. The experiment was then further carried out by addition of anion (100 μL) (7.5 mM in CH_3CN solution) to the $\mathbf{4_e \bullet K^+}$ solution. The UV–vis spectra were recorded immediately after mixing. The excitation wavelength was 343 nm.

^{1}H NMR titration experiments of $\mathbf{4_e}$, $\mathbf{4_e \bullet K^+}$, $\mathbf{4_e \bullet K^+}$ ***with*** $\mathbf{Cl^-}$ ***and*** $\mathbf{4_e \bullet K^+}$ ***with*** $\mathbf{Br^-}$. The ^{1}H NMR titration experiment was investigated by addition 10 μL of KSO_3CF_3 (2.2×10^{-1} M) to the solution of $\mathbf{4_e}$ ($CDCl_3$–DMSO, 10:1, v/v) (4×10^{-3}M) in NMR tube (560 μL). Then further experiment was carried out by addition of increasing concentrations of Bu_4NCl or Bu_4NBr in CH_3CN solution (2.2×10^{-1} M). The spectra were recorded after mixing and the temperature of the NMR probe was kept constant at 298K.

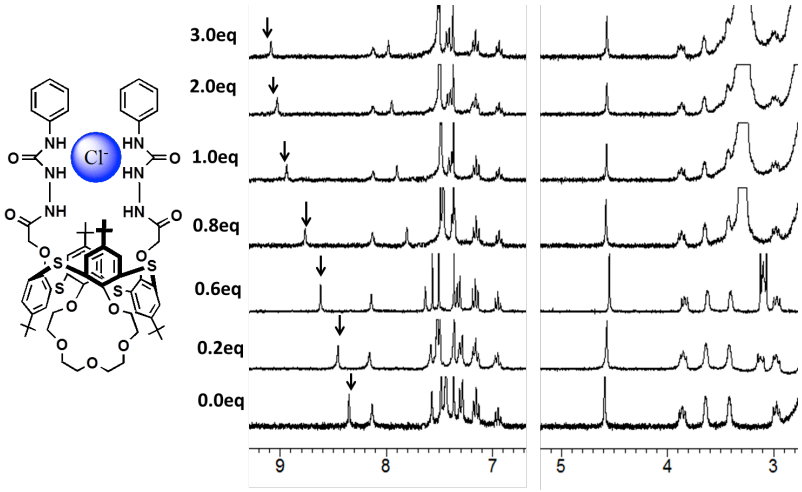

Figure S**17.** ^{1}H NMR stack plot of a $CDCl_3$–DMSO (10:1, v/v) solution of **4a** (4.0×10^{-3} M) upon addition of Bu_4NCl in CD_3CN. K_a = 6816 (±545) M^{-1}.

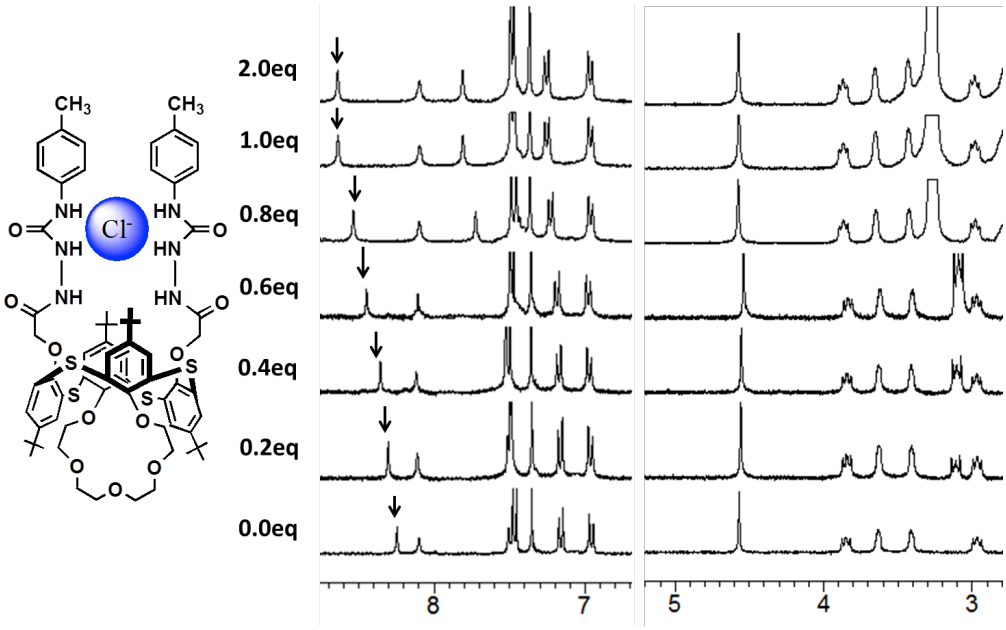

Figure S18. ^{1}H NMR stack plot of a $CDCl_3$–DMSO (10:1, v/v) solution of **4b** (4.0×10^{-3} M) upon addition of Bu_4NCl in CD_3CN. K_a = 6945 (±625) M^{-1}.

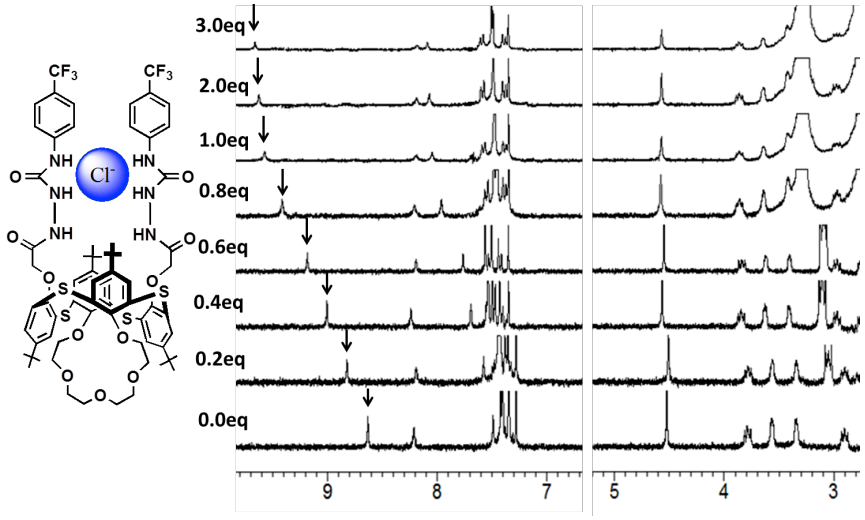

Figure S19. ^{1}H NMR stack plot of a $CDCl_3$–DMSO (10:1, v/v) solution of **4c** (4.0×10^{-3} M) upon addition of Bu_4NCl in CD_3CN. K_a = 3021 (±242) M^{-1}.

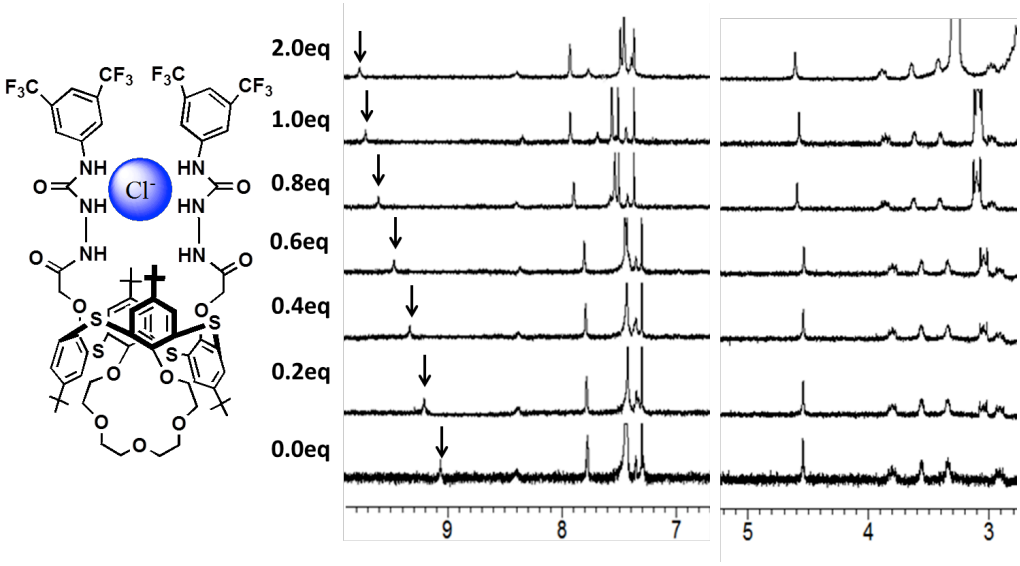

Figure S20. ^{1}H NMR stack plot of a $CDCl_3$–DMSO (10:1, v/v) solution of **4d** (4.0×10^{-3} M) upon addition of Bu_4NCl in CD_3CN. K_a = 34411 (±2400) M^{-1}.

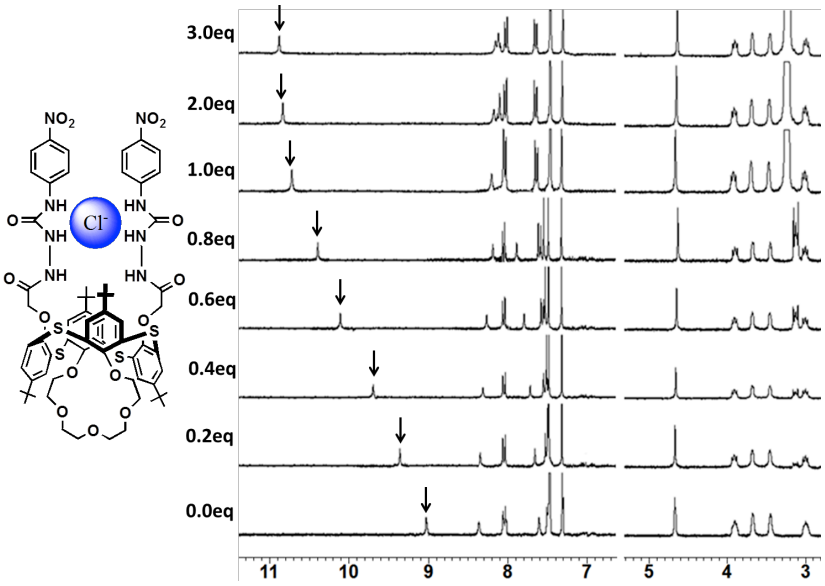

Figure S21. ^{1}H NMR stack plot of a $CDCl_3$–DMSO (10:1, v/v) solution of **4e** (4.0×10^{-3} M) upon addition of Bu_4NCl in CD_3CN. K_a = 34411 (±2400) M^{-1}.

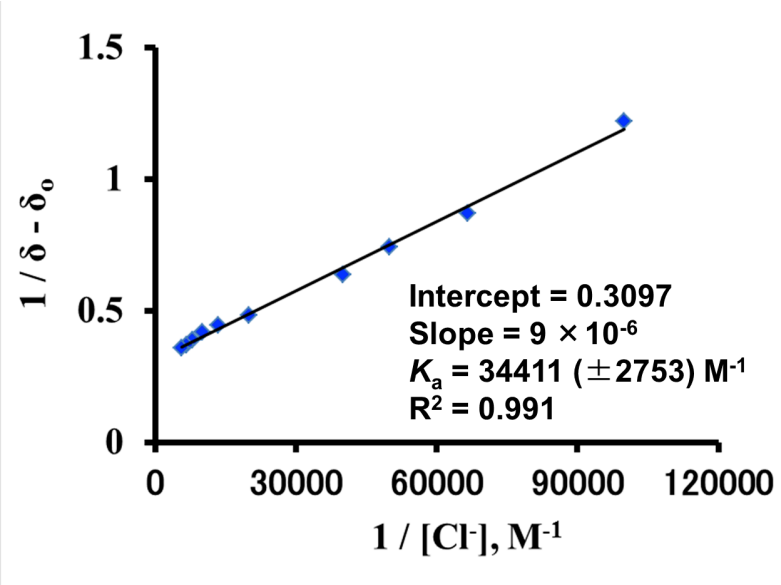

Figure S22. Benesi-Hildebrand plot of **4e** for various concentrations of Cl^- ion at 298K by the ^{1}H NMR titration method. The associate constant (K_a) was calculated to be 34411 (±2753) M^{-1}.

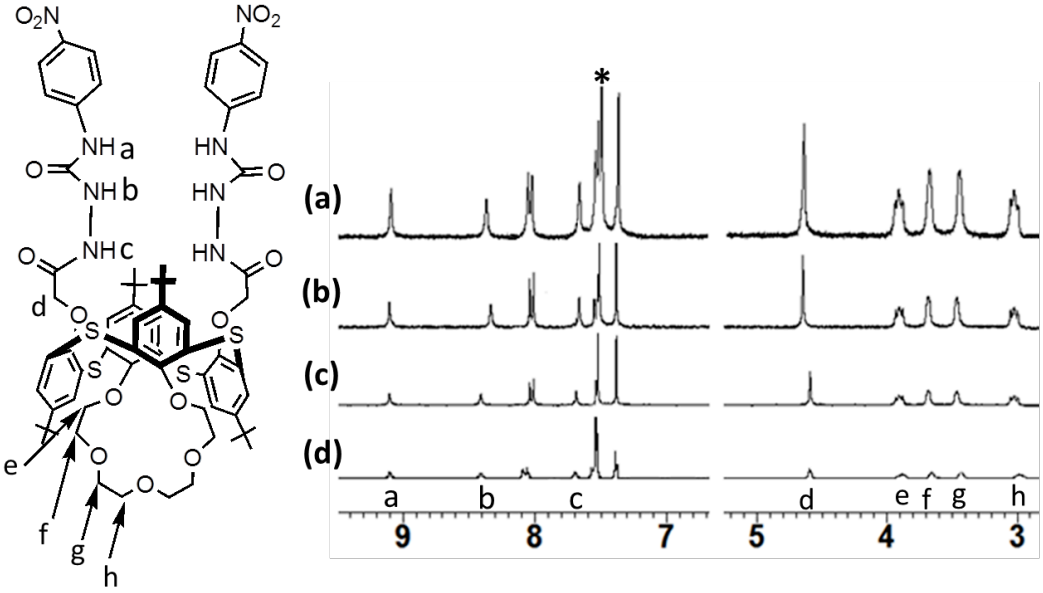

Figure S23. Concentration-dependent ^{1}H NMR spectra of **4$_e$** in $CDCl_3$–DMSO (10:1, v/v). (a = 4.0×10^{-2} M, b = 4.0×10^{-3} M, c = 8.0×10^{-4} M, d = 4.0×10^{-4}). *Denotes the solvent peak.

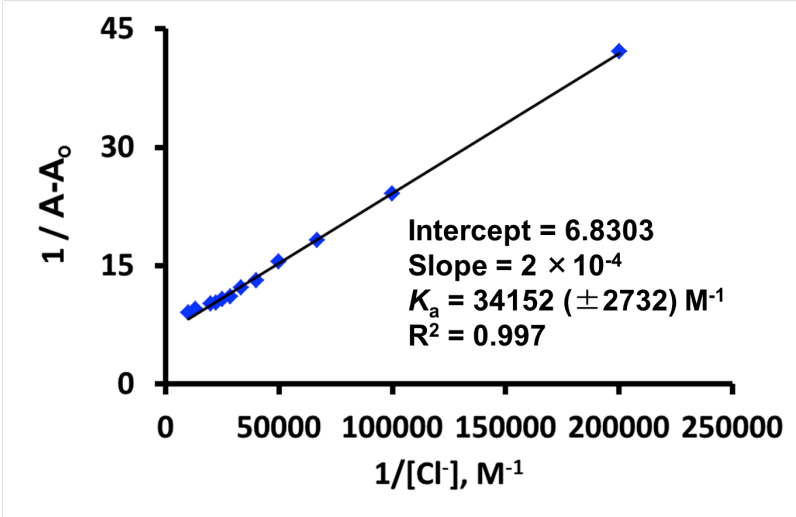

Figure S24. Benesi-Hildebrand plot of **4$_e$** for various concentrations of Cl^- at 298K by the UV-vis titration method. The associate constant (K_a) was calculated to be 34152 (±2732) M^{-1}.

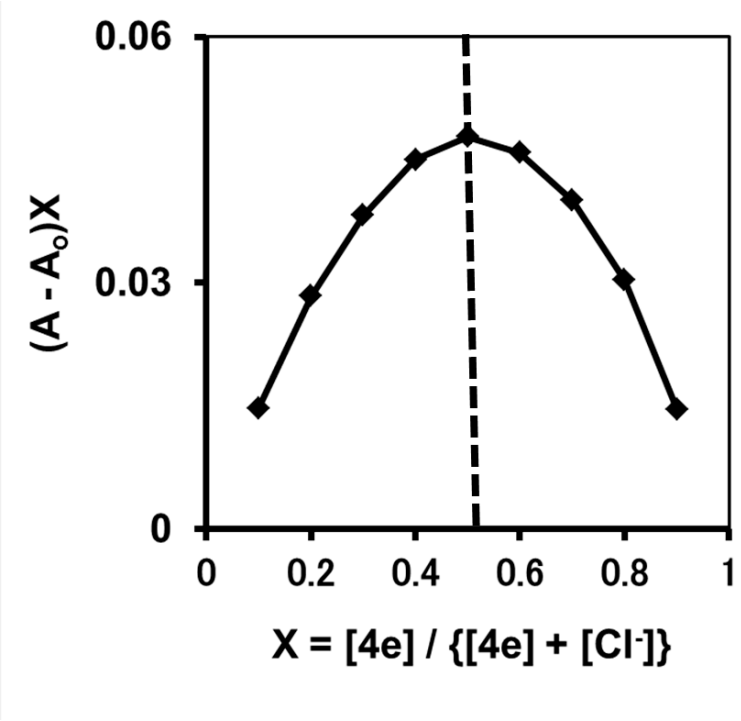

Figure S25. Job's plot showing the 1:1 binding of $\mathbf{4_e}$ to Cl^- ion from the UV-vis titration method at 390 nm in CH_2Cl_2–DMSO (10:1, v/v).

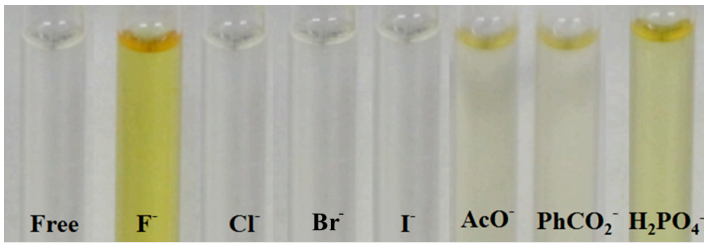

Figure S26. The solution color of reseptor $\mathbf{4_e}$ (2.5μM) in the absence and presence of 5 equivalents of various anions.

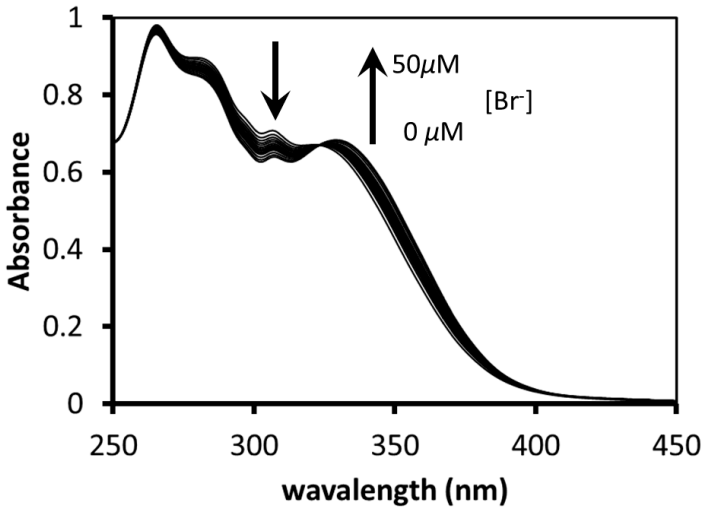

Figure S27. UV–vis absorption spectra of $\mathbf{4_e}$ (2.5μM) upon the addition of increasing concentrations of Br^- ion in CH_2Cl_2–DMSO (10:1, v/v).

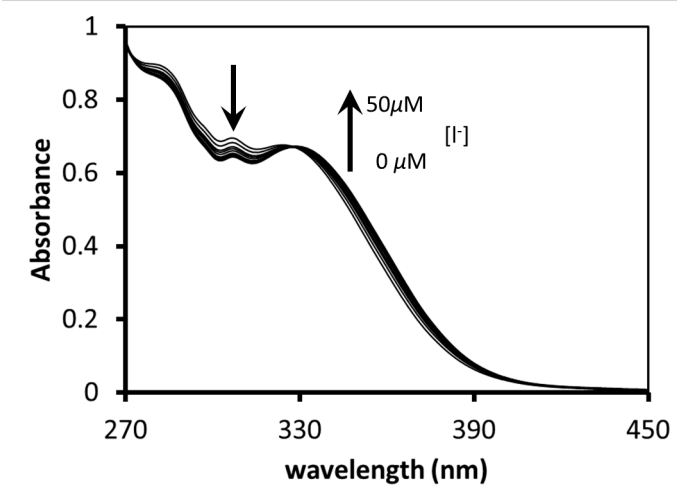

Figure S28. UV–vis absorption spectra of $\mathbf{4_e}$ (2.5μM) upon the addition of increasing concentrations of I^- ion in CH_2Cl_2–DMSO (10:1, v/v).

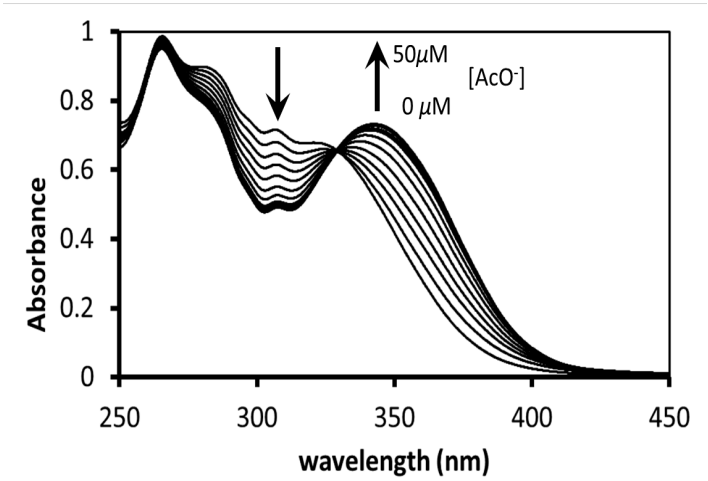

Figure S29. UV–vis absorption spectra of $\mathbf{4_e}$ (2.5μM) upon the addition of increasing concentrations of AcO^- ion in CH_2Cl_2–DMSO (10:1, v/v).

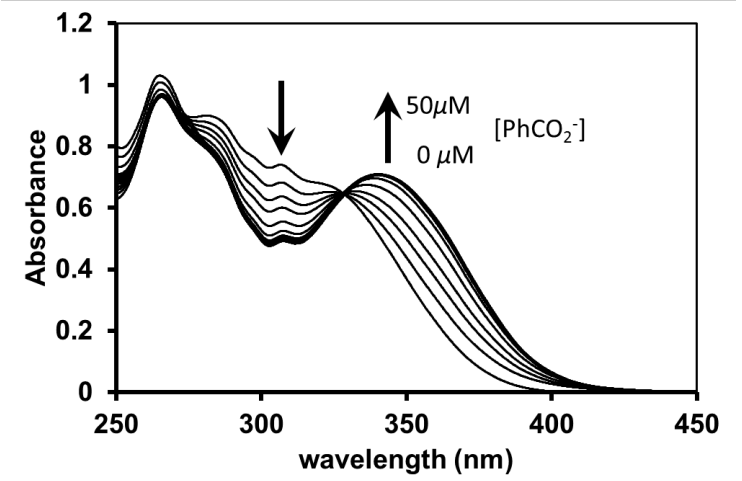

Figure S30. UV–vis absorption spectra of $\mathbf{4_e}$ (2.5μM) upon the addition of increasing concentrations of $PhCO_2^-$ ion in CH_2Cl_2–DMSO (10:1, v/v).

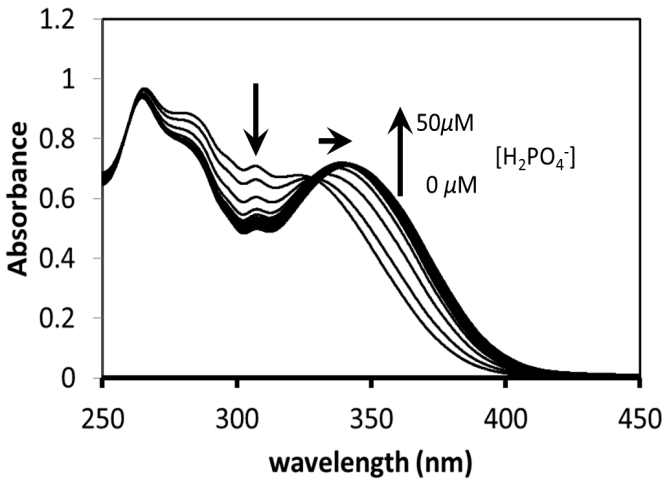

Figure S31. UV–vis absorption spectra of $\mathbf{4_e}$ (2.5μM) upon the addition of increasing concentrations of $H_2PO_4^-$ ion in CH_2Cl_2–DMSO (10:1, v/v).

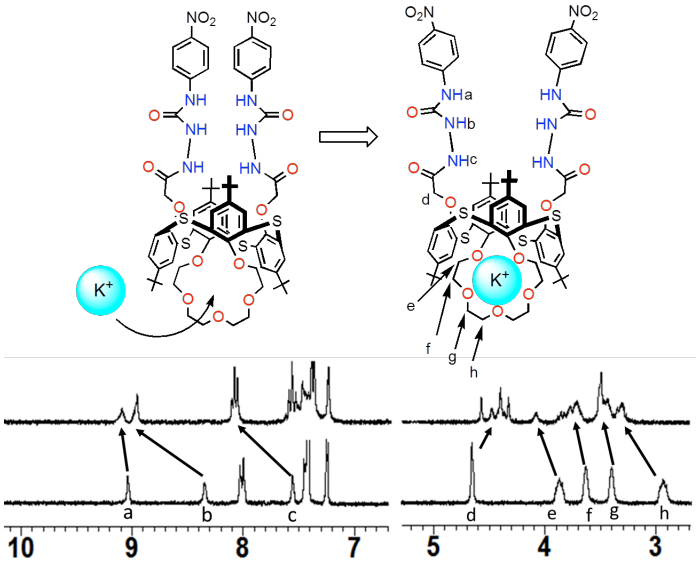

Figure S32. ^{1}H NMR stack plot of a $CDCl_3$–DMSO (10:1, v/v) solution of $\mathbf{4_e}$ (4.0×10^{-3} M) upon addition of KSO_3CF_3 in CD_3CN. Binding mode of receptor $\mathbf{4_e}$ upon complexation with K^+ ion.

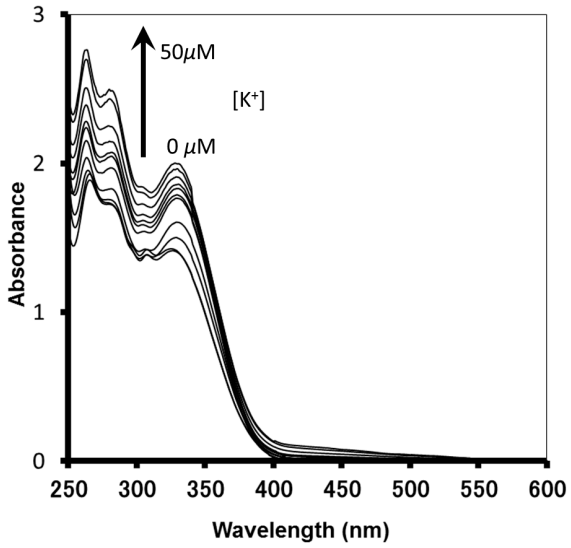

Figure S33. UV–vis absorption spectra of receptor $\mathbf{4_e}$ (2.5 μM) upon the addition of KSO_3CF_3 (0-50 μM) in CH_2Cl_2–DMSO (10:1, v/v).

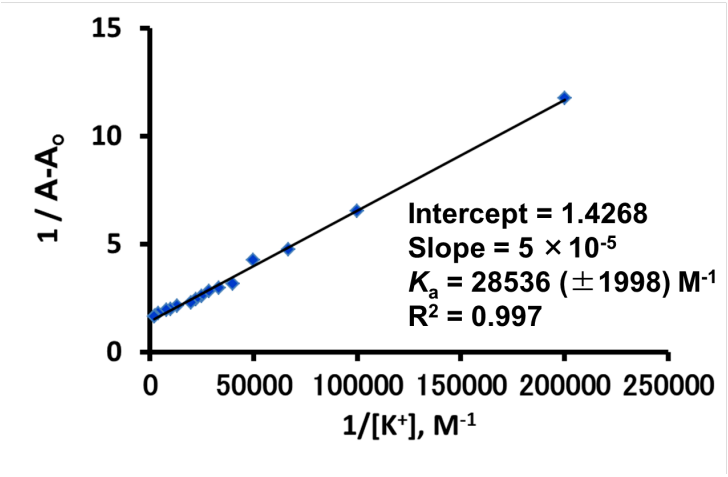

Figure S34. Benesi-Hildebrand plot of $\mathbf{4_e}$ with varied concentrations K^+ ion at 298K. The associate constant (K_a) was calculated to be 28536±1998 M^{-1} in CH_2Cl_2–DMSO (10:1:1, v/v).

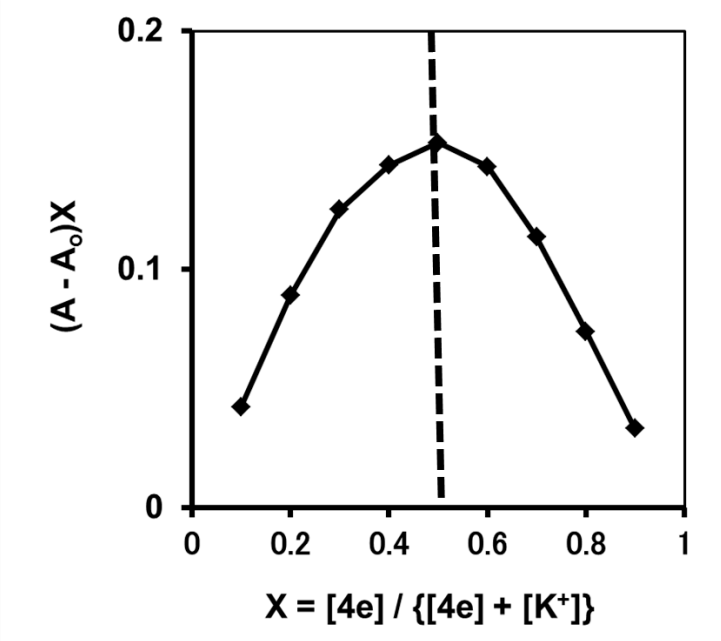

Figure S35. Job's plot showing the 1:1 binding of $\mathbf{4_e}$ to K^+ ion from fluorescence methods at 390 nm in CH_2Cl_2 –DMSO (10:1, v/v).

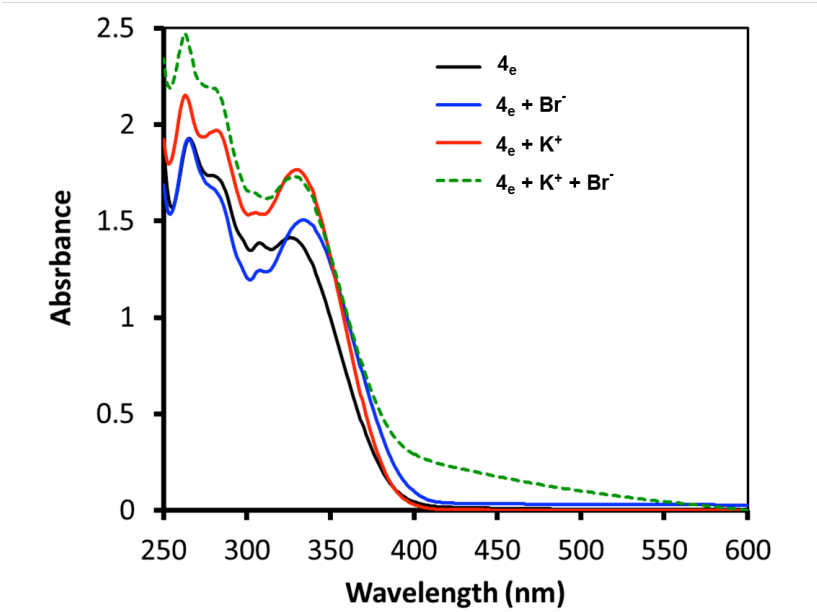

Figure S36. Proposed positive allosteric behaviour of receptor $\mathbf{4_e}$ with Br^- and K^+ ions. UV–vis absorption spectra of $\mathbf{4_e}$/guest (H/G = 1:1); free $\mathbf{4_e}$ (black full line), $\mathbf{4_e}\subset KSO_3CF_3$ (red full line), $Bu_4NBr\supset[\mathbf{4_e}\subset K^+]$ (green broke line), $\mathbf{4_e}\subset Bu_4NBr$ (blue full line). Solvent: CH_2Cl_2–DMSO (10:1, v/v). 300 MHz at 298 K.