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 S4. \( ^{13}\)C–NMR spectra of 3 (75 MHz, CDCl\(_3\), 293 K).
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Figure S12. $^{13}$C–NMR spectra of $4_d$ (100 MHz, CDCl$_3$–DMSO, 293 K).
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**Figure S14.** $^{13}$C–NMR spectra of 4e (100 MHz, CDCl$_3$–DMSO, 293 K).
Figure S15. a) X-ray crystal structure of the asymmetric unit of receptor 4b. 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.
Figure S16. X–ray crystal structure of the asymmetric unit of receptor 4. 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 4a–e to various anions. The UV–vis titration experiments of 4a–e were investigated by addition of anions (100 µL) (7.5 mM in CH$_3$CN solution) to 3 mL of 4a–e solution (2.5 µM in CDCl$_3$–DMSO, 10:1, v/v), respectively. The excitation wavelength was 343 nm.

$K^+$ titration of receptor 4e solution determined by absorption. The UV-vis titration experiment of 4e was investigated by adding increasing concentrations of KSO$_3$CF$_3$ (50 µL) (3.8 mM in CH$_3$CN solution) to 3 mL of 4e 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 4e•$K^+$ to various anions. The fluorescent response of L•$K^+$ to different anions was investigated by addition of KSO$_3$CF$_3$ (50 µL) (4.5 mM in CH$_3$CN) to 3 mL of 4e 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$_3$CN solution) to the 4e•$K^+$ solution. The UV–vis spectra were recorded immediately after mixing. The excitation wavelength was 343 nm.

$^1$H NMR titration experiments of 4e, 4e•$K^+$, 4e•$K^+$ with Cl$^-$ and 4e•$K^+$ with Br$. The $^1$H NMR titration experiment was investigated by addition 10 µL of KSO$_3$CF$_3$ (2.2 × 10$^{-1}$ M) to the solution of 4e (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$_4$NCl or Bu$_4$NBr in CH$_3$CN 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 S17. $^1$H NMR stack plot of a CDCl$_3$–DMSO (10:1, v/v) solution of 4$_a$ (4.0 × 10$^{-3}$ M) upon addition of Bu$_4$NCl in CD$_3$CN. $K_a = 6816$ (±545) M$^{-1}$.

Figure S18. $^1$H NMR stack plot of a CDCl$_3$–DMSO (10:1, v/v) solution of 4$_b$ (4.0 × 10$^{-3}$ M) upon addition of Bu$_4$NCl in CD$_3$CN. $K_a = 6945$ (±625) M$^{-1}$. 
Figure S19. $^1$H NMR stack plot of a CDCl$_3$–DMSO (10:1, v/v) solution of 4e (4.0 \times 10^{-3} \text{ M}) upon addition of Bu$_4$NCl in CD$_3$CN. $K_a = 3021 \ (\pm 242) \ \text{M}^{-1}$.

Figure S20. $^1$H NMR stack plot of a CDCl$_3$–DMSO (10:1, v/v) solution of 4d (4.0 \times 10^{-3} \text{ M}) upon addition of Bu$_4$NCl in CD$_3$CN. $K_a = 34411 \ (\pm 2400) \ \text{M}^{-1}$.
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$_4$NCl in CD$_3$CN. $K_a = 34411$ (± 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 4e 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 4e 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$^{-1}$. 

 Intercept = 6.8303
Slope = 2 × 10$^{-4}$
$K_a = 34152$ (±2732) M$^{-1}$
$R^2 = 0.997$
**Figure S25.** Job's plot showing the 1:1 binding of 4e to Cl\(^-\) ion from the UV-vis titration method at 390 nm in CH\(_2\)Cl\(_2\)-DMSO (10:1, v/v).

**Figure S26.** The solution color of reseptor 4e (2.5µM) in the absence and presence of 5 equivalents of various anions.
Figure S27. UV–vis absorption spectra of 4e (2.5µM) upon the addition of increasing concentrations of Br⁻ ion in CH₂Cl₂–DMSO (10:1, v/v).

Figure S28. UV–vis absorption spectra of 4e (2.5µM) upon the addition of increasing concentrations of I⁻ ion in CH₂Cl₂–DMSO (10:1, v/v).
Figure S29. UV–vis absorption spectra of 4e (2.5µM) upon the addition of increasing concentrations of AcO− ion in CH2Cl2–DMSO (10:1, v/v).

Figure S30. UV–vis absorption spectra of 4e (2.5µM) upon the addition of increasing concentrations of PhCO2− ion in CH2Cl2–DMSO (10:1, v/v).
Figure S31. UV–vis absorption spectra of 4e (2.5µM) upon the addition of increasing concentrations of H$_2$PO$_4^-$ ion in CH$_2$Cl$_2$–DMSO (10:1, v/v).

Figure S32. $^1$H NMR stack plot of a CDCl$_3$–DMSO (10:1, v/v) solution of 4e (4.0 × 10$^{-3}$ M) upon addition of KSO$_3$CF$_3$ in CD$_3$CN. Binding mode of receptor 4e upon complexation with K$^+$ ion.
Figure S33. UV–vis absorption spectra of receptor 4e (2.5 µM) upon the addition of KSO$_2$CF$_3$ (0-50 µM) in CH$_2$Cl$_2$–DMSO (10:1, v/v).

Figure S34. Benesi-Hildebrand plot of 4e with varied concentrations K$^+$ ion at 298K. The associate constant ($K_a$) was calculated to be 28536 ± 1998 M$^{-1}$ in CH$_2$Cl$_2$–DMSO (10:1:1, v/v).
**Figure S35.** Job's plot showing the 1:1 binding of 4e to K\(^+\) ion from fluorescence methods at 390 nm in CH\(_2\)Cl\(_2\) –DMSO (10:1, v/v).

**Figure S36.** Proposed positive allosteric behaviour of receptor 4e with Br\(^-\) and K\(^+\) ions. UV–vis absorption spectra of 4e/guest (H/G = 1:1); free 4e (black full line), 4e \(\subset\) KSO\(_2\)CF\(_3\) (red full line), Bu\(_4\)NBr \(\supset\)[4e \(\subset\) K\(^+\)] (green broke line), 4e \(\subset\) Bu\(_4\)NBr (blue full line). Solvent: CH\(_2\)Cl\(_2\)–DMSO (10:1, v/v). 300 MHz at 298 K.