Synthesis and inclusion behaviour of a heterotritopic receptor based on hexahomotrioxacalix[3]arene

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Figure S1. $^1$H NMR spectrum of cone-7 (300 MHz, CDCl$_3$, 298 K).
The corresponding chemical shifts were marked on the $^1$H NMR spectrum.
Figure S2. $^{13}$C NMR spectrum of cone-7 (75MHz, CDCl$_3$, 298 K).
Figure S3. Mass spectra of cone-7 in CH$_2$Cl$_2$. 
Figure S4. UV-vis absorption spectra response of cone-7 (1 × 10^{-6} M) in CH2Cl2-CH3CN (10:1, v/v) to 1 × 10^{-5} M various tested metal ions. λ_{max} = 290 nm, ε = 1.89 × 10^5 cm^{-1} M^{-1}.
Figure S5. Partial $^1$H NMR titration of $cone$-$7$/guest complex (H/G = 1:1); a) free $cone$-$7$; b) $cone$-$7$ ⊃ $K^+$; Solvent: CDCl$_3$/CD$_3$CN(10:1, v/v).

Figure S5’. Partial $^1$H NMR titration of $cone$-$7$/guest complex (H/G = 1:1); a) free $cone$-$7$; b) $cone$-$7$ ⊃ $Ag^+$; c) KClO$_4$ ⊂ [$cone$-$7$ ⊃ $Ag^+$]; Solvent: CDCl$_3$/CD$_3$CN(10:1, v/v).

$^1$H NMR titration experiments of $cone$-$7$ with $K^+$ ions were conducted. An equivalent of KClO$_4$ was added to the solution of $cone$-$7$ in the absence and presence of $Ag^+$ ion; no obvious chemical shift of $cone$-$7$ was observed.
Figure S6. Partial $^1$H NMR titration of cone-7/guest complex (H/G = 1:1); a) free cone-7; b) cone-7 ⊃ Cs$^+$. Solvent: CDCl$_3$/CD$_3$CN(10:1, v/v).

$^1$H NMR titration experiments of cone-7 with Cs$^+$ ions were conducted. An equivalent of CsClO$_4$ was added to the solution of cone-7 in the absence of Ag$^+$ ion; no obvious chemical shift of cone-7 was observed.
Figure S7. Partial $^1$H NMR titration of cone-7/guest complex (H/G = 1:1); a) free cone-7; b) cone-7 ⊃ Li$^+$; c) AgClO$_4$ ⊂ [cone-7 ⊃ Li$^+$]; Solvent: CDCl$_3$/CD$_3$CN(10:1, v/v).

After changing the binding sequence of metal ions, first to form the complex cone-7 ⊃ Li$^+$ then to form the complex AgClO$_4$ ⊂ [cone-7 ⊃ Li$^+$], we observed the same $^1$H NMR spectrum as shown in Figure S7c and Figure 3c was observed. This was consistent with the cone-hexahomotrioxacalix[3]arene triamide derivatives cone-7 serving as heteroditopic receptors for Ag$^+$ and Li$^+$ simultaneously.
Figure S8. Partial $^1$H NMR titration of cone-7/guest complex (H/G = 1:1); a) free cone-7; b) cone-7 $\supset$ AgClO$_4$; c) LiClO$_4$ $\subset$ [cone-7 $\supset$ Ag$^+$]; d) Na$^+$ $\subset$ {Li$^+$ $\subset$ [cone-7 $\supset$ Ag$^+$]}; Solvent: CDCl$_3$/CD$_3$CN (10:1, v/v).

We observed the same $^1$H NMR spectrum after changing the binding sequence of metal ions as shown in Figure S8d and Figure 6d, which was consistent with the cone-hexahomotrioxacalix[3]arene triamide derivatives cone-7 serving as heterotritopic receptors for Ag$^+$, Li$^+$ and Na$^+$ ions simultaneously.
The stoichiometry of the *cone*-7 complexes with Li$^+$ was also determined by UV-vis absorption spectrum (CH$_2$Cl$_2$/CH$_3$CN), using the continuous variation method; the absorption reached a maximum at 0.5 mol fraction for this cation, indicating that Li$^+$ forms a 1:1 complex with *cone*-7.

**Figure S10.** Molar ratio of Na$^+$ with host *cone*-7.
Figure S11. Bensei-Hilderbrand plot of *cone-7* for various concentrations of Ag⁺ at 298 K. The association constant \((K_a)\) was calculated to be \(2.24 \times 10^5\) M⁻¹.

Figure S12. Bensei-Hilderbrand plot of *cone-7* for various concentrations of Li⁺ at 298 K. The association constant \((K_a)\) was calculated to be \(2.58 \times 10^5\) M⁻¹.
Figure S13. Bensei-Hilderbrand plot of *cone-7* for various concentrations of Na$^+$ at 298 K. The association constant ($K_a$) was calculated to be $1.55 \times 10^5$ M$^{-1}$. 

The plot is shown with the equation $y = 1E-04x + 15.517$ and the association constant $K_a = 1.55 \times 10^5$ (±1536), with a $R^2 = 0.9926$. 

The diagonal line represents the linear relationship between the reciprocal of Na$^+$ concentration and the observed absorbance difference. The linear equation $y = 1E-04x + 15.517$ is derived from the data, indicating a slight positive deviation from the expected linear fit, as evidenced by the $R^2$ value of 0.9926.