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

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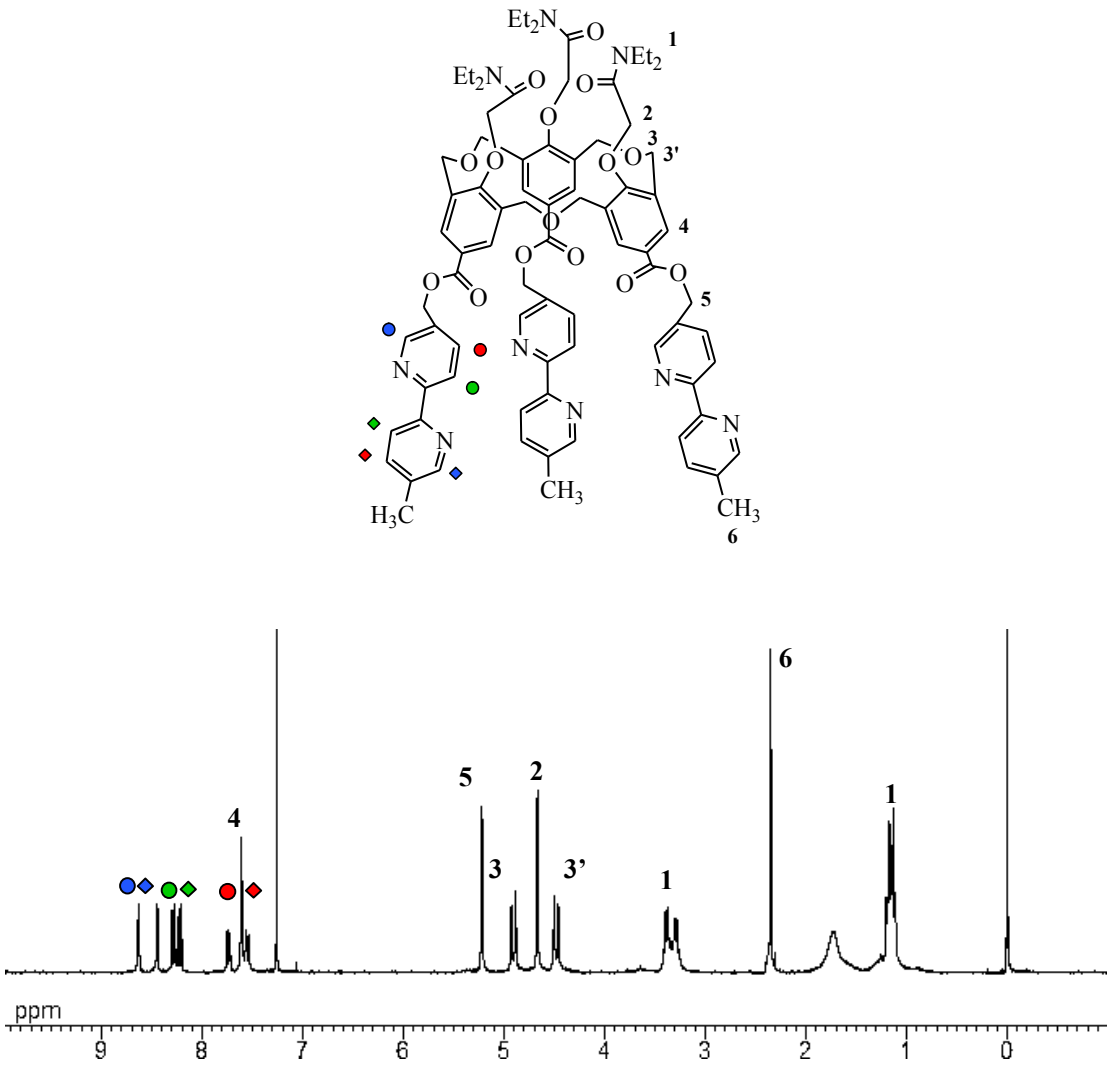

Figure S1. ^{1}H NMR spectrum of *cone*-**7** (300 MHz, $CDCl_3$, 298 K).
The corresponding chemical shifts were marked on the ^{1}H NMR spectrum.

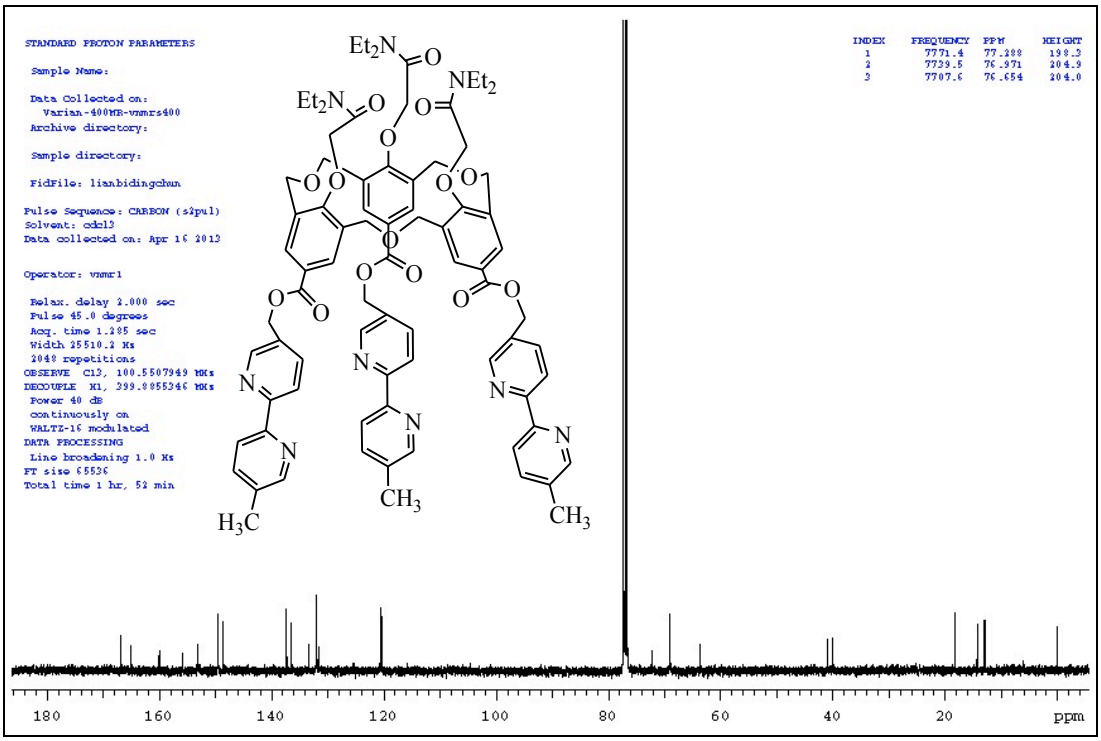

Figure S2. ^{13}C NMR spectrum of *cone*-**7** (75MHz, $CDCl_3$, 298 K).

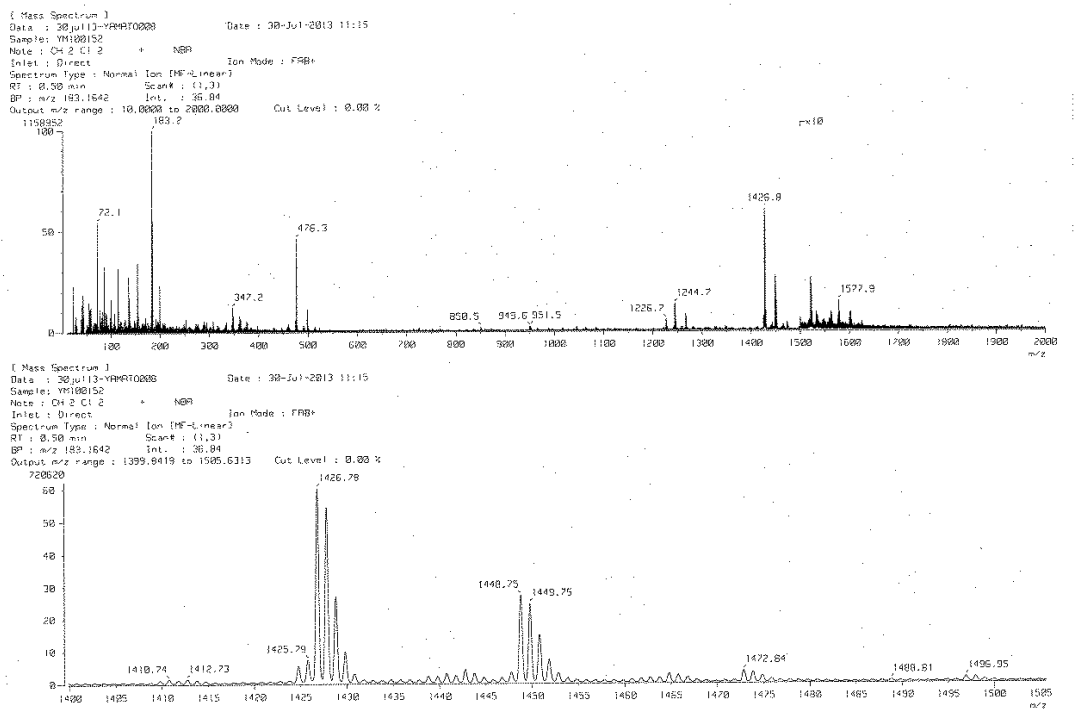

Figure S3. Mass spectra of *cone*-**7** in CH_2Cl_2.

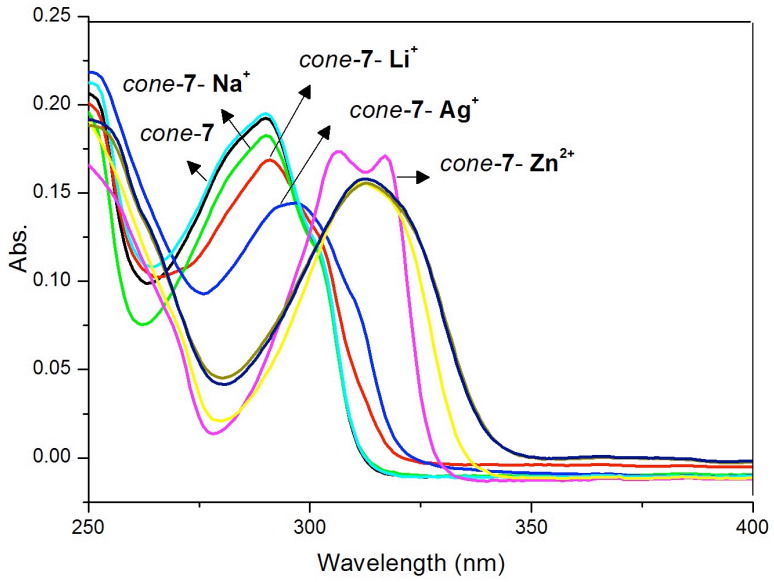

Figure S4. UV-vis absorption spectra response of *cone*-**7** (1×10^{-6} M) in CH_2Cl_2-CH_3CN (10:1, v/v) to 1×10^{-5} M various tested metal ions. λ_{max} = 290 nm, ε = 1.89×10^5 $cm^{-1}M^{-1}$.

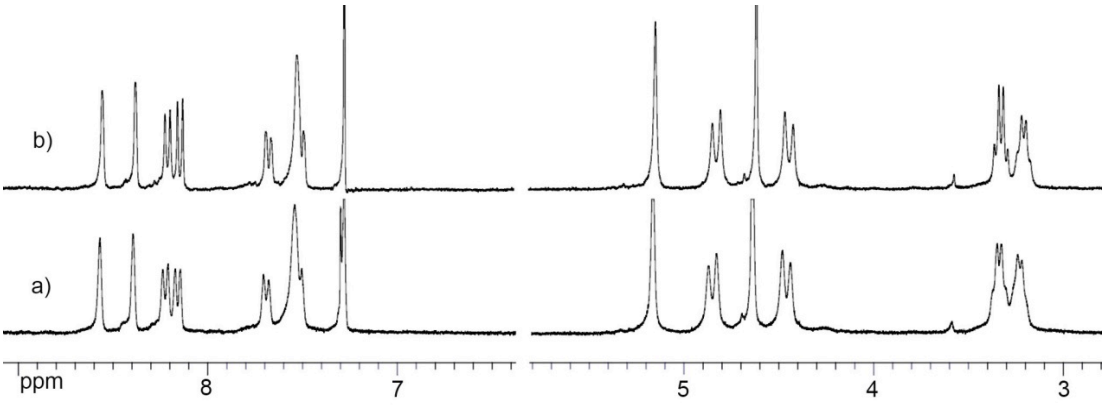

Figure S5. Partial ^{1}H NMR titration of *cone*-**7**/guest complex (H/G = 1:1); a) free *cone*-**7**; b) *cone*-**7** ⊃ K^+; Solvent: $CDCl_3/CD_3CN$(10:1, v/v).

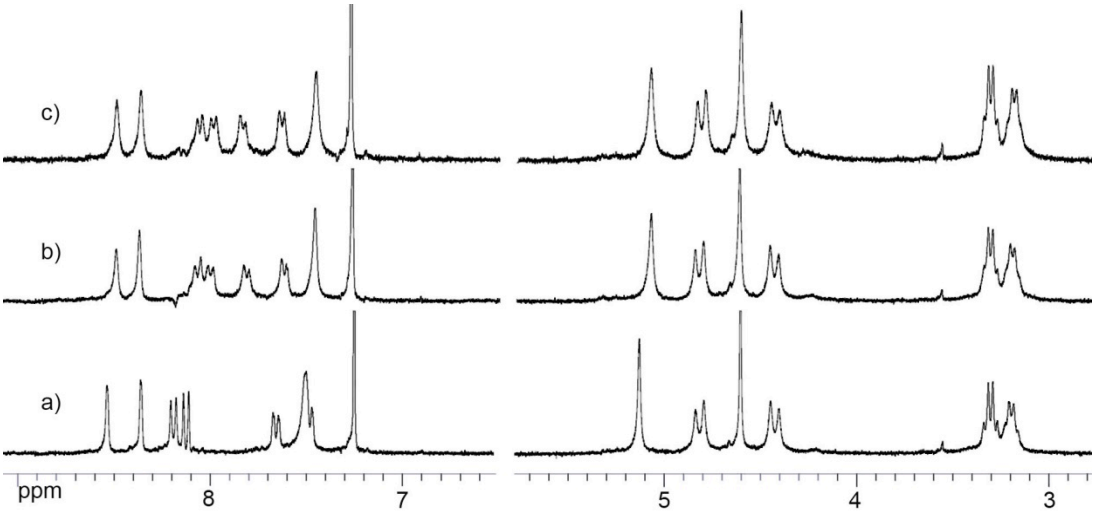

Figure S5'. Partial ^{1}H NMR titration of *cone*-**7**/guest complex (H/G = 1:1); a) free *cone*-**7**; b) *cone*-**7** ⊃ Ag^+; c) $KClO_4$ ⊂ [*cone*-**7** ⊃ Ag^+]; Solvent: $CDCl_3/CD_3CN$(10:1, v/v).

^{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.

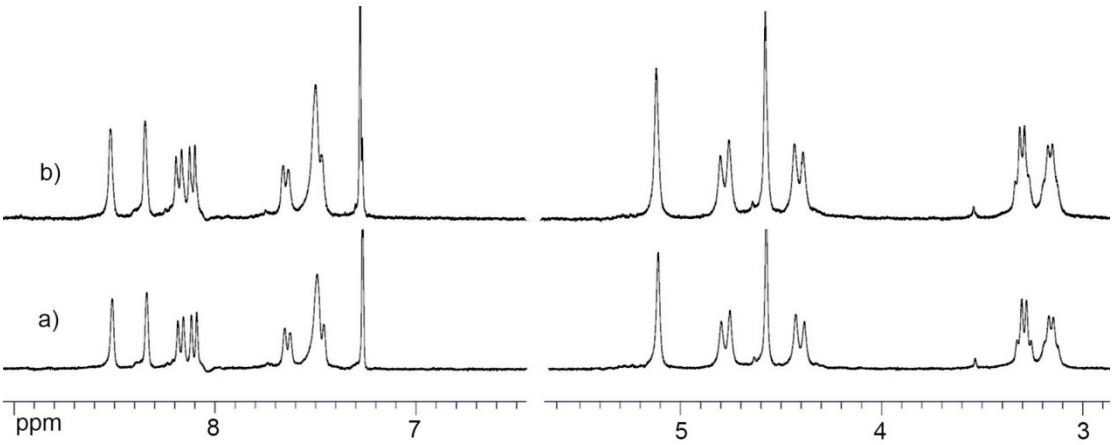

Figure S6. Partial ^{1}H NMR titration of *cone*-**7**/guest complex (H/G = 1:1); a) free *cone*-**7**; b) *cone*-**7** ⊃ Cs^+; Solvent: $CDCl_3/CD_3CN$(10:1, v/v).

^{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.

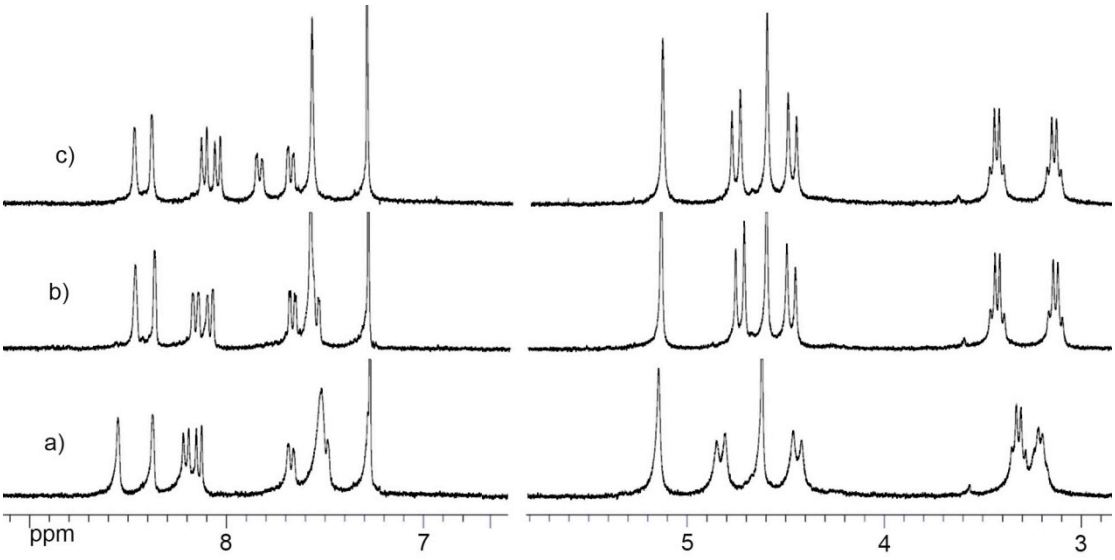

Figure S7. Partial ^{1}H NMR titration of *cone*-**7**/guest complex (H/G = 1:1); a) free *cone*-**7**; b) *cone*-**7** ⊃ Li^+; c) $AgClO_4$ ⊂ [*cone*-**7** ⊃ Li^+]; Solvent: $CDCl_3/CD_3CN$(10:1, v/v).

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.

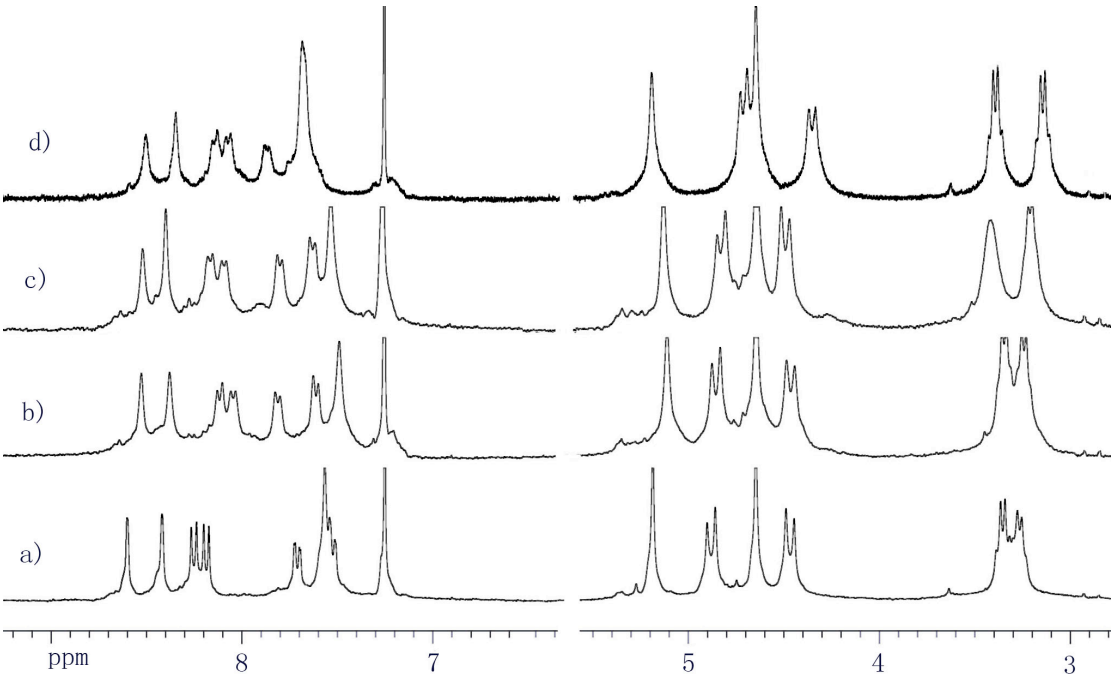

Figure S8. Partial ^{1}H NMR titration of *cone*-**7** /guest complex (H/G = 1:1); a) free *cone*-**7**; b) *cone*-**7** ⊃ $AgClO_4$; c) $LiClO_4$ ⊂ [*cone*-**7** ⊃ Ag^+]; d) Na^+ ⊂ {Li^+ ⊂ [*cone*-**7** ⊃ Ag^+]}; Solvent: $CDCl_3/CD_3CN$ (10:1, v/v).

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.

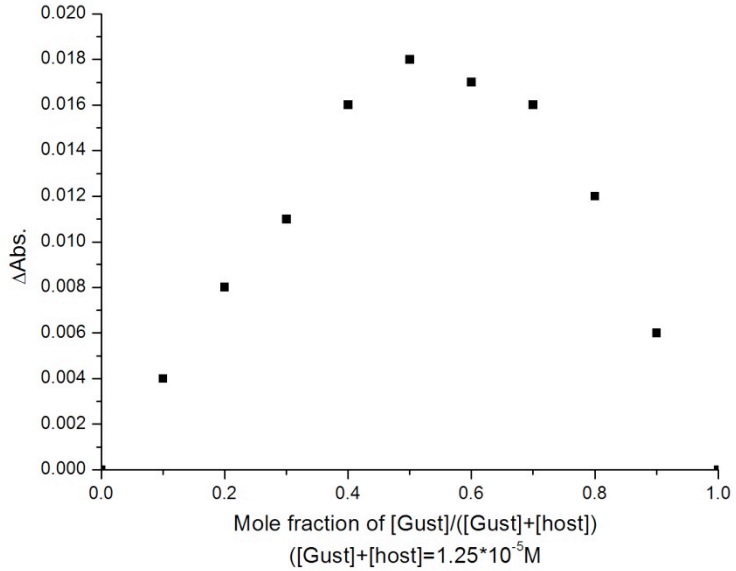

Figure S9. Job's plot of the extractions of Li^+ with host *cone*-**7**.

The stoichiometry of the *cone*-**7** complexes with Li^+ was also determined by UV-vis absorption spectrum (CH_2Cl_2/CH_3CN), 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**.

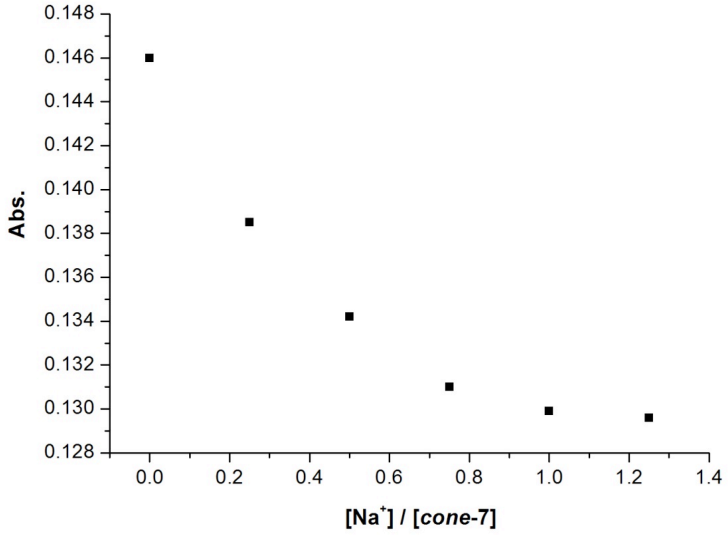

Figure S10. Molar ratio of Na^+ with host *cone*-**7**.

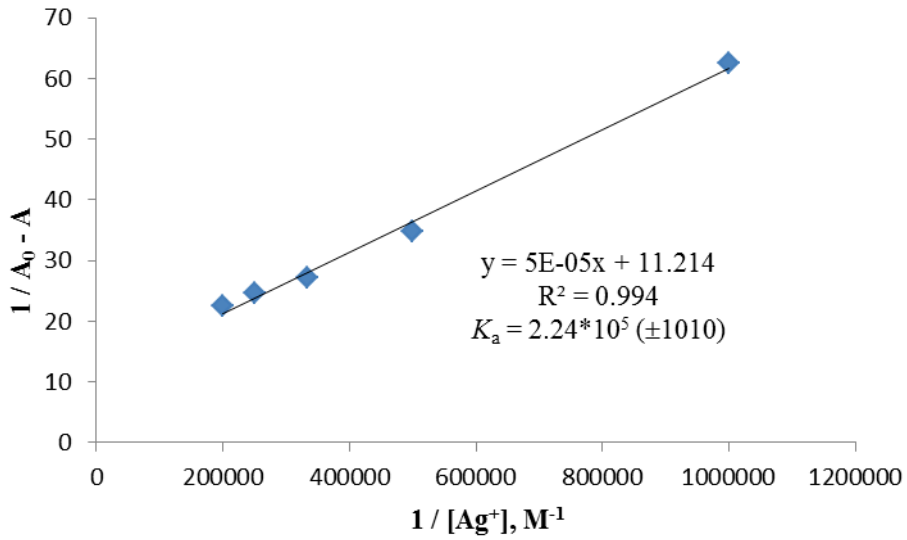

Figure S11. Bensei-Hilderbrand plot of *cone*-**7** for various concentrations of Ag^+ at 298 K. The association constant (K_a) was calculated to be 2.24×10^5 M^{-1}.

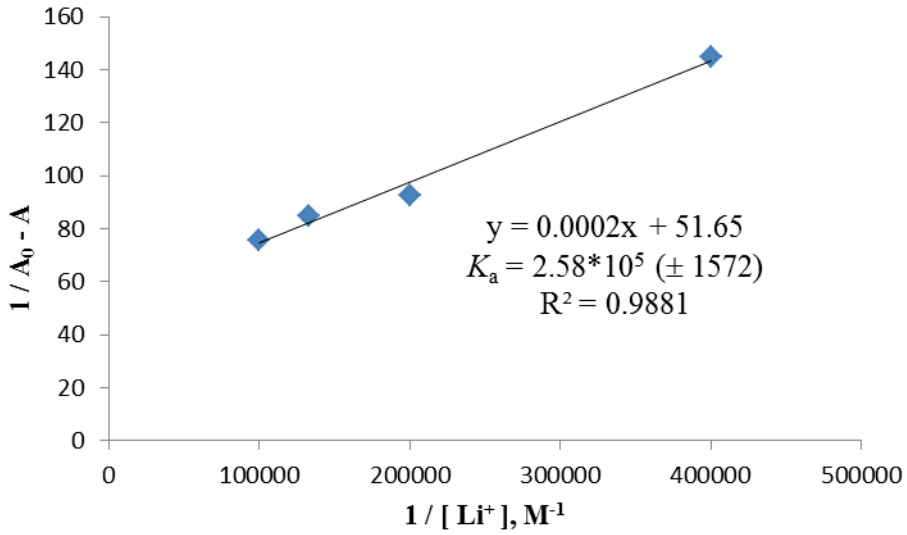

Figure S12. Bensei-Hilderbrand plot of *cone*-**7** for various concentrations of Li^+ at 298 K. The association constant (K_a) was calculated to be 2.58×10^5 M^{-1}.

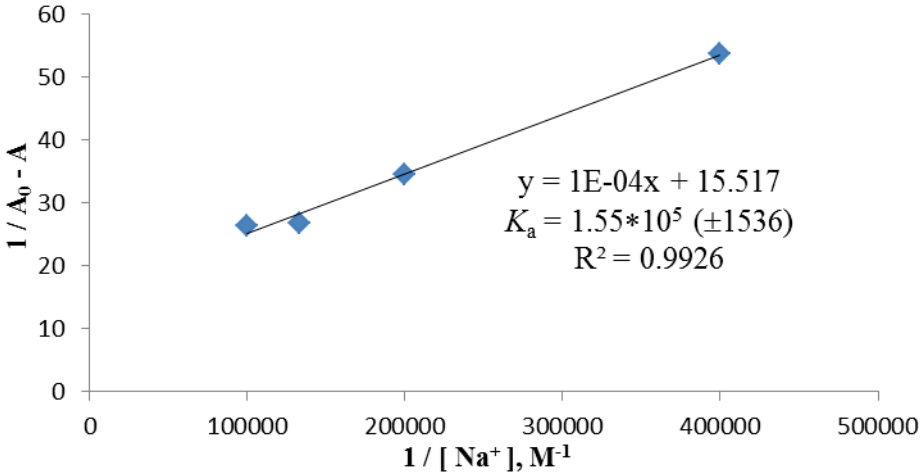

Figure S13. Bensei-Hilderbrand plot of *cone*-**7** for various concentrations of Na^+ at 298 K. The association constant (K_a) was calculated to be 1.55×10^5 M^{-1}.