Supporting Information

Selective Templated Complexation of Cylindrical Macrotricyclic Host with Neutral Guests: Three Cation-Controlled Switchable Processes

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1. $^1$H NMR, $^{13}$C NMR and MS spectra of host 1 and guest 2

Figure S1. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 1.

Figure S2. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of host 1.
Figure S3. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of guest 2.

Figure S4. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of guest 2.
Figure S5. MALDI-TOF MS of host 1.

Figure S6. ESI-MS MS of guest 2 (Negative mode; Voltage: 70V; Temperature: 550°C).
II. ESI-MS spectra of complexes between host I and metal ions

**Figure S7.** ESI-MS spectrum of complex 1·2Li⁺.

**Figure S8.** ESI-MS spectrum of complex 1·2Na⁺.
Figure S9. ESI-MS spectrum of complex 1·2K⁺.

Figure S10. ESI-MS spectrum of complex 1·Mg²⁺.
Figure S11. ESI-MS spectrum of complex 1·Ca$^{2+}$.

III. UV-Vis spectra of 1, 2, and their mixture in the absence and presence of LiBr

Figure S12. UV-Vis spectra of the indicated species (3 mM) in 1:1 CHCl$_3$/CH$_3$CN solution.
IV. Low temperature $^1$H NMR spectrum of the complex 1·2·2Li$^+$

![Low temperature $^1$H NMR spectrum of the complex 1·2·2Li$^+$](image)

**Figure S13.** $^1$H NMR spectrum of 1·2·2Li$^+$ ([1]$_0$=3 mM, [2]$_0$=4.5 mM, [LiBr]=30 mM) at 233K, c and uc denote ‘complex’ and ‘uncomplex’, respectively.

V. The $^1$H NMR spectra of 1:1 mixture of 1 and 2 in the presence of different cations

![Partial $^1$H NMR spectra](image)

**Figure S14.** Partial $^1$H NMR spectra (300 MHz, CD$_3$CN : CDCl$_3$=1:1, 295K) of a) 1 and 1.0 equiv of 2, b) 1 and 1.0 equiv of 2 in the presence of 10 equiv of LiBr, c) 1 and 1.0 equiv of 2 in the presence of 10 equiv of NaClO$_4$, d) 1 and 1.0 equiv of 2 in the presence of 10 equiv of KPF$_6$, e) 1 and 1.0 equiv of 2 in the presence of 10 equiv of Mg(ClO$_4$)$_2$, f) 1 and 1.0 equiv of 2 in the presence of 10 equiv of Ca(ClO$_4$)$_2$. [1]$_0$ = 2 mM
VI. The $^1$H NMR spectra of 1:1 mixture of 1 and 3 in the presence of different cations

Figure S15. Partial $^1$H NMR spectra (300 MHz, CD$_3$CN:CDCl$_3$=1:1, 295K) of (a) 1 and 1.0 equiv of 3, (b) 1 and 1.0 equiv of 3 in the presence of 10 equiv of LiBr, (c) 1 and 1.0 equiv of 3 in the presence of 10 equiv of NaClO$_4$, (d) 1 and 1.0 equiv of 3 in the presence of 10 equiv of KPF$_6$, (e) 1 and 1.0 equiv of 3 in the presence of 10 equiv of Mg(ClO$_4$)$_2$, (f) 1 and 1.0 equiv of 3 in the presence of 10 equiv of Ca(ClO$_4$)$_2$. [1]$_0$ = 2 mM.
VII. Mole ratio plots, and determination of the association constants for the complexes $\text{1·2·2Li}^+$, $\text{1·3·2K}^+$ and $\text{1·4}$

**Figure S16.** Mole ratio plot for the complex $\text{1·2·2Li}^+$ in 1:1 chloroform/ acetonitrile solution at 295K.

**Figure S17.** Scatchard plot for the complex $\text{1·2·2Li}^+$ in 1:1 chloroform/ acetonitrile solution at 295K.
**Figure S18.** Mole ratio plot for the complex 1·3·2K⁺ in 1:1 chloroform/ acetonitrile solution at 295K.

**Figure S19.** Scatchard plot for the complex 1·3·2K⁺ in 1:1 chloroform/ acetonitrile solution at 295K.
Figure S20. Mole ratio plot for the complex 1·4 in 1:1 chloroform/acetonitrile solution at 295K.

Figure S21. Scatchard plot for the complex 1·4 in 1:1 chloroform/ acetonitrile solution at 295K.
VIII. Comparison of $^1$H NMR spectra of 1:1 mixture of 1 and 2 in the presence of LiBr and LiClO$_4$

![Figure S22](image)

Figure S22. Partial $^1$H NMR spectra (300 MHz, CD$_3$CN : CDCl$_3$=1:1, 295K) of (a) 1 and 1.0 equiv of 2 in the presence of 10 equiv of LiClO$_4$, (b) 1 and 1.0 equiv of 2 in the presence of 10 equiv of LiBr. $[1]_0 = 2\text{mM}$.

IX. Comparison of $^1$H NMR spectra of host 1 and guest 3

![Figure S23](image)

Figure S23. Partial $^1$H NMR spectra (300 MHz, CD$_3$CN : CDCl$_3$=1:1, 295 K) of (a) free host 1, (b) free guest 3, (c) 1 and 1.0 equiv of 3. $[1]_0 = 1\text{mM}$, (d) the mixture obtained after adding KPF$_6$ (4 equiv) to solution c.
X. Comparison of $^1$H NMR spectra of host 1 and guest 4

![NMR spectra](image)

**Figure S24.** Partial $^1$H NMR spectra (300 MHz, CD$_3$CN : CHCl$_3$=1:1, 295K) of (a) free host 1, (b) free guest 4, (c) 1 and 1.0 equiv of 4. $[1]_0 = 3 \text{ mM}$. 

XI. ESI-MS spectra of complexes 1·3·2K$^+$ and 1·4

![ESI-MS spectrum](image)

**Figure S25.** ESI-MS spectrum of the complex 1·3·2K$^+$: $m/z$ 575.6 $[1\cdot2K^+]^2+\,$, 737.6 $[1\cdot3\cdot2K^+]^2+\,$, 1111.5 $[1\cdotK^+]^+$. 

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Figure S26. ESI-MS spectrum of the complex $1 \cdot 4$ ($m/z$ at 657.8 for $[1 \cdot 4 \cdot 2\text{PF}_6^-]^2^+$.)

XII. Crystal structure of the complex $1 \cdot 3 \cdot 2\text{K}^+$

Figure S27. Crystal structure of $1 \cdot 3 \cdot 2\text{K}^+$. Solvent molecules, $\text{PF}_6^-$ counterions, and hydrogen atoms are omitted for clarity.