Binding of carboxylatopillar[5]arene with alkyl and aryl ammonium salts in aqueous medium

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1. Characterization of G1 ⊃ CP5A complex

1.1 DOSY NMR spectrum

Figure S1. DOSY spectrum of an equimolar (10 mM) mixture of CP5A and G1 in D$_2$O. 
Same diffusion coefficient for both the species indicates them to be constituents of a single complex. Impurity (acetone) is represented by “x”.
1.2 NOESY NMR spectrum

Figure S2. 2D NOESY spectrum of a mixture of CP5A and G1 in D_2O. The concentrations of host and guest are 10 and 15 mM, respectively. NOE correlations were observed between aromatic proton H_1 of CP5A and methylene protons H_a, H_b and H_c of G1. The NOE cross-peaks labelled as “a/1, b/1, c/1” confirm the pseudo[2]rotaxane formation.
1.3 Determination of the association constant and stoichiometry

NMR titration was done to determine the association constant ($K_a$) for the present host-guest systems since complex formation is in fast exchange on NMR time scale. NMR titrations were done with solutions having fixed and varying concentration of guest (G1-G3) and host CP5A respectively. Using the nonlinear curve-fitting method, the association constant was obtained for 1:1 host-guest combination from the following equation:

$$\Delta \delta = \left( \Delta \delta_\infty / [G]_0 \right) \left( 0.5[H] + 0.5([G]_0 + 1/K_a) - (0.5([H] + 2[H] (1/K_a - [G]_0)) + (1/K_a + [G]_0)^2)^{0.5} \right)$$

Eq. 1

Where $\Delta \delta$ is the chemical shift change of H$_{\delta}$ of the guest G at [H], $\Delta \delta_\infty$ is the chemical shift change of H$_{\delta}$ when the guest is completely complexed, [G]$_0$ is the fixed initial concentration of the guest, and [H] is the varying concentrations of the host CP5A.

For 1:2 guest-host combination, the association constant was obtained from the following equation:

$$\Delta \delta = (\Delta \delta_{GH}K_1[H] + \Delta \delta_{GH2}K_1K_2[H]^2)/(1 + K_1[H] + K_1K_2[H]^2)$$

Eq. 2

Where $\Delta \delta$ is the chemical shift change of H$_{\delta}$ of the guest G at [H], $\Delta \delta_{GH}$ is the chemical shift change of H$_{\delta}$ of the guest G when it is completely complexed by the first CP5A, $\Delta \delta_{GH2}$ is the chemical shift change of H$_{\delta}$ of the guest G when it is completely complexed by the second CP5A, and [H] is the varying concentration of the host CP5A.
**Figure S3.** Partial $^1$H NMR spectra (400 MHz, D$_2$O) of G1 at a concentration of 3.0 mM upon addition of CP5A (126.8 mM): a) 0 µL, b) 2 µL, c) 2 µL, d) 2 µL, e) 2 µL, f) 4 µL, g) 4 µL, h) 4 µL, i) 4 µL, j) 6 µL.
**Figure S4.** The chemical shift changes of H$_d$ on G1 upon addition of CP5A. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

**Figure S5.** Mole ratio plot for the complexation between G1 and CP5A, indicating a 1:1 stoichiometry.
2. Characterization of $\text{G}_2 \supset \text{CP5A}$ complex

2.1 DOSY NMR spectrum

Figure S6. DOSY spectrum of an equimolar (10 mM) mixture of CP5A and G2 in D$_2$O. Same diffusion coefficient for both the species indicates them to be constituents of a single complex. Impurity (acetone) is represented by “x”.
2.2 NOESY NMR spectrum

Figure S7. 2D NOESY spectrum of an equimolar (10 mM) mixture of CP5A and G2 in D$_2$O. NOE correlations were observed between aromatic proton H$_1$ of CP5A and methylene protons H$_a$, H$_b$ and H$_c$ of G2. The NOE cross-peaks labelled as “a/1, b/1, c/1” confirms the pseudo[2]rotaxane formation. Impurity (acetone) is represented by “x”.
2.3 Determination of the association constant and stoichiometry

Figure S8. Partial $^1$H NMR spectra (400 MHz, D$_2$O) of G2 at a concentration of 2.9 mM upon addition of CP5A (127.6 mM): a) 0 µL, b) 2 µL, c) 2 µL, d) 2 µL, e) 2 µL, f) 2 µL, g) 2 µL, h) 2 µL, i) 2 µL, j) 2 µL, k) 2 µL, l) 4 µL.
Figure S9. The chemical shift changes of $H_a$ on G2 upon addition of CP5A. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

Figure S10. Mole ratio plot for the complexation between G2 and CP5A, indicating a 1:1 stoichiometry.
3. Characterization of $\text{G3} \supset \text{CP5A}$ complex

3.1 DOSY NMR spectrum

**Figure S11.** DOSY spectrum of an equimolar (10 mM) mixture of $\text{CP5A}$ and $\text{G3}$ in $\text{D}_2\text{O}$. Same diffusion coefficient for both the species indicates them to be constituents of a single complex.
3.2 NOESY NMR spectrum

Figure S12. 2D NOESY spectrum of an equimolar (10 mM) mixture of CP5A and G3 in D$_2$O. NOE correlations were observed between aromatic proton H$_1$ of CP5A and methylene protons H$_d$, H$_e$ and H$_g$ of G3. The NOE cross-peaks labelled as “1/d, 1/e,g” confirms the pseudo[2]rotaxane formation.
3.3 Determination of the stoichiometry

Figure S13. Partial $^1$H NMR spectra (400 MHz, D$_2$O) of G3 at a concentration of 3.6 mM upon addition of CP5A (120.6 mM): a) 0 µL, b) 5 µL, c) 5 µL, d) 5 µL, e) 5 µL, f) 5 µL, g) 5 µL, h) 5 µL, i) 5 µL, j) 5 µL, k) 5 µL. Protons $H_{b-h}$ can be first seen upfield shifted only when the [CP5A] = 3.5 mM (entry d). Further addition of CP5A (entry e – entry k) hardly affected the chemical shift of $H_{b-h}$ protons of G3, confirming 1:1 stoichiometry for the CP5A $\supset$ G3 complex.

Determination of association constant was not possible as for [CP5A]<[G3], the NMR solutions are turbid and no signal could be obtained even after sonication and heating for long time. Mixed solvents did not improve the case. Titration of G3 into a fixed concentration solution of CP5A was not possible due to poor solubility of G3 (hindering the possibility of making stock solution of G3).
4. Characterization of G4 ⊃ CP5A complex

4.1 Determination of the association constant and stoichiometry

Figure S14. Partial $^1$H NMR spectra (400 MHz, D$_2$O) of CP5A at a concentration of 3.08 mM upon addition of G4 (97.2 mM): a) 0 µL, b) 3 µL, c) 3 µL, d) 3 µL, e) 3 µL, f) 3 µL, g) 3 µL, h) 3 µL, i) 3 µL, j) 3 µL, k) 3 µL, l) 3 µL.
Figure S15. The chemical shift changes of H₁ on CP5A upon addition of G4. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

Figure S16. Mole ratio plot for the complexation between G₄ and CP5A, indicating a 1:1 stoichiometry.
5. Characterization of $G_5 \supset CP5A$ complex

5.1 DOSY NMR spectrum

Figure S17. DOSY spectrum of a mixture of CP5A and G5 in D$_2$O. The concentrations of host and guest are 12 and 10 mM, respectively. Same diffusion coefficient for both the species indicates them to be constituents of a single complex.
5.2 NOESY NMR spectrum

**Figure S18.** 2D NOESY spectrum of a mixture of CP5A and G5 in D$_2$O. The concentrations of host and guest are 11 and 17 mM, respectively. NOE correlations were observed between aromatic proton H$_1$ of CP5A and methylene protons H$_a$, H$_c$ and H$_d$ of G5. The NOE cross-peaks labelled as “1/a, 1/c,d” confirm the pseudo[2]rotaxane formation.
5.3 Determination of the association constant and stoichiometry

Figure S19. Partial $^1$H NMR spectra (400 MHz, D$_2$O) of G5 at a concentration of 3.2 mM upon addition of CP5A (75.6 mM): a) 0 µL, b) 3 µL, c) 3 µL, d) 3 µL, e) 3 µL, f) 3 µL, g) 3 µL, h) 3 µL, i) 3 µL, j) 3 µL, k) 3 µL, l) 6 µL, m) 6 µL, n) 6 µL, o) 6 µL.
Figure S20. The chemical shift changes of H_d on G5 upon addition of CP5A. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

Figure S21. Mole ratio plot for the complexation between G5 and CP5A, indicating a 1:1 stoichiometry.
6. Characterization of $\text{G6} \supset \text{CP5A}$ complex

6.1 DOSY NMR spectrum

Figure S22. DOSY spectrum of a mixture of CP5A and G6 in D$_2$O. The concentrations of host and guest are 16 and 7.2 mM, respectively. Same diffusion coefficient for both the species indicates them to be constituents of a single complex.
6.2 Determination of the association constant and stoichiometry

![Chemical Structure](image)

**Figure S23.** Partial $^1$H NMR spectra (400 MHz, D$_2$O) of G6 at a concentration of 2.97 mM upon addition of CP5A (51.1 mM): a) 0 µL, b) 5 µL, c) 5 µL, d) 5 µL, e) 5 µL, f) 5 µL, g) 5 µL, h) 5 µL, i) 5 µL, j) 10 µL, k) 10 µL, l) 15 µL, m) 15 µL, n) 15 µL.
**Figure S24.** The chemical shift changes of H_d on G6 upon addition of CP5A. The red solid line was obtained from the non-linear curve-fitting using Eq. 2.

**Figure S25.** Mole ratio plot for the complexation between G6 and CP5A, indicating a 1:2 stoichiometry.
7. References:
