Supporting Information

Complexation of Polyvalent Cyclodextrin Ions with Oppositely Charged Guests. Entropically Favorable Complexation due to Dehydration

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**SI Fig. 1.** This figure shows the saturated complexation-induced shifts ($\Delta\delta_{\text{sat}}$) for the proton signals of the hosts upon addition of the carboxylate anions. The $\Delta\delta_{\text{sat}}$ values were determined from the computer-aided curve fitting for the $^1$H NMR titration curves. The shift in the chemical shift of the NMR signal upon complexation is represented as

$$\Delta\delta = \frac{\Delta\delta_{\text{sat}}(\beta - (\beta^2 - 4K[H][G])^{1/2})}{2K[G]} \tag{1}$$

$$\beta = 1 + K[H] + K[G] \tag{2}$$

In the $p$-CH$_3$-Ph-CO$_2^-$/per-NH$_3^+$-$\beta$-CD system, both signals of the H$_3$ and H$_5$ protons of the host shift to higher magnetic fields due to the shielding effects by the phenyl ring. This means the deep penetration of the guest into the host cavity. Meanwhile, the signal due to H$_5$ proton of per-NH$_3^+$-$\alpha$-CD shifts to lower magnetic field while the H$_3$ proton signal shifts to higher magnetic field upon addition of $p$-CH$_3$-Ph-CO$_2^-$ . The downfield shift of the H$_5$ proton signal suggests that the H$_3$ protons are placed at the deshielding region of the phenyl ring. This means that this guest anion is bound shallowly to the per-NH$_3^+$-$\alpha$-CD cavity. The units for the y axes are $\Delta\delta_{\text{sat}}$/ppm.

**SI Fig. 2.** The cross peaks in the ROESY spectrum of the $p$-CH$_3$-Ph-CO$_2^-$-$\alpha$-CD system was observed between the H$_n$ protons of the guest and the H$_3$ protons of the host and between the CH$_3$ protons of the guest and the H$_5$ and/or H$_6$ protons of the host. These results clearly indicate the orientation of this guest anion in the $\alpha$-CD cavity as shown in SI Fig. 2.
SI Fig. 3. The ROESY spectra of the alkanoate-per-NH$_3^+$-β-CD systems clearly indicate the formation of the complexes where the CO$_2^-$ group of the alkanoate is located in the vicinity of the NH$_3^+$ groups of the host. Coulomb interactions determine the orientation of the guest anion in the CD cavity.

SI Fig. 4. In all cases, the linear relationship was observed in the van’t Hoff plots. It is better to compare the results determined from the NMR measurements with those from microcalorimetry. However, we could not carry out the experiments using the microcalorimeter in the present study. Good linear relationship in the van’t Hoff plots suggests negligibly small effects of $\Delta C_p$. The units for the y axis are $\Delta G$ KJmol$^{-1}$.

SI Fig. 5. The ROESY spectrum of the p-CH$_3$-Ph-CH$_2$NH$_3^+$-per-CO$_2^-$β-CD system clearly suggests the structure of the inclusion complex as shown in this figure. The phenyl group is pulled up by the Coulomb interactions between the SCH$_2$CO$_2^-$ groups of the host and the NH$_3^+$ group of the guest.

SI Fig. 6. The complexation-induced shifts (CIS) in the $^1$H NMR shifts of the neutral guests upon addition of per-CO$_2^-$β-CD suggest that these neutral guests are incorporated deeply into the host cavity. Deep penetration seems to be ascribed to the elongation of the hydrophobic cavity by the
SCH$_2$CO$_2^-$ groups attached to the rim of the host cavity. The units (y axes) are $\Delta\delta_{\text{sat}}$/ppm.
SI Fig. 1. Saturated complexation-induced shifts ($\Delta\delta_{\text{sat}}$) in $^1$H NMR spectra of various CDs upon complexation with anionic guests in D$_2$O at pD 6.0 and 25 °C.
SI Fig. 2. ROESY spectrum of the \( p\text{-CH}_3\text{-Ph-CO}_2^- \) - \( \alpha\text{-CDx} \) system in D\(_2\)O at pD 9.0 and 25 °C.  

\[ [p\text{-CH}_3\text{-Ph-CO}_2^-] = [\alpha\text{-CDx}] = 1 \times 10^{-2} \text{ M}. \]
SI Fig. 3. ROESY spectra and complex structures for C$_5$-CO$_2^-$ - per-NH$_3^+$-β-CD (left) and C$_3$-CO$_2^-$ - per-NH$_3^+$-β-CD (right) in D$_2$O at pD 6.0 and 25°C. [per-NH$_3^+$-β-CD] = [C$_n$-CO$_2^-$] = 1 x 10^{-2} M.
SI Fig. 4. Van’t Hoff plots for complexation of $p$-CH$_3$-Ph-CO$_2^-$ with β-CD (●), mono-NH$_3^+$-β-CD (▲), di-NH$_3^+$-β-CD (m), per-NH$_3^+$-β-CD (n), and per-NH$_3^+$-α-CD (Δ) in D$_2$O at pD 6.0.
**MI Fig. 5.** ROESY spectrum of $p$-CH$_3$-Ph-CH$_2$NH$_3^+$-per-CO$_2^-$ \(\beta\)-CD system in D$_2$O at pD 6.0 and 25 °C. \([\text{per-CO}_2^-\beta\text{-CD}] = 1.2 \times 10^{-2} \text{ M}, \ [p$-\text{CH}_3$-Ph-\text{CH}_2\text{NH}_3^+] = 1.6 \times 10^{-2} \text{ M}.$
SI Fig. 6. Saturated complexation induced shifts (Δδ_{sat}) in $^1$H NMR spectra of per-CO$_2$-β-CD upon complexation with neutral guests in D$_2$O at pD 6 and 25 °C.