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Structural effects of ditopic azoprobe–cyclodextrin complexes on the selectivity of guest-induced supramolecular chirality†

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Benzo-15-crown-5 and dipicolylamine are contained as the binding sites in a ditopic azoprobe (15C5-Azo-*n*-dpa). However, the selectivities of guest-induced supramolecular chirality for cations and anions were dramatically altered by a slight change in the spacer length of (15C5-Azo-*n*-dpa)₂- γ -CyD complexes in water.

Chirality control by supramolecular assemblies and helical polymers based on chiral templates has attracted much attention in recent years.¹ Especially guest-induced chirality control is expected to apply for the development of versatile chiral switching and sensing systems.² To obtain the supramolecular chirality function, cyclodextrins (CyDs) are quite attractive host molecules.³ Optically inert CyDs have a chiral nature in their cavities and can be efficiently combined with various achiral chromoionophores and fluoroionophores to induce chiral nature by forming an inclusion complex with CyDs.⁴ In the previous study, we have reported a ditopic azoprobe (15C5-Azo-2-dpa) bearing benzo-15-crown-5 (B15C5) and dipicolylamine (dpa) as recognition sites. 15C5-Azo-2-dpa was found to form a 2:1 complex with γ -CyD and show a unique response function based on guest-induced supramolecular chirality in water.⁵ By allowing ditopic azoprobes to be incorporated into γ -CyD, we revealed the response behavior of the supramolecular (15C5-Azo-2-dpa)₂- γ -CyD complex in the presence of each cationic and anionic species by measuring induced circular dichroism (ICD) spectra and UV-visible (Vis) absorption spectra. We confirmed that only when K⁺, Zn²⁺, and CO₃²⁻ were all present, a large split-type Cotton effect appeared in the measured ICD spectra and a significant short-wavelength shift took place in the measured UV-Vis spectra. The result clearly demonstrates that the (15C5-Azo-2-dpa)₂- γ -CyD complex can exhibit supramolecular chirality due to the twisted

structure of the azoprobe dimer inside the γ -CyD cavity, only when it recognizes K⁺ and Zn²⁺ in the presence of CO₃²⁻.⁵ From the ICD spectral change, we can estimate the spatial changes of the azoprobe dimer inside γ -CyD, which induce a change in the UV-Vis spectra.⁶ Therefore each guest ion can be selectively detected in the presence of the other guest ions by measuring the spectral changes.

Herein we report how the 15C5-Azo-*n*-dpa structure affects the selectivity of guest-induced supramolecular chirality. The dramatic selectivity changes of supramolecular chirality were found to be noted for (15C5-Azo-*n*-dpa)₂- γ -CyD complexes by controlling the spacer length of 15C5-Azo-*n*-dpa from ethylene (*n* = 2) to propylene (*n* = 3) to butylene (*n* = 4) units (Fig. 1). Also, while 15C5-Azo-*n*-dpa has a dpa binding site for heavy metal ions, the selectivity of guest-induced supramolecular chirality changed from Zn²⁺ for the (15C5-Azo-2-dpa)₂- γ -CyD complex to

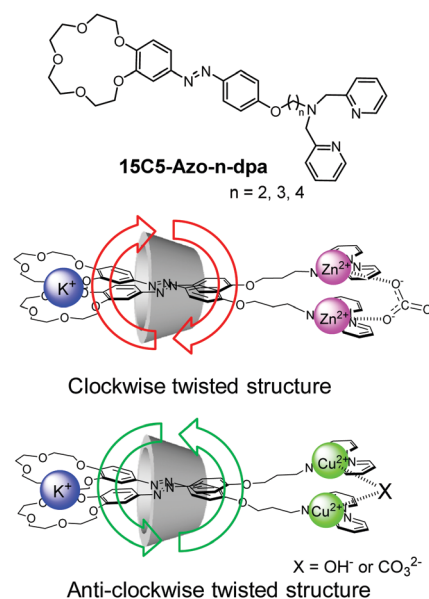
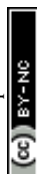


Fig. 1 Structure of 15C5-Azo-*n*-dpa and the twisted structures.

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Cu^{2+} for the $(\mathbf{15C5-Azo-4-dpa})_2\text{-}\gamma\text{-CyD}$ complex. However, most dpa-based chemosensors display Zn^{2+} and/or Cd^{2+} selectivity in water.⁷ Thus this is a unique example where the dpa-based supramolecular sensor exhibits a selectivity change from Zn^{2+} to Cu^{2+} caused by a change in the spacer length. We also report the specific selectivity changes of guest-induced supramolecular chirality for alkali-metal cations and anions based on the change in the spacer length of $(\mathbf{15C5-Azo-n-dpa})_2\text{-}\gamma\text{-CyD}$ complexes in water.

The synthesis of $\mathbf{15C5-Azo-n-dpa}$ was carried out by the azocoupling of 4'-aminobenzo-15-crown-5 with phenol, followed by the introduction of bromoethylene, bromopropylene, and bromobutylene spacers using the Williamson ether synthesis.⁸ Then a dpa moiety was introduced under basic conditions with K_2CO_3 , and the obtained products were purified using silica gel column chromatography. The structures of $\mathbf{15C5-Azo-n-dpa}$ were confirmed *via* ^1H NMR and combustion analyses. Details of the synthesis are available in the ESI.[†]

Job's plot analyses clearly revealed that $\mathbf{15C5-Azo-n-dpa}$ formed a 2 : 1 inclusion complex with $\gamma\text{-CyD}$ in 4% DMSO–96% water (v/v) (Fig. S6, ESI[†]). The ICD spectra of $(\mathbf{15C5-Azo-n-dpa})_2\text{-}\gamma\text{-CyD}$ complexes are depicted in Fig. 2. For $\mathbf{15C5-Azo-2-dpa}$ (Fig. 2a), the selective ICD response was only noted for Zn^{2+} over other metal ions (Mg^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} , as nitrate salts) in the presence of 50 mM K_2CO_3 . The split ICD from the negative peak at 351 nm to the positive peak at 394 nm indicates the clockwise twisted structure of the two azoprobes inside the $\gamma\text{-CyD}$ cavity.⁶ For $\mathbf{15C5-Azo-3-dpa}$, however, the ICD response was found to be observed not only for Zn^{2+} but also for Cu^{2+} in the presence of 50 mM K_2CO_3 . Interestingly the ICD peak shape for Cu^{2+} was opposite compared with that for Zn^{2+} , indicating that the Cu^{2+} complex formed an anti-clockwise twisted structure inside the $\gamma\text{-CyD}$ cavity. This change in the twisted structure may be due to the difference in the coordination configuration; Cu^{2+} was capable of forming a coordination bond with the phenoxy ether oxygen in the dpa complexes,⁹ whereas only a few coordination bonds with the phenoxy ether oxygen were noted for the Zn^{2+} –dpa complexes.¹⁰ For $\mathbf{15C5-Azo-4-dpa}$, the selective ICD response was only noted for Cu^{2+} over other metal ions (Mg^{2+} , Fe^{3+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} , as nitrate salts) in the presence of 50 mM K_2CO_3 . Although $\mathbf{15C5-Azo-n-dpa}$ possesses the same dpa binding site for heavy metal ions, the selectivity was dramatically changed from Zn^{2+} for the $(\mathbf{15C5-Azo-2-dpa})_2\text{-}\gamma\text{-CyD}$ complex to Cu^{2+} for the $(\mathbf{15C5-Azo-4-dpa})_2\text{-}\gamma\text{-CyD}$ complex in the presence of K_2CO_3 . The $(\mathbf{15C5-Azo-3-dpa})_2\text{-}\gamma\text{-CyD}$ complex exhibited selectivity for both Zn^{2+} and Cu^{2+} , indicating an intermediate selectivity between $\mathbf{15C5-Azo-2-dpa}$ and $\mathbf{15C5-Azo-4-dpa}$.¹¹ It is evident that the spacer length of $\mathbf{15C5-Azo-n-dpa}$ played an important role in controlling the selectivity of guest-induced supramolecular chirality. As shown in Fig. 2, it should be noted that the shapes of split Cotton effects based on $\pi\text{-}\pi^*$ transition are not symmetric, indicating the overlap of the Cotton effect based on $n\text{-}\pi^*$ transition at the longer wavelength. In addition, the location of azobenzenes along the z-axis of CyD is known to strongly affect the sign and intensity of the Cotton effect.⁶ Although we consider that the bulky and hydrophobic B15C5 moieties restrict the movement of azobenzenes along the

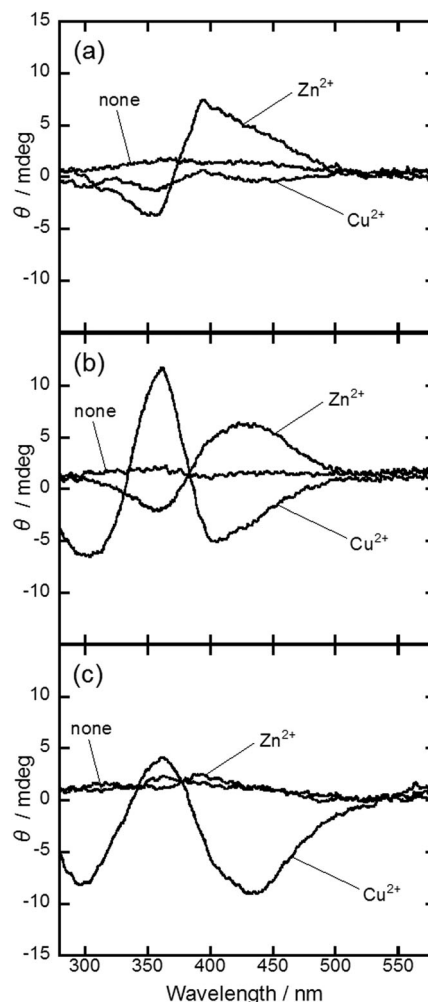
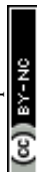


Fig. 2 ICD spectra of $\mathbf{15C5-Azo-n-dpa}/\gamma\text{-CyD}$ sensors in 4% DMSO aq.: (a) $(\mathbf{15C5-Azo-2-dpa})_2$; (b) $(\mathbf{15C5-Azo-3-dpa})_2$; (c) $(\mathbf{15C5-Azo-4-dpa})_2$. $[\mathbf{15C5-Azo-n-dpa}] = 0.04$ mM, $[\text{Zn}(\text{NO}_3)_2] = 0.04$ mM, $[\text{Cu}(\text{NO}_3)_2] = 0.04$ mM, $[\gamma\text{-CyD}] = 5$ mM, $[\text{K}_2\text{CO}_3] = 50$ mM.

z-axis of the $\gamma\text{-CyD}$ cavity, the abovementioned factors make the detailed understanding of guest-induced ICD responses difficult. To obtain further evidence for the guest-induced ICD responses, additional analysis based on molecular mechanics and TD-DFT calculations as well as X-ray crystallography analysis are to be conducted.

In the presence of equivalent amounts of Zn^{2+} with $\mathbf{15C5-Azo-n-dpa}$ (20 μM), and 50 mM CO_3^{2-} , the ICD intensities at the maximum wavelength are plotted against the alkali metal ion diameter (Fig. 3a). As we reported previously, the $(\mathbf{15C5-Azo-2-dpa})_2\text{-}\gamma\text{-CyD}$ complex exhibited high K^+ ion selectivity over other alkali metal ions in the presence of Zn^{2+} and CO_3^{2-} . This selectivity is consistent with the selectivity of sandwich complex formation of the two benzo-15-crown-5 derivatives with alkali metal ions.^{8,12} However, for the $(\mathbf{15C5-Azo-3-dpa})_2\text{-}\gamma\text{-CyD}$ complex, the alkali metal ion selectivity was significantly reduced (Fig. 3a). This indicates that the formation of the clockwise twisted structure is dominated only by the bridge formation of CO_3^{2-} with the two dpa- Zn^{2+} complexes in the



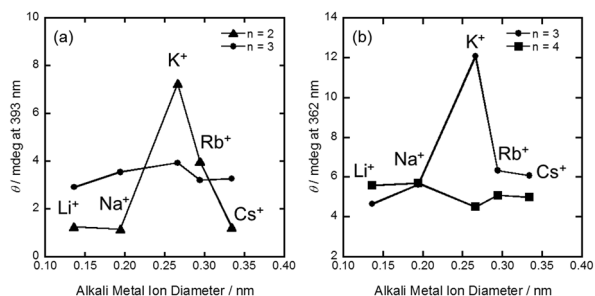


Fig. 3 Selectivity of **15C5-Azo-*n*-dpa**/γ-CyD sensors toward alkali metal ions in 4% DMSO aq., [γ-CyD] = 5 mM, [alkali metal ion] = 50 mM: (a) [**15C5-Azo-2-dpa**], [**15C5-Azo-3-dpa**] = 0.04 mM, [Zn(NO₃)₂] = 0.04 mM; (b) [**15C5-Azo-3-dpa**], [**15C5-Azo-4-dpa**] = 0.04 mM, [Cu(NO₃)₂] = 0.04 mM.

(**15C5-Azo-3-dpa**)₂-γ-CyD complex. The enhanced flexibility of **15C5-Azo-*n*-dpa** upon changing the spacer from ethylene (*n* = 2) to propylene (*n* = 3) should be the reason of this selectivity change. On the other hand, in the presence of equivalent amounts of Cu²⁺ with **15C5-Azo-*n*-dpa** (20 μM), and 50 mM CO₃²⁻, the (**15C5-Azo-3-dpa**)₂-γ-CyD complex exhibited high K⁺ ion selectivity similar to the Zn²⁺ system of the (**15C5-Azo-2-dpa**)₂-γ-CyD complex (Fig. 3b). However, for the (**15C5-Azo-4-dpa**)₂-γ-CyD complex, no alkali metal ion selectivity was observed in the anti-clockwise twisted structure of the two azoprobes inside the γ-CyD cavity (Fig. 3b). This is also ascribed to the enhanced flexibility of **15C5-Azo-*n*-dpa** upon changing the spacer from propylene (*n* = 3) to butylene (*n* = 4).

The effect of anion species on the ICD responses was also examined for (**15C5-Azo-*n*-dpa**)₂-γ-CyD complexes. For the Zn²⁺ complex system of (**15C5-Azo-*n*-dpa**)₂-γ-CyD complexes (*n* = 2, 3), the effects of salt species on ICD responses were examined in the presence of 50 mM KX (X = NO₃⁻, CH₃CO₂⁻, and OH⁻). The results are depicted in Fig. 4. Similar to the (**15C5-Azo-2-dpa**)₂-γ-CyD complex, the (**15C5-Azo-3-dpa**)₂-γ-CyD complex exhibited high CO₃²⁻ selectivity, indicating that CO₃²⁻ bridging with the two Zn²⁺-dpa binding sites induced the clockwise twisted structure of the azoprobe dimer inside the γ-CyD cavity. In addition, direct evidence of the relative orientation of the azoprobes and the macrocyclic ring was obtained *via* NOESY experiments. Cross-peaks between H3 protons inside the CyD cavity and protons of the azoprobes were clearly observed (Fig. S7, ESI†).

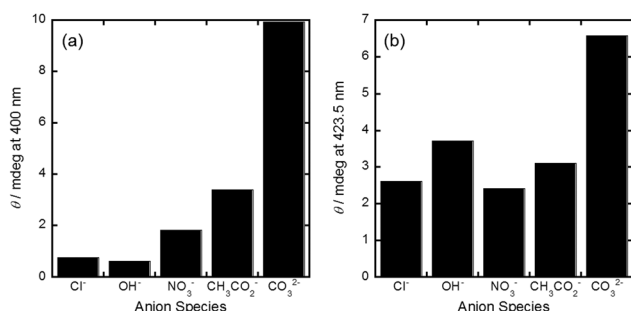


Fig. 4 Selectivity of (**15C5-Azo-*n*-dpa-Zn²⁺**)₂-γ-CyD sensors toward anions in 4% DMSO aq.: (a) [**15C5-Azo-2-dpa**] = 0.04 mM; (b) [**15C5-Azo-3-dpa**] = 0.04 mM, [Zn(NO₃)₂] = 0.04 mM, [γ-CyD] = 5 mM, [Cl⁻], [OH⁻], [NO₃⁻], [CH₃CO₂⁻], [CO₃²⁻] = 50 mM.

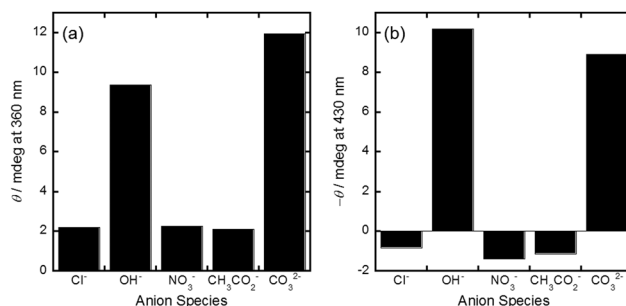


Fig. 5 Selectivity of (**15C5-Azo-*n*-dpa-Cu²⁺**)₂-γ-CyD sensors toward anions in 4% DMSO aq.: (a) [**15C5-Azo-3-dpa**] = 0.04 mM; (b) [**15C5-Azo-4-dpa**] = 0.04 mM, [Cu(NO₃)₂] = 0.04 mM, [γ-CyD] = 5 mM, [Cl⁻], [OH⁻], [NO₃⁻], [CH₃CO₂⁻], [CO₃²⁻] = 50 mM.

On the other hand, for the Cu²⁺ complex system of (**15C5-Azo-*n*-dpa**)₂-γ-CyD complexes (*n* = 3 and 4), the (**15C5-Azo-*n*-dpa**)₂-γ-CyD complexes showed both CO₃²⁻ and OH⁻ selectivity (Fig. 5). This indicates that hydroxo-bridging between the two Cu²⁺-dpa binding sites induced the anti-clockwise twisted structure of the azoprobe dimer in the (**15C5-Azo-*n*-dpa**)₂-γ-CyD complex. Thus, by changing the metal species of the dpa binding sites, the anion selectivity of the (**15C5-Azo-3-dpa**)₂-γ-CyD complex can be easily controlled from the CO₃²⁻ selectivity with the Zn²⁺ system to both CO₃²⁻ and OH⁻ selectivity with the Cu²⁺ system in water. These are apparently a unique function of guest-induced supramolecular chirality based on (**15C5-Azo-*n*-dpa**)₂-γ-CyD complexes.

In conclusion, we have shown a novel guest-induced supramolecular chirality induced by twisted structural switching of the two **15C5-Azo-*n*-dpa** molecules inside the γ-CyD chiral cavity due to multi-point recognition of guest ions by the ditopic azoprobes in water. Although the two recognition sites are the same, a slight change in the spacer length of **15C5-Azo-*n*-dpa** was found to significantly affect the ICD response selectivity of (**15C5-Azo-*n*-dpa**)₂-γ-CyD complexes. To the best of our knowledge, this is a novel selectivity control based on guest-induced supramolecular chirality which completely differs from the design strategy of conventional molecular recognition systems.

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Conflicts of interest

There are no conflicts to declare.

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