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Social Self-Sorting: Alternating Supramolecular Oligomer Consisting of Isomers

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Abstract: The isomers of cinnamoyl α -CDs (2-CiO- α -CD and 3-CiO- α -CD) organize by themselves to give different types of supramolecular complexes in aqueous solutions. 2-CiO- α -CD was found to form a double-threaded dimer, which was characterized by single crystal X-ray analysis. The molecular sizes of supramolecular complexes consisting of CiO- α -CDs were estimated by pulsed field gradient spin-echo NMR, which gives the diffusion coefficient (D). D of 2-CiO- α -CD was found to be 2.3×10^{-10} m²/s at concentrations over 10 mM and D was saturated. It should be noted that the hydrodynamic radius derived from D of 2-CiO- α -CD was found to be 9.6 Å, which closely matched the result from the single crystal X-ray analysis. D of 3-CiO- α -CD, however, was smaller than that of 2-CiO- α -CD at concentrations over 32 mM, indicating that 3-CiO- α -CD formed a supramolecular oligomer. Two-dimensional (2D)-ROESY spectra of the mixture of 2-CiO- α -CD and 3-CiO- α -CD did not show a correlation between the same species; rather, correlation peaks between 2-CiO- α -CD and 3-CiO- α -CD were observed. D 's of a mixture of 2-CiO- α -CD and 3-CiO- α -CD were found to be larger than those of 2-CiO- α -CD and 3-CiO- α -CD, respectively, indicating that the mixture of 2-CiO- α -CD and 3-CiO- α -CD formed an alternative supramolecular oligomer and not a self- or random- supramolecular complex. CDs recognize a guest molecule and the substitutional position of a guest molecule on CD, suggesting that CDs have social self-sorting capability.

Introduction

Biological materials, such as microtubules¹ and hemoglobin,² are composed of two kinds of building blocks. These molecules exhibit a high affinity for one another and, hence, are referred to as social self-sorting.³ Notable self-sorting systems have been constructed on the basis of the formation of hydrogen bonds,⁷

coordination bonds,^{8–17} solvophobic effects,^{18,19} dynamic covalent bonds.^{20–22} In recent years, supramolecular assemblies^{23–26} and supramolecular polymers^{27–29} from enantiomers were designed by researchers. In many cases, the mixture of isomers led to formation of homosupramolecular assemblies and supramolecular polymers, indicating that in the process of narcissistic self-sorting,³⁰ molecules that show a high affinity for

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themselves operate in these systems. Social self-sorting is comparatively rare in supramolecular assemblies^{31–33} because two hetero units often form a thermodynamically unfavorable structure to assemble to a less compact structure. Therefore, although there have been reports on the preparation of supramolecular alternating copolymers,^{34–42} two heterochiral units make

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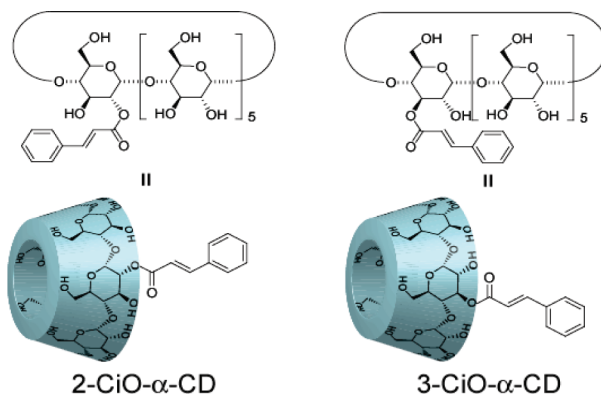


Figure 1. Structures of 2-CiO- α -CD and 3-CiO- α -CD.

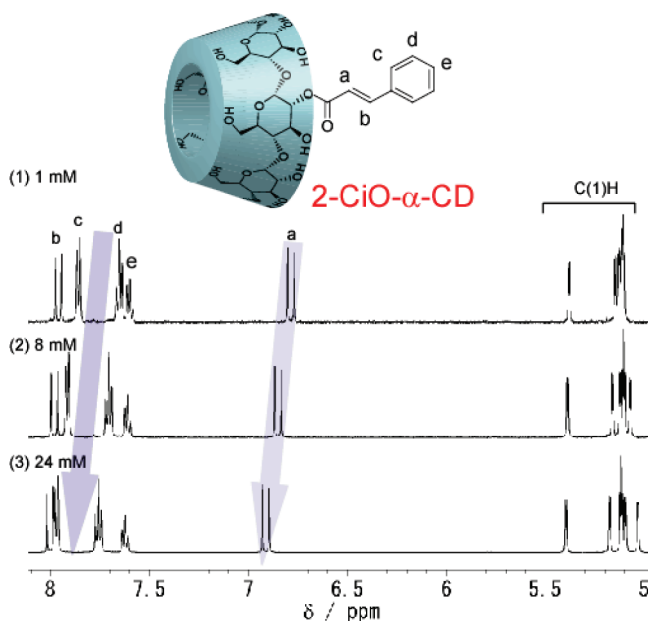


Figure 2. ^1H NMR spectra at various concentrations (1.0 mM, 8.0 mM, and 24 mM) of 2-CiO- α -CDs in D_2O at 30 °C.

it extremely difficult to form an alternating supramolecular polymer using a mixture of isomers. In our study, we have prepared isomers of cinnamoyl α -CD. We observed the formation of homosupramolecular complexes by each isomer, and the formation of an alternating supramolecular oligomer by the mixture of isomers in such a way that represents a social self-sorting system.

Results and Discussion

Preparation of Cinnamoyl- α -CDs (2-CiO- α -CD and 3-CiO- α -CD). Cinnamoyl α -CDs (CiO- α -CD) on the secondary hydroxyl group were prepared by the reaction of *m*-nitrophenyl cinnamate with α -CD in a basic aqueous solution (pH = 9).

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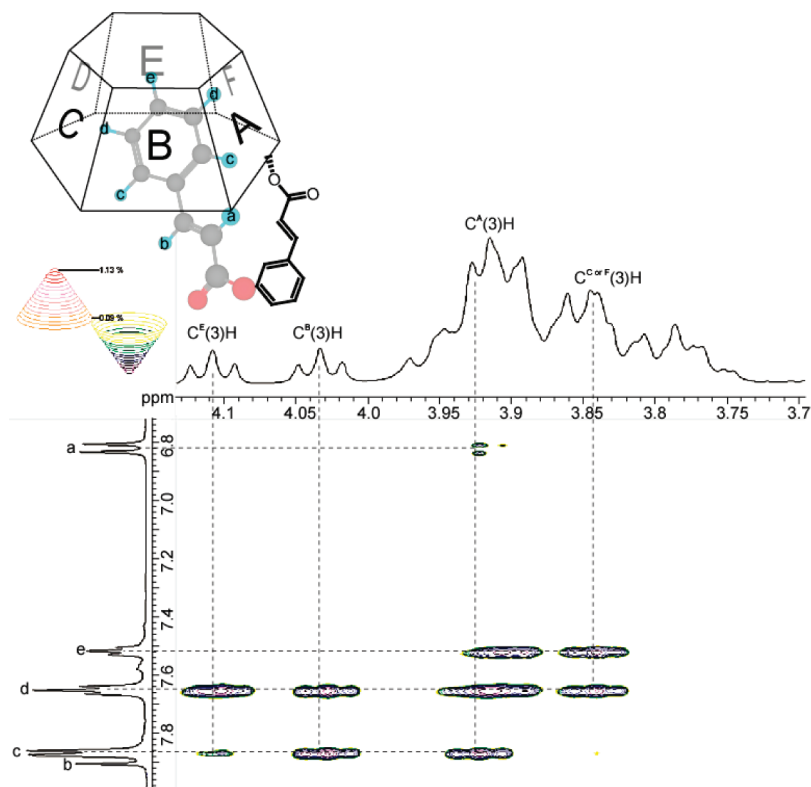


Figure 3. 600 MHz ROESY spectrum of 2-CiO- α -CD in D₂O (24 mM) at 20 °C (mixing time = 100 s).

The reaction involved an ester exchange by way of inclusion of the ester in the CD cavity. The product was found to be a mixture of 2-cinnamoyl α -CD (2-CiO- α -CD) and 3-cinnamoyl α -CD (3-CiO- α -CD) (Figure 1). Both isomers were purified by reversed phase HPLC.

Formation of Homosupramolecular Oligomer from 2-CiO- α -CD or 3-CiO- α -CD. The ^1H NMR spectra of 2-CiO- α -CD showed that the peaks of 2-CiO- α -CD shifted downfield with an increase in the concentration (Figure 2), suggesting the intermolecular supramolecular complex in aqueous solutions. The 2D ROESY spectrum of 2-CiO- α -CD showed correlation peaks between C(3)-H in the inner protons of α -CD and cinnamoyl protons in D₂O, whereas the C(5)-H of the inner protons of α -CD did not show correlation peaks with protons of the cinnamoyl group (Figure 3). These results indicate that the cinnamoyl group is included from the secondary hydroxyl group side (wider rim). We obtained a single crystal of 2-CiO- α -CD suitable for X-ray crystallographic analysis. The X-ray crystallographic analysis showed formation of a double-threaded dimer (Figure 4). This result is in an excellent agreement with the 2D ROESY experiments.

The correlation peaks of the 2D ROESY spectrum of 3-CiO- α -CD were similar to that of 2-CiO- α -CD (Figure 5), suggesting that the cinnamoyl part is included from the wider rim of the α -CD.

To compare the molecular size of supramolecular complexes incorporating CiO- α -CDs, diffusion coefficients (D 's) of the supramolecular complexes were determined by the pulse field gradient spin-echo (PFG) NMR technique. Although the D of 2-CiO- α -CD shows an unvarying value over 10 mM and reached $2.3 \times 10^{-10} \text{ m}^2/\text{s}$ at 32 mM, the D of 3-CiO- α -CD decreased monotonously with increasing concentration, then reached $1.7 \times 10^{-10} \text{ m}^2/\text{s}$ at 64 mM. The hydrodynamic radius of 2-CiO- α -CD calculated by D 's at concentrations over 10 mM

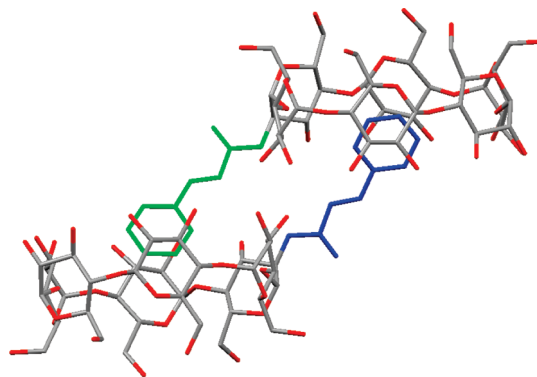


Figure 4. Crystal structure of 2-CiO- α -CD. Carbon and oxygen of α -CD are shown in gray and red, respectively. Carbon and oxygen of cinnamoyl groups are shown in blue and light green, respectively.

was found to be 9.6 Å, which is in agreement with that calculated from single crystal X-ray analysis. These results indicate that 2-CiO- α -CD forms a double threaded dimer over 10 mM. It should be noted that the D 's of 3-CiO- α -CD showed a concentration dependence, but D 's of 2-CiO- α -CD did not. These results indicate that 3-CiO- α -CD forms a supramolecular oligomer at concentrations greater than 32 mM in aqueous solutions.

Formation of Heterosupramolecular Oligomer from the Mixture of 2-CiO- α -CD or 3-CiO- α -CD. Although 2-CiO- α -CD is sparingly soluble in D₂O, when 2-CiO- α -CD was mixed with 3-CiO- α -CD in water, 2-CiO- α -CD was easily solubilized and gave a clear solution. This result suggests that 2-CiO- α -CD formed complexes with 3-CiO- α -CD to give soluble supramolecules. The 2D ROESY spectrum of the mixture of 2-CiO- α -CD and 3-CiO- α -CD clearly showed that olefin and aromatic protons of 3-CiO- α -CD correlated with inner protons

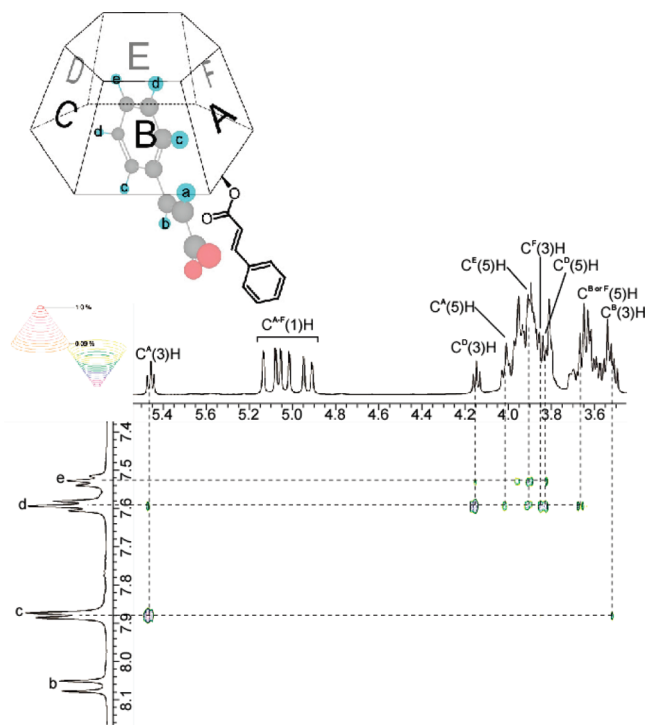


Figure 5. 600 MHz ROESY spectrum of 3-CiO- α -CD in D₂O (24 mM) at 20 °C (mixing time = 200 ms).

(C(3)-H) of 2-CiO- α -CD and vice versa (Figure 6). However, cinnamoyl protons of 3-CiO- α -CD and 2-CiO- α -CD, respectively, did not correlate with their own inner protons (C(3)-H). It should be noted that although correlation peaks between 2-CiO- α -CD and 3-CiO- α -CD were observed, correlation peaks between the same species were not. These results indicate that a mixture of 2-CiO- α -CD and 3-CiO- α -CD forms an alternating supramolecular complex and not a self-supramolecular complex.

D 's of a 1:1 mixture of 2-CiO- α -CD and 3-CiO- α -CD were calculated from the proton intensity decay of 2-CiO- α -CD and 3-CiO- α -CD, respectively. Figure 7 shows the D 's of the mixture of 2-CiO- α -CD and 3-CiO- α -CD calculated from the **2a** proton intensity of 2-CiO- α -CD. Even though calculated by a **2a** proton, the D 's of the mixture showed much lower values than those of individual isomers, especially those of 2-CiO- α -CD. These results indicate that the mixture of 2-CiO- α -CD and 3-CiO- α -CD did not form individual self-supramolecular complexes, but rather cooperatively formed heterosupramolecular oligomers.

The turbo ion spray TOF mass spectrum provides direct evidence of the formation of a supramolecular oligomer. The mass spectrum of the 1:1 mixture of 2-CiO- α -CD and 3-CiO- α -CD showed oligomeric peaks assigned as sodium cation adducts in aqueous solutions (Figure 8). The spectrum showed that the peaks appeared at intervals of av. 1102.4 Da, which corresponded to a CiO- α -CD monomer unit. These results indicate that the mixture of 2-CiO- α -CD and 3-CiO- α -CD formed a supramolecular oligomer in an aqueous solution.

Association Constants for Formation of Homo- and Hetero-supramolecular Oligomers. Formations of supramolecular complexes consisting of CiO- α -CDs are summarized in Figure 9. The association constant (K) of 2-CiO- α -CD for dimerization is found to be $K_{2\text{-CiO}} = 4.1 \pm 0.55 \times 10^2 \text{ M}^{-1}$, and that of 3-CiO- α -CD is $K_{3\text{-CiO}} = 1.0 \pm 0.17 \times 10^2 \text{ M}^{-1}$. Single crystal X-ray analysis of 2-CiO- α -CD indicated the formation of a double

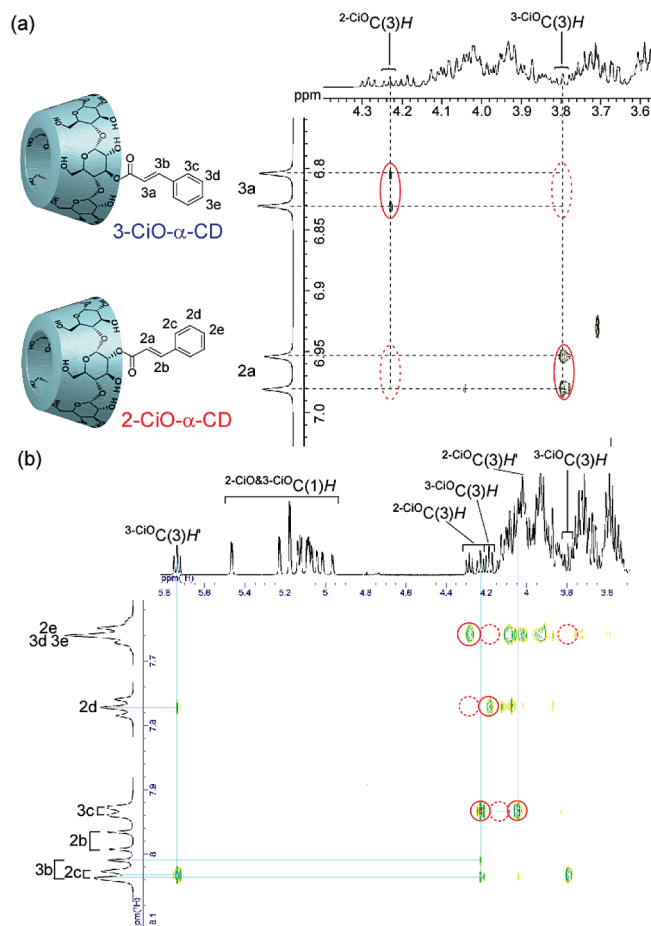


Figure 6. Two-dimensional ROESY NMR spectra of the mixture of 2-CiO- α -CD and 3-CiO- α -CD in D₂O (32 mM) at 20 °C. The spectrum shows the partial area between inner protons of CiO- α -CDs and olefin protons of the cinnamoyl group. The correlation peaks were observed in the area of solid circles, whereas in the dash circles were not observed. Full spectrum is shown in Figure S5 in Supporting Information.

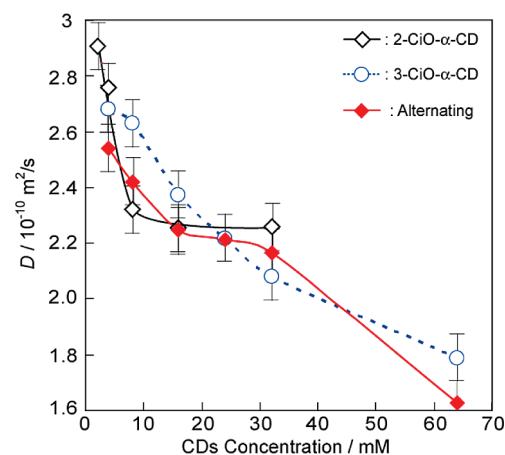


Figure 7. Plots of diffusion coefficients (D 's) of 2-CiO- α -CD (red \diamond), 3-CiO- α -CD (black \circ) and the mixture of 2-CiO- α -CD and 3-CiO- α -CD (red \blacklozenge). D 's of 2-CiO- α -CD, 3-CiO- α -CD, and the mixture of 2-CiO- α -CD and 3-CiO- α -CD were calculated by using a **2a** proton, a **3a** proton, and a **2a** proton, respectively, in D₂O at 30 °C.

threaded dimer. The complementary dimerization of 2-CiO- α -CD led $K_{2\text{-CiO}}$ to be larger than $K_{3\text{-CiO}}$. In contrast, K_{Hetero} between 2-CiO- α -CD and 3-CiO- α -CD was found to be $K_{\text{Hetero-1}} = 2.1 \pm 0.33 \times 10^3 \text{ M}^{-1}$ (dimerization) and $K_{\text{Hetero-2}} = 1.5 \pm 0.23 \times$

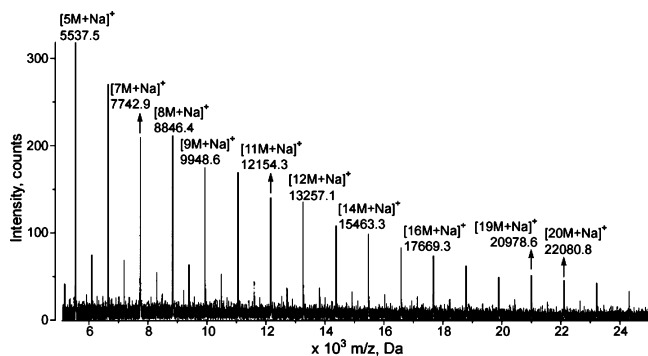


Figure 8. Turbo-ion spray TOF mass spectrum of the 1:1 mixture of 2-CiO- α -CD (8.0 mM) and 3-CiO- α -CD (8.0 mM) in an aqueous solution (total concentration; 16 mM).

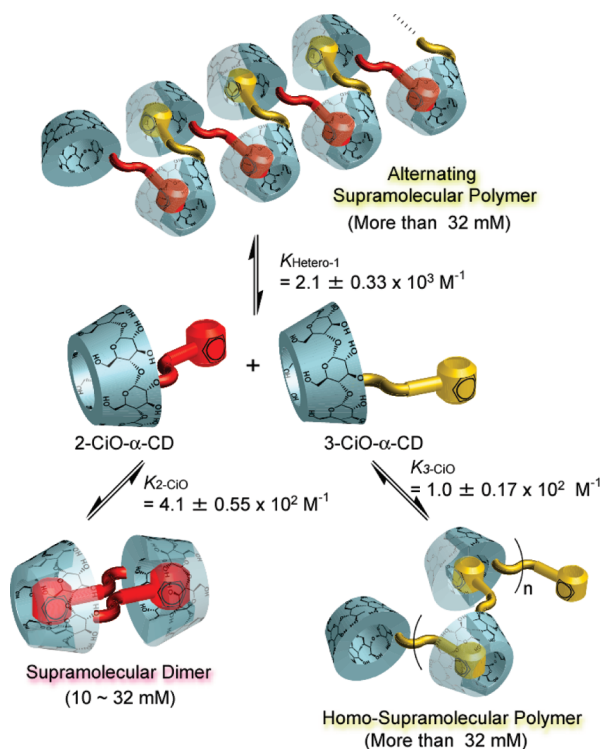


Figure 9. Illustration of the formation of supramolecular complexes using CiO- α -CDs.

10^3 M^{-1} (trimerization), which are much higher than those of individual homocomplexes. These results indicate that the formation of heterosupramolecular complexes between 2-CiO- α -CD and 3-CiO- α -CD have a priority over that of the homosupramolecular complexes in diluted conditions. Previously, Meijer has reported that the maximum degree of polymerization, $n_{\text{max}} = (KC)^{1/2}$, in which K is the association constant and C is the concentration. When we follow this equation, the mixture of 2-CiO- α -CD and 3-CiO- α -CD formed

$n_{\text{max}} = 8$ at 32 mM and $n_{\text{max}} = 11$ at 64 mM.^{43–49} On the basis of these studies of the diffusion coefficients, the mass spectrum,⁵⁰ and the association constant, K_{Hetero} , the mixture of 2-CiO- α -CD and 3-CiO- α -CD forms alternating supramolecular oligomer.

Conclusion

2-CiO- α -CD and 3-CiO- α -CD organized by themselves to give a double threaded dimer and a supramolecular oligomer at high concentrations, respectively. The addition of 2-CiO- α -CD to an aqueous solution of 3-CiO- α -CD triggered the formation of heterosupramolecular complexes by a social self-sorting system. It should be noted that CiO- α -CDs recognized the difference in the substitution position on a glucopyranose unit. Moreover, the mixture of 2-CiO- α -CD and 3-CiO- α -CD formed alternating supramolecular oligomer over 32 mM and not self- or random-supramolecular complexes. We conclude that it is important not only that hydrophobic interactions but also π - π stacking and hydrogen-bonding interactions function cooperatively to create social-self-sorting system.

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Supporting Information Available: Selected NMR data (1D NMR and ROESY spectra), determination of the association constant and the diffusion coefficient; movie file of the crystal structure of 2-CiO- α -CD; CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (50) The species of supramolecular oligomer up to the 20 mer were observed in the mass spectrum in Figure 7 because the supramolecular oligomer has a distribution and the desolvation process of ionizations leads to formation of larger supramolecular oligomeric species by an increase in the concentration.