

Guest-Free Self-Assembly of α -Cyclodextrins Leading to Channel-Type Nanofibrils as Mesoporous Framework

Jae Woo Chung, Tae Jin Kang, and Seung-Yeop Kwak*

Department of Materials Science and Engineering, Seoul National University, San 56-1, Sillim-dong, Gwanak-gu, Seoul 151-744, Korea

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Guest-free α -cyclodextrin self-assembly (α -CD-SA) was successfully obtained through a simple treatment such as sonication of α -CD in a specific solvent. From wide-angle X-ray diffraction (WAXD), it was found that the crystalline structure of α -CD changed upon increasing the treatment time, resulting in α -CD-SA in which the α -CDs were closely packed in the vertical direction and hexagonally aligned in the horizontal direction (what is called as “channel structure”). In particular, these structures were developed only in tetrahydrofuran (THF) as a specific solvent. In addition, it was found by inclusion experiment and field-emission scanning electron microscopy (FE-SEM) that propionic acid was able to be included into the channel of α -CD-SA and that α -CD-SA had α -CD bundles with a fibril-like shape, respectively. These results demonstrate that the α -CD-SA consists of nanofibril-like α -CD bundles with cylindrical nanopores open at least at one end, resulting from the dispersion of α -CD molecules by sonication in THF and the subsequent re-formation of strong hydrogen bonding between the α -CDs with the aid of THF (so-called “slow recrystallization”). Interestingly, it was observed from FE-SEM and nitrogen adsorption–desorption measurement that the α -CD-SA had a wormhole-like mesopore with inkbottle shape (average desorption pore size = ca. 25 nm). This mesoporous structure was considered to be attributed to the formation of a mesoporous framework by the disordered aggregation of the nanofibril-like α -CD bundles.

Introduction

In recent decades, cyclic compounds have found wide application in supramolecular chemistry as building blocks for the creation of ordered and functionalized assemblies.^{1–5} In particular, much attention has focused on the ordered stacking of cyclic compounds, resulting in the formation of tubular assemblies with a channel structure. The cyclic oligomers of glucose known as cyclodextrins (CDs) are ideal candidates, capable of providing a channel structure, attributed to their stacking.⁶ Covalent and noncovalent tubular assemblies with channel structures based on CDs have recently been reported. Covalent tubular assemblies have been obtained by cross-linking CDs in inclusion complexes (ICs) with epichlorohydrin and the subsequent removal of the included polymeric guest.⁶ Noncovalent tubular assemblies have been constructed by removing the included polymer from an IC under the action of a selective organic solvent that is inert in relation to the CD.⁷ These CD tubular assemblies are of interest as highly ordered structures that possess extensive cylindrical nanopores due to the channel structure and have the potential to be used as nanoscopic filters, biosensors, catalysts, and photoresponsive materials.^{8,9} However, these approaches involve painstaking procedures, such as the

inclusion and dissociation of guest molecules in the CD cavity in order to obtain cylindrical nanopores, although they provided noteworthy methods for constructing tubular structures with cylindrical nanopores based on CDs. Tonelli et al.¹⁰ have reported that tubular CD assemblies with cylindrical nanopores can be achieved without the use of guest molecules by recrystallization of the CD using a solvent–nonsolvent system (e.g., water–chloroform or water–acetone system), so attention has increasingly been paid to the formation without the use of guest molecules of CD self-assemblies with cylindrical nanopores.

In this study, we achieved a guest-free α -cyclodextrin self-assembly (α -CD-SA) by means of a simple method consisting of the sonication of the α -CD in a specific solvent. We report herein that a nanofibril-like α -CD bundle with a cylindrical nanopore open at least at one end can be simply constructed and then used as a framework for the generation of a mesoporous structure by reorganization of α -CD attributed to sonication in a specific solvent, which opens up the possibility of creating novel and functional materials from CDs with self-assembly.

Experimental Section

Materials. α -Cyclodextrin (α -CD) and tetrahydrofuran (THF, 99%) was supplied from Walker-GmbH and Daejung Chemicals & Metals, respectively. Propionic acid (PA, 99%) was purchased from Tokyo Kasei Kogyo Co., Ltd. All samples were used as received without any additional purification.

Self-Assembly of α -CD. For the construction of the α -CD self-assembly (α -CD-SA), 0.15 g of α -CD was added to 30 mL of THF and sonicated using a Bransonic 3510 sonicator (Branson) for 12 h. During the sonication, reaction temperature slightly increased from 25 to 37 °C. After THF treatment, dispersed products were collected by filtering and dried overnight in a vacuum oven at room temperature.

Inclusion of Guest Molecule into the Channels of the α -CD-SA. α -CD-SA (0.15 g) was added to 10 mL of PA. The resulting

* Correspondence author. Tel: +82-2-880-8365. Fax: +82-2-885-1748. E-mail: sykwak@snu.ac.kr.

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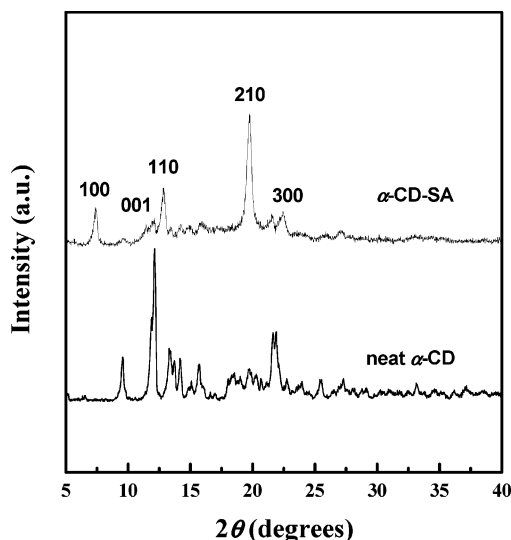


Figure 1. WAXD profiles of neat α -CD and α -CD-SA.

suspension was allowed to stand overnight at room temperature. The precipitate was separated by vacuum filtration and then washed several times with THF to remove the unincorporated PA. The final precipitate (i.e., PA- α -CD-SA) was vacuum-dried at room temperature.

Measurements. Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature on a MAC/Science MXP 18XHF-22SRA diffractometer with a Cu K α radiation source (wavelength = 0.154 nm). The supplied voltage and current were set to 50 kV and 200 mA, respectively. Powder samples were mounted on a sample holder and scanned at a rate of $2\theta = 5^\circ \text{ min}^{-1}$ between $2\theta = 5^\circ$ and 40° . Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum GX spectrometer at frequency ranging from 400 to 4000 cm^{-1} . Differential scanning calorimetry (DSC) analysis was performed using a TA instruments DSC 2920 under nitrogen flow. DSC thermograms were recorded during heating from -70 to 220°C at a heating rate of $10^\circ \text{C min}^{-1}$. The morphologies of the neat α -CD and α -CD-SA were visualized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F). The FE-SEM samples were coated with a thin conductive Pt layer prior to observation. The specific surface area and pore size distribution were evaluated by analyzing the nitrogen adsorption and desorption isotherms obtained at 77 K using Micrometrics ASAP 2000 equipment. All the samples were degassed at 150°C and 10^{-6} Torr for 4 h prior to these measurements. The surface areas of the samples were calculated with the Brunauer–Emmett–Teller (BET) equation, and their pore size distributions were determined by using the Barrett–Joyner–Halenda (BJH) equation from the desorption branch.

Results and Discussion

Crystalline structures of neat α -CD and α -CD-SA, which was prepared by sonication of neat α -CD in THF for 12 h, were investigated using WAXD. As shown in Figure 1, neat α -CD exhibits a cage-type single crystalline structure. For α -CD-SA, however, peaks at $2\theta = 7.4^\circ$ (100), 12.7° (110), and 22.5° (300) are clearly observed with a ratio between the $\sin^2(\theta)$ values for the (100), (110), and (300) peaks of 1:3:9, suggesting the presence of hexagonal symmetry in the horizontal direction.¹¹ In addition, a sharp reflection with prominent (210) peak at $2\theta = 19.6^\circ$ is observed for α -CD-SA. These demonstrate that α -CDs are closely packed in the vertical direction (what is called the “channel-type structure”) and α -CD channels are hexagonally aligned in the

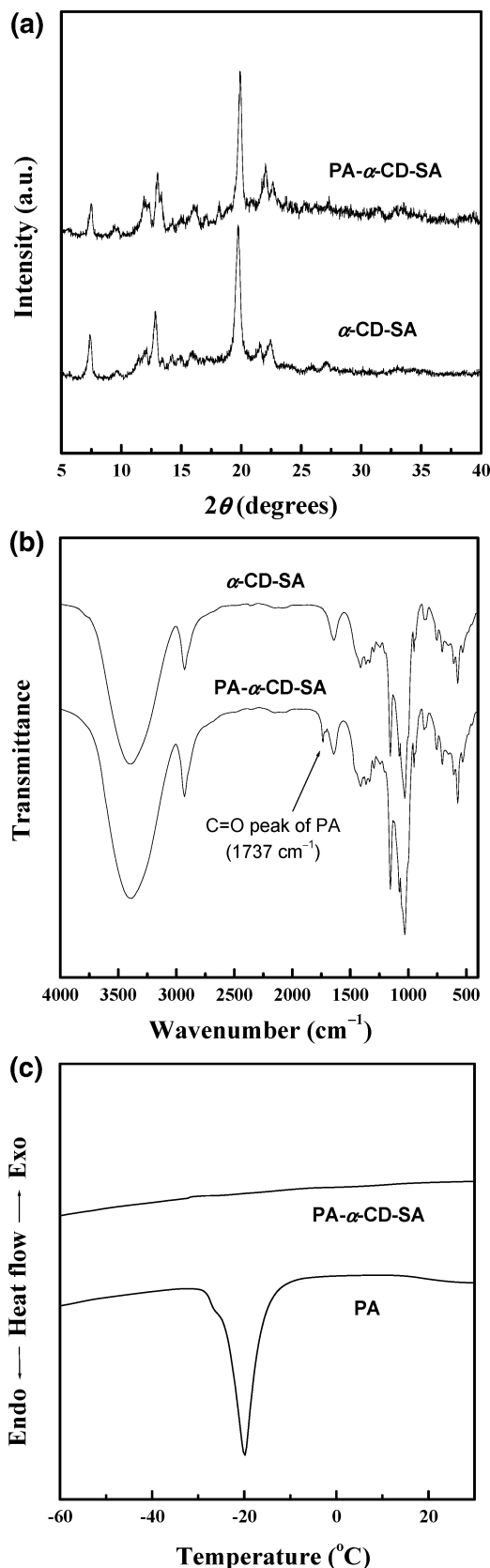


Figure 2. Inclusion test of α -CD-SA with PA: (a) WAXD profiles, (b) FT-IR spectra, and (c) DSC scans of α -CD-SA and PA- α -CD-SA.

horizontal direction during the sonication in THF (see Figure 6a).^{11–17} In particular, it was found that the crystalline structure of α -CD slowly changed as the THF treatment progresses without a critical threshold time for structural change (Supporting

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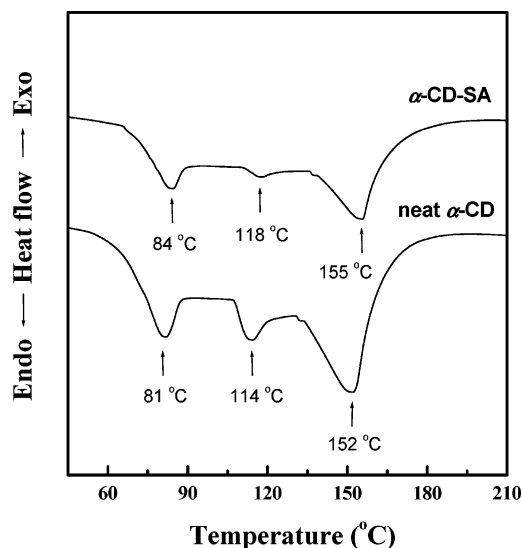


Figure 3. DSC scans of neat α -CD and α -CD-SA.

Information, Figure S-1). In order to verify the presence of cylindrical nanopores attributed to channel formation in α -CD-SA, an inclusion test of α -CD-SA with PA was carried out. It has already been known that PA was able to be included into the cavity of α -CD, resulting in a cage-type inclusion complex.¹⁸ As shown in Figure 2a, however, α -CD-SA treated with PA (PA- α -CD-SA) has a similar WAXD profile compared to α -CD-SA, in spite of the PA treatment. This reveals that the channel structure of α -CD-SA is still maintained. Moreover, the FT-IR spectrum of PA- α -CD-SA clearly shows a carbonyl peak at 1737

cm^{-1} attributed to the inclusion of PA in the channel of α -CD-SA, whereas no carbonyl peak is observed for α -CD-SA (Figure 2b). DSC scans of PA and PA- α -CD-SA in Figure 2c also demonstrate that PA is fully included in the channel of α -CD-SA without free PA adsorbed onto the outer surface of PA- α -CD-SA; if the PA component is not included, then an endothermic peak for fusion of free crystalline PA will be observed in DSC scans. These give strong evidence that PA is well-included into the channel of α -CD-SA and that α -CD-SA has a cylindrical nanopore structure open at least at one end. In fact, Tonelli et al. have suggested that hydrogen bonding between CDs, which is mediated by the water molecules, is a critical factor for reorganization of α -CD resulting in the formation of the channel structure.¹⁰ As shown in Figure 3, it is found that neat α -CD has three endothermic peaks (81, 114, and 152 °C) brought about by the dehydration of water molecules presented in the cavity and outer surface of α -CD, which is consistent with results of Tonelli.¹⁰ α -CD-SA is also observed to have endothermic peaks similar to those of neat α -CD, indicating the existence of water molecules. However, it is found that the dehydration temperatures of α -CD-SA (84, 118, and 155 °C) are higher than those of α -CD. This reveals that strong hydrogen bonding is re-formed in α -CD-SA compared to α -CD. Furthermore, we observed that the channel structure was not developed for the α -CD treated by THF without sonication and the α -CD treated by other solvent with sonication (Supporting Information, Figure S-2 and S-3, respectively). Thus, reorganization of α -CD, which results in the generation of α -CD-SA, is thought to be due to the breaking of innate water-mediated hydrogen bonding between α -CDs by sonication in THF and the subsequent re-formation of strong

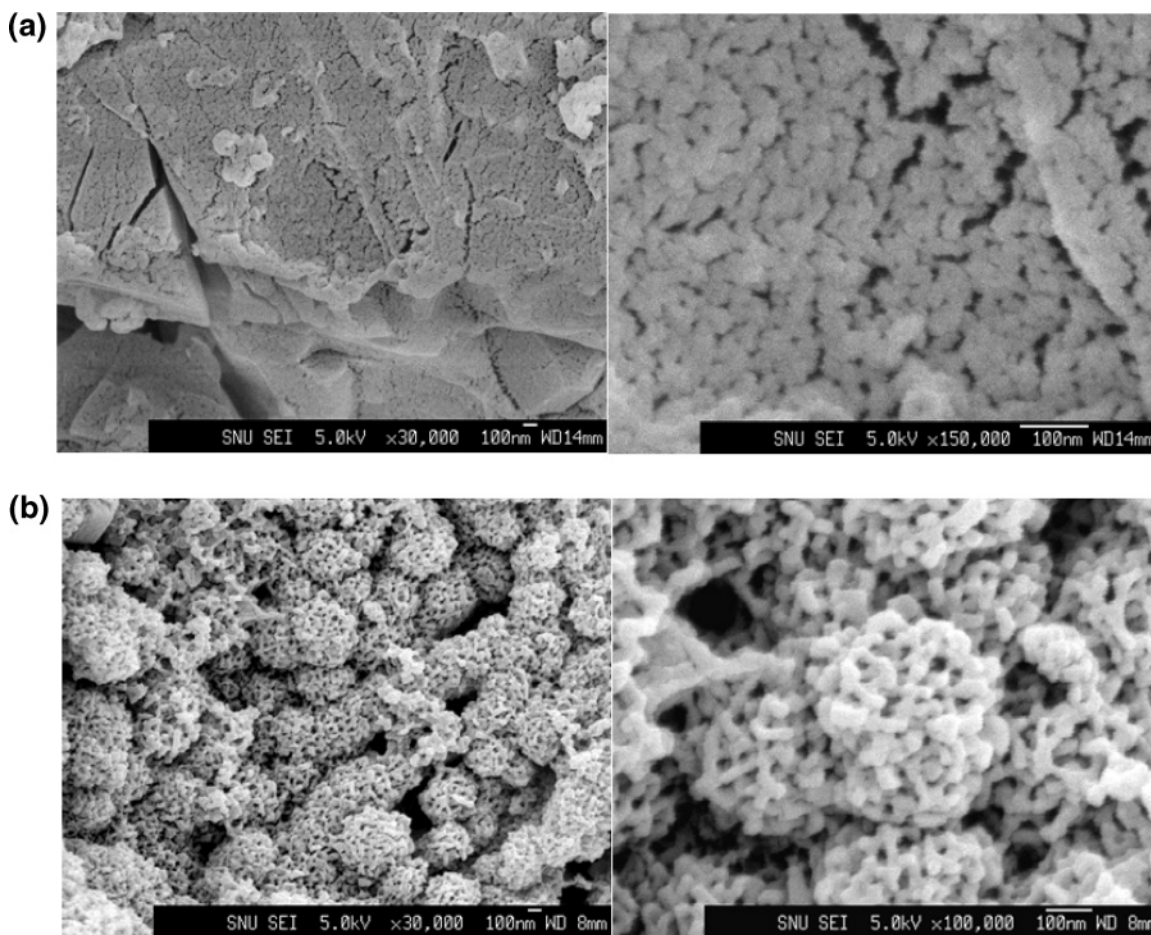


Figure 4. FE-SEM images of (a) neat α -CD and (b) α -CD-SA.

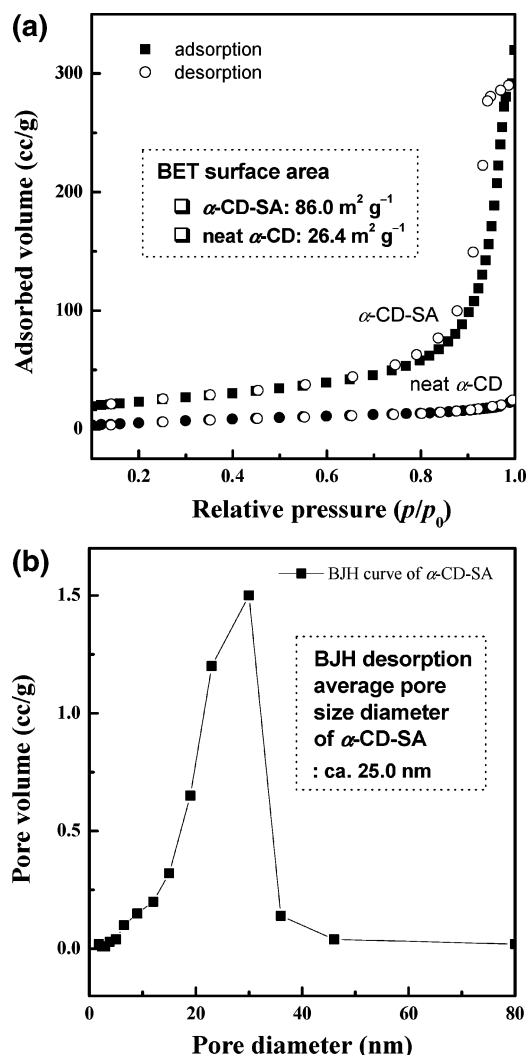


Figure 5. (a) Nitrogen adsorption–desorption isotherms of neat α -CD and α -CD-SA. (b) Pore size distribution of α -CD-SA.

water-mediated hydrogen bonding between the α -CDs with the aid of THF (so-called “slow recrystallization”). To the best of our knowledge, this is the first report that cylindrical nanopores open at least at one end can be produced through the reorganization of α -CD by carrying out a simple sonication treatment in a specific

solvent without guest molecules. To further investigate the change in structure from neat α -CD to α -CD-SA, their morphologies were investigated with FE-SEM. As shown in Figure 4, the morphology of α -CD-SA is quite different from that of neat α -CD. α -CD-SA contains the nanofibril-like α -CD bundles (see Figure 6b,c), whereas neat α -CD contains the agglomerate without noticeable specific shape resulting from the cage-type crystalline structure. These results are well-consistent with that of the crystallographic study of α -CD-SA, which showed the presence of a channel-type crystalline structure with the horizontally hexagonal alignment and the vertically ordered stacking of α -CD. Interestingly, Figure 4b exhibits that a wormhole-like pore is present in α -CD-SA. Thus, the specific surface area and pore size distribution of neat α -CD and α -CD-SA were evaluated with the BET and BJH methods in order to investigate the pore structure of α -CD-SA observed from the FE-SEM image of Figure 4 in more detail. As shown in Figure 5a, the BET analysis obtained from the nitrogen adsorption–desorption measurements shows that α -CD-SA produces type IV isotherms with H2 hysteresis loops, whereas neat α -CD does not produce hysteresis loops between the adsorption and desorption of nitrogen gas. Moreover, the specific surface area of α -CD-SA ($86.0 \text{ m}^2 \text{ g}^{-1}$) is found to be considerably higher than that of neat α -CD ($26.4 \text{ m}^2 \text{ g}^{-1}$). From BJH analysis (Figure 5b), it was verified that the average desorption pore size of α -CD-SA is about 25 nm (pore size distribution = approximately 10–40 nm), whereas no pore is detected for α -CD. These observations indicate that wormhole-like mesopores with inkbottle shape are present in α -CD-SA. The mesoporous structure is considered to be attributed to the formation of mesoporous framework by the nonordered aggregation of the nanofibril-like α -CD bundles (see Figure 6 c).

Conclusion

We successfully obtained the guest-free α -cyclodextrin self-assembly (α -CD-SA) by simply sonicating α -CD in THF as a specific solvent. The combined results of WAXD, FT-IR, DSC, and FE-SEM showed that α -CD-SA consists of nanofibril-like α -CD bundles, in which the α -CDs are closely packed in the vertical direction and hexagonally aligned in the horizontal direction, with cylindrical nanopores open at least at one end. Moreover, it was verified by FE-SEM and nitrogen adsorption–desorption measurements that α -CD-SA has a mesoporous structure ascribed to the random aggregation of nanofibril-like

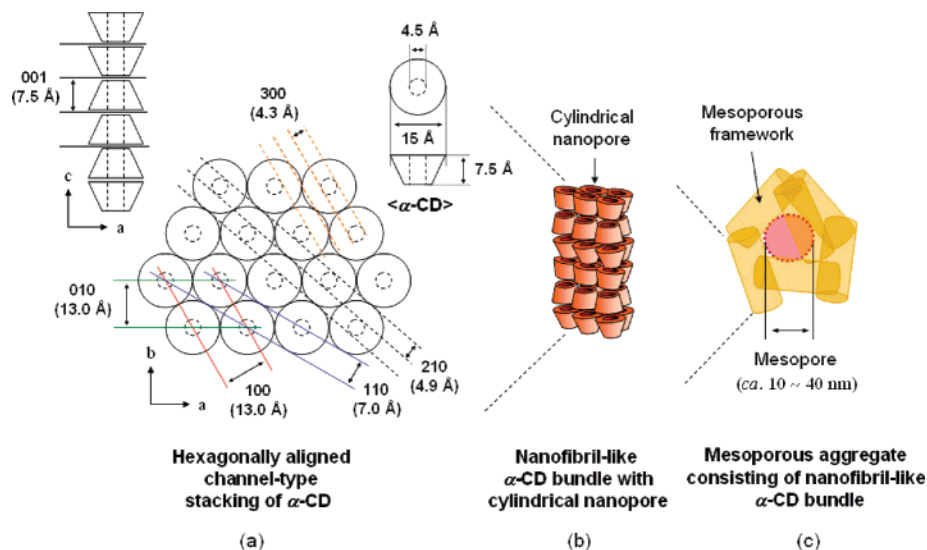


Figure 6. Schematic illustration of the hierarchical structure of α -CD-SA.

α -CD bundles. The formation of α -CD-SA is thought to be ascribed to the slow recrystallization of α -CD by sonication in THF, and these results open up the possibility of creating novel and functional materials from CDs with self-assembly.

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Supporting Information Available: Additional WAXD data to show the change of crystalline structure of α -CD with THF treatment time, the effect of sonication on the crystalline structure of α -CD, and the difference of the crystalline structure of α -CD with solvent type. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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