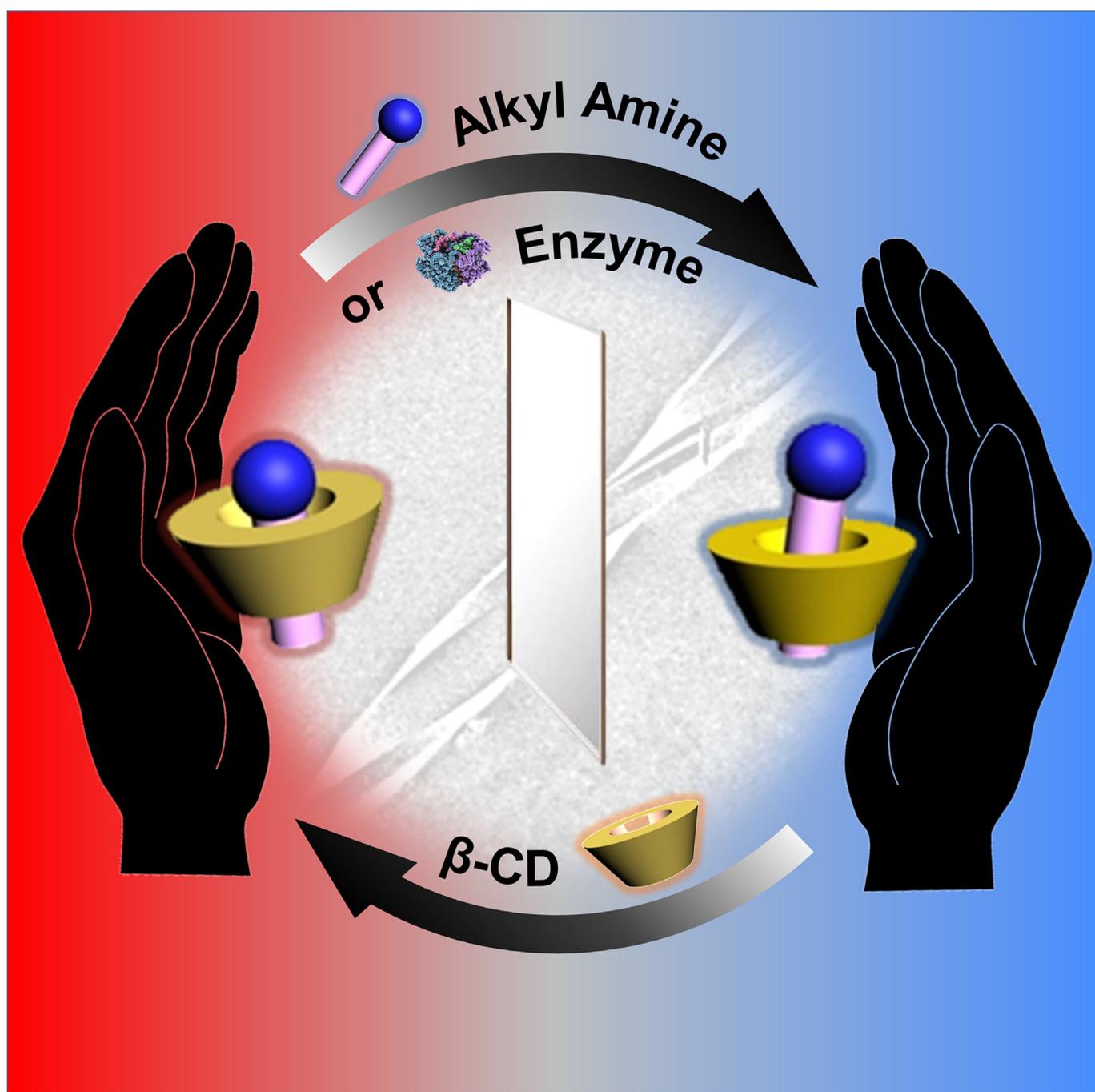


| Chirality | *Very Important Paper* |**VIP** Reversible Manipulation of Supramolecular Chirality using Host-Guest Dynamics between β -Cyclodextrin and Alkyl AminesXuejiao Wang, Maodong Li, Pengbo Song, Xiaolin Lv, Zhirong Liu,* Jianbin Huang,* and Yun Yan*^[a]

Abstract: Host–guest interactions are widely employed in constructing responsive materials, although less is known to manipulate the chiral property of materials using such host–guest dynamics. With the supramolecular self-assembly based on β -cyclodextrin (β -CD) and alkyl amines ($\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$), we report that faster host–guest dynamics induces a dipole located above the cavity of β -CD, whereas slower dynamics create in-cavity dipole. These two scenarios correspond to negative and positive chiral signals, respectively. Considering that a larger fraction of amines facilitates faster exchange between the threaded and unthreaded amines, the chiral signal for the right-handed helical ribbons can be manipulated simply by alternatively increasing the fraction of amines and β -CD. Excitingly, enzyme responsive supramolecular chirality is obtained as a result of shifting the molar ratio by enzyme triggered hydrolysis of β -CD. We expect that this strategy may open up an area of rationally designed chiral supramolecular materials based on host–guest chemistry.

Chirality is ubiquitous in nature, ranging from biomolecules to galaxy.^[1] Understanding the origin of chirality and manipulating chirality of materials are challenging topics in the field of physics, chemistry, biology, and material science. Nowadays, people are able to create various chiral architectures, such as single or double helical ropes, helical ribbons, or nanotubes.^[2] These chiral assemblies can be generated from both chiral^[2c,3] molecules and achiral^[4] ones. Considering that chiral molecules are able to spontaneously self-assemble into chiral structures with promising applications in material science,^[5] tremendous efforts have been conducted to design various chiral building blocks either covalently or non-covalently. Compared to the covalent strategy, noncovalent interactions allow the fabrication of chiral supramolecules easily in a controllable way. For instance, time-programmable chirality switching is possible by using coordination chemistry on the basis of the same starting coordinating organic molecules.^[6] Chirality switching of supramolecular self-assemblies formed with the same building blocks is also possible by controlling the polarity of solvent,^[7] the direction of mechanical force^[8] and other physical parameters.^[9] These marvelous studies have laid the foundation for fabrication of various chiral materials.

However, so far, most reported chirality switching in supramolecular system is based on discovery of serendipity among numerous newly synthesized molecules,^[6b,7a] and it is still a

challenge to rationally design a new supramolecular system that is able to undergo chirality switching. The main reason is that the knowledge about the chirality switching for materials based on new molecules is very limited. In contrast to the tremendous efforts devoted to the design of novel chiral molecules, the chiral property of many well-known supramolecular systems has not yet been sufficiently utilized. For instance, cyclodextrins (CD) are known to have a chiral cavity that can induce supramolecular chirality for achiral aromatics harboring in their cavity.^[10] Interestingly, the sign of the induced chiral signal depends on the location of the electronic dipoles of the guests in CDs. For a guest with parallel dipole to that of CD, the chiral signal is positive when it locates inside the cavity, whereas it is negative in case of above (outside) the cavity.^[11] This clear picture suggests that, if we are able to control the position of the electronic dipole of the guest in the cavity of CD, it is possible to manipulate the chirality of the self-assembled supramolecular materials with expectable results. However, this scenario has not been verified so far, partially because of two insurmountable obstacles. First, it is difficult to control the threading direction of the guest into the cavity of CD, and the coexistence of threading from the wider and narrower rim will result in enantiomers that display achiral property. Second, the host–guest supramolecules can hardly self-assemble into hierarchical structures that are of interest in material science. Fortunately, the latter has been made possible by us in recent years. We have found that the host–guest supramolecules of CDs and surfactants or alkanes can further self-assemble into crystalline self-assemblies of rhombics,^[12] microtubes,^[13] fibers,^[14] lamellae,^[15] or vesicles^[14,16] by hydrogen bonding between CDs, and the hydrogen bonding driven hierarchical self-assembly has displayed attractive ability in restricted assembly of colloidal particles.^[17] Therefore, we anticipate that if we are able to control the orientation of the guest in the cavity of CD, it is possible to achieve chirality switching in the host–guest supramolecular self-assembly of CDs.

The key that leads to the orientation of the guest in the cavity of CD is to create a different strength or probability of the guest with the wider and narrower rim. Considering that the wider rim of CDs has one extra fold of OH groups than the narrower rims, we expect hydrogen bonding of guest with the wider rim should be stronger than that with the narrow rim, which may act as the driving force for the orientation of the guest. With this in mind, we chose alkyl amines, instead of surfactants used in the previous study,^[13b,15,18] as the guest to form crystalline self-assembly with CDs in this study. We found that oriented threading of the amines into the cavity of CDs is controllable through the chain length of the alkyl amines. Theoretical calculations based on molecular dynamics (MD) revealed that the oriented threading of the alkyl amines with proper length in the cavity of the CDs is exactly driven by the superior hydrogen bonding between the NH_2 and OH groups at the wider rim of CDs. When the chain is too long, the polar amine head would protrude away from the rims, and the discriminatory interactions with the wider and narrower rims disappear. As a result, the amines lost their ability of orientation with increasing chain length from C8 to C10. Notably, we show

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that once oriented threading of the amines is achieved, we are able to manipulate the supramolecular chirality by controlling the molar ratio between the host and guest. The underlying principle is that a faster exchange rate between the hosted and free guests lead to the polar amine head being further away from the rim of CDs. Considering that increasing the molar ratio of alkyl amines facilitates faster exchanging rate of the guest, we are able to reverse the supramolecular chirality of the host–guest system simply by varying the molar ratio between β -CD and the guest, and the chirality switching is reversible by alternatively creating a situation with excess host or guest. Microscopic studies reveal that the chiral supramolecules can further self-assemble into right-handed helices, and the helical pitch can be varied by the dynamics. Furthermore, the molar ratio dependent reversible chirality switching allows creating enzyme responsive supramolecular chirality because the molar fraction of β -CD can be decreased by enzyme triggered decomposition of β -CD. To the best of our knowledge, this is the first case of rational manipulation of the chirality of supramolecular materials based on the dynamic non-covalent interactions. We expect the present work establishes a new paradigm for constructing chiral supramolecular materials with expectable and controllable chirality.

The alkyl amines with carbon chain length (6–10) are used to build host–guest systems with β -CD (Figure 1 a). The inclusion complexes were prepared by addition of organic amines $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n=6-10$) into the clear saturated solution of β -CD under vortex mixing (see Supporting Information). The shorter chain amines of $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n=6, 7$) cannot thread into the cavity of β -CD, as confirmed by NMR and FT-MS measurements (Figure S1, Supporting Information), and no Tyndall effect was observed in the $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD ($n=6, 7$) system, indicating no colloidal particles are formed. However, white precipitates were observed in systems formed with $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n=8, 9, 10$) (Figure 1 b). For a given amount of β -CD, the quantity of precipitates increases with increasing fraction of the alkyl amines. SEM images reveal the formation

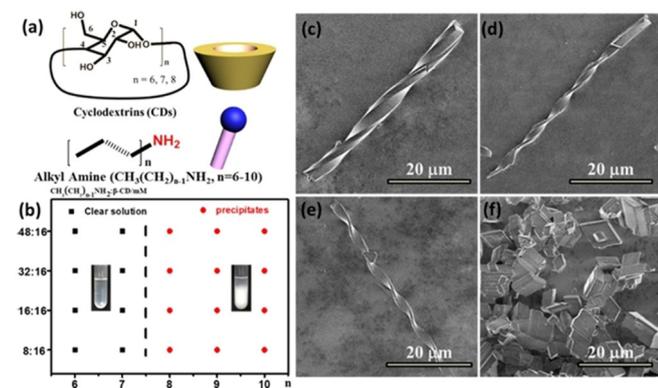


Figure 1. a) The molecular structure of CDs ($n=6, 7, 8$ for α, β, γ -CD, respectively) and alkyl amines. b) Phase diagram of $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD ($n=6-10$) systems with varying chain length and molar ratio between alkyl amines and β -CD in water. SEM images of the self-assembled structure: c) $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@ \beta$ -CD, d) $16:16$ mM, and e) $48:16$ mM, f) $\text{CH}_3(\text{CH}_2)_9\text{NH}_2@ \beta$ -CD $48:16$ mM; f) $\text{CH}_3(\text{CH}_2)_{10}\text{NH}_2@ \beta$ -CD $16:16$ mM.

of mesoscopic right-handed helical ribbons in the precipitates of with $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD ($n=8, 9$) systems (Figure 1 c–e). In contrast, planar bulk bricks are formed in $\text{CH}_3(\text{CH}_2)_9\text{NH}_2@ \beta$ -CD system (Figure 1 f), similar to the lamellar structures observed in alkane@ β -CD systems.^[16b,19] NMR and FT-MS measurements reveal the formation of the 1:1 complexes in all these systems (Figure S2, Supporting Information), which is in clear contrast with the 1:2 building blocks obtained in the $\text{SDS}@2\beta$ -CD system in a previous study.^[15,20] The building blocks are always in a 1:1 complex regardless of the initial feeding ratio between the amines and β -CD, indicating the 1:1 complexation is preferred in all three systems.

The formation of helical structures in the $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD ($n=8, 9$) system indicates that the oriented threading of the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ into the cavity of β -CD may have occurred. To verify this conclusion, 2D-NMR measurements were performed for the $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD ($n=8, 9$) and the $\text{CH}_3(\text{CH}_2)_9\text{NH}_2@ \beta$ -CD systems. Figure 2 shows that the occur-

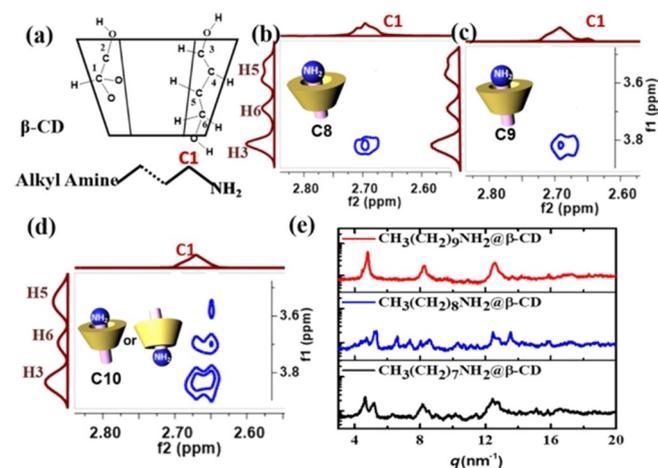
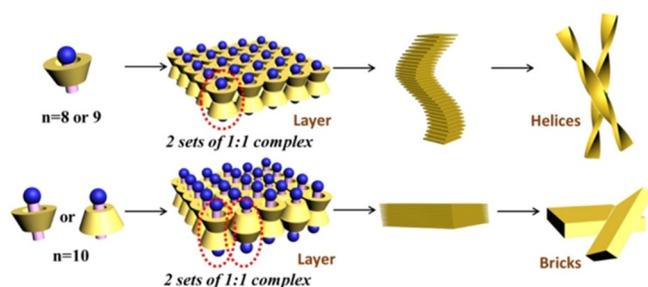


Figure 2. a) Schematic illustration of the structure of β -CD and alkyl amine; 2D-NMR (ROESY) and the schematic illustration (insets) of b) $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@ \beta$ -CD, c) $\text{CH}_3(\text{CH}_2)_8\text{NH}_2@ \beta$ -CD, and d) $\text{CH}_3(\text{CH}_2)_9\text{NH}_2@ \beta$ -CD. e) SAXS patterns of lyophilized self-assemblies of $\text{CH}_3(\text{CH}_2)_{7-9}\text{NH}_2@ \beta$ -CD.

rence of the correlation between the protons at the C1 of the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ and that at the C3 of β -CDs (further details in Figure S3, Supporting Information). Considering that C3 is on the wider rim of β -CD, this result indicates that the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ are oriented predominantly toward the wider rim of β -CD. In contrast, correlations occur between the protons at C1 of the $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ and both the C3 and C5 protons of β -CD, suggesting the amine head of $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ has threaded through both the narrower and the wider rim of β -CD (Scheme 1). The threading and packing of the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2@ \beta$ -CD and $\text{CH}_3(\text{CH}_2)_9\text{NH}_2@ \beta$ -CD is illustrated in Scheme S1 (Supporting Information).

Due to the β -CD having a truncated cone structure,^[21] we expect that the dual orientation of $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ in β -CD may lead to better supramolecular packing than that in the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ systems. To test this hypothesis, SAXS and synchrotron radiation measurements (Figure 2 e and Figure S4,



Scheme 1. $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ is oriented toward to the wider rim of β -CD, and $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ is oriented toward to both the wider and narrower rims of β -CD. The selective orientation of the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ leads to helices, whereas the dual orientation of $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ results in planar bricks.

Supporting Information) were performed. Indeed, all the three systems show channel-type arrangement of β -CD, which is confirmed by the characteristic diffractions at $q=8.2$ and 12.4 nm^{-1} , respectively.^[15,19,22] However, three distinct individual peaks with nearly the same distance of q between each other in the $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ system (the red line in Figure 2e) indicate a perfect channel-type lamellar structure, whereas the peaks in the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ systems (the blue and black line in Figure 2e) are mixed and irregular, suggesting the building blocks are not oriented uniformly in the helical ribbon structures. This is in line with the formation of symmetry breaking building blocks revealed by 2D-NMR, which can hardly pack perfectly. Detailed analysis of the supramolecular packing in the helices is provided in the Supporting Information (Figure S4, and Table S1).

To probe the physical insight of the preferred orientation of the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ chains in the cavity of β -CD, theoretical computation based on molecular dynamics (MD) are performed. Figure 3a reveals that the polar head of $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2$ can form more H-bonds with the wider rim of β -CD (Figure 3b,c) because the number of the OH groups on the wider rim is two times that on the narrower rim, whereas the $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ forms similar amount of H-bonds with both the wider and narrower rims (Figure 3d, e). This is in perfect agreement with our experimental results. We therefore confirm that the nature of the chain length dependence is the ability to form H-bond between the NH_2 group and the OH groups (H-bond in these systems can also be seen in FT-IR results, Figure S5, Supporting Information). If the chain length is similar to the height of the cavity of β -CD, H-bonding is the most efficient. With increasing the chain length of amines, the NH_2 head protrudes outside of the cavity (Figure 3d,e), so that H-bond formation becomes difficult. This explains why $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ has no selective orientation when threading into the cavity of β -CD.

Next, the chirality of the supramolecular system of the $\text{CH}_3(\text{CH}_2)_{7,8}\text{NH}_2@ \beta$ -CD is examined. β -CD is known to have a chiral cavity that can induce chirality for a guest molecule. Considering that β -CD (and also other cyclodextrins) has no absorption in the UV/Vis range, β -CD solution does not exhibit chiral signal. However, a positive chiral signal is observed at wavelength corresponding to the UV adsorption (Figure S6,

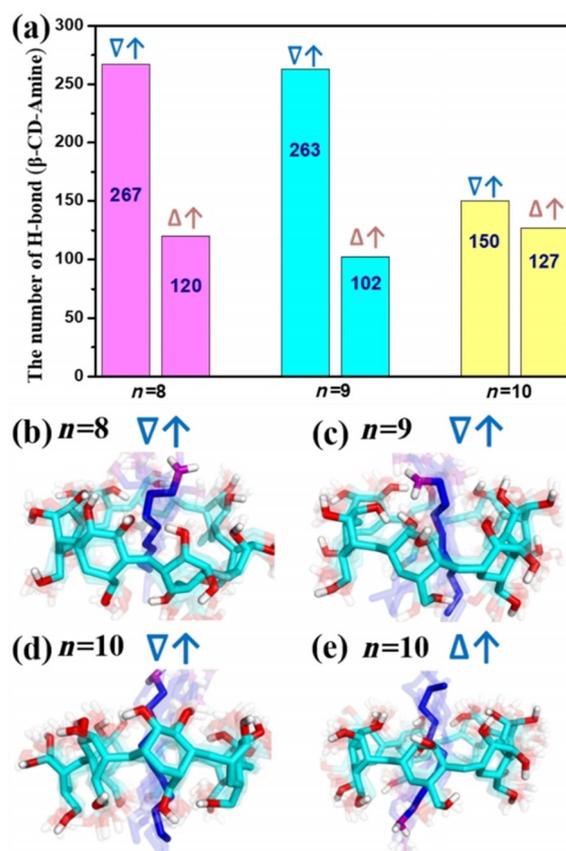


Figure 3. a) The number of β -CD-alkyl amine H-bond in $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD system. Representative results are obtained in the first 10 ns MD simulations for 6 initial conformations each with 3 trajectories stored information. b–e) Stable structures obtained from MD for the $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD host-guest complex. The NH_2 group of b) $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$, and c) $\text{CH}_3(\text{CH}_2)_8\text{NH}_2$ are predominantly oriented toward the wider rim of β -CD, which are designated with the symbol of $\nabla\uparrow$; whereas the NH_2 group of d, e) $\text{CH}_3(\text{CH}_2)_9\text{NH}_2$ can orient toward both the wider ($\nabla\uparrow$) and narrower rim ($\Delta\uparrow$) of β -CD with equal probability. Colors in the model: red: O; purple: N, white: H; cyan: the skeleton of β -CD; blue: the carbon chain of $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2@ \beta$ -CD.

Supporting Information) of the NH_2 group in Figure 4a for the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@ \beta$ -CD supramolecular system, and a negative one is observed for the $\text{CH}_3(\text{CH}_2)_8\text{NH}_2@ \beta$ -CD system. Meanwhile, the $\text{CH}_3(\text{CH}_2)_9\text{NH}_2@ \beta$ -CD system is CD silent. To prove the authenticity of the CD spectra, HT curves were plotted and are given in Figure S7 (Supporting Information). According to Harata^[23] and Kodaka's^[24] rule, the sign of the induced chiral signal is positive if a parallel electronic dipole is inside the cavity of CDs, whereas it is negative if outside the cavity. This means that the NH_2 in the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ system, albeit located at the rim of β -CD, is still inside the cavity territory of β -CD, whereas that of $\text{CH}_3(\text{CH}_2)_8\text{NH}_2$, connected to an alkyl chain only one carbon longer than the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ chain, is just outside the cavity. This picture can be clearly observed in the MD simulations in Figure 3.

The fine chain-length dependence of the sign of the induced chirality suggests that we can manipulate the supramolecular chirality in the host-guest system by controlling the host-guest dynamics because a faster exchange between the threaded and unthreaded $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ may lead to a larger

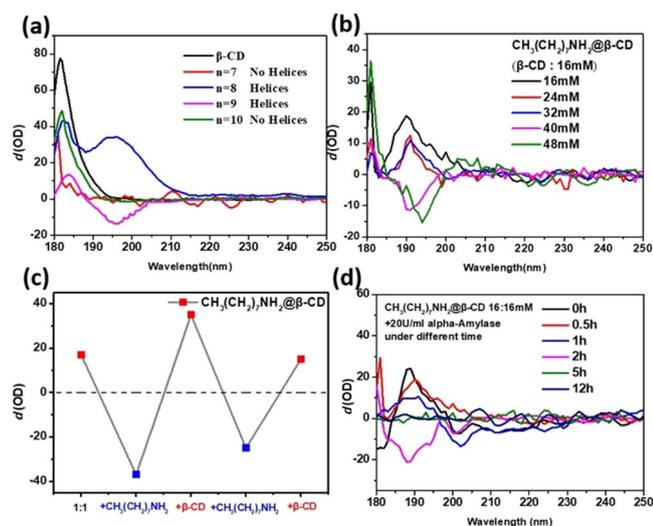


Figure 4. Circular dichroism spectroscopy (CD spectrum) of a) $\text{CH}_3(\text{CH}_2)_n\text{NH}_2@β\text{-CD}$ ($n = 7-10$) systems, b) $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ systems with increasing the concentration of $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ (from 16 mM to 48 mM) at a fixed concentration of $β\text{-CD}$. c) Reversal of chiral signal of $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ system with alternatively adding the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ and $β\text{-CD}$ (refer to Figure S9 for details). d) Variation of the circular dichroism signal of the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ (16:16 mM) solution since the addition of $α\text{-amylase}$ at $t = 12$ hours.

distance between the NH_2 group and the rim of $β\text{-CD}$. To verify this argument, the molar ratio between $β\text{-CD}$ and $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ is increased from 1:1 to 1:4. Excitingly, reversed circular dichroism signals are indeed observed. Figure 4b shows that the circular dichroism signal is positive as the molar ratio is 16:16, 16:24, and 16:32, whereas it becomes negative as the ratio increases to 16:40 and 16:48. In particular, the chirality-switching is completely controlled by the dynamics of the host-guest process and it is reversible. As we revert the molar ratio between $β\text{-CD}$ and $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ by adding extra $β\text{-CD}$ to the 16:48 system, which has negative chiral signal, to reach the ratio of 32:48, 48:48, the chiral signal is reversed again (Figure S8, Supporting Information). As shown in Figure 4c, this recyclable switching of chiral signal from the positive signal to negative signal could be achieved by alternatively adding the moderate $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ and $β\text{-CD}$.

The excellent reversible molar ratio dependent supramolecular chirality in the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ system suggests that we can manipulate the chiral signal by the addition of $α\text{-amylase}$, which is an enzyme that can specifically catalyzes the hydrolysis of the $α\text{-1,4}$ -linkages between glucose units of starch molecules including CDs, and cleave off two glucose units at a time.^[25] Therefore, addition of $α\text{-amylase}$ will decrease the molar fraction of $β\text{-CD}$. Figure 5d displays the variation of the circular dichroism signal upon addition of 20 U mL^{-1} of $α\text{-amylase}$ to the 16:16 mM $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ solution in real-time. In the very beginning ($T = 0 \text{ h}$), the signal is positive; whereas the signal gradually reverses within 1 h, indicating the molar fraction of $β\text{-CD}$ is reduced. The supramolecular chirality vanishes completely after 5 h when all the $β\text{-CD}$ s have been degraded. This experiment clearly demonstrates that supramolec-

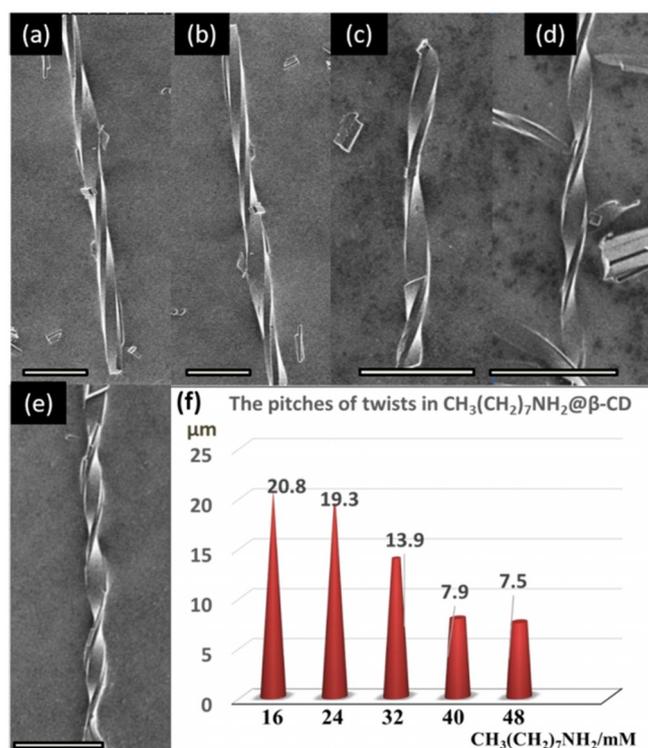


Figure 5. SEM images of the ribbons with different pitches formed in the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ supramolecular systems with increased concentration of $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$. The concentration of $β\text{-CD}$ is 16 mM for all the panels, whereas the concentration of $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ is: a) 16; b) 24; c) 32; d) 40; e) 48 mM. Scale bars are $10 \mu\text{m}$. f) Variation of the average pitches of the helices with the molar ratio between $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ and $β\text{-CD}$, according to the statistics counting of 50 helical ribbons.

ular chirality of the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ system indeed displays enzyme responsiveness, which is useful in a number of fields ranging from enzyme activity detection and responsive chiral materials.

Interestingly, switching of the chiral signal in the $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$ does not change the handedness of the self-assembled structure, although this is often observed in many chirality switching systems.^[7a,b,26] The SEM observation (Figure 5) reveals that all the helices remain right-handed, but the average helical pitch is reduced notably from 20.8 to 7.5 μm as the molar ratio between $β\text{-CD}$ and $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ changes from 16:16 to 16:48. This is attributed to the increased concentration of the building block of $\text{CH}_3(\text{CH}_2)_7\text{NH}_2@β\text{-CD}$, which forms more "crystal seeds" to develop helical structures. It is also noticed that the right-handed supramolecular chirality is not caused by the directional shear force during sample preparation. Changing the direction of vortex mixing will result in helices of the same right-handedness (Figure S9, Supporting Information).

In conclusion, we have shown that the chiral signal can be manipulated by the dynamic nature of the host-guest chemistry between CD and alkyl amines. The fast exchange between the threaded and the unthreaded guest determines the distance between the polar amine head and the rim of CD, which impacts the sign of the chiral signal of the host-guest supra-

molecular building block. As the molar fraction of CD is reduced by an enzyme that can hydrolyze CD, a faster exchange of threaded and unthreaded amines occurs, which results in enzyme responsive supramolecular chirality. The fast dynamics also lead to smaller helical pitches in the resultant right-handed helical ribbons. We expect that by using the dynamic host-guest chemistry, it is possible to rationally manipulate the supramolecular chirality. This work opens a new paradigm for constructing supramolecular materials with expected chirality.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: chirality switching · enzyme responsiveness · host-guest dynamics · supramolecular chirality · β -cyclodextrins

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