



Chirality manipulation of supramolecular self-assembly based on the host-guest chemistry of cyclodextrin

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Abstract

Chiral materials have been of the interests of scientists for nearly a century. People have endeavored a great effort to manipulate the chirality of various self-assembled materials. Among these efforts, cyclodextrins are used only in recent years, although it has long been recognized that the chirality of cyclodextrin can be transferred to the guest. In this review, we for the first time summarize the recent advancement of the supramolecular chirality manipulation on the basis of the host-guest chemistry of cyclodextrins. By using the simple Harata-Kodaka's rule, natural cyclodextrins can be exploited in a dynamic manner to create chirality inversion materials through crystalline self-assembly, which is facile and environment-friendly. What is more, we also discussed the remarks on future outlooks at the end of this article and expect it to stimulate a rapid development on both the theory and application level.

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Current Opinion in Colloid & Interface Science 2021, 56:101526

This review comes from a themed issue on **Colloid Science for a Sustainable Future**

Edited by **Paschalis Alexandridis, Stephanie Reynaud and Marina Tsianou**

For a complete overview see the [Issue](#) and the [Editorial](#)

<https://doi.org/10.1016/j.cocis.2021.101526>

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Keywords

Chirality manipulation, Cyclodextrin, Harata-Kodaka's rule, Crystalline self-assembly.

Introduction

Chirality refers to the characteristic that an object cannot be superimposed on its mirror image. Chirality is a widespread phenomenon of nature and is crucial to the organization and function process of living matter [1,2],

which could be obtained at various levels, ranging from molecular (amino acids), supramolecular (DNA double helix), macroscopic (mountain-climbing vines) to galactic scales [3]. Generally speaking, the origin of molecular chirality is from the tetrahedral configuration of carbon atoms, which can be categorized into point, axis, and plane chirality, whereas the supramolecular chirality originates from nonsymmetric arrangement of molecules. In the past decades, diversified artificial chiral supramolecular materials have been created [4–6], which have displayed attractive applications in multidisciplinary fields such as communication, photo-electronic devices, and smart sensors.

Chirality manipulation is one of the most crucial issues in the chiral supramolecular system [7]. Nowadays, chirality manipulation at supramolecular or mesoscales is possible in several ways. For example, people are able to tune supramolecular chirality on the basis of metal-coordination chemistry by using the same organic ligand but different metal ions [8–10]. Because dipole–dipole interaction is closely related to the induced supramolecular chirality, variation of solvent in which self-assembly occurs is also possible to modulate the chirality or handedness of the self-assembled materials [11–13]. Besides, chirality could be altered by external factors such as addition of chiral enantiomers, application of mechanical forces, irradiating by polarized light, or other physical parameters such as pH and temperature [14–18].

Among these efforts, cyclodextrins (CDs) are used only in recent years, although it has long been recognized that the chirality of CD can be transferred to the guest, leading to a considerable induced circular dichroism (ICD). As a natural macrocyclic molecule with chirality, CD can induce the chirality of both organic molecules and inorganic particles through host-guest interaction. Inouye et al. [19,20] found that the host-guest complex formed by pyrene or perylene derivatives and γ -CD exhibits strong circularly polarized luminescence (CPL, chiral luminescence). Falaise et al. [21,22] revealed a size-exclusion mechanism in host-guest complexes of CDs and inorganic particles such as octahedral rhenium clusters and polyoxometalates, where the inclusion depth of the inorganic particles

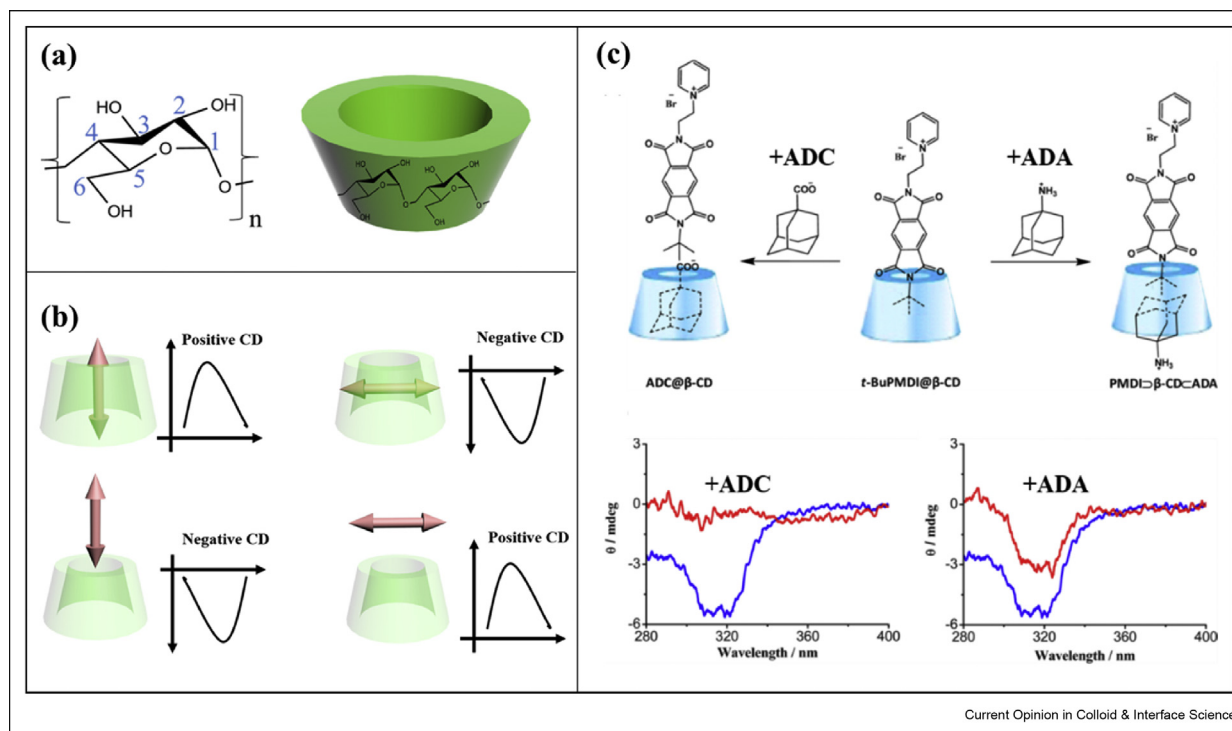
relies on the size matching degree between the cavity and the guest. In the system of γ -CD and rhenium clusters with relatively matching sizes, the deep inclusion of the cluster inside γ -CD provokes a remarkable chirality induction. While most literatures report the ICD at molecular level, recently, Yan et al. found that the host-guest chemistry between CDs and amphiphiles can also be used to create chiral supramolecular self-assembled materials, and the handedness of the chiral self-assembled materials can be rationally designed on manipulating the host-guest dynamics. The cavity of CD is chiral, which has long been recognized to induce circular dichroism (ICD) for the achiral guest it hosts, and the sign of ICD can be predicted by Harata-Kodaka's rule (H–K rule). However, the H–K rule is mainly used to predict the position of the guest in CD's cavity and has never been used to create chiral supramolecular self-assemblies until recent work on the crystalline self-assembly of CDs. In this review, we systematically overviewed the history of the chiral-inducing ability of CDs and the supramolecular handedness manipulation on the basis of the crystalline self-assembly of CDs. The following contents are included: (1) brief introduction of H–K rule in predicting the sign of induced circular

dichroism (ICD); (2) supramolecular chirality of the crystalline self-assembly on the basis of the host-guest complexes of amphiphile@CD; (3) manipulating the handedness of the crystalline self-assembled materials by using H–K rule; (4) conclusions and perspectives.

Harata-Kodaka's rule: principle to induce supramolecular chirality based on cyclodextrin

As a family of ring-like oligosaccharides, CDs are doughnut ring-like structures composed of six, seven, or eight D-glucopyranose molecules (noted as α -, β -, and γ -CD, respectively) linked together by α -1,4 glycoside bonds. CDs are green, economic, and versatile hosts in assembly, which show great potential in application [23–30]. The height of the ring for various CDs is 0.78 nm, but the diameter of the cavity increases with the number of its sugar unit. The upper rim of CD is wider than the lower rim, thus CD displays a toroidal structure, as illustrated in Figure 1a. Owing to the existence of abundant hydroxyl groups, the exterior of CD is highly hydrophilic, but the cavity is lipophilic endowed by the methylene groups [27]. The unique characteristic of CD makes it a fascinating host to selectively bind hydrophobic guests of various sizes,

Figure 1



H-K rule and its application. (a) Schematic structure of cyclodextrin. (b) Schematic description of Harata-Kodaka's rule and the induced cotton effects of guest@CD derivatives. The red arrows illustrate the orientation of the electric dipole transition moment of the sheltered guest relative to the host cavity of CD. (c) Schematic diagram of inclusion behavior of the t-BuPMDI@ β -CD inclusion complex with ADC and ADA and the induced circular dichroism spectra of t-BuPMDI with the absence (blue trace) and presence (red trace) of the adamantane derivatives [45]. ADA, adamantane-1-ammonium; ADC, adamantane-1-carboxylate; CD, cyclodextrin; t-BuPMDI, butylpolydiphenylmethane diisocyanate.

which finds wide applications in pharmacy, food chemistry, catalysis, agriculture, and environmental science [31–37].

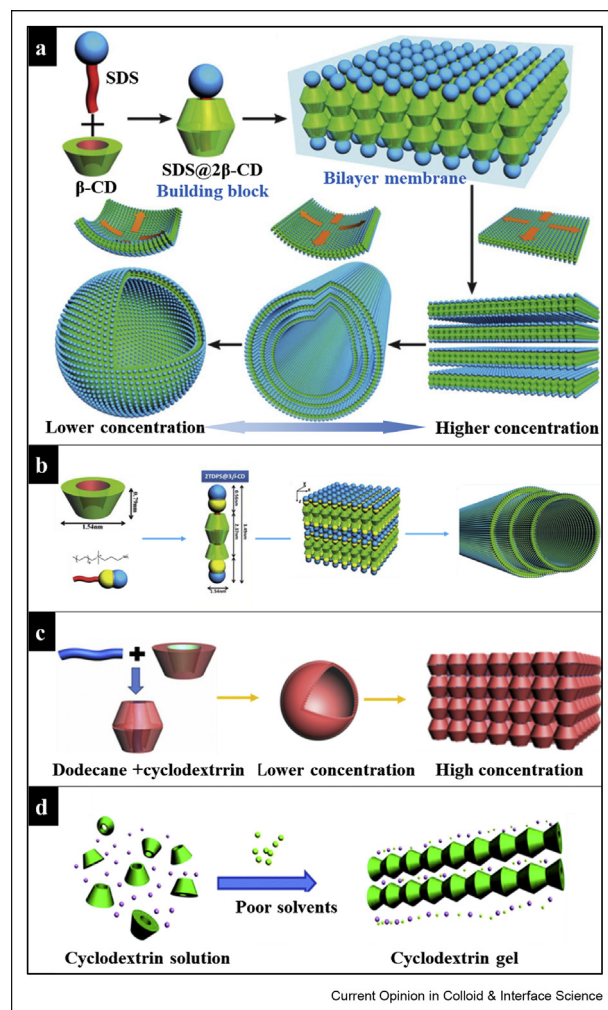
One of the most crucial properties of CD that differentiates it from most other common hosts, such as podand, cucurbituril, pillararene, coronand, cryptand, and so on, is its intrinsic chirality, namely, the characteristic that distinguishes a substance from its mirror image [38,39]. As is shown in Figure 1a, the carbon atoms labeled with 1–5 in CD are all chiral, which endows the cavity of CD with molecular chirality. Because CD has no absorbance peak in the UV–vis (ultraviolet–visible) region, the molecular chirality of CD would not give a circular dichroism signal. However, as a guest with UV–vis absorbance is threaded into the cavity, the molecular chirality of CD will transfer to the guest through dipole–dipole interactions between them, leading to an induced circular dichroism (ICD) signal for the guest.

During the past years, the phenomena which CDs could induce optical activity in the electronic transitions of various guests have been observed by a large number of scientists [38–40]. Harata and Kodaka *et al.* [41–44] used the Tinoco theory of the coupled oscillator model of Kirkwood to calculate the induced Cotton effects. In short, if the electric dipole transition moment μ of the included guest is aligned exactly parallel to the cavity axis of the CD molecule, the signal of the induced Cotton effect in circular dichroism spectra is positive. On the contrary, when the dipole transition moment μ is aligned perpendicular to the axis, the corresponding Cotton effect is thus negative. The previous statement is under the circumstance that the chromophore is in the cavity of CD. If the guest is outside of the cavity, the signal is reversed. These scenarios are vividly illustrated in Figure 1b.

An in-depth research of the experimental result indicates the signal and strength of the ICD signal rely closely on the intensity of polarization and the electronic dipole transition moments in the guests, from which it could be summarized that the appearance of the ICD signal is a suggestion of the formation of an inclusion complex with highly ordered structure. By exploring, either theoretically or phenomenologically, the relationship between the ICD spectra and the conformation of the inclusion complex, as well as the intrinsic nature of the electric dipole transition moment of the included guest molecule, the recording of ICD spectra can serve as a facile tool to estimate either the conformation of the CD complex or the orientation of the transition in the guest. For example, Gopidas (Figure 1c) *et al.* used ICD spectra to probe the complexation of tertiary-butylpolydiphenylmethane diisocyanate (t-BuPMDI) with β -CD. ICD spectra of the t-BuPMDI@ β -CD in the absence (blue trace) and

presence (red trace) of the adamantane derivatives are shown in Figure 1c. If the conformation matches the structure in Figure 1c, the addition of adamantane-1-carboxylate would have replaced the t-PMDI completely, resulting in the absence of the ICD signal. However, if adamantane-1-carboxylate is replaced with adamantane-1-ammonium, part of t-PMDI would still be in the β -CD's cavity, as represented in Figure 1c, a reduced ICD intensity was observed. It was noticed that the chiroptical signals were negative corresponding to absorbance, which indicated that the chromophore of PMDI is outside of the cavity of CD, in line with the expected host-guest conformation [45].

Figure 2



Cyclodextrin-based crystalline self-assembly. (a) Schematic diagram of crystalline self-assembly behavior of guest SDS and host β -CD [49]. (b) A schematic diagram of the self-assembly process of 2 tetradecyl dimethylammonium propane sulfonate (TDPS) @ β -CD building block, from a multilayer structure to a microtube structure [50]. (c) Schematic diagram of the self-assembly process of the dodecane @ β -CD inclusion complex [51]. (d) Schematic diagram of the formation process of cyclodextrin gel triggered by poor solvents [52]. β -CD, β -cyclodextrin; SDS, sodium dodecyl sulfate.

CD-based crystalline self-assembly and ICD (induced circular dichroism) for the crystalline tube and lamellae

CD has long been considered a destructor for self-assembly because of its hydrophilic property. Although scientific researchers have already been able to create self-assembled structures exploiting the host-guest chemistry between CD and a very hydrophobic guest [46,47], the role of CD is to act as hydrophilic portion of the host-guest complexes, thus creating a supramolecular amphiphile. Until 2010, when Jiang et al. [48,49] reported that the channel type host-guest inclusions formed with CD and sodium dodecyl sulfate (SDS) are able to build nonamphiphilic self-assemblies through the hydrogen bonding between CDs (Figure 2a), the crystalline self-assembly of the CD-amphiphile complex was established.

It has been found that the channel-type CD building blocks threaded by different alkyl chains, which may either be from long-chain surfactants (Figure 2b) [50,53–55], or merely alkanes (Figure 2c)) [51,56], are all capable to form supramolecular crystalline self-assembly.

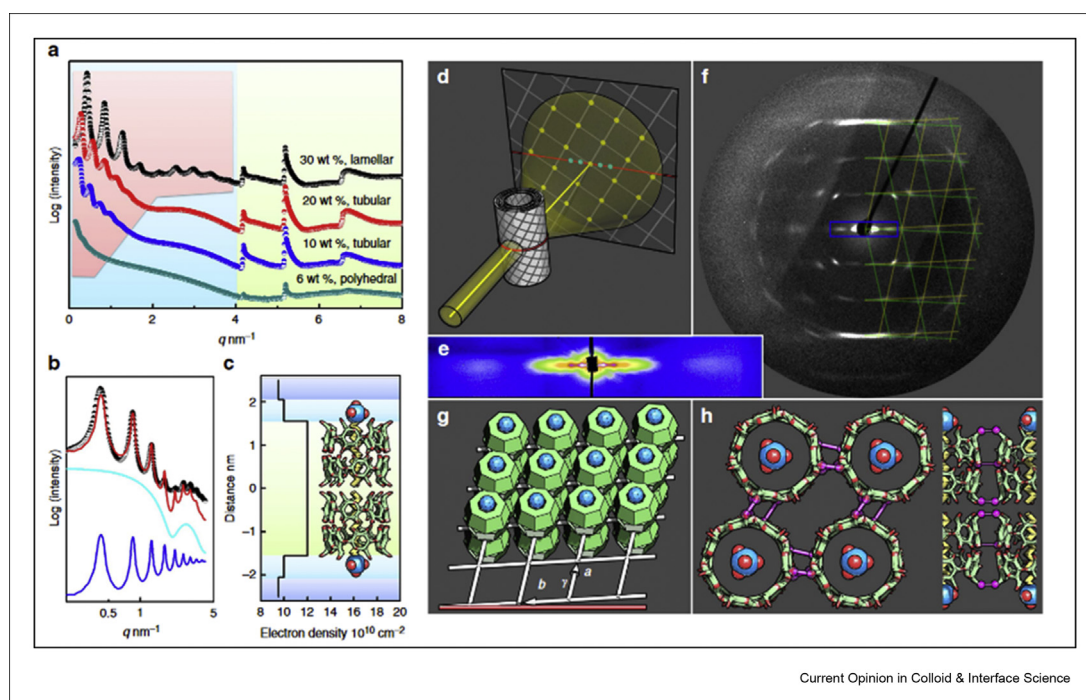
Interestingly, Hao et al. [52] reported a variety of organogels based on regular assemblies of CDs induced by

poor solvents (Figure 2d). Hydrogen bonding is also verified to be the driving force for crystalline assembly. Specially, the excellent symmetric channel-type structure of the complexes allows formation of rigid microtubes and lamellar structures in the concentrated regime.

In 2017, Yang et al. [57] further revealed that in SDS@2 β -CD crystalline self-assembly, the SDS@2 β -CD building blocks are arranged to form an in-plane lattice with a rhombic unit cell $a = b = 1.52$ nm, $\gamma = 104^\circ$ and the b axis-to-equator angle = 3° , as shown in Figure 3.

Different types of intermolecular interactions can lead to different structures. Wu et al. [58] systematically compared the driving force of the CD-based crystalline self-assembly with soft assembly. Soft assemblies with lower-ordered structure are mainly formed by the hydrophobic interactions of low strength and nondirectionality, where the flexibility and fluidity are emphasized. In contrast to soft assembly, these lattice structures of CD-based crystalline assembly with high rigidity and crystallinity mainly rely on strong and directional driven forces such as H-bonds or π - π stacking. The extensive network of hydrogen bonding among the CD complexes is the main driving force for

Figure 3



The proof for the crystalline structure. X-ray scattering of the SDS@2 β -CD structures and mechanism for the microtube formation. (a) Small-angle X-ray scattering (SAXS) curves of the lamellar, tubular, and polyhedral phases with different SDS@2 β -CD concentrations. (b) The SAXS curve (30 wt%, black dots) up to 4 nm^{-1} is fitted by form factors. (c) The electron density profile across the bilayer. (d) A scheme of wide-angle X-ray scattering of aligned multilamellar tubes with in-plane crystallinity. (e) Scattering patterns along the equator at a small angle. (f) The scattering pattern at a large angle is superpositioned by the mirrored yellow and green grids. (g) The in-plane lattice with a rhombic unit cell. (h) Top and side views of the SDS@2 β -CD lattice, highlighting the possible, inter-CD H-bonds [57]. SDS@2 β -CD, sodium dodecyl sulfate@2 β -cyclodextrin.

CD-based assembly, which leads to the highly-ordered structure in the crystalline self-assembly.

The high extent orientation of the CDs in the resultant crystalline self-assembly makes it possible to generate amplified circular dichroism signals for the guest through the chirality transfer process. For instance, the strong ICD signal was found in the microtubes formed with SDS@2 β -CD (Figure 4a) [59]. In line with HK's rule, the positive ICD signal indicates that the electronic dipole moment of SDS, which is close to the sulfate group, is included inside the β -CD's cavity. This is indeed the case. The height of a β -CD monomer is about 0.8 nm, and the channel structure formed by two β -CDs is about 1.6 nm long. However, the extending length of SDS is about 1.25 nm, which is much shorter than the depth of the channel. As a result, the sulfate group is sheltered in the cavity of SDS (Figure 4b). Interestingly, the ICD of SDS in this microtube crystalline self-assembly can be further transferred to fluorescent dyes thioflavin T (ThT) and Nile red, which allows generating of CPL (Figure 4c) [59]. It is worth noting that the whole process of chirality transfer is multilevel, mimicking the multiple chirality transferring process in nature. First, the intrinsic molecular chirality of β -CD is successfully transferred to the building block

of supramolecular assemblies consisting of SDS@2 β -CD. The supramolecular building block furthermore assembles into a nanoarray structure driven by the abundant hydrogen bonding between β -CDs. The strong ICD and CPL signals for the dye-doped nanosheet indicate the following level of chirality transfer from the channel type host-guest building block to a chiral nanosheet. Furthermore, the chiral nanosheet would curl into chiral microtubes, which is the third transfer of chirality. Finally, doping with achiral fluorescent dyes (ThT and Nile red) was considered the final level of successful chirality transfer, which directly leads to strong CPL with a large unsymmetrical factor of $g_{lum} = 0.1$ (Figure 4c).

Chirality manipulation of supramolecular self-assembly based on host-guest dynamics

In the past decades, H—K rule is only used to identify the absolute conformation of the host-guest inclusion complex, although various CD-based dynamic materials have been developed [60,61]. Recently, it was found that the threading depth of the guest's dipole transition moment in β -CD's cavity can be manipulated via host-guest dynamics, which may alter the position of the dipole transition moment of guest inside the cavity. As a result, the ICD signal might be inverted, making it a feasible method to intelligently design and construct chiroptical switching materials by using the host-guest crystalline self-assembly of CDs.

Host-guest dynamics to control chirality inversion

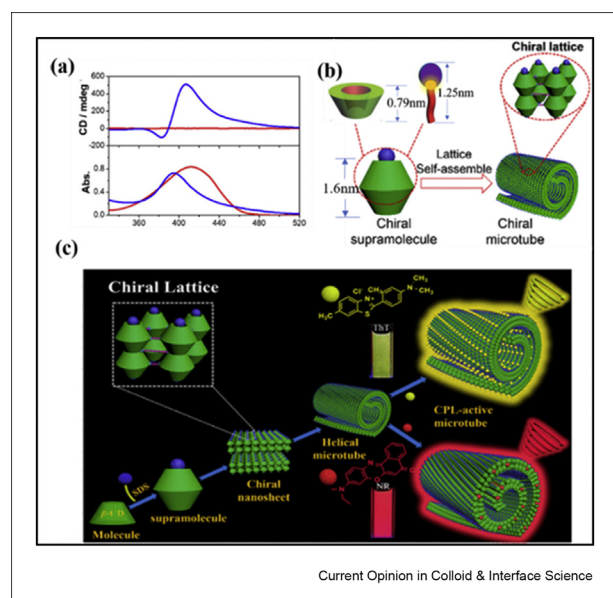
Alkyl amide chain length-dependent ICD (induced circular dichroism)

Based on the principle mentioned previously, Yan et al. [62] used the alkyl amines with the carbon number of 8 and 9 to construct host-guest complexes with β -CD. Mesoscopic right-handed helical ribbons were formed both in the C₈NH₂@ β -CD and C₉NH₂@ β -CD systems. Two-dimensional NMR (nuclear magnetic resonance) demonstrates that the oriented threading of C₈NH₂ and C₉NH₂ into the cavity of β -CD has happened in both systems, but molecular simulations suggest that the amino group for the C₉NH₂ outcrops the cavity of β -CD, whereas that for the C₈NH₂ remains inside. On the basis of H—K rule, the former should have a negative ICD, whereas the latter is positive. This is indeed the case. Experimentally, they observed this chain length-dependent chirality inversion of the ICD (Figure 5).

Host-guest dynamics to control chirality

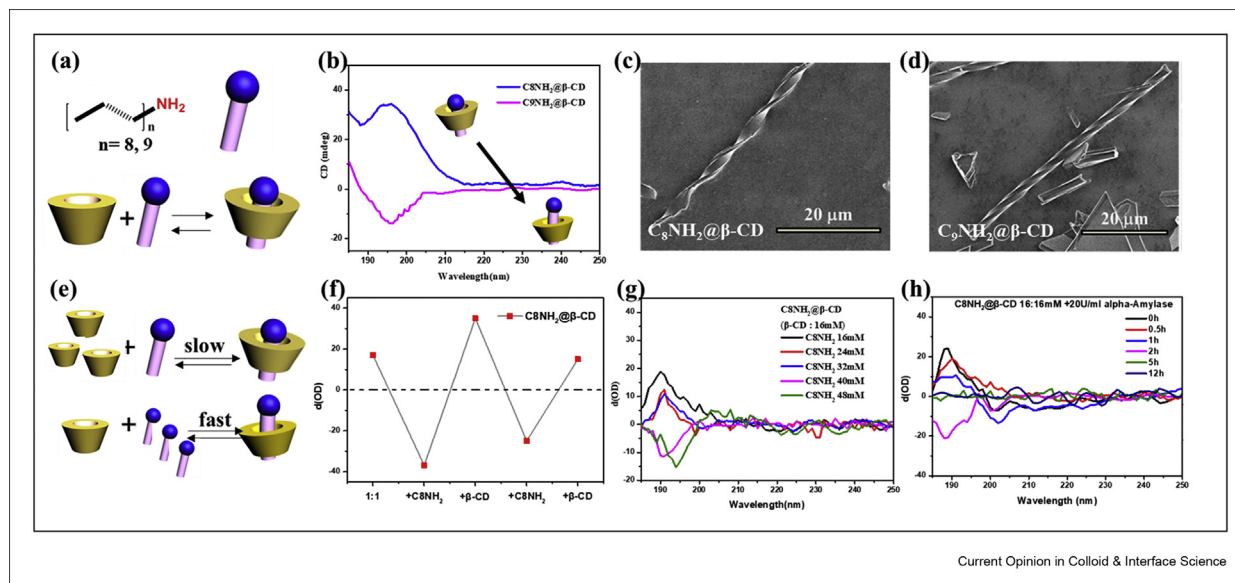
Because the chain length of the two alkyl amines in 4.1.1 is only different from each other by 1 carbon, this inspires that a shallower threading of the C₈NH₂ in the β -CD's cavity would result in inversion of the ICD of the helices. In the next step, they confirmed this hypothesis by controlling the host-guest dynamics. The rationale is

Figure 4



ICD for the crystalline tube and lamellae. (a) ICD (induced circular dichroism) and corresponding UV-vis (ultraviolet -visible) absorption spectra obtained from a sole ThT aqueous solution (red line) and 10% SDS@2 β -CD/ThT complex (15/1) (blue line). (b) Schematic description of the construction of a chiral microtube on the basis of the crystalline self-assembly of SDS@2 β -CD building block (The yellow dot represents the center of the dipole transition moment in SDS). (c) A schematic description of the host-guest crystalline self-assembly process of SDS@2 β -CD and dye [59]. SDS@2 β -CD/ThT, sodium dodecyl sulfate@2 β -cyclodextrin/thioflavin T.

Figure 5



Host-guest dynamics to control chirality. (a) Schematic diagram of the molecular structure of C_nNH_2 ($n = 8, 9$) and host-guest equation between C_nNH_2 ($n = 8, 9$) and β -CD. (b) Circular dichroism spectrometry and schematic diagram of $C_8NH_2@\beta$ -CD and $C_9NH_2@\beta$ -CD systems. SEM (scanning electron microscope) photographs of the mesoscopic helix of (c) $C_8NH_2@\beta$ -CD and (d) $C_9NH_2@\beta$ -CD. (e) Schematic diagram of two host-guest dynamic illustrations. Induced circular dichroism spectroscopy (ICD spectrum) change of the (f) $CH_3(CH_2)_7NH_2@\beta$ -CD inclusion system with alternatively changing the molar ratio of $CH_3(CH_2)_7NH_2$ and β -CD, (g) $CH_3(CH_2)_7NH_2@\beta$ -CD systems on adding $CH_3(CH_2)_7NH_2$ (from 16 mM increasing to 48 mM) at a settled amount of β -CD. (h) $CH_3(CH_2)_7NH_2@\beta$ -CD (at a settled 16:16 mM) complex solution after the addition of 20U/mL alpha-amylase in 12 h [62]. B-CD, β -cyclodextrin.

that for the host-guest inclusion of $C_8NH_2@\beta$ -CD, a faster guest exchange between those in and out of the cavity of β -CD would result in a shallower threading of C_8NH_2 in β -CD, thus shifts the $-NH_2$ group from inside to outside of the β -CD's cavity, leading to ICD signal inversion (Figure 5e). To testify this assumption, the authors changed the relative molar fraction between β -CD and C_8NH_2 guest from 1:1 gradually to 1:4⁶². Inspiringly, reversed chiroptical spectra are obtained as expected. As is shown in Figure 5g, the positive Cotton effect corresponding to the molar fraction of 16:16, 16:24, and 16:32 turns into negative when adding guest to a molar ratio of 16:40 and 16:48. Furthermore, the host-guest dynamics-caused chirality switching is completely reversible. By supplementing extra β -CD to the 16:48 negative chiroptical system, the chiral signal is positive again when arriving at a molar ratio of 48:48. Figure 5f illustrates that the reversible inversion of the chiroptical signal between two opposite states could be alternatively obtained by changing the molar fraction between β -CD and C_8NH_2 .

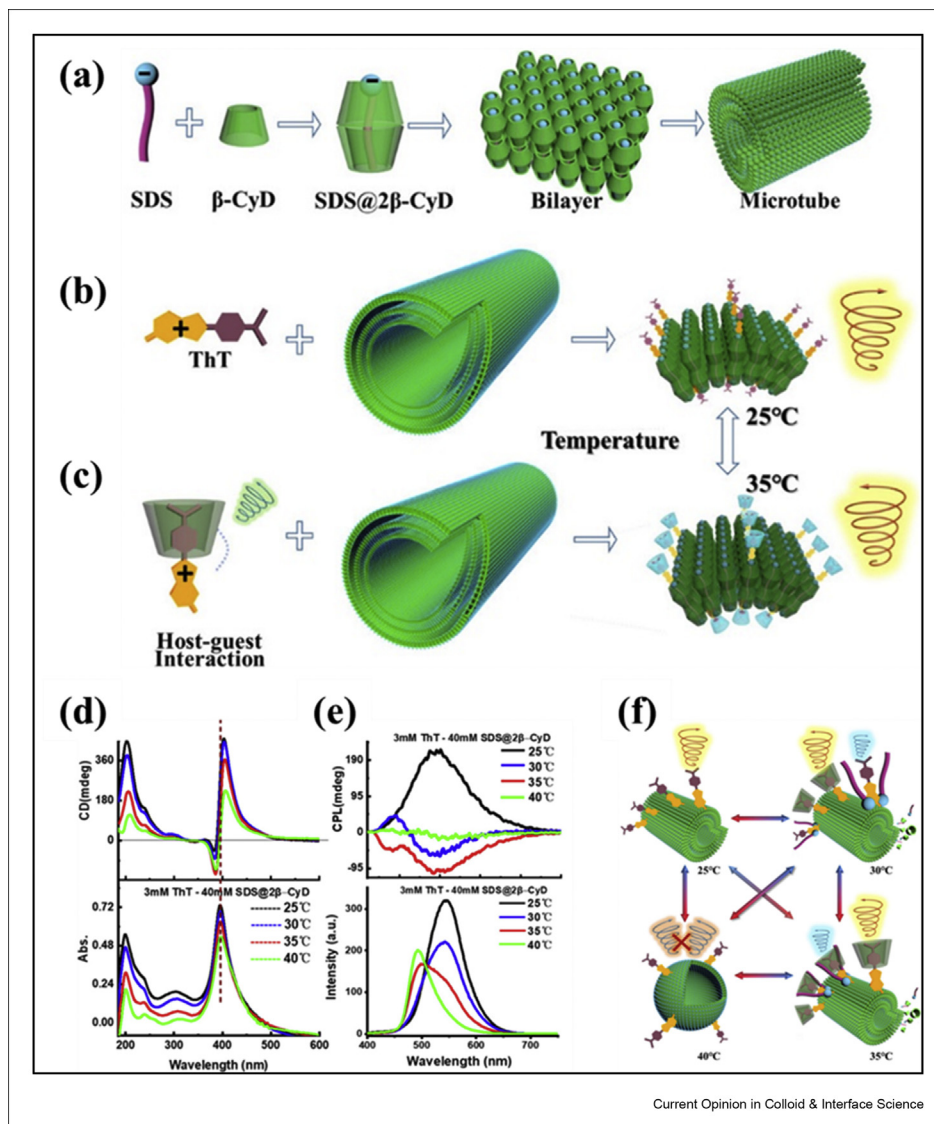
The host-guest dynamics-directed chirality inversion can also be achieved by addition of α -amylase to hydrolyze β -CD, because this will reduce the absolute amount of β -CD, which is equivalent to increasing the molar ratio of C_8NH_2 : β -CD. Excitingly, through changing the molar fraction by α -amylase-induced

hydrolysis of β -CD, enzyme-responsive supramolecular chirality manipulation is achieved. Figure 5h shows the real-time shift of the circular dichroism signal on addition of α -amylase to the 16:16 mM $C_8NH_2@\beta$ -CD system. As is illustrated in the figure, the chiroptical peak is positive at the very beginning, whereas it switches into negative gradually in the subsequent 1 h, demonstrating the decrease of β -CD. When all the rest β -CDs have been hydrolyzed in 5 h, the ICD signal is thoroughly silent. The previous research clearly expounds that supramolecular host-guest dynamics can be used to intelligently control chirality inversion and may initiate a new era of rationally designed chiroptical supramolecular materials.

Chirality manipulation based on crystalline self-assembly transition

On the basis of Jiang and Duan's multilevel chirality transfer using the crystalline self-assembly of $SDS@2\beta$ -CD microtube, Yan et al. [63] moved a further step by creating temperature-triggered reversible CPL (chiral luminescence) handedness inversion (Figure 6). Because the crystalline self-assembly would gradually disassemble with increasing temperature, the released free β -CD would tend to host the dye. In this case, the dipole transition moment of the dye is outside of β -CD's cavity, leading to a negative ICD. This ICD is reverse to the case when the dye binds directly to SDS via

Figure 6



Chirality manipulation based on crystalline self-assembly transition. Schematic diagram of (a) the crystalline self-assembly process of SDS@2 β -CD microtubes, (b) the coassembly of a nonchiral dye ThT with the SDS@2 β -CD microtube to give an l-CPL at 25 °C, (c) temperature-induced (from 25 °C to 35 °C) CPL inversion (from l-CPL to r-CPL) in the complex system of ThT-SDS@2 β -CD microtubes [63]. (d) Circular dichroism spectra and UV-vis (ultraviolet-visible) absorbance spectra. (e) Circularly polarized luminescence spectra and FL (fluorescence) emission of 3 mM ThT/40 mM SDS@2 β -CD suspension by alternately changing temperature. (f) Schematic diagram of six basic CPL switching modes under different temperatures [63]. CPL, circularly polarized luminescence; SDS@2 β -CD, sodium dodecyl sulfate@2 β -cyclodextrin; ThT, thioflavin T.

electrostatic interaction, where a positive ICD for the dye is generated owing to the chirality transfer from SDS to the dye. Because the dye would also be induced to give chiral fluorescence with opposite handedness, they are able to regulate the CPL handedness of the system. It should be pointed out that this CPL inversion is achieved by combining the two situations of H–K rule into the same host-guest crystalline self-assembly at different temperatures. Using the different molecular interacting modes at various temperatures, they are able to create different combinations of the two scenarios illustrated by H–K rule.

As is shown in Figure 6e, a strong positive CPL peak around 580 nm is obtained at 25 °C. The left-handedness of the nonchiral fluorescent dye ThT originates from the successful chirality transfer from the guest SDS, as the coassembly between ThT and the host-guest crystalline self-assembly of SDS@2 β -CD microtubes occurs because of electrostatic interaction. As temperature increases, the scenario changes. First, the hydrophobic part of ThT is sheltered in the β -CD's cavity owing to hydrophobic interaction, leaving the positive charge part of ThT outside. Therefore, a negative CD signal should be induced at the absorbance

area corresponding to H–K rule. Therefore, as temperature increases to around 30 °C, the chiroptical signal is reversed as the ThT@ β -CD inclusion on the SDS@ β -CD microtube wall gives a right-CPL at 580 nm, whereas the ThT@SDS complex still generates an l-CPL peaked at 495 nm. Moreover, when temperature is increased to around 35 °C, the l-CPL peaked at 495 nm also reverses to give an r-CPL, which clearly indicates that those dyes interacting with SDS have also changed into the β -CD's cavity. As temperature further increases to 40 °C, all CPL become silent as the assemblies are destroyed. This study affords a facile strategy to intelligently manipulate the handedness of CPL, which may prosper future applications in various areas such as smart photoelectric devices, intelligent chiroptical switches, and high-class data encryption systems.

Conformation-selective chiral manipulation

Guest-dependent chirality manipulation

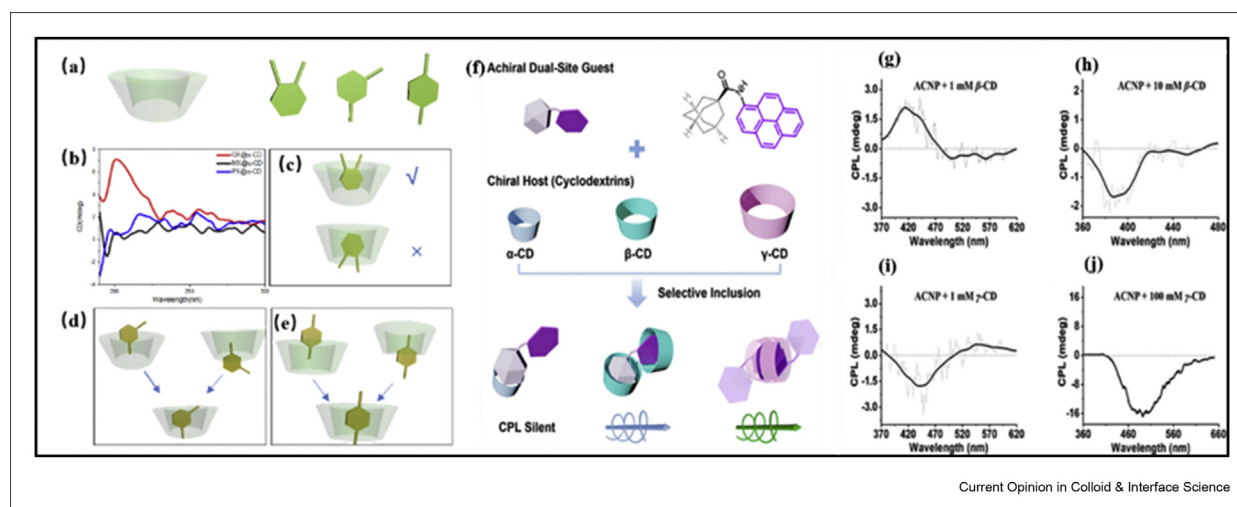
Recently, Huang et al. [64] have found that chirality could not only be manipulated by chain length of the guest but also by isomers. Xylene isomers are used to construct host–guest crystalline assembly systems with size-matching α -CD. ^1H NMR (1 hydrogen nuclear magnetic resonance) and mass spectra prove that the building blocks in the three xylene isomers@ α -CD systems have exactly the same composition. However, their self-assembling behaviors are drastically different. Further study reveals the host-guest conformations for the three xylene isomers@ α -CD are quite different. Circular dichroism measurements indicate only the OX (ortho-xylene) @ α -CD system displays a positive ICD

signal at 206 nm corresponding to the UV absorption spectrum of OX, whereas there is no ICD signal observed for the metaxylene @ α -CD and paraxylene @ α -CD system (Figure 7b). The molecular modeling study suggests that the OX threads into α -CD's cavity predominantly from the wider rim, and its dipole transition moment is precisely inside the cavity of α -CD, thus a positive ICD signal is induced. This oriented threading of OX is attributed to the matching of its size with the wider rim of α -CD. In comparison, both meta-xylene and para-xylene are narrower than OX, so that they are capable of threading into the cavity of α -CD from either rim. This nonoriented threading results in a racemic host-guest complex. Accordingly, no ICD is detected. This isomer-regulated handedness of the crystalline self-assembly indicates that small differences in the isomer conformation can result in significant distinction in the chirality of the crystalline self-assembly, inspiring that people can regulate chirality through fine-tuning of the guest structure in the future without requiring complex chemical synthesis.

Host-dependent chirality manipulation

Liu et al. have found that different sizes of CDs will also affect the chiroptical properties of the formed supramolecular assemblies. Although H–K rule can be perfectly used to explain CD spectra of ground state chirality, it still remains unknown how the CPL, which expresses the chirality of excited state, will change when the lumiphores interact with CDs. A recent work by Liu et al. [65] [66] has filled the blank by focusing on the excited state CPL induction of the CD-based host-guest system. They designed an achiral compound

Figure 7



Conformation-selective chiral manipulation. (a) Schematic structures of cyclodextrin and xylene isomers. (b) Chiroptical spectroscopy (CD spectrum) and (c, d, e) schematic illustrations of different host-guest inclusion positions of xylene isomers@ α -CD complexes [64]. (f) Illustration of designed host-guest interaction systems. The CPL spectrum of ACNP assemblies in 1 mM (g) and 10 mM (h) β -CD aqueous solutions. The CPL spectrum of ACNP assemblies in 1 mM (d) and 100 mM (e) γ -CD aqueous solutions [65]. ACNP, N-(pyren-1-yl) adamantane-1-carboxamide; β -CD, β -cyclodextrin; CPL, circularly polarized luminescence.

N-(pyren-1-yl) adamantane-1-carboxamide (ACNP) to investigate their induced CPL properties by the CDs with different cavity sizes (Figure 7f). ACNP exhibits dual host-guest interaction sites, adamantly group (Ada) and pyrenyl group (Pyr), which could selectively interact with CDs owing to their size match. What is more, Ada is nonemissive, whereas Pyr is emissive. ACNP itself could not display CPL property even after assembly because it is achiral. However, at a lower concentration of β -CD, Ada could be predominantly captured by the β -CD, where chirality of CD could be transferred indirectly to pyrene, and a complex showing positive CPL signals is formed. When β -CD's concentration is increased, β -CD could directly include pyrene, producing a negative CPL. In contrast, γ -CD could directly include Pyr at any concentration. Because the chirality of γ -CD is directly transferred to the Pyr, the signs of CPL signals are always negative. In the case of α -CD, owing to the weak interaction between either group of ACNP and α -CD's cavity, no chirality could be induced to Pyr, and thus, no CPL could be detected. This work has provided a deep insight into the selective interaction of achiral luminophores with the chiral host and the generation of induced CPL in host-guest systems.

Conclusions and perspectives

The crystalline self-assembly chemistry based on the host-guest interaction of CDs and guests is an intriguing platform leading to chiral supramolecular self-assembly with controllable chiroptical properties. The formation of sheets or tube-like self-assembled crystalline structures of CDs allows orientation of the guest in the self-assembly, thus leading to an ICD signal. It should be noticed that the oriented conformation of the guest in the CD's cavity is crucial for the generation of the ICD. The sign of the ICD can be predicted by H-K rule for a given host-guest conformation. Because the host-guest conformation can be regulated by varying the host-guest dynamics, the same host-guest system may display reverse ICD. This offers an opportunity to control the chiroptical property of the self-assembled materials by controlling any physiochemical conditions that may impact the host-guest dynamics, such as concentration, host-guest ratio, or chemicals that may consume either the host or the guest. It should also be noted that a qualified system that is able to undergo chirality inversion should have an electronic transition dipole that is near the rim of the CDs. Only under such circumstances, the variation of the host-guest dynamics would impact the location of the dipole transition moment (μ) of the guest relative to the CD's cavity, namely, in or out of the cavity. Under this circumstance, the chiroptical signal of the self-assembled system can be precisely predicted by H-K rule, and the chirality inversion can be rationally manipulated based on the H-K rule.

Clearly, the host-guest dynamic chemistry would open a new paradigm in manipulating the chiroptical property of self-assembled materials. Up to now, the available examples are based on the host-guest crystalline self-assembly of CDs, because it is capable of providing rigid sheet or tube-like structures that orient the guest. However, we envision that the chiroptical self-assembled materials might also be possible if the host-guest complex is coassembled on the base of an achiral sheet or tube-like structures. In this case, the achiral sheet or tubes may act as a substrate that has the ability of orienting the host-guest complex, so that the guest with induced chirality is well-aligned. In this way, the formation of the crystalline self-assembly is not necessary, and a vast number of molecules of interest can be used for general chiral materials. This is especially useful in creating a smart CPL system, where people are able to use economic materials to form sheets or tubes, and smart CPL materials can be formed simply by coassembling the host-guest complex of a fluorescent material and CDs. By elegant design or careful selecting fluorescent molecules with electronic transition dipoles near the rim of CDs, the resultant CPL materials are expected very smart so as to undergo CPL handedness inversion under external stimuli, paving the way for their practical application in the field of data storage, anticounterfeiting, display, biological science, and advanced optics, and so on.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (21633002, 91856120, 21972003).

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