Surface Chirality

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Remote Chiral Communication in Coadsorber-Induced Enantioselective 2D Supramolecular Assembly at a Liquid/Solid Interface**

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Abstract: *Remote chiral communication in 2D supramolecular assembly at a liquid/solid interface was investigated at the molecular level. The stereochemical information in a chiral coadsorber was transmitted over a flexible spacer with a length of up to five methylene groups to a 2D supramolecular assembly of achiral building blocks with the cooperation of specific hydrogen bonding between the chiral coadsorber and achiral building blocks and the confinement effect during 2D crystallization. When the position of the stereogenic center was changed with respect to the stereocontrolling moiety, an odd–even effect was found. A stereogenic center closer to the stereocontrolling moiety transmitted the stereochemical information to the 2D supramolecular assembly more reliably. This result is beneficial not only for mechanistic understanding of chiral communication in 2D supramolecular assembly on surfaces but also for the rational design of homochiral supramolecular assemblies on surfaces.*

Chiral communication is common in many biological and chemical processes. For example, in stereoselective reactions, a small amount of a chiral catalyst may favor the formation of one enantiomer of the product. Similarly, in polymer synthesis and supramolecular organization, the introduction of a stereogenic center in the monomers or building blocks usually leads to supramolecular architectures with a specific handedness. In these processes, the generation of a specific chirality in the product or the supramolecular architecture is closely related to the efficient communication of the stereochemical information. In general, stereochemical information is introduced by including one or more stereogenic center in the molecule by direct covalent binding, as has been described for helical polymers,[1] metal–organic ensembles,[2] and 1D, 2D, and 3D supramolecular assemblies.[3] In these cases, the molecular structure, including the number of the stereogenic center(s)and their positions, the spacer between the stereogenic center, and the stereocontrolling moiety, acts a major factor for the communication of the stereochemical information.[4] In the case of 1D helical polymers or supramolecular organizations, for example, a stereogenic center linked directly or through a rigid spacer to the stereocontrolling moiety is preferred for efficient chiral communication.[1] Moreover, when the position of the stereogenic center relative to the stereocontrolling moiety is changed, the chiral features of the helical supramolecular architecture follow an odd–even rule.[3a,b,5] The reliability of the chiral communication with respect to the molecular structure is a result of a complex interrelation of steric, stereoelectronic, kinetic, and thermodynamic effects,[4c] and different results have been reported depending on the molecular system.[5d,e]

Recently, some studies showed that chiral guest molecules or chiral solvents that can specifically interact through noncovalent bonds with achiral hosts can efficiently transmit their stereochemical information to the achiral building blocks to enable asymmetric control in the supramolecular assembly of achiral molecules in solution.[6] This approach avoids the tedious asymmetric synthesis of chiral building blocks and is considered to be a simple strategy to induce the formation of homochiral supramolecular architectures. For example, Schenning and co-workers found that the enantioselective supramolecular self-assembly of achiral oligo(*p*-phenylenevinylene) (OPV) derivatives can be induced by both chiral regulators (*R*- or *S*-citronellic acid) and chiral solvents (*S*- or *R*-citronellol).[6e,f] Moreover, the approach is also applicable to 2D supramolecular assembly at a liquid/solid interface.[7] De Feyter and co-workers reported that the introduction of a chiral solvent or a chiral auxiliary or "handle" induced the formation of a supramolecular assembly of achiral OPV derivatives with a preferred handedness.[7a–d] We reported the induction of homochirality in enantiomorphous molecular networks as triggered by chiral coabsorbers at a liquid/solid interface.[7e] In view of the great convenience of using a noncovalent interaction rather than a covalent bond to bias the homochiral assembly, it is of great interest to understand the chiral communication in such chiral-guest-induced enantioselective 2D supramolecular assembly at the liquid/solid interface. In particular, the dependence of chiral transmission on the characteristics of the noncovalent interactions, such as the specificity and the

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strength, needs to be clarified. However, there is little information available about remote chiral communication in 2D supramolecular assembly at solid surfaces, even for molecular systems in which the stereogenic center is covalently introduced, although it has been studied extensively in solution. Supramolecular assembly at the liquid/solid interface is a confined 2D crystallization process. The effects of some pivotal factors, such as specific noncovalent interactions, the configuration and position of the stereogenic center, the spacer, and the substrate are still unclear for chiral communication at solid surfaces.

In this study, we investigated remote chiral communication through noncovalent interactions in enantioselective 2D supramolecular assembly at a liquid/solid interface. Molecular assemblies of 5-(benzyloxy)isophthalic acid (BIC) derivatives, which form 2D enantiomorphous porous networks at the liquid/solid interface when codeposited with alkyl alcohols, were studied as a model system (Figure 1).[7e] It was

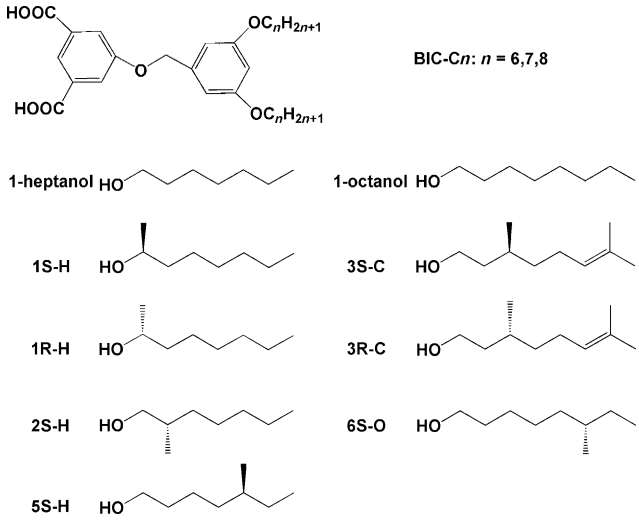

Figure 1. Chemical structures of BIC derivatives and alkyl alcohols. BIC derivatives are abbreviated as BIC-C*n*, in which *n* is the number of carbon atoms in the alkyl chain. In the nomenclature of the coadsorbers, the first two characters indicate the position and spatial configuration of the stereogenic center, and the last letter denotes the backbone structure of the coadsorber, that is, H, C, and O represent heptanol, citronellol, and octanol, respectively.

found that a stereogenic center could transmit its stereochemical information to the achiral BIC building blocks and further to the 2D nanoporous network even when it was separated from the stereocontrolling BIC moieties by five methylene groups and a hydrogen-bonding group (−OH). The handedness of the 2D nanoporous networks followed an odd–even alternation rule when the position of the stereogenic center was changed with respect to the hydroxy end group. Moreover, the reliability of the remote chiral communication increased when the stereogenic center was shifted closer to the hydroxy group. Molecular mechanistic (MM) simulations provide quantitative understanding of the remote chiral communication.

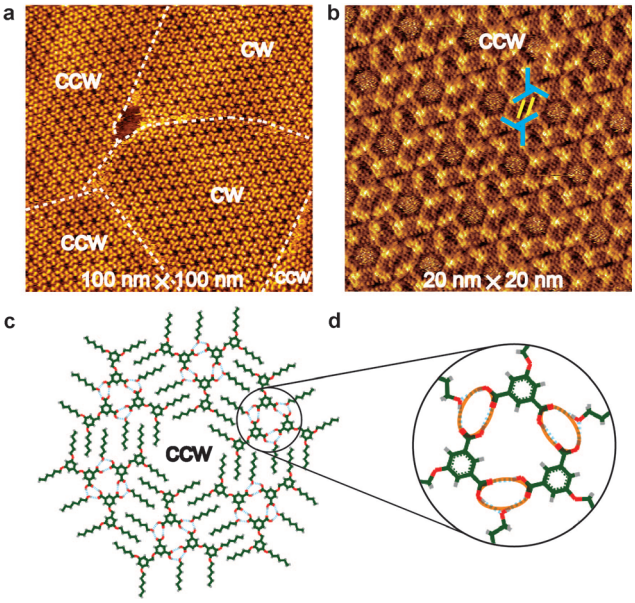

Figure 2. a) Typical STM image of the enantiomorphous networks of BIC-C6 coassembled with 1-heptanol. b) High-resolution STM image of the CCW domain. c) Proposed structural model of the CCW network. d) Illustration of intermolecular interactions within the trimeric aggregations. Tunneling conditions: a) $I = 0.600$ nA, $V_{bias} = 0.900$ V; b) $I = 0.900$ nA, $V_{bias} = 0.700$ V.

The codeposition of BIC analogues with achiral 1-heptanol and 1-octanol was first explored. The porous network formed by BIC-C6 and 1-heptanol is composed of windmill-shaped molecular trimers (Figure 2a). According to the rotational direction of the molecular trimers (clockwise or anticlockwise), two mirror domains, named the CW network and the CCW network, respectively, are discerned in the adlayer. Statistical analysis of more than 200 STM images recorded at different positions suggests that the CW network and the CCW network are present in the adlayer with nearly the same probability, thus implying that the network is locally chiral but globally racemic. In a high-resolution STM image of the CCW network (Figure 2b), the solvent molecules (denoted with yellow lines) were clearly resolved. Figure 2c is a proposed structural model of the CCW network. The intermolecular hydrogen bonding between 1-heptanol and BIC-C6 is illustrated in Figure 2d. The configuration of the hydroxy group exactly fits the chiral hydrogen-bonding pockets of the BIC trimers to form a 10-membered ring stabilized by three O−H···O hydrogen bonds (outlined by the orange circles). A high-resolution STM image and proposed structural model of the CW network are shown in Figure S1 of the Supporting Information. We also investigated the coassembly of BIC-C7 or BIC-C8 with achiral 1-heptanol and 1-octanol. Similar porous networks were formed by BIC-C7 or BIC-C8 with 1-octanol, except that the periodicity increased from 4.6 to 4.8 and 5.0 nm, respectively (see Figure S2 in the Supporting Information). The length of the coadsorber is crucial for the formation of the coassembly: The codeposition of BIC-C7 or BIC-C8 with 1-heptanol led to the disappearance of the porous networks. This result is ascribed to the size

mismatch between the length of 1-heptanol and the vacant space enclosed by neighboring BIC-C7 (or BIC-C8) trimers.

We next examined the codeposition of BIC derivatives with chiral alcohols. We found a similar size-matching effect between the BIC derivatives and the chiral alcohols. Nevertheless, whenever a nanoporous network was possible, all analyzed domains in the coassembly possessed the same handedness. As shown in Table 1, homochiral induction not only exists for **1S-H** and **1R-H**, which have a stereogenic center adjacent to the hydroxy end group, but is also possible with a chiral coadsorber that has a stereogenic center far away from the hydroxy end. In the coassembly of BIC analogues with **6S-O**, for example, a stereogenic center separated by six covalent bonds from the hydroxy end group resulted in a preference for one porous network with a specific handedness, thus implying efficient remote chiral communication in the 2D supramolecular assembly at the liquid/solid interface. Typical STM images of the homochiral networks of BIC-C6 and **1S-H** or **1R-H** are shown in Figure S3 of the Supporting Information. Although chiral-solvent-mediated asymmetric molecular assembly at a liquid/solid interface has been reported previously,[7a,b,f,g] the role of chiral alcohols in the present system can be unambiguously identified as that of a coadsorber on the basis of the high-resolution STM image.[7e]

Table 1: Results of the supramolecular assembly of BIC analogues codeposited with pure achiral and chiral alcohols.[a]

	BIC-C6	BIC-C7	BIC-C8
1-heptanol	CW, CCW	–	–
1-octanol	CW, CCW	CW, CCW	CW, CCW
1S-H	CCW	–	–
2S-H	CW	–	–
3S-C	–	–	CCW
5S-H	CCW	–	–
6S-O	CCW	CW	CW
1R-H	CW	–	–
3R-C	–	–	CW

[a] CW and CCW indicate that the CW network and the CCW network are formed in the coassembly, respectively. A dash indicates that no porous network was present in the coassembly.

The handedness of the 2D supramolecular assembly is closely dependent on the absolute configuration and the position of the stereogenic center. Stereogenic centers at the same position with mirror absolute configurations induce opposite handedness in the 2D assembly. If the absolute configuration is kept the same but the stereogenic center is moved from one atom to the next along the alkyl backbone, the handedness of the resulting network follows an odd–even alternation rule. A special case is the coassembly of BIC-C6 and **6S-O**, which gives a CCW network rather than the expected CW network, thus implying a violation of the odd–even alternation rule. It was inferred that the adsorbed conformation of the stereogenic center is inverted as compared to that of other chiral coadsorbers owing to steric hindrance (see Figure S4 for further analysis and details of MM simulation).

Dilute solutions of a chiral alcohol in nonselective achiral 1-heptanol as the solvent were used to study the chiral-transmission efficiency. For chiral alcohols **1S-H** and **5S-H**, the coverage of the CCW network on the surface increased nonlinearly with the concentration of the chiral alcohol even if only a small amount of the chiral alcohol was present in the solution (Figure 3). All of the networks were CCW when the concentration of the chiral coadsorber reached 20%. However, in the lower concentration range (< 20%), the coverage of the CCW network with **1S-H** was higher than that with **5S-H** at the same concentration of the chiral coadsorber. For example, when 5% of the chiral coadsorber was present in the solution, (80 ± 2)% of the networks were CCW with **1S-H**, whereas only (68 ± 5)% of the networks were CCW with **5S-H**. As the CW and CCW networks are present in nearly equal amounts when coassembled with the diluent achiral 1-heptanol, we propose that the excess of the CCW network formed on the surface when a chiral coadsorber is present in the solution reflects the reliability of the chiral communication during 2D supramolecular assembly. Such a dilution experiment has not been performed for the chiral-solvent-induced asymmetric assembly process.[7a,b,f,g] The efficient chiral communication in the presence of a small amount of a chiral alcohol further validated the hypothesis that the coadsorber molecules, rather than a chiral environment imposed by a chiral solvent, were important for the induction of homochirality in the present study.[7e]

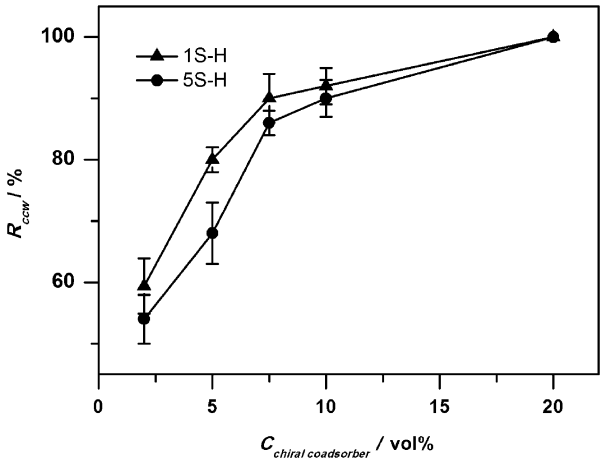

Figure 3. Correlation of the coverage of CCW networks on the surface with the concentration of the coadsorber **1S-H** or **5S-H** as a solution in achiral 1-heptanol. The coverage percentage of CCW networks was deduced on the basis of the number of domains.

To further verify the difference in the chiral-communication efficiency for stereogenic centers at different positions, a mixture of **1R-H** and **5S-H** (1:1, v/v), which induce CW and CCW assembly, respectively, was used as the solvent and codeposited with BIC-C6. Of the resulting networks, 79% of were CW and the remaining 21% were CCW, which correspond to coassembly with **1R-H** and **5S-H**, respectively. This result confirms that the stereochemical information of a stereogenic center at the 1-position can be more efficiently transmitted to the 2D supramolecular assembly at the liquid/

solid interface than that of a stereogenic center at the 5-position.

There is a long-standing argument about the induction mechanism of supramolecular homochirality. One viewpoint is that the domain boundary plays an important role in the chiral induction.[8] The formation of a homochiral surface with a large superstructure of the major enantiomer and a disorganized minor enantiomer can maximize entropy and is thus thermodynamically favored.[8a] On the other hand, the asymmetric interaction of disordered molecules with the building unit of the homochiral assembly at the domain boundary can also induce homochirality.[8b] We explored the dependence of the domain size on the concentration of the chiral coadsorber in the solution and found that the domain size only relates to the concentration of BIC derivatives. For example, when the concentration of BIC-C6 was kept at 4×10^{-4} M for the dilution measurements, the domain size is found to be about 400–900 nm^2, independent of the concentration of the chiral coadsorber. Moreover, the binding of disorganized molecules at the domain boundaries was not observed in the present study. Thus, it is supposed that the role of the domain boundary in the chiral induction is limited. Another perspective is that the chirality of the supramolecular assembly is determined by the conformational preference.[7] We used MM simulation to understand the contribution of the conformational preference to the chiral communication. We simulated the adsorption energy of the alcohols as coabsorbers of the CW and CCW BIC-C6 spiral aggregations (Figure 4, Table 2), which are the essential chiral structural units of the networks. The adsorption energy of achiral 1-heptanol coadsorbed with the CW or CCW BIC trimer is comparable, thus suggesting there is no preference for the CW or CCW chiral unit. When a stereogenic center is present in the coadsorber, a conformational preference appears: The chiral unit with the methyl branch oriented away from the surface is energetically favored (see Figure S5). The adsorption energy of the energetically favored conformation is higher than that of the chiral unit composed of BIC-C6 and 1-heptanol, which is consistent with the ability of the chiral coadsorber to control

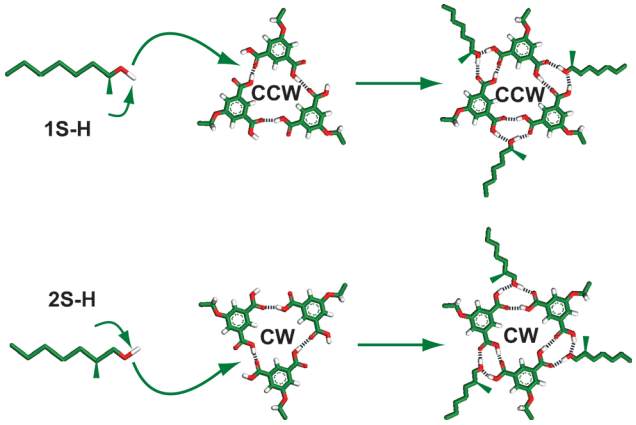

Figure 4. Illustration of the remote chiral transmission in the coassembly of BIC derivatives with **1S-H** and **2S-H**. The hydrogen atoms on the alkyl backbones of **1S-H** and **2S-H** are not shown for clarity. The BIC aggregations are simplified to clearly reveal the chiral hydrogen-bonding pockets.

Table 2: Adsorption energy (in kcal mol^{-1}) of the alcohols as coabsorbers in the CW and CCW BIC-C6 trimeric chiral units.[a]

Adsorption energy	1-Heptanol	**1S-H**	**2S-H**	**3S-H**	**4S-H**	**5S-H**
E_{CW}	263.89	257.53	267.86	257.81	265.34	260.61
E_{CCW}		268.01	257.60	266.06	258.94	265.55
ΔE_{CW-CCW}[b]	0	10.48	10.26	8.25	6.4	4.94
$\Delta E_{chiral-achiral}$[c]	0	4.12	3.97	2.17	1.45	1.66

[a] The chiral structural unit of the coassembly of BIC-C6 and **1S-H**, **2S-H**, or **5S-H** is drawn according to the STM images. The analogous chiral units composed of BIC-C6 and **3S-H** or **4S-H** are proposed by analogy. [b] ΔE_{CW-CCW} is the difference in adsorption energy between the CW and CCW units (absolute value). [c] $\Delta E_{chiral-achiral}$ is the difference in adsorption energy between the energetically favored enantiomer of the chiral alcohol in a coassembly with BIC and the achiral 1-heptanol in a coassembly with BIC.

the homochirality of the surface even when diluted by an achiral nonselective solvent in the dilution experiment. Moreover, when the stereogenic center is moved away from the hydroxy end of the coadsorber, the difference in adsorption energy between the CW and CCW chiral units decreases gradually. At the same time, the difference in adsorption energy between the energetically favored chiral units of BIC-C6 with the chiral coadsorber and achiral 1-heptanol also decreases gradually. This result suggests that a stereogenic center closer to the hydroxy end group has a stronger effect on the adsorption of the chiral unit and induces a clearer preference for one of two mirror configurations. The adsorption energy of individual chiral alcohols does not change much with the position of the stereogenic center. This result is in sharp contrast to that obtained for the chiral coassemblies (Table 2). A plausible reason for the difference is that 2D coassembly at the liquid/solid interface is a confined process. The adsorption of the coadsorber is not only affected by the substrate but also constrained by the neighboring molecules. The violation of the odd–even alternation rule in the coassembly of BIC-C6 and **6S-O** is an example of such a confinement effect.

Overall, it is believed that in the present system, the stereochemical information is communicated through conformational preference during supramolecular assembly. We found that the degree to which the stereochemical information could be communicated through conformational preference was significantly affected by the spacer between the stereogenic center and the interaction site.[1a–d,3b,9] A rigid spacer facilitates efficient long-range transmission of stereochemical information in 1D helical polymers or organizations. In our system, although the spacer, that is, the alkyl backbone between the stereogenic center and the hydroxy group, is generally believed to be flexible, the conformational preference originating from the stereogenic center can be transmitted over this long flexible spacer to determine the handedness of the 2D assembly. It is proposed that the cooperation of noncovalent interactions during the 2D crystallization plays an important role in the efficient remote chiral communication.

Figure 4 illustrates the remote chiral transmission in the coassembly of BIC derivatives with **1S-H** and **2S-H**. Owing to

the steric effect, the stereogenic center has the same conformation in all chiral coadsorbers adsorbed on the surface; that is, the methyl group points towards the solution. Meanwhile, 2D crystallization of the alkyl chains on graphite surface, as induced by van der Waals interactions, makes the flexible alkyl chains act as rigid spacers.[10] Therefore, the conformational preference of the stereogenic center can be transferred over a long distance to determine the orientation of the hydroxy group. Subsequently, the hydroxy group with a specific orientation selectively interacts with BIC trimers of a specific handedness to form the exact geometric complement and the unique hydrogen-bonded ring. The conformational preference is further transmitted through the noncovalent bonding to the BIC trimers. For coadsorbers with stereogenic centers that have the same absolute configuration but at neighboring positions, for example, **1S-H** and **2S-H**, the configuration of the hydroxy group is opposite, and BIC trimers of opposite handedness are formed. As a result, the handedness of the 2D supramolecular assembly follows an odd-even alternation rule when the stereogenic center moves from one position to the next along the alkyl chain. This effect is similar to the *Sol-Rel*, *Sed-Rod* alternation rules developed for cholesteric liquid crystals and odd–even effects later described for polymers and a variety of self-assembled systems.[5a–c,11]

The experimental results and MM simulations suggest that the stereochemical information is communicated more efficiently when the stereogenic center is located closer to the hydroxy group. To induce asymmetric 2D supramolecular assembly, the conformational preference of the stereogenic center should pass through the spacer to the hydroxy end group and finally to the BIC assembly through intermolecular hydrogen bonds. The flexibility of the spacer increases with its length owing to the rotation of the C–C bonds. Thus, the conformational preference is transferred less effectively to the hydroxy end group as the length of the spacer increases. As a result, the ability of the chiral coadsorber to control the 2D supramolecular assembly decreases as the stereogenic center is moved away from the hydroxy end. Furthermore, coassembly of the diluent, that is, 1-heptanol, which forms enantiomorphous networks with BIC derivatives, cannot be excluded. The adsorption energy of the energetically favored chiral unit in **5S-H** is only a little higher than that of achiral 1-heptanol. Therefore, 1-heptanol may readily coassemble with BIC-C6, thus leading to a decreased enantiomeric excess in the adlayer.

In conclusion, communication of the stereochemical information in chiral alcohols induced 2D asymmetric supramolecular assembly of achiral BIC derivatives at a liquid/solid interface was demonstrated. The cooperation of noncovalent interactions, including the hydrogen-bonded rings connecting BIC derivatives and the coadsorber and the van der Waals interactions during 2D crystallization, plays an important role in efficient chiral communication at the liquid/solid interface, that is, in the transmission of stereochemical information through a flexible spacer to the achiral building blocks. Experimental and MM simulations indicate that the presence of a stereogenic center closer to the hydroxy end of the chiral coadsorber is more reliable for the remote chiral communication. The chirality of the supramolecular assembly follows an odd–even alternation rule with respect to the position of the stereogenic center owing to the alternation of the spatial configuration of the stereogenic center when the coadsorber is adsorbed on a surface. This result provides mechanistic insight at the molecular level into the transmission of stereochemical information during supramolecular assembly on a 2D surface. The tunable reliability of the chiral communication within the supramolecular assembly may benefit the rational design of supramolecular chiral structures and materials.

Keywords: chiral communication · interfaces · scanning tunneling microscopy · supramolecular assembly · surface chirality

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