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Amplification of Chirality from Molecules into Morphology of Crystals through Molecular Recognition

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Abstract: We have found a novel type of morphological chiral tuning on inorganic helical crystals through stereochemical recognition of organic molecules. Helical forms consisting of twisted twins emerged from triclinic crystals under diffusion-limited conditions. The proportion of the right- and left-handed helices was precisely tuned with the addition of a specified amount of chiral molecules, such as D- and L-glutamic acids. The chiral molecules recognized the enantiomeric surface of the triclinic crystal and then changed the growth behavior of the helical morphology. As a result, the microscopic chiral information, at a molecular level, was amplified into the macroscopic helices consisting of inorganic achiral components.

Introduction

The concept of "left" or "right", as it relates to various scales and fields in nature, is a fundamental and fascinating phenomenon in any age.[1−5] Biological architectures, including those for amino acids, sugars, DNA, proteins, shells, and tendrils, have chirality at a specified level.[5−7] The chiral architectures in different hierarchies and categories are correlated with each other. For example, the right- and left-handed forms of a snail's body are induced by a single gene speciation.[4] The recognition of chirality is imperative for the understanding of living organisms. Many complex phenomena in life are easily understood through the recognition of molecular chirality; examples of such phenomena are enzymes and substrates or antibodies and antigens. A considerable amount of attention has been given to understanding the phenomena related to chirality and its recognition process because of its significance and broad range of influence.

Recently, much effort has been devoted to clarification of various types of molecular recognition.[8] The concept of stereochemical recognition between a chiral molecule and an inorganic crystal surface has been explored over the past decade.[2,8d,9−16] Many reports suggest the significance and potential for applications, such as biomimetic synthesis, heterogeneous catalysis, and chemical sensors.[9−11] Selective adsorption of a chiral molecule onto the high-Miller-index surface of face-centered-cubic metal has been observed in many combinations.[9,10] Addadi, Mann, and co-workers reported that crystals, including calcite,[12] magnetite,[13] and calcium oxalate,[14] grown in a biological process through stereochemical interaction, have macroscopic chiral morphology.[2,8d,11] Habit modification with stereochemical adsorption of a chiral molecule on a specified crystal plane has also been experimentally demonstrated.[15,16] However, the influence of the chiral molecule just appeared as a reduction of geometrical symmetry on the forms.

Microscopic chirality at a molecular level is well investigated in modern chemistry.[17−22] The asymmetric synthesis and optical resolution of various chiral organic compounds, using asym-

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metric catalysis and several other methods, are essential for our life.[17] Chiral symmetry breaking on crystallization of sodium chlorate[19] and 1,1′-binaphthyl,[20] which provide optically active crystals, has also been demonstrated in both theoretical and experimental studies.[18−20] Helical sense of supramolecular structures, including polymer chains,[21] liquid crystals,[22] and helicates (metal−ligand complexes),[23] is generally determined by the chirality in unit molecules.[5,21−23] Helical arrangement of atoms or ions in several inorganic crystals was demonstrated in cesium copper chloride[24] and gold nanowire,[25] both by experimental and theoretical studies. The study of open-framework materials with helically arranged molecules and micropores was focused on their ability to participate in chiral catalysis or act as separation media.[26]

Macroscopic helical forms found on the assembly of macromolecules[5,27−33] and polymers[34−36] are a typical morphology having chirality, or handedness. The presence of chirality on the unit molecules plays an essential role for the formation of the helical morphology through a twisted assembly. Sugawara et al. prepared a composite of peptides and calcium carbonate with right- and left-handed helical ribbons.[37] The formation of the helical morphology is also ascribed to the chirality of the peptides. In these cases, the handedness of the macroscopic helices is naturally determined by the microscopic chirality of the components.[33,34,37]

In recent years, macroscopic inorganic helices have attracted considerable interest; examples of such materials are carbonates,[38] potassium dichromate,[39] barium sulfate,[40] silica−surfactant composite,[41] manganese oxide,[42] and carbon coils.[43] However, these new classes of chiral architectures consisting of inorganic components have not been fully understood because the helical forms were not composed of chiral components. Moreover, the chirality of the macroscopic inorganic helices was hardly controlled in the previous studies.

We have already reported the emergence of the helical morphology consisting of inorganic crystals without chiral molecules.[44,45] Helical forms were produced upon diffusion-limited growth of triclinic crystals, such as potassium dichromate and boric acid, in various kinds of gel media. The backbone of the helical architecture was found to be composed of twisted-twin crystals of the platy subunit crystals.[45] We observed an equal amount of right- and left-handed helical forms in gel media composed of synthetic polymers including poly(vinyl alcohol) and poly(acrylic acid). In these cases, the main role of the gel media was formation of a diffusion field with suppression of the diffusion of solutes.[44,45] On the other hand, right-handed helices were dominantly obtained in a gel matrix consisting of a biological macromolecule, such as gelatin, agar, and pectin. These results suggest that biological molecules with chirality had a remarkable influence on the morphological chirality of the macroscopic helical forms of the twisted twins. However, the detailed mechanism for the transfer of molecular chiral information into the crystal morphology was not to be clarified because of its complexity.

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In the present study, we investigated the fundamental effects of chiral additives on the macroscopic helical forms and its potential for the chiral tuning behavior. Potassium dichromate was selected as the triclinic crystal to form helical morphology. Poly(acrylic acid) was adopted as gel medium to achieve a diffusion-limited growth condition because it fundamentally provides equal amounts of right- and left-handed helices. Thus, the influence of simple chiral additives, such as two enantiomers each of glutamic acid (Glu) and aspartic acid (Asp), on the handedness of the macroscopic helices could be estimated. Here we successfully demonstrated that the microscopic chirality at a molecular level on the additives was transferred onto the right- or left-handed helices of the twisted-twin crystals at a macroscopic level. Moreover, the proportion of the right- or left-handed helices was precisely tuned by the mixing ratio of the two enantiomers. Stereochemical recognition between a chiral molecule and a specified crystal plane played a key role in controlling the morphological chirality.

Experimental Section

A triclinic crystal of potassium dichromate ($K_2Cr_2O_7$, Kanto Chemical, 99.5%) was grown in a poly(acrylic acid) (PAA, $M_w = 250\,000$, 35 wt % aqueous solution, Aldrich Chemical) gel medium to achieve diffusion-limited growth conditions. Two enantiomers each of glutamic acid (D- and L-Glu, Junsei Chemical, 99.0%) and aspartic acid (D-Asp, Wako Pure Chemical, 98.0%; L-Asp, Tokyo Kasei Kogyo, 98.0%), a total of four different molecules, were adopted as the chiral additives. Iminodiacetic acid (IDA, Tokyo Kasei Kogyo, 98.0%), citric acid (CA, Junsei Chemical, 99.5%), and malonic acid (MloA, Junsei Chemical, 99.0%) were used as the achiral molecules in a contrasting experiment. Stock solutions containing 20 g dm^{-3} of $K_2Cr_2O_7$ and a 20 g dm^{-3} commercial PAA aqueous solution (35 wt %) were prepared using purified water at room temperature. The chiral or achiral additives were added into 10 cm^3 of the stock solutions while the solutions were stirred. Two enantiomers of the chiral additives were mixed at a specified ratio. The total amount of chiral additives was kept at 3 g dm^{-3}. The mixing ratio of the two enantiomers was described as enantiomeric excess (ee), which is defined as the relative concentration difference $(C_D - C_L)/(C_D + C_L)$. Enantiomeric excess was varied in ee $= -1.0$ (pure L-additives), -0.5, 0 (racemic), 0.5, and 1.0 (pure D-additives). After the additive was completely dissolved, 1−3 mm^{-3} (μL) of the precursor solution were dropped on glass slides. The substrate was maintained at 25 °C in the ambient atmosphere, and then crystal growth was achieved by the evaporation of water from the droplets. Crystal morphologies were observed using a field-emission scanning electron microscope (FESEM, Hitachi S-4700).

Results and Discussion

Emergence of Helical Morphology in Gel Media. We have already reported on helical forms of $K_2Cr_2O_7$ crystals grown in various kinds of gel media, as shown in Figure 1.[45] The backbone of the helices was composed of platy subunits through a twisted assembly with a specific direction and angle. The angle of the twisted assembly was fixed at 12° for $K_2Cr_2O_7$, though the rotated direction was just reversed for right- (Figure 1a−c) and left-handed helices (Figure 1d). Figure 1e shows an FESEM image for the starting point of the helical growth, such as the center of a spherulitic morphology shown in Figure 2. The right- and left-handed twists were produced on the opposite sides of the starting point (Figure 1e−h). The results of FESEM observation and XRD measurement indicated that the subunits of the backbone were a tilted component of $K_2Cr_2O_7$, which is surrounded with the {010}, {001}, and {2−11} planes, as shown in Figure 1f.[44,45] According to these facts, we proposed a twisted-twin model for the helical morphology, as shown in Figure 1g,h.[45] In the helical backbone, the tilted subunits are aligned along the ⟨010⟩ direction, with a counterclockwise rotation of ca. 12°. This model implied that right- and left-handed helices consisting of the twisted twins are formed along [0−10] and [010] with regard to the opposite directions from the primary subunit at the nucleation site, respectively. Therefore, we could obtain the equal amounts of right- and left-handed helices. The helical forms were produced with the triclinic crystals, grown with a diffusion-limited condition in gel media.[44,45] The forma-

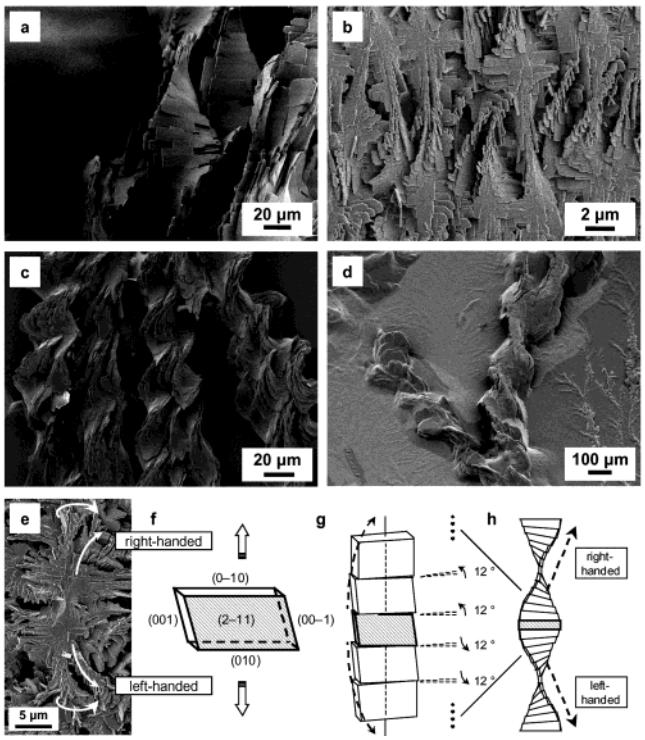

Figure 1. Typical FESEM images (a−e) and structure (f−h) of the helical architectures. (a and b) The backbone of the helical morphologies consisting of platy crystals with a specific twisted assembly. (c and d) Typical right- and left-handed helices, respectively. (e) FESEM image around the starting point, which provides right- and left-handed helices on the opposite sides. (f) A tilted subunit of a $K_2Cr_2O_7$ crystal. (g and h) A schematic model for right- and left-handed helices composed of twisted twins with the tilted subunits.

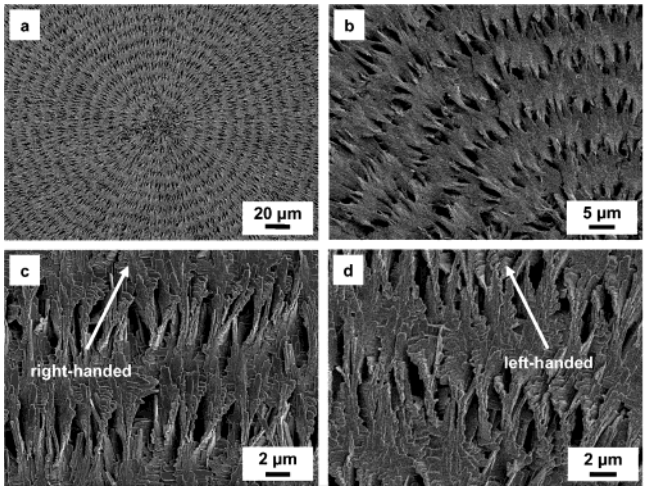

Figure 2. Typical FESEM images of the $K_2Cr_2O_7$ helical architectures grown in PAA gel matrix without the additives after evaporation of water. (a) Spherulitic morphology. (b) Branches having a helical architecture in the spherulite. (c and d) Right- and left-handed helical forms, respectively.

Table 1. Average Proportion of the Right- and Left-Handed Helices

	PAA only	achiral			chiral			
additives	no.	IDA[a]	CA[b]	MloA[c]	D-Glu	L-Glu	D-Asp	L-Asp
right (%)	49.9	49.7	44.4	47.0	69.2	30.9	65.2	32.0
left (%)	50.1	50.3	55.6	53.0	30.8	69.1	34.8	68.0
error[d] (%)	2.8	3.7	7.1	4.1	4.1	3.4	4.3	4.5
samples	17	4	5	3	6	6	12	8

[a] IDA = iminodiacetic acid. [b] CA = citric acid. [c] MloA = malonic acid. [d] Standard deviation.

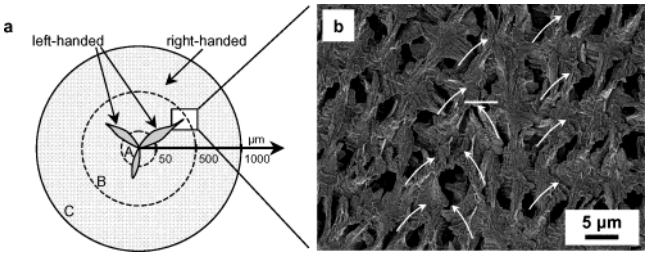

Figure 3. Influence of the chiral additives on growth of the right- and left-handed helical forms. (a) Schematic illustration for distribution of the right- and left-handed helices with addition of D-Glu and D-Asp. Regions A, B, and C are the area surrounded by a circle with a radius of ca. 50, 500, and 1000 μm, respectively. (b) A typical FESEM image for the fade-out of left-handed helices, with frequent branching of the right-handed growth.

tion of twisted twins with a certain rotational direction could be explained considering a diffusion-limited growth in a specific diffusion field around the growing surface of the tilted subunits. However, the detailed mechanism for the formation of the unique morphology is now under investigation, including computer simulation.

Influence of Chiral Additives on the Helical Morphology. After evaporation of water, within several hours, from the droplet of $K_2Cr_2O_7$ solution, the helical forms were obtained on the branches of a spherulitic morphology (Figure 2a,b). Typical images of right- and left-handed helical-twin crystals are shown in parts c and d of Figure 2, respectively. The proportion of the right- and left-handed structures (%) listed in Table 1 was estimated from the area of right- and left-handed helices in the central region of spherulites (region A in Figure 3a). The chiral symmetry of the macroscopic helices was kept in the PAA gel matrix with and without the achiral additives. On the other hand, chiral molecules remarkably influence the morphological chirality. About 70% of right- and left-handed helices were obtained with the addition of d- and l-additives, respectively. Figure 3a shows a schematic illustration for the distribution of the right- and left-handed helices in a spherulitic morphology with addition of D-Glu and D-Asp (ee = −1.0).

Since the chiral symmetry breaking was more extreme in the area farthest from the center, domination of right-handed helices was accelerated with growth of the helical branches from region A to region C. The right-handed helical forms, which account for 70% of the growth in region A, increased with the growth in region B and then completely occupied region C. On the other hand, left-handed helices were swallowed up by the growth of the right-handed forms with frequent branching (Figure 3b). The addition of L-Glu and L-Asp (ee = 1.0), in contrast, induced left-handed dominance with the disappearance of right-handed forms. The selection and amplification of the macroscopic chirality with the crystal growth, as described here, are very interesting phenomena that are similar to the natural selection.

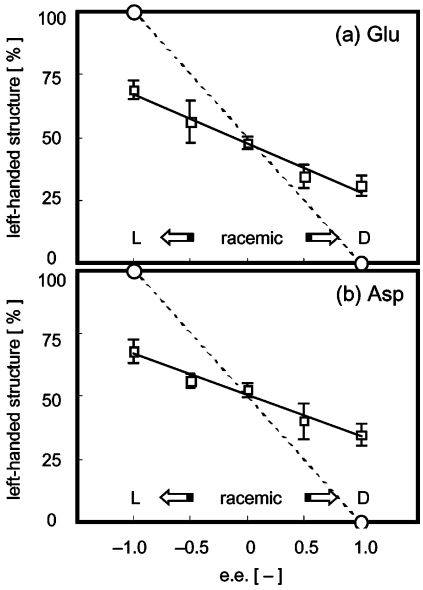

Figure 4. Macroscopic chiral tuning in region A (open squares) and region C (open circles) with increasing ee value. (a and b) The proportion of the left-handed helices with addition of D-, L-Glu and D-, L-Asp, respectively.

On the other hand, the chiral symmetry was kept everywhere in a spherulitic morphology with and without achiral additives.

Precise Tuning of the Morphological Chirality. We successfully tuned the proportion of the right- and left-handed helices by varying the ee of Glu and Asp (Figure 4). Open squares in Figure 4 indicate the proportion of left-handed helices with variation of ee in region A of Figure 3a. The initial proportion of the left-handed helices (70%) at ee = −1.0 decreased to approximately 55% at ee = −0.5. Almost equal amounts of right- and left-handed structures were then obtained at ee = 0. Finally, the dominance of the handedness was changed to 70% of the right-handed forms at ee = 1.0. Tuning the proportion of right- and left-handed forms was achieved using the ee value. Moreover, open circles in Figure 4 show the proportion estimated in region C of Figure 3a. Considering the distribution of the right- and left-handed helices, the more remarkable tuning was achieved in the region surrounding the spherulites.

The macroscopic chiral tuning is ascribed to stereochemical interaction between the chiral additives and the specific crystal planes of $K_2Cr_2O_7$. Although morphological modification by the stereochemical interaction was widely reported,[2,8d,9,11−16] the interaction of the chiral molecules was only observed as a habit modification and a reduction of symmetry on the shape. In this study, we recognized that the influence of the microscopic chirality appeared as a tuning effect of the morphological chirality on helical forms of inorganic crystals prepared without chiral information. The presence of the chiral molecules was not important for construction of the helical morphology, but it was essential for tuning of the handedness of helices through stereospecific interaction at the interface.

Chiral Symmetry Breaking on the Helices through Molecular Recognition. It is generally accepted that chirality resides at the crystal surface in the lower symmetry of crystal systems, even if the bulk structure is not chiral. Many previous studies indicated that stereochemical interaction of the "top" surface with chiral molecules would be different from that of the "bottom".[2,8d,9,11−16] Thus, the crystal growth at the specified planes, such as (010) and (0−10), would be selectively inhibited by adsorption of a chiral molecule through stereochemical

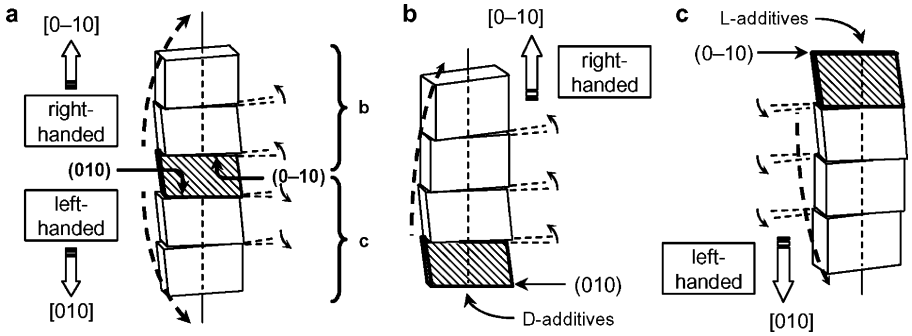

Figure 5. Schematic illustrations for (a) the fundamental structure of the helical morphology and (b and c) preferential formation of right- and left-handed helices by selective inhibition of the growth in the [010] and [0−10] directions, respectively.

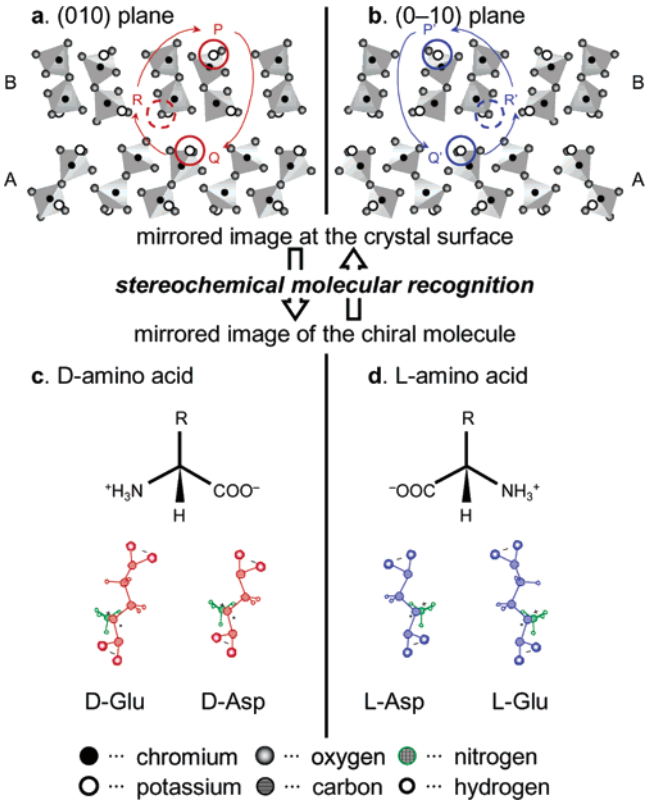

Figure 6. Schematic model for stereochemical recognition between the {010} planes of $K_2Cr_2O_7$ and chiral molecules. (a and b) The surface cleavage of the (010) and (0−10) planes. (c and d) The structures of the enantiomers for the amino acids.

recognition (Figure 5a). Assuming the crystallographic direction of a $K_2Cr_2O_7$ subunit, as shown in Figure 1f, the formation of right- and left-handed helices is attributed to twisted assembly, with a counterclockwise rotation in the [0−10] and [010] directions, respectively (Figure 5a). The fact that the right-handed structure was dominantly obtained at ee = 1.0 (Table 1 and Figure 4) could be explained by the stereospecific interaction of D-additives with the (010) plane. The stereochemical adsorption of the enantiomers selectively inhibits the growth in the [010] direction. In a similar manner, the preferential formation of left-handed helices is also ascribed to the specific adsorption of the L-additives on the (0−10) plane (Figure 5c). Consequently, we observed that the proportion of right- and left-handedness was precisely tuned with variation of the ee value.

A schematic model in Figure 6 shows the concept of stereochemical recognition on the (010) and (0−10) planes of $K_2Cr_2O_7$ with chiral molecules. If the setting of the crystallographic axes is reversed in the unit cell, the spatial positions of the (0−10) and (010) planes are also reversed in Figures 1f, 5, and 6. The essence for the morphological chiral tuning on the helical morphology is the selective interaction of D- and L-additives with the top and bottom planes of the inorganic crystals. The structures of chiral molecules, such as D- and L-amino acids, are reflected images of each other (Figure 6c,d). Two carboxy groups and an amino group arranged around an asymmetric carbon atom would play an important role for the interaction with a solid surface. The surface cleavage of the {010} planes composed of the A and B layers is illustrated in Figure 6a,b.[46−48] The arrangements of the cations (K^+) and anions (O^{2-}) on the {010} planes are also mirror images, as shown in P−Q−R and P′−Q′−R′ in Figure 6a,b.

These enantiomeric crystal surfaces could stereochemically recognize the chiral molecules. The right-handed dominance with addition of D-Glu and D-Asp implies affinity between the D-additives and the (010) plane through stereospecific adsorption. In the same manner, L-additives also selectively adsorbed on the (0−10) plane. Finally, the stereospecific adsorption of the amino acids on the {010} plane would change the growth behavior (Figure 5) and then control the proportion of the right- and left-handed forms (Figures 3 and 4). In this way, the microscopic chirality at a molecular level was transferred and amplified into macroscopic chirality through a stereochemical recognition process.

Conclusion

Helical twins were composed of triclinic inorganic crystals without a chiral component. The morphological chirality at a macroscopic level was precisely tuned with the addition of chiral organic molecules. Stereochemical recognition between the enantiomeric molecules and crystal surfaces was essential for the chiral amplification. The molecular recognition mediating chirality is extremely important for understanding complex phenomena in biological systems. Moreover, crystal design with the use of molecular recognition is expected to be widely applicable to various types of material fabrication.

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(48) The atomic arrangement of potassium dichromate on the (010) plane in Figure 6 was illustrated by Crystal Designer (version 6.02, Crystal Structure Design AS, 1997) and ref 46. The atomic parameters were taken from ref 47.