

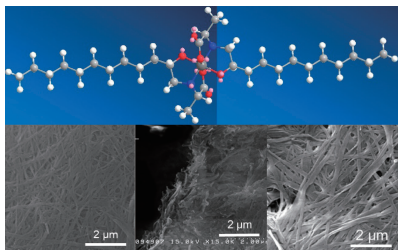
Coordination Lamellar Nanofibers Consisting of *N*-(2-Hydroxydodecyl)-substituted Amino Acid and Divalent Copper Cation

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Lamellar nanoribbons consisting of 1:2 complexes of divalent copper and *N*-(2-hydroxydodecyl)-substituted amino acid were newly developed. When racemic ligand was used, the lamellar size showed shrinkage and the stability of the fibrous nanostructures were enhanced compared to that consisting of pure enantiomer.

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Lamellar nanoribbons consisting of 1:2 complexes of divalent copper and *N*-(2-hydroxydodecyl)-L-alanine (L-AlaC₁₂OH) and related *N*-(2-hydroxydodecyl)-substituted amino acid were newly developed. When racemic ligand was used, the lamellar size showed shrinkage and the stability of the fibrous nanostructures were enhanced, reflecting the spontaneous effective mixing of L and D complexes to form supramolecular racemic compounds.

Coordination compounds show a wide variety of unique properties such as magnetism, optical, redox, and catalytic activities. These properties originate from the arrangement of the metal center and ligands, whereas their functionalities are often determined in the nanometer or subnanometer scale. That is, when these coordination compounds are fabricated for application, structure of some tenth nanometers or submicron-scale critically affects these properties. For example, the total catalytic activity is not only affected by the reactivity of the active site but also by the diffusion of the reactant for accessing to and eliminating from these active sites. Thus, the catalytic function requires a design both for the active site and the mesoscale structure that direct the mass transport of the substrates and reactants. In contrast to the brightful success in developing the structures of nanometer or subnanometer scale by suitably programming covalent or coordination bonds,¹ control of coordination architectures and their functions in the mesoscale is in the developing world.²

We focused here on the programming of mesostructures by using weak interactions between amphiphilic chiral metal complexes. Although the formation of chiral nanostructures from chiral organic molecules has been widely investigated,³ the self-assembly of chiral and racemate metal complexes as a tool to regulate their molecular alignment has been largely unexplored.

In this study, a family of chiral lipophilic ligands, alanine and valine modified with hydroxydodecyl groups, *N*-(2-hydroxydodecyl)-L-alanine (L-AlaC₁₂OH), *N*-(2-hydroxydodecyl)-D-alanine (D-AlaC₁₂OH), and *N*-(2-hydroxydodecyl)-L-valine (L-ValC₁₂OH), were synthesized. They are known to form twisted fiber structures with sodium or magnesium salt;^{4,5} however, the complex with copper has not been investigated.

The ligands D/L-AlaC₁₂OH and L-ValC₁₂OH were synthesized according to the previous report.⁴ NMR and elemental analyses showed a good purity of the obtained compounds. They were easily soluble in methanol but not in water, and they become soluble in water when excess amount of sodium hydroxide was added. These alkaline aqueous solutions afforded precipitates when mixed with aqueous solution of copper nitrate. Similar ligands construct 1:2 complex with copper ion where

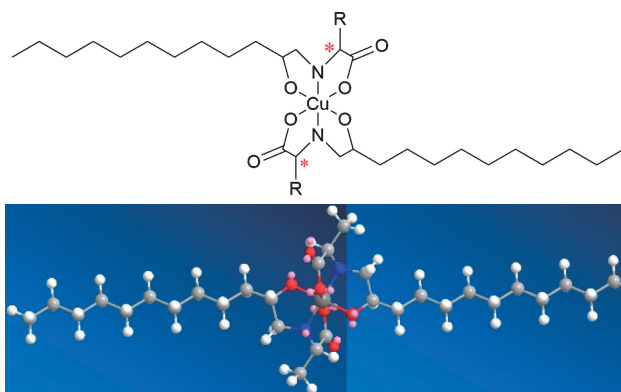


Figure 1. Suggested coordination geometry (top) and optimized structure (bottom) of [Cu(L-AlaC₁₂OH)₂].

two nitrogen atoms and two oxygen atoms of carboxylate groups coordinate in the *trans*-fashion and construct square-planar copper center coordination geometry.⁶ Two oxygen atoms of the hydroxy groups, on the other hand, weakly coordinate to the axial site of the copper, as shown in Figure S1.^{6–8} A presumable structure for the obtained complex is shown in Figure 1. This structure is also supported by the Job's plot of L-ValC₁₂OH and copper, as shown in Figure S2. A peak is observed at the metal to ligand ratio of approximately 0.37:0.73, and the complexation ratio of 1:2 was also supported by the result of elemental analysis. This result is reasonable because no nitrate ion was detected in the IR spectrum. From MM2 optimization, the molecule has two alkyl chains elongated to the opposite direction and the C–C distance of both ends is ca. 30 Å, as shown in Figure 1.

When the reaction was executed in a mixture of water and methanol (1:4 vol/vol), the resultant complexes were stably dispersed. Interestingly, in the circular dichroism (CD) spectra of CT absorption band at 250 nm, the L and D forms showed positive and negative Cotton effects, respectively, whereas the equimolar racemic mixture was CD silent (Figure S3). Because the complex [Cu(L-AlaC₁₂OH)₂] is hydrophobic, it is expected to self-assemble even in a water/methanol solution.⁹ The CD signals observed for pure enantiomer complexes seem to reflect the interactions between the adjacent molecules. When the racemic ligand was reacted with copper, naturally both types of stacking averaged the CD signals and thus no peaks were observed.

The coordination structure of [Cu(L-AlaC₁₂OH)₂] was further investigated by IR spectra (Figure S4). The IR spectra of L-AlaC₁₂OH ligand showed N–H stretching at 3075 cm⁻¹, NH₂ rocking at 1595 cm⁻¹ and scissoring at 1466 cm⁻¹, and

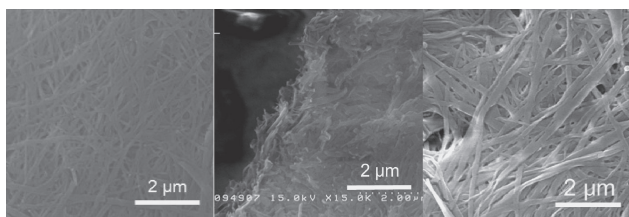


Figure 2. SEM images of [Cu(L-AlaC₁₂OH)₂] (left), [Cu(D-AlaC₁₂OH)₂] (center), and [Cu(D,L-AlaC₁₂OH)₂] (right).

C=O asymmetric and symmetric stretching of carboxylate at 1567 and 1400 cm⁻¹, respectively. These peaks are almost the same as those in pristine alanine, along with the O–H stretching at 3381 cm⁻¹ and indicative of the zwitterionic structure. Meanwhile, when the ligand coordinates to copper, the O–H stretching mode showed a shift to 3168 cm⁻¹. It clearly demonstrates that the hydroxy group coordinates to copper ion without the loss of proton. The peaks at 1634 cm⁻¹ corresponds to C=O asymmetric stretching peak of carboxylate that coordinate monodentately to copper ions. These IR peaks clearly support the coordination geometry of the copper center, as shown in Figure 1.

Scanning electron microscopic (SEM) images are shown in Figure 2. [Cu(L-AlaC₁₂OH)₂] showed nanofibrous structures with ca. 150 nm in width and 50 nm in thickness. The lengths of these nanofibers are quite long. The nanofiber structures are directed by the solvophobic self-assembly of the lipophilic complexes, which would be stabilized by the intermolecular hydrogen bonds between the carboxylate and hydroxy groups. The X-ray diffraction measurement revealed that [Cu(L-AlaC₁₂OH)₂] has lamellar basic structure, as shown in Figure 3. The (001) peak can be observed at 2.70° that corresponds to a *d* value of 32.7 Å, which is in good agreement with the size of the molecule that stacks to the lamellar structure without interdigitation. The ligand alone afforded fibrous lamellar structures; however, it afforded XRD peaks at 4.61 and 5.15°, which corresponded to the long periods of 19.2 and 17.1 Å, respectively (Figure S5). These data are in good agreement with the interdigitated lamellar structures. It should be noted that the ligand has two optically active centers at the alanine part (C^α) and a carbon atom adjacent to the hydroxy group (C^β), as schematically shown in Scheme S1. The chirality of C^α is determined by the amino acid used for the preparation, while both the configurations are possible for C^β. Thus, it is reasonable that the XRD pattern of the ligands revealed two types of lamellar structure *d*-spacings. It is notable that the XRD patterns of copper complexes do not have such side peaks, indicating that regular lamellar structures are formed.

When the copper ion was reacted with a mixture of D-AlaC₁₂OH and L-AlaC₁₂OH, similar ribbon-like nanofibers can be observed with the width and thickness of ca. 250 and 50 nm, respectively (Figure 2). The obtained ribbon for the racemic complex is slightly broader than that obtained for the chiral complex. The XRD pattern of racemic [Cu(D,L-AlaC₁₂OH)₂] was found to be similar to that observed for chiral [Cu(L-AlaC₁₂OH)₂], with a slight shift to higher angle ((001) peak at 2.78° and *d*-spacing of 31.9 Å) (Figure 3). This shrinkage is probably due to the tight packing of the D and L compounds compared to the chiral complexes. The tight packing is also

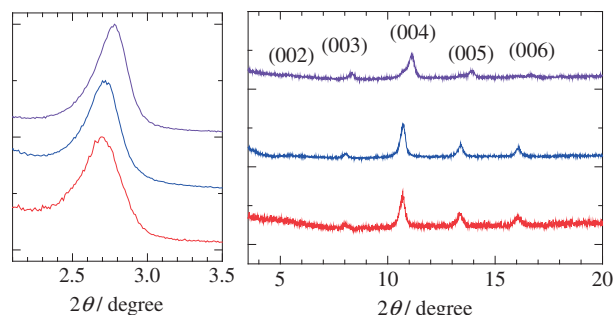


Figure 3. XRD patterns of [Cu(L-AlaC₁₂OH)₂] (red), [Cu(D-AlaC₁₂OH)₂] (blue), and [Cu(D,L-AlaC₁₂OH)₂] (purple).



Figure 4. Photograph of [Cu(L-AlaC₁₂OH)₂] (left), [Cu(D-AlaC₁₂OH)₂] (right), and [Cu(D,L-AlaC₁₂OH)₂] (center).

supported by the fact that the racemic complex is much more stable against the damage caused by the high-voltage electron beam in the SEM measurement. Interestingly, when the water/methanol (1:4) solutions of [Cu(L-AlaC₁₂OH)₂] and [Cu(D-AlaC₁₂OH)₂] were mixed, the solution quickly became cloudy, as shown in the center of Figure 4. It also reflects the interaction of enantiomer complexes to self-assemble into racemic compounds. This result can be attributed to the so-called “Wallach’s rule,” which states that racemic compounds tend to construct denser crystals than their chiral counterparts.¹⁰ Here, the lamellar nanoribbons also show a similar behavior with the previous compounds.

When alanine was replaced with valine, rigid nanofibers were obtained with a reaction of copper ions (Figure S6). From the IR spectra, the copper center was isolated compared to that of alanine, and a free O–H stretching mode can be observed at 3520 cm⁻¹ (Figure S7). The other peaks are quite similar to those with alanine derivatives, and similar stacking was also achieved by the valine derivative. The XRD patterns of the valine derivative were also quite similar to those of the alanine derivative and have typical lamellar patterns from 2.72°, corresponding to the periodic structure of 32.5 Å. These results indicate that the lamellar structures are obtained regardless of the amino acid structure, indicating that the hydrophobic interactions among the alkyl chains determine the molecular alignment in the crystalline structures.

In summary, we have demonstrated lipophilic chiral copper complexes self-assemble to form nanoribbon structures in the water/methanol mixtures. Upon mixing pure enantiomer complexes, they self-assemble into racemic compounds. It indicates that interactions between chiral groups can be employed as a tool to regulate the molecular organization of metal complexes.

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