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A cyclic dipeptide cyclo[–L-methionyl–L-methionyl–] and gold(I) cation were found to form a complex in a 1:2 ratio. Pouring a DMF solution of the complex into ethyl acetate afforded fibers with lengths of more than $20 \,\mu\text{m}$ and 100– $400 \,\text{nm}$ in width, which consisted of fibrous nanostructures 50– $100 \,\text{nm}$ in diameter. Treatment of this supramolecular fiber with catechol gave linearly aligned Au nanoparticles on the original fibers.

Supramolecular polymers are one-dimensionally (1D) aligned small molecules, formed through noncovalent intermolecular interactions such as hydrogen bonding, electrostatic interactions, and π - π interactions. Supramolecular polymers are interesting soft materials because of their flexibility, reversibility, and directionality.¹ They are known to form nanostructures such as fibers, tubes, or wires, which can behave as scaffolds or templates for nanoparticles (NPs). This unique feature of supramolecular polymers is of significance because 1D-aligned metal NPs, especially Ag and Au NPs, can be applied in optical and electronic devices where the particle size, shape, and aggregation state of the arrays influence their physical properties.²

Two main methods have appeared for the introduction of metallic components to fabricate 1D-aligned precious metal NPs. One is the deposition of the NPs on supramolecular polymer scaffolds,^{3–6} and the other involves the fixation of metal cations to supramolecular polymer templates and subsequent electroless-plating-like reduction in the presence of externally added metal cations to form NPs.^{7–12} In the former case, because NPs are generally not stable and tend to aggregate, they must either be used immediately after preparation or be chemically modified by organic molecules. Solutions of noble cations used in the latter case are also unstable, and the complexation conditions need to be controlled carefully.

On the other hand, if the supramolecular polymer can be prepared from metal-ion-containing monomers, incorporation of the metal species in every building unit is ensured, and this would make the formation of 1D-aligned metal cations easier. Concerning this, Nishi et al. reported that nanowire-shaped crystals of silver(I) phenylacetylide could be converted into 1Daligned Ag NP arrays via photoreduction of this organosilver species.¹³ In this example, the organometallic monomer was insoluble, and potentially pyrophoric PMe₃ was needed as a temporal ligand to dissolve the monomers. Lecante et al. reported the formation of quasi-1D-aligned Au NPs from rodlike crystals of AuCl-n-octylamine complexes via autoreduction of Au(I) species in air.¹⁴ The transformation is spontaneous and not controllable. Moreover, in both these cases, the construction of 1D-aligned NPs was based on the nanorod-like crystal structure of the metal-containing species, the formation of which is hardly predictable. In this letter, we report the formation of



Figure 1. Chemical structure of compounds used in this study.

1D-aligned Au NPs from a supramolecular polymer by utilizing the known ability of cyclic dipeptides to make supramolecular polymers and the Au–S interaction. Sulfides are known as temporal ligands for the Au⁺ cation,¹⁵ but there are no examples in which sulfide moieties are utilized as binding sites in supramolecular fibers. Cyclic dipeptides are known to form a tape or layer supramolecular structure owing to the multiple intermolecular hydrogen bonds between rigid diketopiperazine rings,¹⁶ however, they have not been utilized as building blocks for functional materials.¹⁷ Thus, we designed cyclo[–L-methionyl–L-methionyl–] (cyclo[–Met–Met–]) **1** (Figure 1), which is considered to interact with Au(I) cations and to be transformable into a 1D-aligned structure.

Cyclo[-Met-Met-] 1 was synthesized in three steps starting from *N-tert*-butoxycarbonyl-L-methionine, through carboxy group activation, amino group deprotection, and cyclization.¹⁸ The Au⁺ stock solution was prepared through the reduction of Na[AuCl₄] with 2,2'-thiodiethanol (TDE) in methanol according to the method described in the literature.¹⁹ Addition of the Au⁺ solution into a suspension of 1 in chloroform or methanol followed by stirring for 25 h at room temperature in the dark afforded a white solid that was soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The ¹H NMR spectrum of a DMSO- d_6 solution of this solid showed peaks similar to those of 1 but shifted downfield in the range of less than 0.1 ppm for the diketopiperazine rings and 0.12-0.39 ppm for the side chains of the Met residues (see Supporting Information).^{18,20} Elemental analysis of the precipitate indicated that it consists of AuCl and the ligand 1 in 2:1 stoichiometry.²¹ Furthermore, the positive-ion fast-atom bombardment mass spectrum of the precipitate showed a peak with m/z = 329.1, which could correspond to the monocation of the digold complex of 1. From these observations, it is most likely that the precipitate is a 2Au⁺-1 complex, of which the two sulfide moieties on the side chains of 1 interact evenly with the Au⁺ ions; hereafter, we denote this compound as complex 2. Next, thermogravimetric analysis was performed (Figure 2). Compound 1 showed a residual weight of 13% at 500 °C. On the basis of this value, the expected residual weights for 1:1 and 1:2 complexes of 1 and AuCl are calculated to be 47% and 59%, respectively. The



Figure 2. TGA thermograms of 1 and 2. N_2 flow (50 mL min⁻¹), 20 °C min⁻¹.

experimental value for **2** was 66%. Although this is not exactly the same as any of the calculated values, the 1:2 stoichiometry is considered to be more plausible. The deviation might be due to the effect of coexisting Au species on the thermal decomposition behavior of $1.^{22}$

The attempted preparation of Au^+ complexes with other cyclic dipeptides, cyclo[–Nle–Nle–] or cyclo[–His–His–] (Nle: norleucine; His: histidine), was not successful. In the case of cyclo[–Nle–Nle–], the chloroform solution was transparent. After mixing the Au⁺ methanol solution, the mixture became turbid immediately. A small amount of brown solid was precipitated after 14 h. In the case of cyclo[–His–His–], the methanol suspension became transparent after mixing. Stirring for 18 h resulted in gold deposition on the wall. It seemed that Au⁺ cations stabilized by TDE aggregated without continuous interaction with the cyclic dipeptides. These results indicated that the interaction of Au⁺ cations with the S atoms of the sulfide moieties of 1 was important for the preparation of a stable complex.

When $20 \,\mu\text{L}$ of a DMF solution of complex **2** (28 mM) was poured into $80 \,\mu\text{L}$ of ethyl acetate,²³ a white precipitate was formed. Scanning electron microscopic observation revealed that the precipitate consisted of fibers more than $20 \,\mu\text{m}$ long and $100-400 \,\text{nm}$ in width (Figure 3a).²⁴ In the atomic force microscopic analysis, thinner fibrous nanostructures of 50–100 nm in width were also observed (Figure 3b). The use of methanol or chloroform as a poor solvent instead of ethyl acetate resulted in the formation of nonfibrous aggregates of **2** (Figure S1).¹⁸ In situ formation of supramolecular fibers was also attempted with the cyclic dipeptide **1**, Au⁺ methanol stock solution, and ethyl acetate. However, long fibers could not be formed in the case of the DMF–ethyl acetate system, which indicated that temporal dissolution of complex **2** toward DMF was important.

FT-IR analysis was performed to obtain structural information on the fibers of **2**. In the amide I region of the spectrum, two peaks were observed at 1680 and 1651 cm^{-1} (Figure 4, right).^{17b,17f,25} The corresponding peaks of the fibers of **1** appeared at 1678 and 1653 cm^{-1} . This indicates that complexation of **1** with AuCl did not significantly affect the mode of hydrogen bonding (Figure S2).¹⁸ It is interesting to note that a crystal of **1** gives only one amide I peak at 1675 cm^{-1} due to a single mode of hydrogen bonding.²⁶ The fact that the fibers of **1** and **2** afforded two amide I peaks should imply that there are two kinds of 1D hydrogen-bonded tapes of these diketopiperazines in the fibrous state. The intensity ratios of the two amide I peaks



Figure 3. (a) SEM micrograph of the fibers of 2. (b) AFM micrograph of the fibers of 2. The profile shows that the height and the width are 30 and 100 nm, respectively.



Figure 4. FT-IR spectra of the fibers of 1 and 2.

were different for 1 and 2, which might reflect a difference in the preference of the two types of tape structures. The N-H stretching regions of the spectra (Figure 4, left) were similar for 1 and 2, which again indicates the resemblance of the hydrogenbonding state between these two species.

Then, the supramolecular fibers of **2** were treated with catechol.²⁷ Catechol is a mild reductant with moderate hydrophobicity, and its oxidized compound, quinone, is known to have a weak binding affinity for metal surfaces.²⁸ When the fibrous nanostructures were immersed into an ethyl acetate solution of 30 mM catechol, small NPs of 10–20 nm in diameter were formed on their surfaces. After 4 h, all the fibers were finally transformed into the aligned NPs (Figure 5). X-ray photoelectron spectroscopic analysis proved that the NPs were composed of Au⁰ and that the sulfide (thioether) moieties were not oxidized to sulfoxides during the conversion of Au⁺ to Au⁰ (Figure S3).^{18,29,30} A qualitative assay with energy-dispersive spectroscopy showed the presence of all elements other than CI



Figure 5. SEM micrographs of a reduced sample of the fibers of **2** by 30 mM of catechol ethyl acetate solution for 4 h.

after the reduction, indicating that the Au⁺ cations were reduced successfully by the catechol (Figure S4).^{18,31} Concerning the mechanism of the Au NP formation, the UV spectral change of the catechol solution phase revealed that oxidation of catechol occurred within 2 h (Figure S5).¹⁸ At the same time, small Au NPs began to appear on the fibers, and the number and size of Au NPs increased gradually with concomitant thinning of the fibers (Figure S6).¹⁸

In conclusion, the interaction between a Au^+ cation and a bissulfide, cyclo[-Met-Met-] **1**, led to the selective and quantitative placement of Au^+ cations on the surface. The complex as a simple monomeric unit successfully formed a supramolecular nanofiber. Subsequently, Au^+ cations were readily reduced to Au^0 atoms by catechol, and the fiber-like template was transformed into aligned NPs.

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