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Self-Assembly of Tubular Microstructures from Mixed-Valence Metal Complexes and Their Reversible Transformation by External Stimuli**

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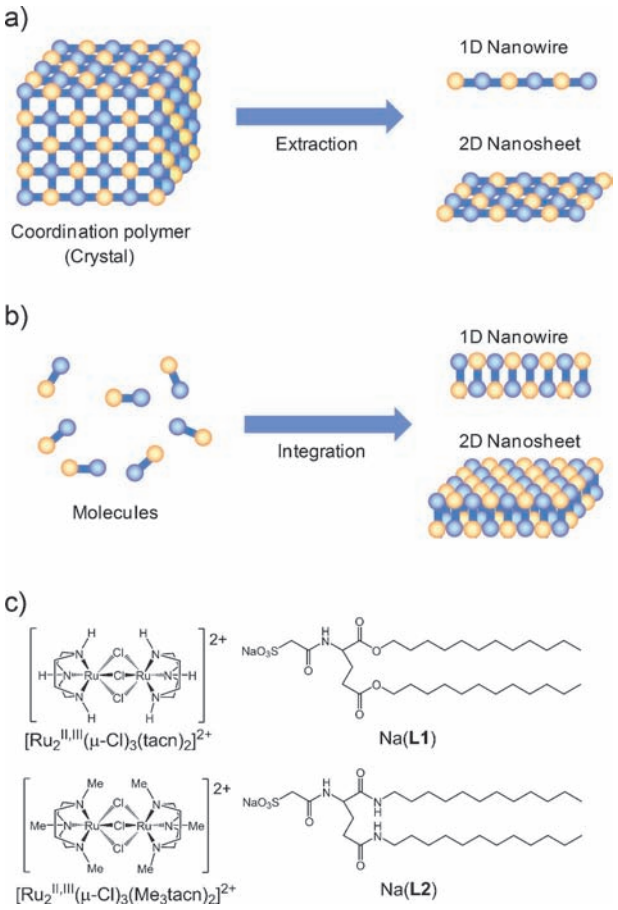
Controlled self-assembly of metal complexes is of high scientific and technological importance for the development of multi-functional materials and devices. Among various types of metal complexes, mixed-valence complexes have attracted much attention because of their wide range of interesting physical and chemical properties from charge-transfer interactions between metal ions linked via bridging ligands.[1–3] In particular, low-dimensional assembly of such mixed-valence complexes gives rise to specific electronic,[4a] magnetic,[4b,c] and optical properties.[4d] Moreover, the assembly of discrete binuclear mixed-valence complexes has been suggested as a basis for forming molecular communication system such as quantum cellular automata.[5] Ideally, the characteristics of such systems would be tunable by controlling the spatial arrangement of the mixed-valence complexes, resulting in electric interaction among metal complexes without covalent or coordinative linkage.

In this context, supramolecular strategies have been developed to construct nanoassemblies of coordination compounds, such as one-dimensional (1D),[6] two-dimensional (2D),[7] and three-dimensional (3D) metal complexes.[8] However, studies to date have focused on the conversion of crystalline coordination polymers to nanowires, nanosheets, and nanoparticles, which can be regarded as isolation of low-dimensional structures from 3D solids (Scheme 1a). In contrast, there exist no reports on the reversible and hierarchical self-assembly of discrete mixed-valence metal complexes (which could not interact with each other) into 1D nanowires, 2D nanosheets, or 3D nanoarchitectures, a concept which would lie at the very heart of bottom-up nanotechnology (Scheme 1b). However, we have developed self-assembled nanowires by amphiphilically modifying such



Scheme 1. Schematic illustrations of the a) isolation and b) integration approaches for constructing nanoassemblies of coordination compounds. c) Chemical structures of lipids and ruthenium complexes.

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mixed-valence coordination compounds.[9,10] The introduction of lipid counteranions to cationic mixed-valence compounds can lead to the dispersion of nanowires in organic media, resulting in the emergence of functionality not available in the solid state.[9–11]

In this study, we first focus on the self-assembly of discrete mixed-valence complexes with lipid amphiphiles. It is well-known that the lipid amphiphiles make it possible to aggregate and self-assemble functional coordination polymers.[6a–e,9–11] Furthermore, this study leads not only to the morphological evolution giving rise to the hypochromic effect, but also to the reversible stimuli-responsive transformation of self-assembled structures. Moreover, this is the first example of reversible, hypochromic effect of discrete mixed-valence complexes formed in organic media. The unusual transformation in solution is discussed based on the results of spectroscopic and microscopic measurements.

Mixed-valence ruthenium complexes with lipid amphiphiles, **L1** and **L2** were synthesized according to literature procedures (Scheme 1 c).[10e,f,11] The composite **1** was obtained by replacement of the counteranion of $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ with **L1** (tacn = 1,4,7-triazacyclononane), while no other combinations of mixed-valence complexes and lipids were found to afford composites worth examining further (see the Supporting Information). This result indicates that $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ and **L1** possess suitable geometry for the formation of a composite. The UV/Vis absorption spectrum of an indigo-colored dispersion of **1** in dichloromethane shows two strong bands centered at 306 and 602 nm (line A in Figure 1 a). The absorption band at 602 nm is similar to that of

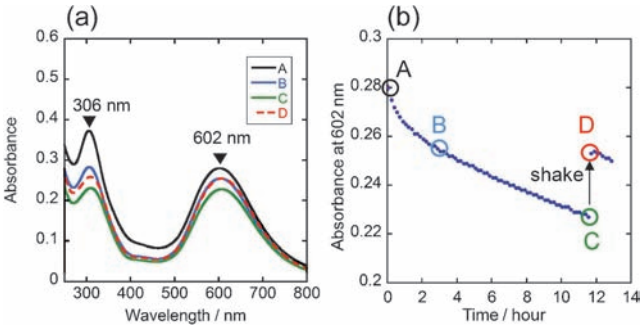
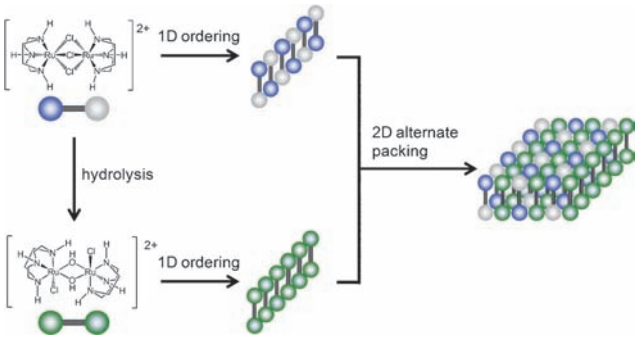


Figure 1. a) UV/Vis absorption spectra of **1** (0.021 mM) in dichloromethane immediately (A); 3 h (B) and 11.5 h (C) after dissolution; and after shaking (D). b) Time dependence of absorption intensity at 602 nm after dissolution of **1** in dichloromethane.

$[Ru_2(\mu\text{-}Cl)_3(tacn)_2](PF_6)_2$ (Figure S2a in the Supporting Information),[12a] indicating that the halogen-bridged mixed-valence structure with Class III state of $[Ru_2^{II,III}(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ is present in the composite **1**. The other strong band ($\lambda_{max} = 306$ nm) corresponds to an absorption band of the hydrolyzed product of $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$, i.e., $[Ru_2^{III,III}Cl_2(\mu\text{-}OH)_2(tacn)_2]^{2+}$ (see Figures S2 and S3).[12] which suggests that the cationic moiety of **1** consists mainly of $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ and $[Ru_2Cl_2(\mu\text{-}OH)_2(tacn)_2]^{2+}$. Interestingly, a simulated spectrum for a 1:1 mixture of $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ and $[Ru_2Cl_2(\mu\text{-}OH)_2(tacn)_2]^{2+}$ is similar to that observed for **1** (Figure S4). Elemental analysis reveals that the composition of **1** is $[Ru_2(\mu\text{-}Cl)_3(tacn)_2][Ru_2Cl_2(\mu\text{-}OH)_2(tacn)_2](\mathbf{L1})_4{\cdot}4\,Na(\mathbf{L1}){\cdot}5\,H_2O$ (Calcd: C 53.09, H 8.78, N 4.55; found: C 53.06, H 8.78, N 4.22), which is consistent with the results estimated from UV/Vis absorption spectroscopy (see Figure S4 for details).

Unexpectedly, after dissolution of **1** in dichloromethane, the absorption bands of **1** gradually decreased, displaying a so-called "hypochromic effect" (Figures 1 and S5).[13] This result suggests that the transition dipole moments of the dinuclear ruthenium complexes are in a parallel arrangement[14] as a result of supramolecular assembly of the dinuclear ruthenium complexes and lipid amphiphiles, as discussed below (Scheme 2). Even more surprisingly, the absorption bands were recovered by simply shaking the solution (C→D in Figure 1). The absorbance change was found to be reversible; the absorbance decreases by standing and recovers by shaking repeatedly (Figure S5).



Scheme 2. Schematic view of the self-assembly of discrete dinuclear ruthenium complexes in the lamellar structure.

To investigate the essential cause of the hypochromic effect and its reversible behavior, the self-assembly structure of **1** was examined by transmission electron microscopy (TEM). TEM images of **1** in dichloromethane taken after aging for various intervals are shown in Figure 2 a–d. The samples taken after dispersing in dichloromethane gave irregular and submicrometer aggregates (Figure 2 a). After aging for 6 h, the blue dispersion gave microtapes with widths of 6–7 μm and lengths of 100–500 μm (Figure 2 b). Surprisingly, upon further aging of the microtapes in dichloromethane for 12 h, tubular aggregates with diameters of 2 μm were obtained (Figure 2 c,d). The image in Figure 2 d clearly indicates the structural transformation from microtapes to microtubes. These aggregates remained dispersed without forming precipitates. Interestingly, upon shaking the dispersion, the microtube structures were transformed to microtape structures, similar to those observed at the aging period of 6 h. This aggregation behavior indicates that the hypochromic effect observed in the UV/Vis absorption spectra is related to the supramolecular self-assembly of dinuclear ruthenium complexes. We suggest that the initial aggregation is fast and kinetically controlled, leading to uniaxial elongation and formation of layered microtapes.[16] In the microtapes, solvophobic region of **1** remains exposed to the surrounding

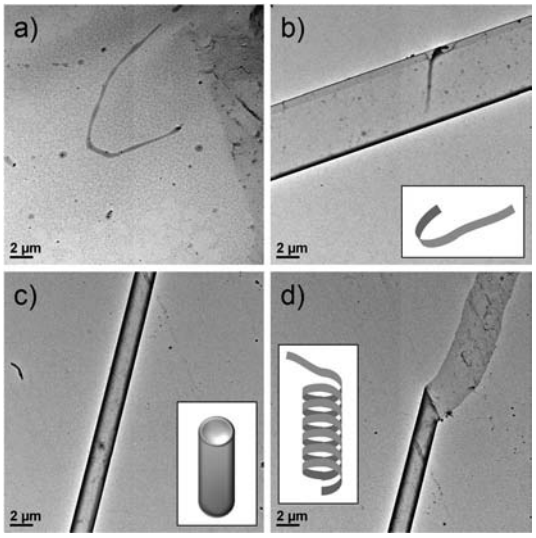


Figure 2. TEM images of **1** upon dissolution in dichloromethane (a), and after 6 h (b) and 12 h (c,d) at room temperature. Samples were observed without negative staining.

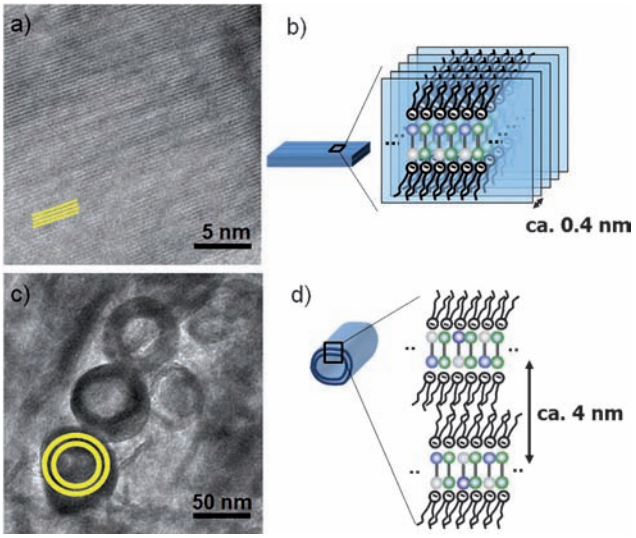


Figure 3. a) HR-TEM image of **1** in dichloromethane after 6 h dissolution at room temperature. The inserted lines mark estimated structures of **1**. b) Schematic view of 2D stacking of lamellar structure of **1** after 6 h estimated based on the HR-TEM image. c) HR-TEM image of **1** in dichloromethane after 12 h dissolution at room temperature. d) Schematic view of double-layered microtube structure of **1** after 12 h dissolution estimated based on HR-TEM image. The inserted circles mark estimated microtubes of **1**. Samples were observed without negative staining.

solvent, and leads to the creation of helical ribbons, and finally microtubes.[15,16] It is noteworthy that these structures can be controlled by external stimuli such as shaking in the case of **1**. The result indicates that the combination of discrete metal complexes and lipid amphiphiles enables some delicate transformation between the dynamic structures.

High-resolution TEM (HR-TEM) images of **1** were therefore obtained to confirm the detailed supramolecular assembly structures of **1**. After 6 h, lamellar patterns in the microtapes were observed with an average spacing of 0.4 nm (Figure 3a). This spacing indicates that the microtape structure is composed of lamellar structures of lipid-packaged complexes (Figure 3b). The double-layered microtubes were observed in abundance after 12 h, as shown by a cross-sectional image, which showed a spacing of around 4 nm (Figures 3c and S6). The number of layers in microtubes is limited to two, and thus lipid-packaged complexes produce double-layered lamellar microtubes with 4 nm spacing in dichloromethane (Figure 3d).

Wide-angle X-ray diffraction (WAXD) measurements of **1** were conducted to further understand the structure of the supramolecular assembly. Figure S7 shows the WAXD pattern (SPring-8 BL02B2, $\lambda = 1.0$ Å) taken for the powder formed by drying solutions of **1** in dichloromethane at room temperature. The WAXD of the powdered **1** showed an intense (001) peak, and weak (002) and (003) peaks at $2\theta =$ 1.55, 3.17, and 4.82°, respectively (Figure S7a). These diffraction peaks indicate the presence of an ordered lamellar structure with a long period of 36.2 Å (Figure S7b). Importantly, this value is consistent with the double-layered structure with approximately 4 nm spacing estimated on the basis of the HR-TEM image (Figure 3c). This value is smaller than twice the molecular length of **L1** (ca. 24 Å, estimated by the CPK model), indicating that the lipid compounds have a tilt orientation with regard to the layer made up of the lipid packaged dinuclear ruthenium complexes. This result suggests that the alkyl chains adopt a more tilted orientation to adapt to the layers consisting of these coordination compounds.

Our spectroscopic and microscopic investigations reveal the details of the self-assembled structure of **1**, as illustrated in Scheme 2. The results of UV/Vis absorption spectroscopy and elemental analysis show that **1** consists of the starting dinuclear complex $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ and the hydrolyzed product $[Ru_2Cl_2(\mu\text{-}OH)_2(tacn)_2]^{2+}$ in a 1:1 ratio. In addition, since hypochromic effects in UV/Vis absorption spectra (Figure 1) are caused by the parallel arrangement of the transition dipole moments,[14] the dinuclear ruthenium complexes are aligned parallel to each other in the bilayer structure of **1**. In particular, the hypochromic effects are observed in both absorptions of $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ and $[Ru_2Cl_2(\mu\text{-}OH)_2(tacn)_2]^{2+}$, indicating that each dinuclear complex forms ordered arrays in the bilayer. Thus, a possible molecular arrangement is proposed to be the alternate 2D packing of 1D $[Ru_2(\mu\text{-}Cl)_3(tacn)_2]^{2+}$ and $[Ru_2Cl_2(\mu\text{-}OH)_2(tacn)_2]^{2+}$ chains (Scheme 2). Indeed, a close-packed simulation of the CPK models of these dinuclear complexes (Figure S8) reveals that the average separation between the closest couple of molecules can be estimated to be 4–5 Å, which is consistent with the interval of the lamellar pattern observed in the HR-TEM images (ca. 0.4 nm; Figure 3).

In conclusion, we have demonstrated that the lipid-packaged mixed-valence complex **1** displays morphological changes with aging of the solution in dichloromethane. Formation of a bilayer structure causes morphological evolution from microtapes to microtubes, giving rise to changes in absorption spectral intensities. Moreover, these morphological and spectral changes can be reversed by

standing or shaking. The technique of combination of lipid molecules and discrete coordination compounds[17,18] makes it possible to design flexible, reversible, and signal-responsive supramolecular coordination systems. The concept of lipid packaging could also be expanded of other useful coordination compounds and should allow us to further develop the nanochemistry of coordination materials.

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