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Nanocrystallization of Insoluble Copper(I) Complex and Formation Mechanism

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We have successfully fabricated insoluble copper(I) complex [Cu(μ-I)dppet]$_2$ nanocrystals by developing the heterogeneous reaction process between rod-like nanocrystals of dppet ligand prepared in advance and added acetonitrile solution of copper(I) halide. During this reaction process, the shape of dppet ligand nanocrystals was dramatically changed from rod-like to spherical. Probably, the complexation reaction and subsequent nanocrystallization would proceed on or near swollen surface of dppet nanocrystals in acetonitrile droplet as restricted reaction field.

Keywords Copper(I) complexes; nanocrystals; heterogeneous reaction process; restricted reaction field

Introduction

Metal-organic complex has attracted much interest so far because of their unique optical [1,2], electronic [3,4] and magnetic [5,6] properties. However, it is difficult to grow the single crystal of organic-metal complex due to their poor solubility. Namely, this fact means that the conventional reprecipitation method cannot be applied to nanocrystallize organic-metal complex. So, we have newly developed and established a useful method to prepare a well-defined metal-organic complex nanocrystals [7]: organic ligand, dppb, was first nanocrystallized by the conventional reprecipitation method [8], and then metal ion solution was further added into the organic ligand nanocrystal dispersion liquid in order to produce complex nanocrystals. As a result, insoluble fluorescent complexes [Cu(μ-Br)dppb]$_2$ [9] were successfully nanocrystallized. During this reaction process, the shape of nanocrystals was changed dramatically from rod-like dppb organic ligands nanocrystals to spherical complex nanocrystal.

In the present study, we have tried to expand the versatility of the novel method to fabricate many kinds of complex nanocrystals, and to investigate the formation mechanism in the novel heterogeneous reaction process. Halogen-bridged binuclear complex [Cu(μ-I)dppet]$_2$ (Fig. 1(a)), which is similar to [Cu(μ-Br)dppb]$_2$, was chosen as a model compound.

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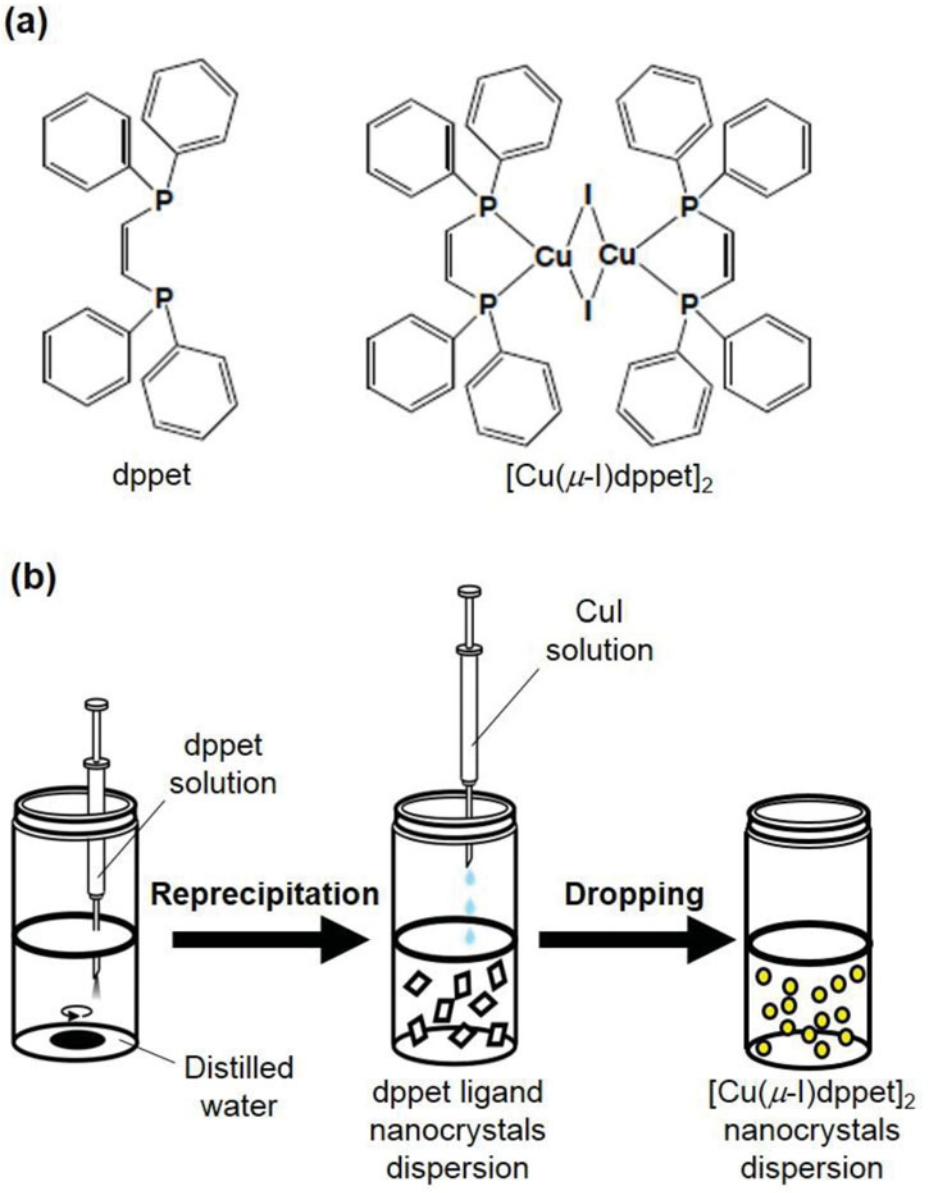

Figure 1. (a) Chemical structure of 1,2-bis(diphenylphosphino)ethylene (dppet) and iodine-bridged copper complex [Cu(μ-I)dppet]$_2$, and (b) scheme of the heterogeneous reaction process to fabricate [Cu(μ-I)dppet]$_2$ nanocrystals.

Experimental

Materials

Copper(I) iodide, 1,2-bis(diphenylphosphino)ethylene (dppet) (Fig. 1(a)), and all solvents were commercially available. All chemicals were used without further purification.

Synthesis of [Cu(μ-I)dppet]$_2$ Bulk Complex

A toluene suspension (2.5 mL) of copper(I) iodide (56 mg, 0.13 mmol) was added into a toluene solution (2.5 mL) of dppet (24 mg, 0.13 mmol). The reaction mixture was stirred for 5 h at room temperature. The pale-yellow precipitate formed was filtrated off and washed successively with toluene, acetonitrile, and methanol, and dried *in vacuo*. The yield of [Cu(μ-I)dppet]$_2$ bulk complex was *ca.* 85%. Elemental analysis of the resulting bulk complex was a good agreement with calculation value.

Fabrication of Low Crystallinity Complex Nanocrystals

Figure 1(b) shows the scheme of the heterogeneous reaction process between dppet ligand nanocrystals and copper(I) iodide dissolved in acetonitrile solvent to fabricate nanocrystals of [Cu(μ-I)dppet]$_2$. In a word, dppet ligand nanocrystals were first prepared by the conventional reprecipitation method (good solvent: acetone, and poor solvent: distilled water), and then acetonitrile solution of copper(I) iodide was added dropwise into dppet ligand nanocrystals dispersion liquid.

Annealing Treatment

The resulting [Cu(μ-I)dppet]$_2$ nanocrystals dispersed in water were filtrated, and then annealed at 160°C for 10 min in nitrogen atmosphere so as to further raise the crystallinity.

Characterization

Samples were observed using scanning electron microscope (SEM; JSM-6700F, JEOL). Powder X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (D8 ADVANCE, Bruker).

Results and Discussion

Fabrication of [Cu(μ-I)dppet]$_2$ Nanocrystals

An acetone solution (200 μL) of dppet (0.8 mg, 2 μmol) was injected into vigorously stirred distilled water (10 mL), so that dppet ligand nanorods were formed in an aqueous dispersion liquid. Subsequently, acetonitrile solution (200 μL) of copper(I) iodide (0.4 mg, 2 μmol) was added into the dppet ligand nanorods dispersion liquid. The colorless dispersion liquid of dppet nanocrystals was gradually turned into pale yellow. During the heterogeneous reaction process between dppet ligand nanorods and copper(I) iodide - acetonitrile solution, dppet ligand nanorods were changed dramatically into spherical as shown in the SEM images of Fig. 2. This shape change was more considerably noticeable, rather than [Cu(μ-Br)dppb]$_2$ nanocrystal [7].

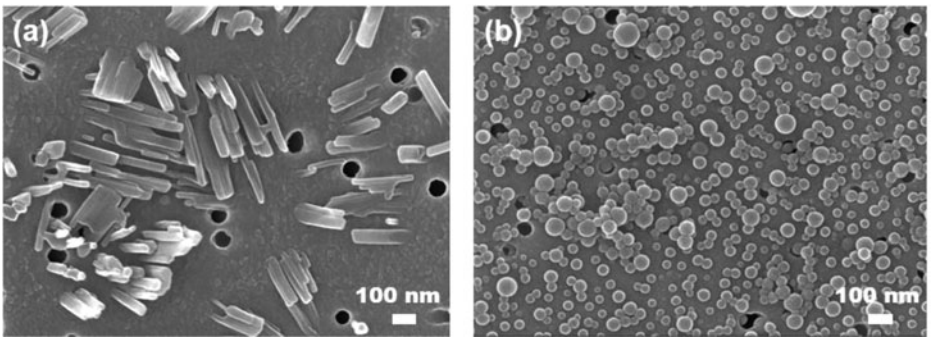

Figure 2. SEM images of (a) dppet nanocrystals and (b) the resulting [Cu(μ-I)dppet]$_2$ nanocrystals.

In XRD pattern of un-annealed [Cu(μ-I)dppet]$_2$ nanorods (Fig. 3(a)), halo pattern was observed. This halo pattern roughly corresponds to the enveloped traced diffraction pattern of bulk crystal of [Cu(μ-I)dppet]$_2$ (Fig. 3(c)), and contained neither peaks of dppet (Fig. 3(d)) nor copper(I) iodide (Fig. 3(e)). This fact suggests that the heterogeneous reaction process could proceed quantitatively even in [Cu(μ-I)dppet]$_2$ system. Anyway, [Cu(μ-I)dppet]$_2$ nanocrystals were not complete amorphous but crystals with too low crystallinity. So, [Cu(μ-I)dppet]$_2$ nanorods were annealed to increase the

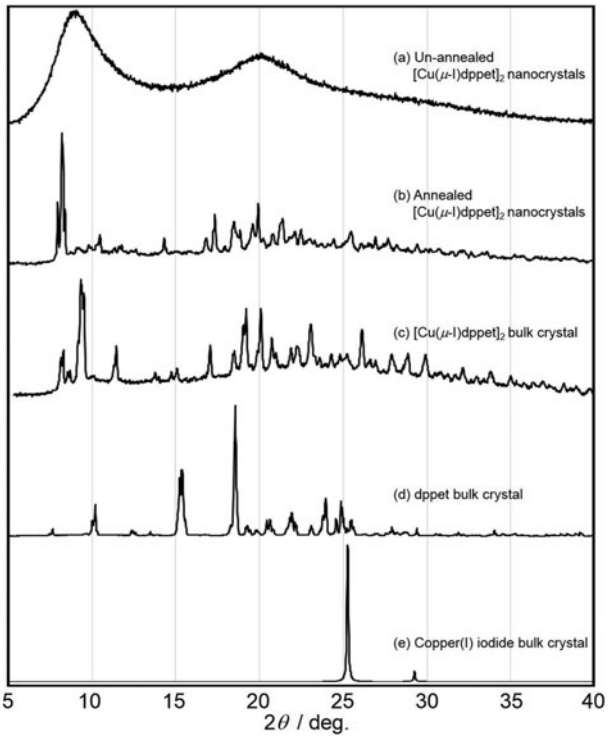

Figure 3. Powder XRD patterns of (a, b) [Cu(μ-I)dppet]$_2$ nanocrystals with and without annealing treatment, (c, d, e) bulk crystals of [Cu(μ-I)dppet]$_2$, dppet, and copper(I) iodide, respectively.

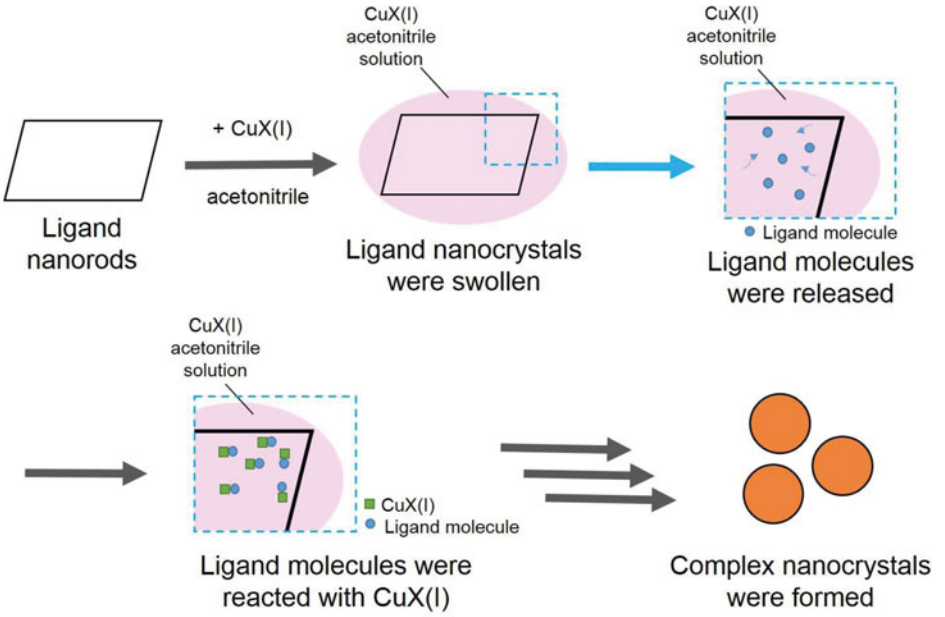

Figure 4. Proposed formation mechanism of [Cu(μ-I)dppet]$_2$ nanocrystals.

crystallinity. As a result, the sharp peaks appeared in XRD patterns, and the crystallinity of [Cu(μ-I)dppet]$_2$ nanocrystals was successfully increased (Fig. 3(b)). Interestingly, although the crystal structure of annealed [Cu(μ-Br)dppb]$_2$ nanocrystals was the same as that of the corresponding bulk crystal [7], the XRD pattern of annealed [Cu(μ-I)dppet]$_2$ nanocrystals shown in Fig. 3(b) was different from that of bulk crystals. This result implies that the different crystal structure of [Cu(μ-I)dppet]$_2$ was created by nanocrystallization through the heterogeneous reaction and/or the annealing treatment.

Formation Mechanism in the Heterogeneous Reaction Process

Finally, we have proposed the formation mechanism in the heterogeneous reaction process (Fig. 4). In the heterogeneous reaction process, the complex formation reaction would proceed on the "swollen or locally dissolved" surface of organic ligand nanorods, after adding of acetonitrile solution of copper(I) halide. In other words, the surface of organic ligand nanocrystals was swollen or partially dissolved by acetonitrile solvent. As a result, ligand molecules were desorbed and released from the nanorods, and then reacted with copper(I) halide in acetonitrile droplet dispersed in an aqueous medium. Further, formed copper(I) complexes were nanocrystallized in an aqueous medium, according to the co-precipitation process [7]. Namely, the shape of organic ligand nanocrystals was changed dramatically induced by the swelling and/or partial dissolution in acetonitrile droplet, and then was converted into the different shape of the subsequently formed complex nanocrystals.

Conclusion

We have succeeded in nanocrystallizing insoluble copper(I) complex $[Cu(\mu\text{-I})dppet]_2$ through the heterogeneous reaction process between dppet ligand nanorods and copper(I) iodide. The crystal structure of the resulting $[Cu(\mu\text{-I})dppet]_2$ nanocrystals was different from that of bulk crystal, which is presumably attributed to thermal softening in organic nanocrystal lattice. In addition, the formation mechanism has been proposed in the heterogeneous reaction process. Anyway, it has become apparent that the present method is effective to fabricate insoluble metal complex nanocrystals.

Acknowledgment

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