論文内容の要旨

論文題目

Developments of Functional Bottom-up Coordination Nanosheets (CONASHs): Bis(dipyrrinato)zinc(II) CONASH with Photoelectric Conversion and Bis(acetylacetonato)copper(II) CONASH with Molecular Recognition
(光電変換特性を有するビスジピリナト亜鉛(II)ナノシートおよび分子認識能を有するビスアセチルアセトナト銅(II)ナノシートによる機能性ボトムアップ型配位ナノシートの展開)

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Introduction

Nanosheets with two-dimensional polymeric planar structures have recently attracted great attention because of their unique properties. Following a discovery of graphene, one of the most promising nanosheets, many kinds of nanosheets such as metal dichalcogenides and metal hydroxides have been studied. While all of them originate from bulk-layered materials, recently molecule-based bottom-up nanosheets have emerged. These nanosheets are prepared by the reaction of chemical components, in which we can customize their chemical structures and properties through appropriately selecting the components. This feature is a big advantage of bottom-up nanosheets. The aim of this study is to design new functions of bottom-up coordination nanosheets by selecting new molecular components: bis(dipyrrinato)zinc(II) and bis(acetylacetonato)copper(II). Bis(dipyrrinato)zinc(II) nanosheets exhibit photofunctionality, while bis(acetylacetonato)copper(II) nanosheets can modulate their physical properties by changing environment.

Photofunctional bis(dipyrrinato)zinc(II) nanosheet

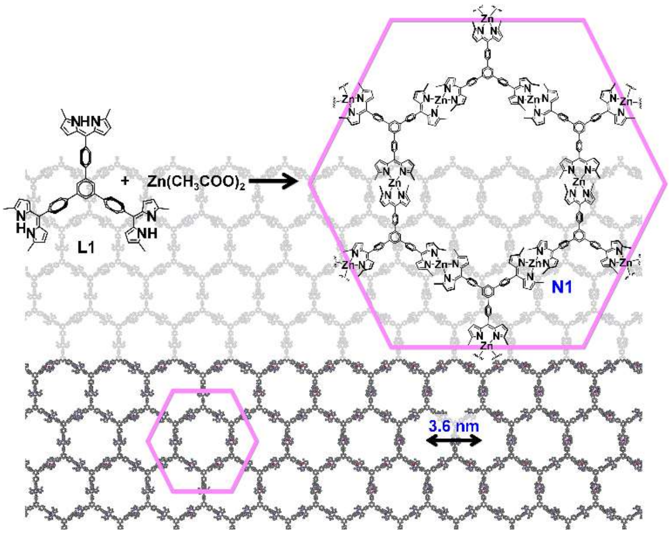

Figure 1. Illustration and chemical structure of bis(dipyrrinato) zinc(II) complex nanosheet.

Bis(dipyrrinato)zinc(II) complex has a strong visible light absorption so that its motif can act as a photofunctional moiety. A bis(dipyrrinato)zinc(II) complex nanosheet (**N1**) was synthesized using a three-way dipyrrin ligand (**L1**) and zinc(II) acetate (Figure 1). The liquid-liquid interfacial synthesis with a dichloromethane solution of **L1** and an aqueous solution of zinc(II) acetate gave multi-layer **N1**, while the gas-liquid interfacial synthesis with a tiny amount of a dichloromethane solution of **L1** and an aqueous solution of zinc(II) acetate gave single-layer **N1** or few-layer **N1**. Optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) revealed the flat film-like morphology of **N1**, and atomic force microscope (AFM) analysis revealed its height could be controlled by the concentration of **L1** in the range from 6 to 800 nm (5-670 layers). The quantitative layering of **N1** was achieved by Langmuir-Blodgett film deposition system with repeated deposition of single-layer **N1**, showing the single-layer absorbance of 0.0010. In order to demonstrate its photofunctionality, a photoelectric conversion system was constructed. **N1** was transferred onto a SnO_2 working electrode and a three-electrode system was set up with triethanolamine(TEA) as a sacrificial electron donor. An anodic current was observed with light irradiation at 500 nm corresponding to the maximum absorption of **N1**. The maximum quantum yield of **N1** photoelectric conversion was 0.86% in the case of single-layer. As a reference, quantum yields were also examined for a self-assembled monolayer (SAM) and a thin film of mononuclear bis(dipyrrinato)zinc(II) complex. Their photoanodes afforded lower efficiencies, indicating superiority of bottom-up nanosheet **N1** over conventional molecular films.

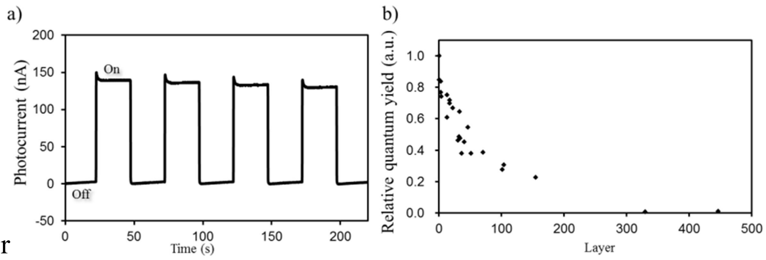

Figure 2. (a) Photocurrent response on irradiation of a working electrode with 500 nm light. (b) Relative quantum yield of each **N1** thickness.

Fabrication and characterization of bis(acetylacetonato)copper(II) nanosheet

A square-planar bis(acetylacetonato)copper(II) complex motif allows for coordination of molecules to the copper(II) ion. The coordination can be utilized to modulate the physical properties or structure of bis(acetylacetonato)copper(II) nanosheet (**N2**). **N2** was synthesized from a three-way acetylacetone ligand (**L2**) and tetraaminecopper(II) sulfate (Figure 3). To synthesize multi-layer **N2**, a liquid-liquid interfacial synthesis was considered. A spontaneous reaction of dichloromethane solution of **L2** and aqueous solution of tetraaminecopper(II) sulfate at room temperature generated a light blue-green film of multi-layer **N2** at the interface. Optical microscope and SEM images revealed its flat, sheet-like morphology and AFM showed its height as 310 nm that corresponds to 260 layers (Figure 4). IR spectra and X-ray photoelectron spectra (XPS) indicated the bis(acetylacetonato)copper(II) complex motif formed quantitatively in the multi-layer **N2.** A 2D grazing incidence wide angle X-ray scattering (2D GIWAXS) measurement with synchrotron radiation suggested a hexagonal unit cell formation in **N2** (3.5 nm for each side). Single-layer **N2** was obtained using a gas-liquid interfacial synthesis method. A tiny amount of **L2** dichloromethane/ethyl acetate (15:1) solution was spread to the surface of aqueous solution of tetraaminecopper(II) sulfate and kept calm for 1 day to be transferred to a silicon(111) substrate modified with 1,1,1,3,3,3-hexamethyldisilazane (HMDS/Si(111)). The sample on HMDS/Si(111) was analyzed using AFM to investigate its morphology and single layer height. An AFM image revealed a flat sheet-like structure of single-layer **N2** with over 10 µm size. The single-layer **N2** was scratched by AFM tip to show its single-layer height of 1.2 nm.

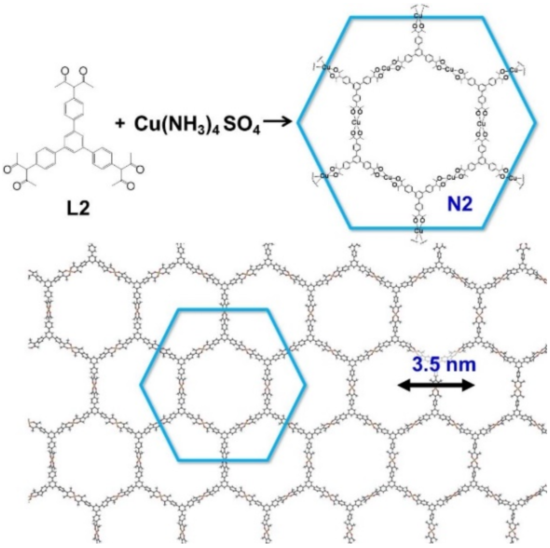

Figure 3. Illustration and chemical structure of bis(acetylacetonato)copper(II) nanosheet.

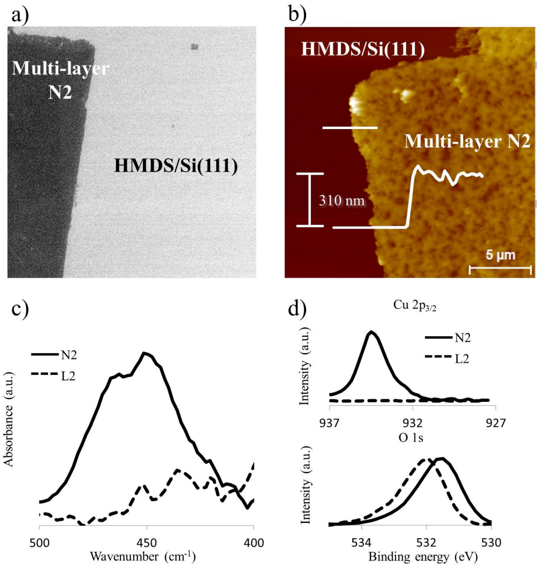

Figure 4. (a) SEM image of multi-layer **N2**. (b) AFM image and line profile of multi-layer **N2**. (c) IR spectra of **N2** and **L2**. (d) XPS of **N2** and **L2** (Cu $2p_{3/2}$, O 1s).

Modulation of bis(acetylacetonato)copper(II) nanosheet by molecular coordination

In order to modify multi-layer **N2** by a coordinative molecules, it was immersed in acetone solution of bis(4’-(4’-pyrydyl)-2,2’:6’,2”-terpyridine)iron(II) ($[\mathrm{Fe(tpypy)_2}]^{2+}$) for 1 day. An UV-vis spectrum showed an absorption band at 576 nm attributed to metal-to-ligand charge transfer (MLCT) centered at $[\mathrm{Fe(tpypy)_2}]^{2+}$. On the other hand, such a MLCT band was not detected when multi-layer **N2** was immersed in the solution of bis(4’-(4’-phenyl)-2,2’:6’,2”-terpyridine)iron(II) ($[\mathrm{Fe(tpyph)_2}]^{2+}$) that does not contain metal-binding sites (**N2**/ $[\mathrm{Fe(tpyph)_2}]^{2+}$). The results suggest the successful coordination of $[\mathrm{Fe(tpypy)_2}]^{2+}$ to **N2** (Figure 5). XPS also revealed the coordination of $[\mathrm{Fe(tpypy)_2}]^{2+}$ to **N2** in **N2**/$[\mathrm{Fe(pyterpy)_2}]^{2+}$ while the absence of $[\mathrm{Fe(tpyph)_2}]^{2+}$ in **N2**/$[\mathrm{Fe(tpyph)_2}]^{2+}$. I also revealed that solvent gases could be used to control the color of **N2**, in which its light green color (vacuum, dichloromethane, chloroform) was changed to light blue-green (ethanol, methanol, H_2O). These results indicate that the properties of the nanosheet can be modulated via the coordination of molecules.

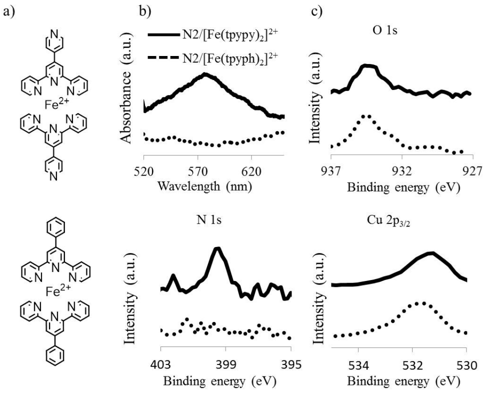

Figure 5. (a) $[\mathrm{Fe(tpypy)_2}]^{2+}$ and $[\mathrm{Fe(tpypy)_2}]^{2+}$ (b) UV-vis spectra of **N2**/$[\mathrm{Fe(pyterpy)_2}]^{2+}$ and **N2**/$[\mathrm{Fe(phterpy)_2}]^{2+}$ (c) XPS of **N2**/$[\mathrm{Fe(pyterpy)_2}]^{2+}$ and **N2**/$[\mathrm{Fe(phterpy)_2}]^{2+}$ (O 1s, N 1s, and Cu $2p_{3/2}$).

[Conclusion]

New functions of bottom-up nanosheets were demonstrated in this research: photofunctionality and molecule coordination in the bottom-up nanosheets. Both functional nanosheets were fabricated by the interlayer synthesis, and their morphology and components were analyzed by optical microscope, SEM, TEM, AFM, XPS, and IR spectroscopy. The bis(dipyrrinato)zinc(II) nanosheet showed photoelectric conversion ability superior to other mononuclear complex sensitizers. The bis(acetylacetonato)copper(II) nanosheet exhibited modulation ability by molecule coordination. These findings will develop the value of bottom-up nanosheets toward molecular electronic devices.