

学位論文 (要約)

Interfacial Synthesis of Coordination Nanosheets Comprising Terpyridine and Dithiolato Ligands and Exploration of Their Functionalities

(テルピリジンおよびジチオラト配位子を用いた
配位ナノシートの界面合成とその機能性の探求)

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東京大学大学院理学系研究科

化学専攻

高田 健司

Abstract

This thesis describes a series of studies on the synthesis of coordination nanosheets and the exploration of their functionalities. In this study, two kinds of ligands were used for the construction of nanosheets. One is terpyridines and the other is a dithiolato ligand. Liquid/liquid interface between two immiscible liquids plays an important role for the synthesis of multi-layered nanosheets.

In Chapter 1, I explain the general introduction of nanosheets. Recent developments of nanosheet studies after the discovery of flagship nanosheet graphene were provided.

In Chapter 2, the preparation and electrochemical properties of bis(terpyridine)iron(II) and cobalt(II) complex nanosheets were described. These nanosheets demonstrated electrochromism upon the oxidation or reduction of their metal centers with rapid response and high durability against redox reactions. These nanosheets were employed in solidified electrochromic devices, which were successfully operated by the application of external voltages. The combination of both iron(II) and cobalt(II) complex nanosheets into one device realized the dual electrochromic device displaying alternately the colorized nanosheets.

In Chapter 3, the bis(terpyridine)metal complex family was expanded to nickel(II) complexes. Electron microscopy observations and spectroscopic measurements confirmed the formation of bis(terpyridine)nickel(II) complex nanosheet. The nanosheet was redox active but did not show electrochromism. In both as-prepared and oxidized states, the nanosheets are transparent in visible light region.

In Chapter 4, the study on a terpyridine-zinc complex nanosheet synthesized by using zinc sulfate is mentioned. Sulfate anions worked not only as counter anions but also nanosheet framework by bridging two mono(terpyridine)zinc(II) complex moieties. The zinc complex nanosheet exhibited luminescence property with lumino-solvatochromism.

In Chapter 5, the preparation of nickeladithiolene nanosheet comprising a porphyrinoid-hybridized dithiolato ligand is described. The electron microscopy images and XP and IR spectra confirmed the formation of the nanosheet. Ultrasonication allowed the exfoliation of the multi-layered nanosheet to several layers.

In Chapter 6, I state the summary of this series of researches.

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Chapter 1

General Introduction

1-1 Dimensionality of Materials

In the history of chemistry, our research started from the study on the chemical compositions of materials in our daily life: what make up our world and how they do that. These curiosities lead to the discovery of atoms, which are examples of zero-dimensional materials. The concept of elements helped our understanding of the structure of three-dimensional bulk material and zero-dimensional molecules.

In early 20th century, the dimensionality was expanded from 0D to 1D systems. One-dimensional organic materials called polymers were evolved as repeating or connection of small molecular units, resulting in the extensive researches of one-dimensional materials.

For a long time after the evolution of one-dimensional materials, materials with new dimensionality were not prepared. It was in 2004 that the first two-dimensional material was obtained, the discovery of graphene.¹ Now, the materials with two-dimensional structures are fascinating a lot of researchers.

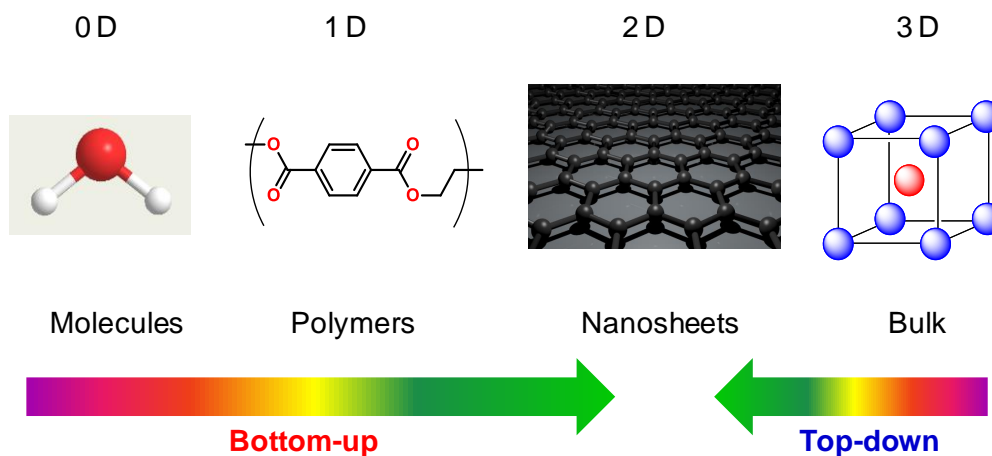


Figure 1-1-1 Dimensionality of materials. 0D molecules, 1D polymers, 2D nanosheets, and 3D bulk materials are illustrated. The two ways to construct 2D systems, top-down method from 3D bulk material and bottom-up method from 0D and 1D materials are depicted.

1-2 Nanosheets

Nanosheets are the materials that have a two-dimensional structure and a thickness of nanometer order. The anisotropic structure endows nanosheets to unique physical or chemical properties.² Due to their properties and ultra-thin structures, many researchers have devoted their efforts to the researches on nanosheets as potential materials for future nano-electronics.

Nanosheets can be categorized into the following 4 types by the components of nanosheets; 1) Graphene, 2) Inorganic nanosheets, 3) Organic nanosheets, and 4) Coordination nanosheets. The former two types of nanosheets were mainly obtained by top-down methods (i.e. exfoliation of bulk materials), because their mother bulk materials originally possess a layered structure. Therefore, the researches on these top-down type nanosheets have proceeded extensively. Herein I introduce the representative examples of top-down nanosheets and their applications.

1-2-1 Graphene

The root of the studies on nanosheets is the discovery of graphene, a two-dimensional network of sp^2 -hybridized carbons with honeycomb periodicity (Figure 1-2-1), in 2004 by Novoselov and Geim.¹ They repeatedly exfoliated highly-oriented pyrolytic graphite (HOPG) using Scotch tapes, and finally obtained few-layered graphene. Although graphene consists of only carbon atoms, it shows fascinating properties. For example, graphene has a unique zero-bandgap band structure³ called Dirac cone, leading to high electron mobility up to $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁴ and balanced ambipolar mobilities for both electron and hole.⁵

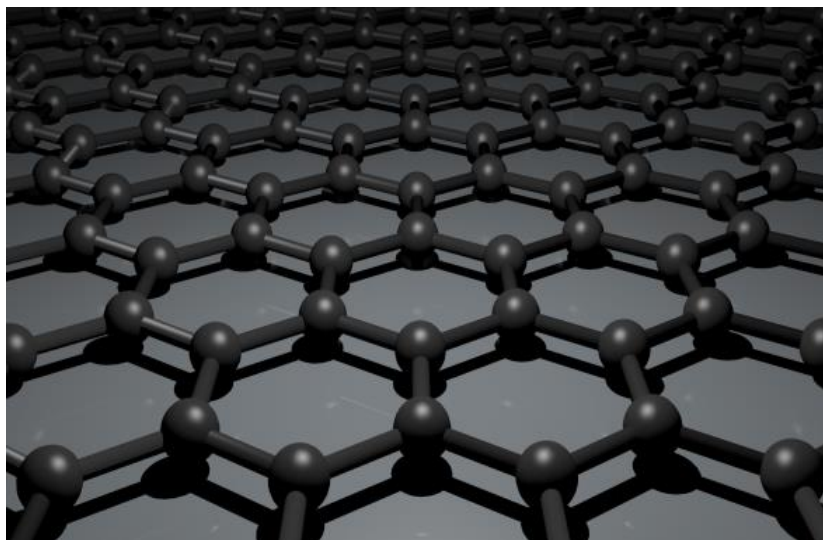


Figure 1-2-1 Structure of graphene.

Due to the attractive properties, a lot of studies on the application of graphene to electronic devices have been reported so far. The high mobility and gapless band structure enable electromagnetic wave detector in terahertz frequency. Vitiello et al. reported the graphene-based field effect transistors worked as terahertz detectors at room temperature.⁶ However, the gap-less band structure of graphene makes it difficult to apply graphenes to electronics, because conventional electronics features silicon-based semiconductors. Thus far, the modulation of the electronic structure is required. To overcome this problem, the functionalization of graphene by both covalent and non-covalent methods has been researched. For example, Haddon's group reported that graphene could be covalently modified with aryl groups using diazonium compounds, resulting in the enhancement of the resistivity in functionalized graphene.⁷ On the other hand, Jang's paper said that the light-modulated carrier doping to graphene was achieved by the non-covalent functionalization of photochromic spiropyran molecules through π - π interaction between graphene and pyrene moiety tethered in the spiropyran molecule (Figure 1-2-2).⁸

The small spin-orbit coupling of carbon atoms in graphene enables spin transportation for long distance. The first long range spin transportation and spin precession were established in 2007.⁹ At this stage, spin was injected to graphene from outside by spin-polarized current. Recently, increasing spin-orbit coupling in graphene toward multifunctional spintronic devices was studied for example by intercalating lead monolayers between graphene and substrates.¹⁰ This work provided a new step towards graphene spintronics.

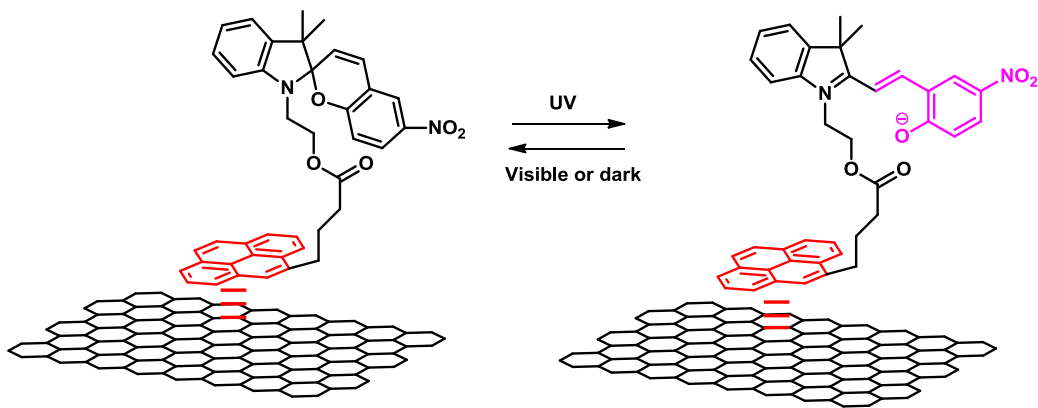


Figure 1-2-2 Non-covalently modified graphene with spiropyran molecules via π - π interaction between graphene and pyrene moiety. Photoisomerization of the spiropyran group changes the carrier density in graphene.

1-2-2 Inorganic nanosheets

The discovery of graphene and its astounding properties encouraged researches on other type of nanosheets. These interests were focused on nanosheets synthesized in top-down methods. In this sense, inorganic materials with a layered structure such as molybdenum disulfide (MoS_2) are potential materials which can be exfoliated to their monolayers. Transition metal chalcogenides are well-known compounds which have layered sheet morphology in bulk crystal. MoS_2 , MoSe_2 , WS_2 , and WSe_2 have been extensively studied,¹¹⁻¹² while other transition metal chalcogenides such as In_2Se_3 and Bi_2Se_3 have also been explored.¹³

Among them, few layer MoS_2 is one of the most popular materials (Figure 1-2-3).¹⁴ Monolayer MoS_2 is a semiconductor with a direct bandgap of 1.8 eV, which is different from that of bulk MoS_2 1.2 eV.¹⁵ This is totally different from graphene with metallic nature, which enables the application of monolayer MoS_2 to conventional silicon semiconductor electronics. Radisavljevic et al. firstly succeeded in implementing a single-layer MoS_2 transistor with a high on/off ratio ($\sim 10^8$).¹⁶ Their success proved the possibility of ultrathin nanosheets for electronics, followed by enthusiastic researches on seeking fabrication of novel electronic devices with MoS_2 .

The direct band gap in MoS_2 attracted optoelectronic application of that inorganic nanosheet. Im et al. reported the fabrication of phototransistors with few-layered MoS_2 . The number of layers significantly affects the band structure of MoS_2 resulting in the thickness-dependent photo-response of the transistors (Figure 1-2-4).¹⁷ A light luminescence of MoS_2 is also the research target. Sundaram et al. reported the electroluminescent from single layer MoS_2 nanosheet field effect transistors.¹⁸

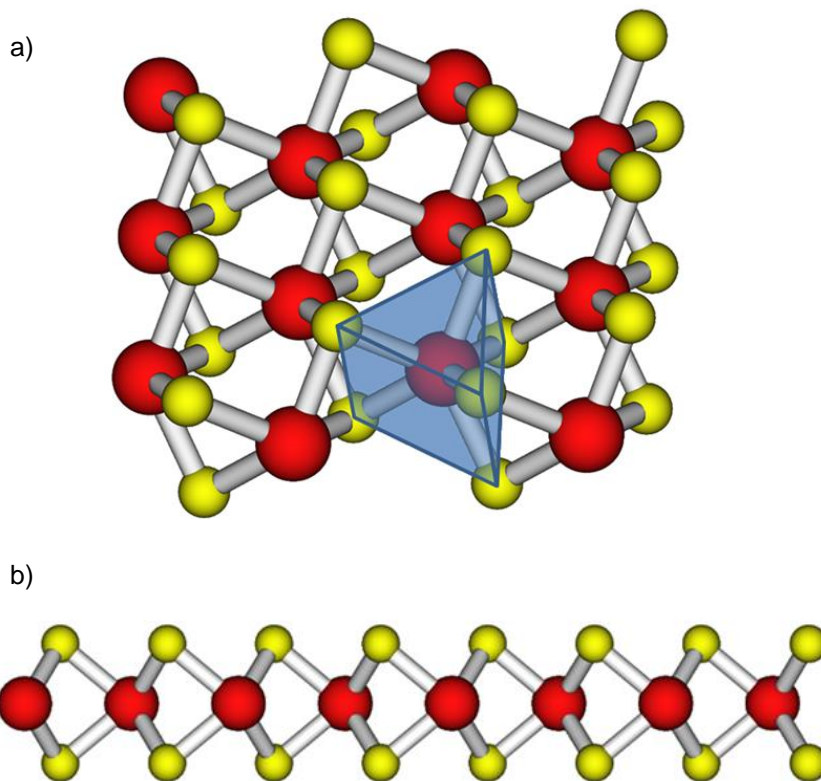


Figure 1-2-3 a) Structure of molybdenum disulfide, MoS₂. Yellow and red spheres represent sulfur atoms and molybdenum atoms respectively. b) Side view of MoS₂. Adapted from ref. 14. Copyright 2014 American Chemical Society.

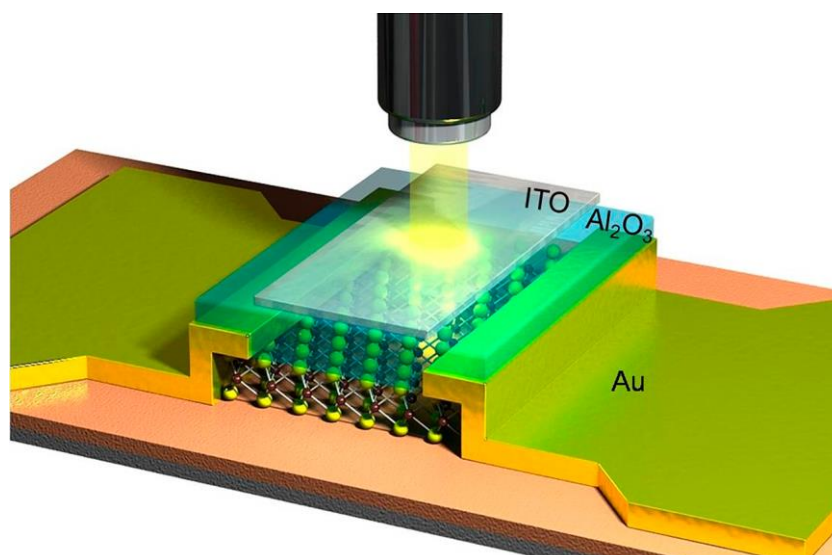


Figure 1-2-4 Phototransistor comprising monolayer MoS₂ as a photoactive layer. Adapted from ref. 17. Copyright 2012 American Chemical Society.

Some metal oxides and hydroxides also possess lamella structure, which means that they can be exfoliated to nanosheets (Figure 1-2-5). For example, Sasaki et al. recently developed the ultrathin (~ 30 nm thickness) capacitors completely comprising metal oxide nanosheets.¹⁹ In their system, $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheet and $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ nanosheet were employed for an electrode material and a dielectric layer respectively. This kind of layer-by-layer structure in electronic devices is ideal for nanosheets application. On the other hand, Ida et al. reported that nickel hydroxide could be exfoliated to its monolayer by the intercalation of large anions (dodecyl sulfonate) between layers followed by heating of the solution. The exfoliated monolayer nanosheet demonstrated the charge-discharge properties in a strong base electrolyte.²⁰

As mentioned above, many types of inorganic nanosheets have been synthesized to date, but I note that all of them have layered structures in their bulk state, which is a large difference from bottom-up type nanosheets explained in Section 1-3.

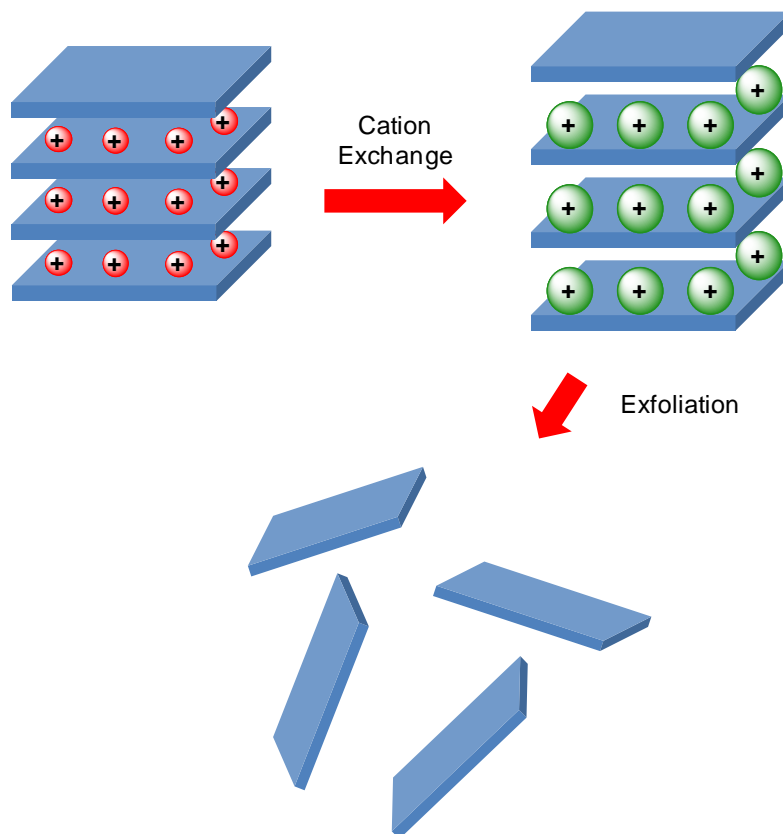


Figure 1-2-5 Schematic illustration of the exfoliation of inorganic nanosheets in the case of anionic nanosheets. The exchange of counter cations between layers to larger ones decreases the stacking interaction, which enables the exfoliation by thermal or ultrasonication treatment.

1-2-3 Bottom-up synthesis of graphene and inorganic nanosheets

Although graphene and inorganic nanosheets are mainly obtained by the exfoliation of mother bulk materials, there are also a large number of reports on bottom-up synthesis of them. One way to obtain these nanosheets in a bottom-up method is chemical vapor deposition (CVD). CVD is a chemical process which prepares thin film materials on substrates through chemical reactions of precursor compounds vapors. While the mechanical exfoliation methods yielded nanosheets with small flakes, CVD technique enables the synthesis of wide nanosheet and their scalable preparation. Sutter et al. reported CVD graphene under ultra-high vacuum conditions on Ru(0001) surface,²¹ and in 2009, Kong's group reported the first CVD graphene prepared under ambient pressure on polycrystalline Ni surface.²² Nowadays, CVD process is inevitable for research on graphene applications for electronic devices. Inorganic nanosheets are also targets of CVD synthesis. Lee et al. fabricated a few layered MoS₂ on SiO₂/Si and other insulating substrate by chemical vapor deposition using MoO₃ and S.²³

One strong advantage of CVD-prepared nanosheets is heteroatom doping to nanosheets, leading to a control of their physical properties. Nitrogen-doped graphene is the most intensively studied because of its decreased charge mobility and electrochemical properties (Figure 1-2-6).²⁴⁻²⁶ The contamination of other elements such as boron, phosphorous, and sulfur have also been achieved to date, though doping of some elements has been achieved via thermal treatment of graphene oxide.²⁷⁻²⁹ The doping of more than two kinds of elements also became possible.³⁰⁻³¹ In inorganic nanosheets, heteroatom-doped transition metal dichalcogenides are reported. Yang et al. reported that the chloride doping to MoS₂ and WS₂ was effective in reducing the contact resistance between Ni and transition metal disulfide nanosheets.³² Mixed-chalcogenide inorganic nanosheets (i.e. MoS_{2-x}Se_x, x = 0~2) were also established for the tuning of their electronic properties.³³ But it is noteworthy that the precise control of doping ratios and positions is almost impossible in the CVD method.

CVD method also enables the vertical layering of two kinds of monolayer nanosheets, so-called van der Waals heterostructure. Hong et al. demonstrated the ultrafast charge transfer in MoS₂/WS₂ heterostructures.³⁴ Attachment of two semiconducting nanosheets induces the fast charge separation across the heterostructure. These heterostructured materials were interesting not only scientifically but also from the view point of the evolution of novel functionality which was not obtained in single component nanosheet structure. The heterostructures of graphene and inorganic nanosheets are also realized where graphene works as an electrode and semiconductive inorganic nanosheet is an active layer.³⁵ This technology will lead to the fabrication of circuits composed of only nanosheets.

Previously it was considered that nanosheets prepared in the CVD process usually suffered from their low quality.³⁶ Compared to mechanically exfoliated nanosheets, nanosheets prepared

by CVD methods possessed polycrystalline nature and defects in the layer resulting in the degradation of their intrinsic properties. But recent studies unveiled the synthesis of CVD-grown nanosheets with large area whose electronic properties are comparable to those of mechanically exfoliated nanosheets.³⁷

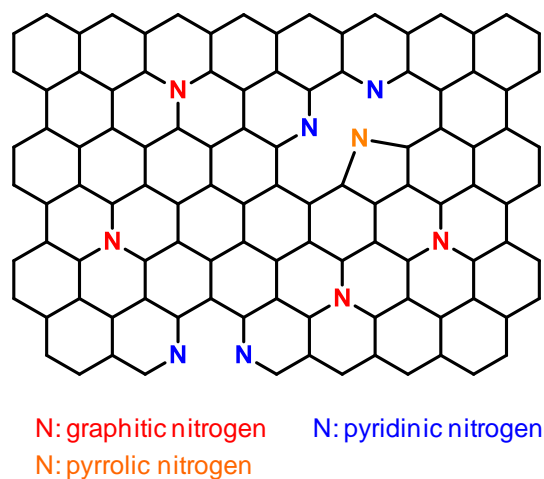


Figure 1-2-6 Illustration of N-doped graphene. Three types of doped nitrogen atoms were illustrated in different colors. Doping of nitrogen generates defects in hexagonal structure of graphene, leading to less developed π -conjugation and decreased charge mobilities.

1-3 Coordination Nanosheets

On the contrary to the graphene and inorganic nanosheets, there have appeared a new type of nanosheets which are constructed from their components, bottom-up nanosheets. Among them, nanosheets woven up with covalent bonds and coordination bonds have attracted increasing attention by the tunability of their components. The utilization of the former bonds results in organic nanosheet, and the latter gives coordination nanosheets (CONASHs, Figure 1-3-1).

Coordination nanosheets were originated from ones prepared under ultra-high vacuum conditions by depositing organic ligands on metal surface. The co-deposition of organic ligands and metal ions afforded the metal-organic coordination networks on metal substrates.³⁸⁻³⁹ Sometimes deposition of only organic ligands resulted in the formation of coordination networks; The ligand spontaneously coordinated to metal adatoms to form a two-dimensional network after thermal annealing.⁴⁰

On the other hand, coordination nanosheets synthesized in solution conditions have appeared recently. Makiura et al. succeeded in fabricating metal-organic framework (MOF) crystals with carboxylate or pyridine tethering porphyrins as ligands using a Langmuir-Blodgett trough.⁴¹⁻⁴³ Meanwhile Sakamoto and Schlüter et al. reported the synthesis of bis(terpyridine) complex nanosheet also using a Langmuir-Blodgett trough.⁴⁴⁻⁴⁶ These studies focused on the preparation and identification of the coordination nanosheet, and no functionality was reported there.

The paradigm shift was the creation of a π -conjugated nickelladithiolene nanosheet by Kambe et al (Figure 1-3-2).⁴⁷⁻⁴⁸ The metalladithiolene nanosheet has a graphene-like hexagonal structure and they demonstrated the electric conductivity of the nanosheet, which was modulated by the oxidation states of nickelladithiolene moieties. To my knowledge, this is the first functional coordination nanosheet. After the report, functionality of coordination nanosheets has attracted considerable attentions. To date, photoelectric conversion by bis(dipyrrinato)zinc(II) complex nanosheet⁴⁹ was realized by Nishihara's group, and other conductive metalladithiolene nanosheet with ligated copper ions were reported.⁵⁰ Other coordination nanosheets comprising metalladithiolene-like redox non-innocent ligands such as 1,2-diimine structure have reported as conducting materials in their stacked multilayer compounds.⁵¹⁻⁵² The theoretical predictions for the electronic properties of metalladithiolene nanosheets and related nanosheets by physicists⁵³⁻⁵⁵ have been published. These researches prove that the coordination nanosheets are promising materials for their applications for electronics, energy conversion, and so on.

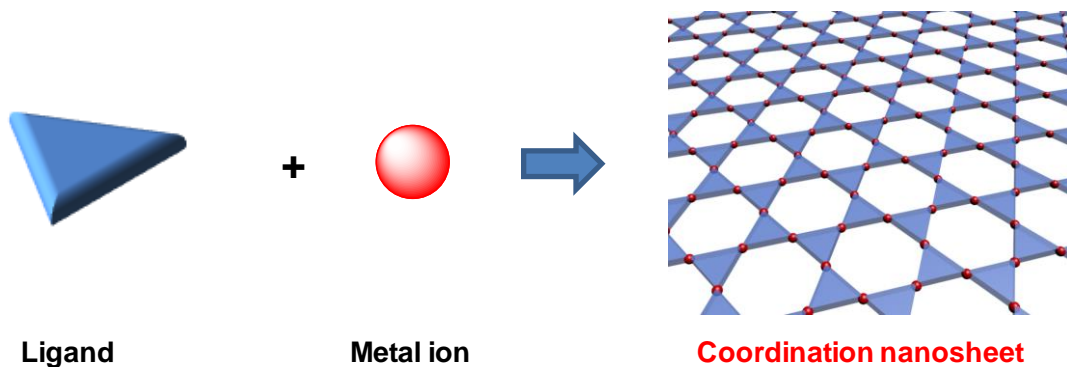


Figure 1-3-1 Schematic image of coordination nanosheets. Illustration of Coordination nanosheets is adapted from ref. 48. Copyright 2014 American Chemical Society.

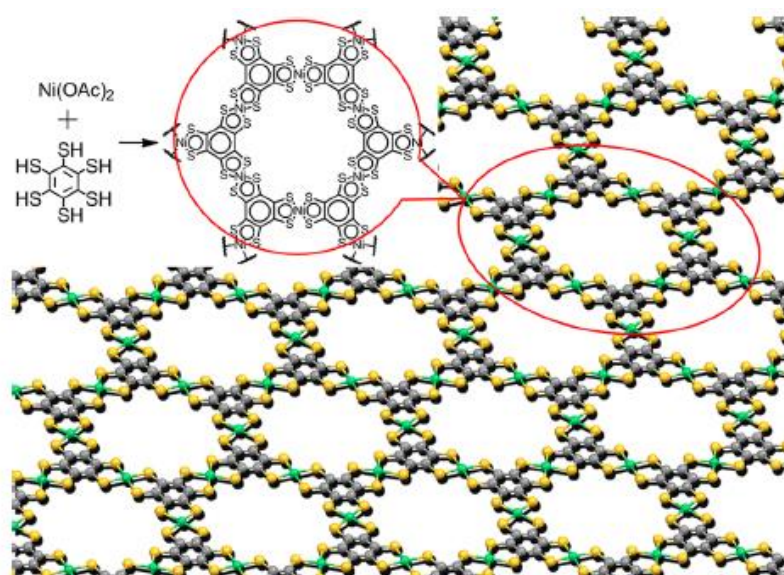


Figure 1-3-2 Structure of nickelladithiolene nanosheet. Adapted from ref. 47. Copyright 2013 American Chemical Society.

1-4 Aim of This Thesis

As mentioned in the previous section, coordination nanosheet is the emerging class of materials with a wide variety of potential applications. However, most of the conventional studies on CONASHs have not elucidated their functionalities and preliminary application to devices, and there are considerable demands for functional coordination nanosheets as nanomaterials.

In my Ph. D. study, I developed novel functional coordination nanosheets families using terpyridine and dithiolato ligands for the sake of their rich chemistry and physics. For the terpyridine-based coordination nanosheets, their properties are still unknown even in nanosheets with simple structures. And for metalladithiolene nanosheet, the hybridization of dithiolato ligands with other functional molecules will lead to development of further functionalities. Thus, in current research, two terpyridine ligands with simple structure, **1** and **2**, and a metalloporphyrazine-hybridized dithiolato ligand **3** were selected for the synthesis of nanosheets (Figure 1-4-1). In my study, the redox or photochemical properties were mainly focused on. I also achieved the device application of coordination nanosheets studied here, promising that the future evolution of practical devices in electronics utilizing coordination nanosheets.

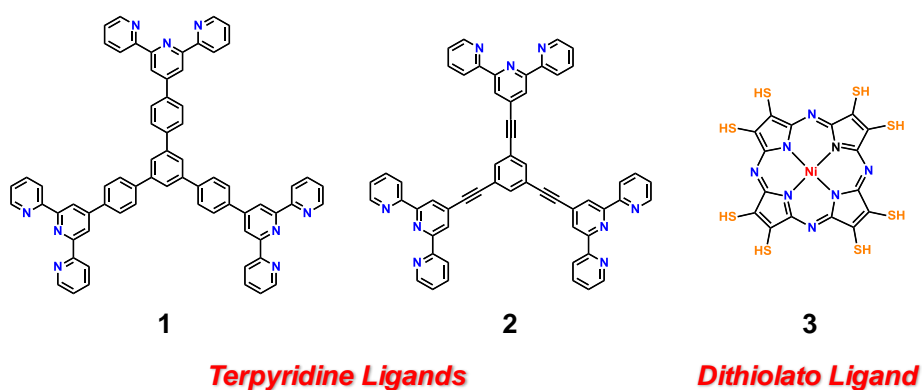


Figure 1-4-1 Terpyridine and dithiolato ligands employed in this study.

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Chapter 2

Electrochromic Bis(terpyridine)iron(II) and Cobalt(II) Complex Nanosheets

インターネット公表に関する共著者全員の同意が得られていないため、この章については、非公開。

Chapter 3

Redox-Active Bis(terpyridine)nickel(II) Complex Nanosheet

本章については, 5 年以内に雑誌等で刊行予定のため, 非公開.

Chapter 4

Fluorescent Zinc-Terpyridine-Based Metal Complex Nanosheet

本章については,5年以内に雑誌等で刊行予定のため,非公開.

Chapter 5

Nickelladithiolene Complex Nanosheet a Comprising Porphyrazine-Conjugated Dithiolato Ligand

本章については, 5 年以内に雑誌等で刊行予定のため, 非公開.

Chapter 6

Concluding Remarks

As I mentioned in Chapter 1, two-dimensional materials, nanosheets have attracted considerable attention for the future nanotechnology. Graphene and inorganic nanosheets such as transition metal dichalcogenides have been extensively studied, but still lack of practical applications. To achieve the practical applications, the preparation of nanosheets with desired properties is necessary, which is enabled by the bottom-up type nanosheets. In this sense, coordination nanosheets, which are constructed their constituting ligands and metal ions, are the promising materials because of the infinite variations in the selection of ligands and metal ions.

In this study, I have developed coordination nanosheets comprising terpyridine ligands and a dithiolato ligand. I have also explored their functionalities that will reach practical applications in future.

In Chapter 2, a series of bis(terpyridine)iron(II) and cobalt(II) complex nanosheets were synthesized by the method of liquid-liquid interfacial coordination reaction. Electron microscopy observation and spectroscopy techniques identified the nanosheets. These nanosheets exhibited the redox activity involving distinctive color changes, electrochromism. Electrochromism of iron(II) complex nanosheets were triggered by the oxidation of iron center to iron(III) state, and that of cobalt(II) complex nanosheet was caused by the reduction of cobalt center to cobalt(I) state. These electrochromism were quickly completed within ca. 0.5 s, and the nanosheets were durable to the repetitive redox cycles. I also confirmed that chemical modification of terpyridine ligands enabled the tuning of colors for electrochromic nanosheets without losing electrochromic properties of bis(terpyridine)metal complex nanosheets.

The electrochromic nanosheets were allowed to device applications. The operation of preliminary solidified electrochromic devices tailoring bis(terpyridine)metal complex nanosheets were successful. The utilization of both oxidation and reduction-induced electrochromic nanosheets into one device realized dual electrochromic device where the nanosheets were colorized alternately.

Chapter 3 describes the expansion of bis(terpyridine)metal complex nanosheet family to the nickel ion system. Bis(terpyridine)nickel(II) complex nanosheet was synthesized via a liquid-liquid interfacial coordination reaction. The multilayered nanosheet with 240 nm thickness was obtained. Electron microscopy observations confirmed the sheet-like morphology, and spectroscopy measurements characterized the nanosheet. This nickel complex nanosheet was redox active as well as bis(terpyridine)iron(II) complex nanosheet described in Chapter 2. Both as prepared state and the oxidized state of nickel complex nanosheet were transparent in visible light region, limiting spectral difference into only UV region.

Chapter 4 mentioned the synthesis of fluorescent terpyridine-zinc complex nanosheet. A liquid-liquid interfacial synthesis of terpyridine ligand in an organic solution and zinc sulfate in an aqueous solution yielded a terpyridine-zinc complex nanosheet. The layered sheet structure was revealed with electron microscopes. The spectroscopic studies clarified that the coordination unit is not bis(terpyridine)zinc(II) complex nanosheet but dinuclear $[\text{Zn}_2(\mu\text{-O}_2\text{SO}_2)_2(\text{terpyridine})_2]$ complex with two sulfate anions bridging two zinc ions. This unique structure led to the luminescent property with emission maximum around 550 nm with 4 % luminescent quantum efficiency. This nanosheet demonstrated solvatochromism in luminescence in solvents with coordination ability, confirmed by the blue-shift of emission maximum by ca. 30 nm in the solvents.

In Chapter 5, the construction of nickelladithiolene complex nanosheet woven up from a porphyrzineoctathiol ligand was discussed. The diffusion of nickel ion into a solution containing porphyrzineoctathiolate resulted in the formation of black precipitate, which consisted of stacked sheet of nickelladithiolene nanosheet confirmed by electron microscopy observation. The X-ray photoelectron spectroscopy and IR spectroscopy also supported the formation of bis(dithiolato)nickel complex moieties in the nanosheet.

In summary, I have achieved the synthesis of a series of coordination nanosheets using terpyridine ligands and dithiolato ligand. I have also explored their electrochemical and photochemical functionalities. Bis(terpyridine)metal complex nanosheets showed electrochromism with rapid and repeatable response, and zinc complex nanosheets exhibited the light emission properties. For the electrochromic nanosheets, fabrication of electrochromic devices with them was established, and the devices were successfully operated by the external voltage.

These studies promise the integration of coordination nanosheets into future electronic and optoelectronic applications.

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Kenji Takada

Publication List

【Publication related to this Thesis】

1. “Electrochromic Bis(terpyridine)metal Complex Nanosheets” Takada, K.; Sakamoto, R.; Yi, S. -T.; Katagiri, S.; Kambe, T.; Nishihara, H. *J. Am. Chem. Soc.* **2015**, *137*, 4681-4689.

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