

論文の内容の要旨

論文題目 : Study on Iron and Zinc Dithiolene 2-D Coordination Frameworks and Lateral Heterojunctions Produced by Transmetallation

(鉄および亜鉛ジチオレンの 2 次元錯体フレームワークとトランスメタル化により作製したヘテロ接合体の研究)

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1. Introduction

The field of two-dimensional (2D) materials, pioneered by the discovery of graphene, has expanded greatly in recent years. Inspired by the exotic physical properties of the monolayer honeycomb structure of graphene with its potential applications, intensive research is being expanded to other 2D materials. Coordination nanosheets are 2D materials formed by coordination between a metal ion and a symmetric ligand, forming an extended structure. Metalladithiolene coordination materials are attractive because the redox activity of the metalladithiolene moiety, together with delocalization of electrons over an extended 2D π -conjugated network leads to unique physical and electronic properties. Various reports on metalladithiolene coordination materials utilizing benzenhexathiol (BHT) have shown that when ligated to different metals, the resulting materials exhibit high conductivity and charge mobility ($M = \text{Cu}, \text{Ag}$), redox tunability ($M = \text{Ni}$), and functions such as hydrogen evolution catalysts ($M = \text{Co}, \text{Pt}$).

Laterally joining two semiconductors to create heterojunctions at the interface is expected to enhance electronic and physical properties. Lateral heterojunctions currently produced using transition metal dichalcogenides show large p-n rectification behavior, high conversion efficiencies and can be used as high mobility FETs. There is thus great potential for lateral heterojunctions in electronics and device applications. However, the fabrication processes (CVD) generate only small domains (few μm) and optimizing synthetic conditions is tedious.

The aim of this study comprises the synthesis of novel coordination materials using BHT and metal ions (Zn^{2+} and Fe^{2+}) together with the fabrication of lateral heterojunctions via transmetallation of zinc dithiolene nanosheets.

2. Fabrication of zinc dithiolene nanosheets

I synthesized zinc dithiolene (**ZnBHT**) nanosheets via a liquid-liquid interfacial reaction between Zn^{2+} and BHT (Fig. 1a) to study its properties. Various spectroscopies such as IR, AFM, TEM, SEM, XPS and CV were used to characterize **ZnBHT**. **ZnBHT** is sheet-like (Fig. 1b) as observed under SEM, with Zn coordinated to the S groups of BHT (from IR and XPS spectroscopies) and is insulating. Electron diffraction studies showed that **ZnBHT** exhibits a hexagonal lattice structure (Fig. 1c). Powder XRD experiments together with molecular modelling and simulations indicate that **ZnBHT** synthesized under heated condition possesses an almost planar non-porous 2-dimensional layered structure. It is likely that heating confers the energy necessary to overcome the torsional energy barrier, leading to the Zn centers adopting a nearly square planar conformation rather than the typical tetrahedral conformation.

3. Fabrication of iron dithiolene nanosheets and determination of chemical structure

Liquid-liquid interfacial synthesis between aqueous FeSO_4 and BHT at 45°C gave **FeBHT** (**1-H**) as a black solid (Fig. 2a). **1-H** was characterized by a variety of spectroscopies, with SEM micrographs showing its sheet-like structure. **FeBHT** synthesized at 45°C (**1-H**) show greatly improved crystallinity to that synthesized at room temperature (**1-RT**). PXRD studies reveal the 2-dimensional non-porous structure formed by eclipsed stacked layers in **1-H** (Fig. 2b). Furthermore, the higher crystallinity of **1-H** leads to lower activation energy barrier to charge hopping (270 meV in **1-H** vs. 360 meV in **1-RT**), and around 20 times higher conductivity of **1-H** (0.68 S cm^{-1} at RT) compared to **1-RT** (0.028 S cm^{-1} at RT) (Fig. 2c). This is due to the reduced number of defects and larger domain sizes in **1-H**.



Figure 1. a) Liquid-liquid interfacial synthesis of **ZnDT**; b) SEM picture showing layered **ZnDT**; c) TEM and SAED pattern implying hexagonal lattice in **ZnDT**.

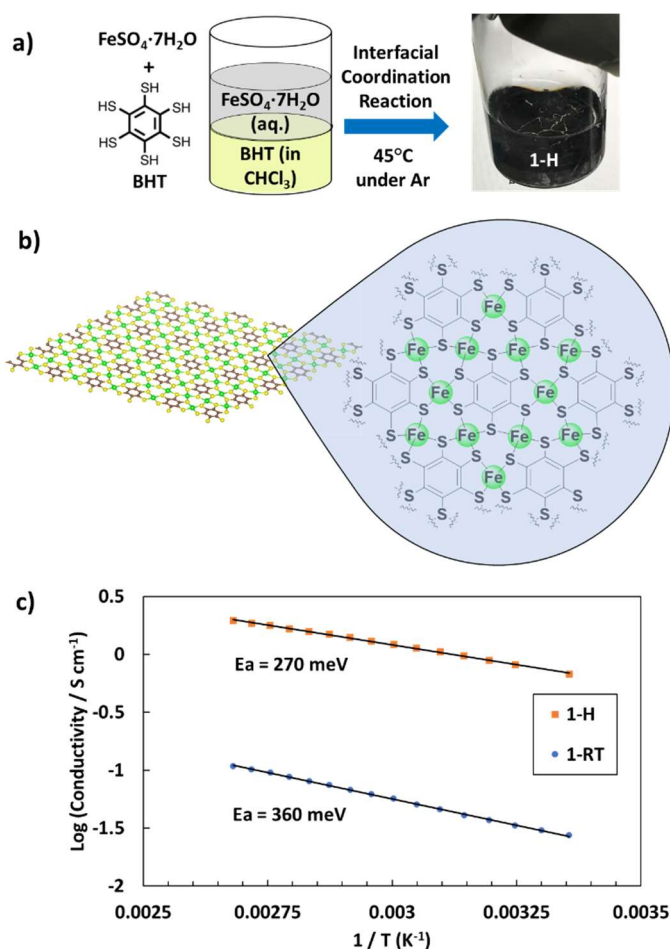


Figure 2. a) Liquid-liquid interfacial synthesis of **1-H**; b) molecular model and chemical structure of **1-H**; c) Temperature dependent conductivity curves of **1-H** and **1-RT**

4. Transmetalation of zinc (II) dithiolene nanosheets with various metal ions

Transmetalation provides a plausible strategy for fabricating lateral heterojunctions in coordination nanosheets. **ZnBHT** provides a ready-made lattice that is modifiable through metal-exchange, ensuring connectivity across the junction. Tunability of physical properties of metalladithiolene nanosheets via changing the metal ion provides various combinations of source materials by which lateral heterojunctions can be constructed.

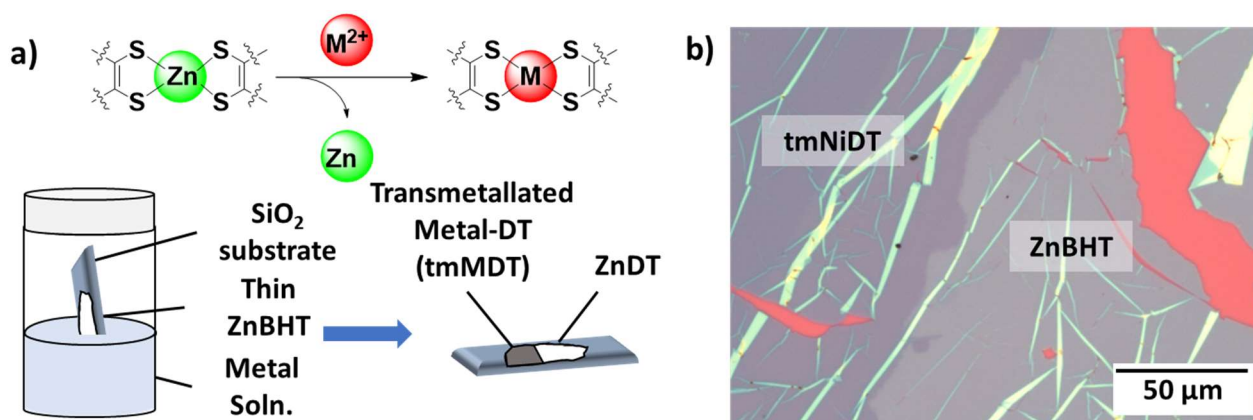


Figure 3. a) Scheme showing area-specific transmetalation process; b) Clear boundary seen between **tmNiDT** and **ZnBHT**.

Liquid-liquid interfacial synthesis of **ZnBHT** while controlling the concentration of reactants and time gave films as thin as 8 nm with large domains ($> 500\mu\text{m}$), which facilitates complete metal-exchange of all the layers. **ZnBHT** thin films deposited on 300 nm SiO₂ substrates were then immersed in various metal-ion solutions ($M = \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Fe}^{2+}$) giving transmetalated metalladithiolene (**tmMDT**) nanosheets (Fig. 3a). Visible darkening of the **ZnBHT** sheets was observable by eye, indicating interaction of the metal ion with the ligand's π -conjugated system (Fig. 3b). Area-selective transmetalation of **ZnBHT** produced a clear boundary between light (**ZnBHT**) and dark areas (**tmMDT**) on the same sheet (Fig. 3b). Transmetalated sheets were characterized by XPS, with appearance of the respective metal ions and disappearance of Zn indicating successful metal-exchange, and atomic ratios from XPS support the as-reported chemical structures. 4-probe electrical conductivity measurements of the transmetalated **tmMDTs** were performed, with the **tmMDTs** showing lower conductivity compared to the as-prepared MDT nanosheets.

5. Electrical properties of lateral heterojunctions of transmetalated metalladithiolene nanosheets

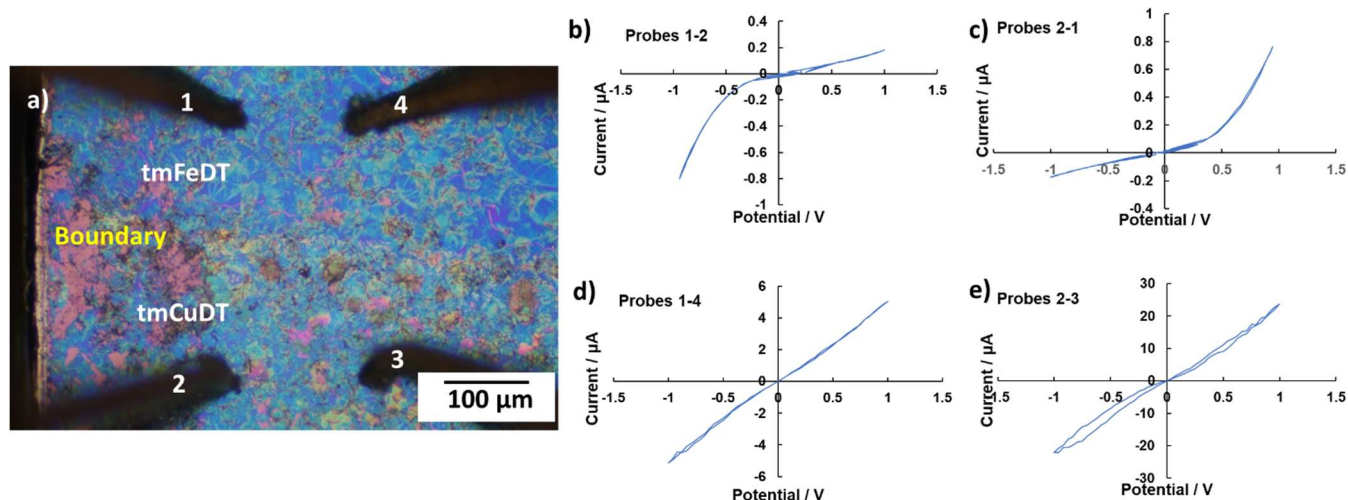


Figure 4. a) I-V curve measurement of **tmFeDT**-**tmCuDT** lateral heterojunction using 4 Au probes; b, c) I-V curves of **tmFeDT**-**tmCuDT** lateral heterojunction showing reversible rectification behavior; d) I-V curve showing Ohmic behavior of **tmFeDT** nanosheet, e) I-V curve showing Ohmic behavior of **tmCuDT** nanosheet.

Area-selective transmetallation of 2 different metal ions on the same **ZnBHT** nanosheet gave 2 different **tmMDT** nanosheets laterally joined together. From a selection of 3 different metal ions, 3 combinations of metal-DT heterojunctions could be produced (**tmNi/tmCu**, **tmNi/tmFe**, **tmFe/tmCu**). The different combinations of heterojunctions were measured using a 2-probe method with Au probes (Fig. 4a). Out of the 3 combinations, only the **tmFeDT-tmCuDT** junction exhibited pronounced diode-like rectifying behavior across the junction (Fig. 4b), within the potential window of -1.0 to 1.0V. The source and drain terminals (Probes 1 and 2) were switched and the potential sweep reapplied, resulting in a reversal of current flow and rectification behavior (Fig. 4c). The presence of Ohmic contacts between the Au probes and the respective **tmFeDT** and **tmCuDT** nanosheets indicate that the rectification behavior is not due to Schottky contacts (Fig. 4d and e).

6. Conclusion

In this study, new iron and zinc dithiolene coordination nanosheets were fabricated, characterized and their chemical structures elucidated. The modification of large domain **ZnBHT** thin films was achieved by transmetallation of the incorporated zinc ions with other divalent metal ions, resulting in conducting films compared to insulating **ZnBHT**. Area-selective transmetallation of **ZnBHT** with metal solutions (Ni^{2+} , Cu^{2+} and Fe^{2+}) allows the fabrication of 3 different combinations of lateral heterojunctions. Out of these combinations, the **tmFeDT-tmCuDT** heterojunction showed significant rectifying behavior. These results are expected to open up new opportunities towards lateral heterojunction research in coordination nanosheets and further its applications to electronic devices.