

論文の内容の要旨

Developments of d/π Electron–Proton-coupled Functionalities in Metal Dithiolene Complex Crystals

(金属ジチオレン錯体結晶における d/π 電子–プロトン相関型機能物性の開拓)

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Chapter 1 General introduction

Functionalities of molecular crystals have been explored based on designing the chemical structure of the constituent molecules and tuning intermolecular interactions, which is decisive to molecular arrangements. Hydrogen bond (H-bond) is one of the important intermolecular interactions to control the molecular arrangements because of its intermediate strength between covalent bonds and van der Waals interactions. In addition to the feature as a structural regulator, H-bond formation and/or proton dynamics act as an additional degree of freedom to significantly modulate the electronic structures of molecular crystals. Our group has recently found proton-(deuteron-) dynamics-coupled magnetism and electrical conductivity switching in the crystal consisting of catechol-fused tetrathiafulvalene: novel phenomena where π electron is coupled with H-bonding.[1–4] Therefore, the proper introduction of H-bond into molecular crystals leads to developments of novel electronic functionalities and phenomena coupled to a proton in H-bonds; however, the number of such examples have been limited.

As the constituent molecules to widely explore such novel phenomena, the author focused on metal dithiolene complexes having d electrons in addition to π electrons. Owing to d - π electron conjugation, various choices of the central metals and the precisely designable dithiolene ligands, they show stable multi-redox abilities and rich electronic properties and functionalities in the solid state (e.g., optical properties, electrical conductivities, and magnetism), leading to the significant discoveries in chemistry and physics, such as two-dimensional π -conjugated nanosheets and the single-component molecular superconductor.[5,6] Therefore, material developments based on metal dithiolene complexes with H-bonding should enable us to explore the novel phenomena unique to a coupling of proton and d/π electrons; however, such phenomena have not been discovered in solid state. Based on the background, this Ph. D. research aims to develop novel functional metal dithiolene complex crystals based on a coupling of proton and d/π electrons.

Chapter 2 Three-dimensional hydrogen-bonded frameworks based on metal dithiolene complex and a role of crystal solvent on the assembled structures

The author first focused on the metal catecholdithiolene complexes with four hydroxy groups, and aimed to develop the crystals with the H-bond network based on metal dithiolene complexes and to control the molecular arrangement. In this chapter, the first three-dimensional (3D) H-bonded frameworks based on metal dithiolene complex have been realized by using the gold catecholdithiolene complex.[7]

New gold catecholdithiolene complex, $[\text{Au}(\text{catdt})_2]^-$ (Fig.1, $\text{catdt} =$ catechol-4,5-dithiolate), was synthesized. The complex was crystallized as 1:1 salts of Ph_4P^+ cation, and three kinds of the crystals containing different crystal solvents were obtained: $(\text{Ph}_4\text{P})[\text{Au}(\text{catdt})_2] \cdot 0.5\text{H}_2\text{O}$ (**3-Au·0.5H₂O**), $(\text{Ph}_4\text{P})[\text{Au}(\text{catdt})_2] \cdot \text{Et}_2\text{O}$ (**3-Au·Et₂O**), and $(\text{Ph}_4\text{P})[\text{Au}(\text{catdt})_2] \cdot 2\text{THF}$ (**3-Au·2THF**) (Fig.2a). In the crystals, the rigid and planar $[\text{Au}(\text{catdt})_2]^-$ complex are connected by multiple intermolecular $[\text{O}-\text{H}\cdots\text{O}]$ H-bonds between the four hydroxy groups (Fig.2b). Interestingly, **3-Au·0.5H₂O** and **3-Au·Et₂O** have 3D H-bonded frameworks, which are different structures from each other (Fig.2a left and middle). The counter cations, Ph_4P^+ , are included in the framework with multiple cation-anion short contacts, which would stabilize these 3D frameworks. These are the first examples of 3D framework structures based on metal dithiolene complexes. On the other hand, **3-Au·2THF** formed a 2D H-bonded sheet structure (Fig.2a right). In order to explain the difference in assembled structures, the author focused on the H-bonding ability, size, and shape of the crystal solvents. The smallness and proton-accepting and -donating properties of the water facilitate the formation of the densely-packed 3D framework (Fig.2a left). On the other hand, bulky Et_2O molecule prevents the gold complexes from approaching each other, resulting in the loosely-packed 3D framework (Fig.2a middle). In **3-Au·2THF**, due to the disk shape of the THF molecule, the THF molecules are positionally disordered, which leads to the formation of the THF-THF H-bonds. These H-bonds would interfere with the formation of the 3D structure. Therefore, in these crystals, the structure and dimensionality of the frameworks can be modulated by changing the crystal solvents, in which interactions between the solvent molecules play an important role.

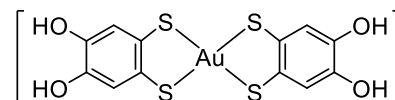


Fig.1 Chemical structure of the gold dithiolene complex, $[\text{Au}(\text{catdt})_2]^-$.

The characteristic molecular assembly which had not been observed for the metal dithiolene complexes will lead to the peculiar functionalities derived from their framework structures. Therefore, these findings indicate that the metal catecholdithiolene complexes are a good building block for constructing H-bonded molecular frameworks with d/π -electrons, leading to the basis of the playground for proton-electron coupled functionalities in the crystal.

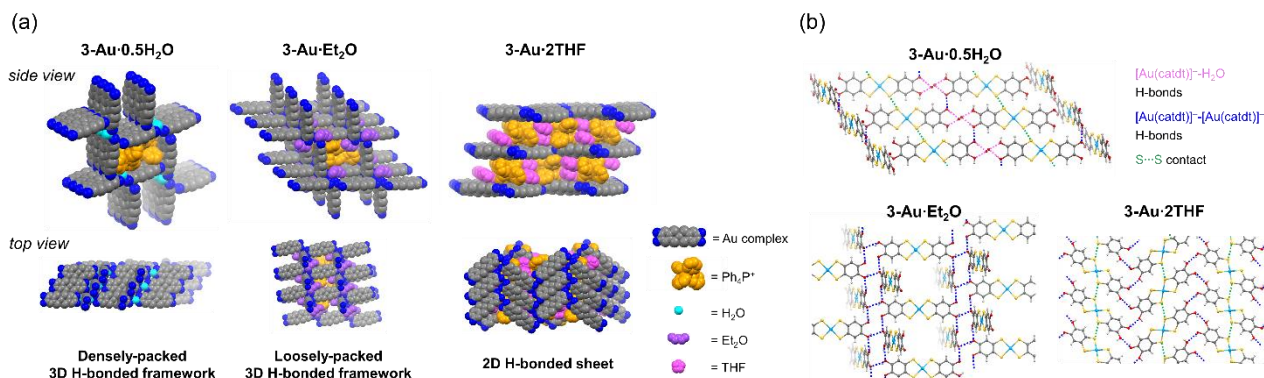


Fig.2 (a) Assembled structures and (b) H-bonding structures based on $[\text{Au}(\text{catdt})_2]^-$ complexes in each crystal.

Chapter 3 Magnetic property change with PCET of metal dithiolene complex and the effect of deprotonation on d/π -electronic states

Proton-coupled electron transfer (PCET) is an important phenomenon upon the development of novel functionalities combining protonic and electronic properties.[8] In this chapter, by exchanging the central metal of the metal catecholdithiolene complexes from gold to nickel (Fig.3), the author realized protonation/deprotonation-coupled magnetic property change of nickel dithiolene complex crystals via PCET in the solution process.

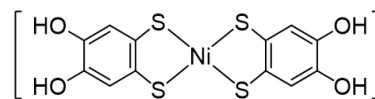


Fig.3 Chemical structure of the nickel dithiolene complex, $[\text{Ni}(\text{catdt})_2]$.

From the reported nickel complex salt, $(\text{Ph}_4\text{P})_3[\text{Ni}(\text{catdt})_2]2\text{Br}$, four kinds of new crystals were successfully obtained by recrystallization: $(\text{Ph}_4\text{P})[\text{Ni}-\text{H}_4(\text{catdt})_2] \cdot \text{DMSO}$, **3-Ni-4H·DMSO**, $(\text{Ph}_4\text{P})[\text{Ni}-\text{H}_3(\text{catdt})_2] \cdot \text{THF}$, **3-Ni-3H·0.5THF**, $(\text{Ph}_4\text{P})[\text{Ni}-\text{H}_3(\text{catdt})_2] \cdot 0.5\text{H}_2\text{O}$, **3-Ni-3H·0.5H₂O**, and $(\text{Ph}_4\text{P})_2[\text{Ni}-\text{H}_2(\text{catdt})_2] \cdot \text{H}_2\text{O}$, **3-Ni-2H·2H₂O**.

Firstly, focusing on the crystal structures, **3-Ni-4H·DMSO** and **3-Ni-3H·0.5H₂O** has a 3D framework structure based on the nickel complexes formed by $[\text{O}-\text{H}\cdots\text{O}]$ H-bonds between nickel complexes and those between nickel complex and crystal solvents (Fig.4a left). On the other hand, **3-Ni-3H·0.5THF** and **3-Ni-2H·2H₂O** had 2D sheet structures formed by $[\text{O}-\text{H}\cdots\text{O}]$ H-bonds based on nickel complexes (Fig.4a right). Interestingly, in **3-Ni-3H·0.5H₂O** and **3-Ni-3H·0.5THF**, the nickel complexes formed anionic $[\text{O}-\text{H}\cdots\text{O}]^-$ H-bonds ($d_{\text{O}\cdots\text{O}} = \sim 2.59 \text{ \AA}$) with each other. Such low-barrier H-bonds have a potential for proton transfer between the O atoms with external-stimuli.[2] Furthermore, a detailed comparison of the bond lengths of the nickel complexes in each crystal revealed

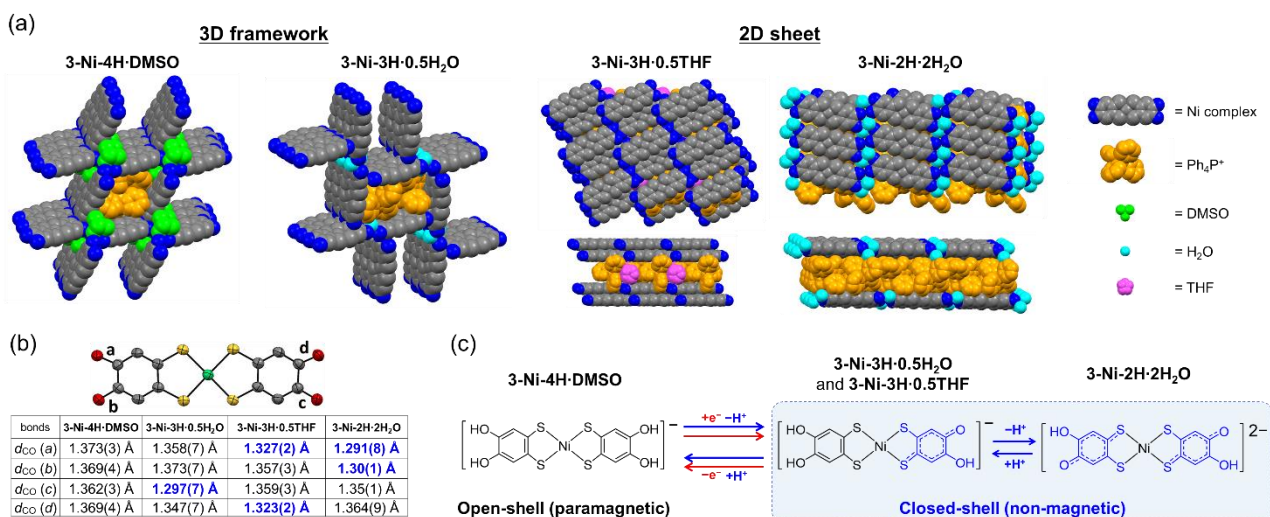


Fig.4 (a) Assembled structures, (b) C–O bond lengths of the nickel complexes, and (c) change of the electronic states of the nickel complexes through PCET in solution processes in each crystal.

that the molecular structures and electronic states are significantly different (Fig.4b). The C–O bond lengths of the nickel complex in each crystal suggest that partial deprotonation of catechol moiety of the nickel complexes should occur in **3-Ni-3H·0.5H₂O**, **3-Ni-3H·0.5THF**, and **3-Ni-2H·2H₂O** (Fig. 4b). Considering that the nickel complexes in **3-Ni-3H·0.5H₂O** and **3-Ni-3H·0.5THF** are monoanionic states and that in **3-Ni-2H·2H₂O** is dianionic state, electronic states and properties should also be changed by oxidation.

In order to investigate the spin-states of the nickel complexes in each crystal, electron spin resonance (ESR) measurements were carried out. The ESR signal was observed for the non-deprotonated crystal, **3-Ni-4H·DMSO**; on the other hand, the deprotonated crystals, **3-Ni-3H·0.5H₂O**, **3-Ni-3H·0.5THF** and **3-Ni-2H·2H₂O**, showed no ESR signals. This result indicates that the nickel complexes of these crystals are singly or doubly deprotonated with one-electron oxidation, as shown in Fig.4c. Therefore, the magnetic properties in the crystals are changed from paramagnetic to non-magnetic through PCET in solution (Fig.4c). In addition, the DFT calculations based on the crystal structures reveal that the d/π electronic states were significantly modulated with the deprotonation. This result indicates that the complex is a good candidate for exploring novel functionalities and phenomena based on d/π electrons coupled to proton dynamics in solid state.

Chapter 4 Vapochromism induced by intermolecular electron transfer coupled with hydrogen bond formation

Vapochromic materials, which respond with color changes when exposed to vapors, have attracted much attention as good candidates for chemical sensors because they can directly visualize external environmental changes.[9] In this chapter, the author successfully developed the novel vapochromic metal-dithiolene-based crystals and realized a new mechanism based on electron transfer coupled with H-bond formation [10].

A zinc complex salt **4-Zn**, (Ph₄P)₂[Zn(4-mx bdt)₂] (4-mx bdt: 4-methoxybenzenedithiolate, Fig.5), was newly synthesized. The methanol-containing salt, **4-Zn·2MeOH**, was obtained by slow evaporation of methanol solution as yellow crystals. In this crystal, methanol molecules formed [S··H–O] H-bonds with S atoms on the [Zn(4-mx bdt)₂]²⁻ complex (Fig.6a top). Interestingly, drying the crystals under vacuum resulted in the color change from yellow to orange, maintaining its single-crystalline state. From the structural analysis, the two methanol in **4-Zn·2MeOH** desorbed completely being converted to the orange crystal **4-Zn** with changes in molecular structure and arrangement. This process is reversible, and a similar color was also observed by the sorption of water vapor in the atmosphere. (**4-Zn·H₂O**; Fig.6a bottom).

To elucidate the mechanism of vapochromism in this crystal, the author firstly compared the crystal structures before and after vapor sorption. Both **4-Zn·H₂O** and **4-Zn·2MeOH** have [S··H–O] H-bonds between the [Zn(4-mx bdt)₂]²⁻ complex and the absorbed vapor molecules (Fig.6a). On the other hand, significant changes in the molecular structure and arrangement of the [Zn(4-mx bdt)₂]²⁻ complexes were observed only in the methanol sorption process. These results suggest that the vapochromism in this crystal is related to H-bond formation, rather

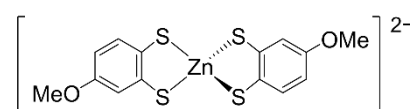


Fig.5 Chemical structure of the zinc dithiolene complex, [Zn(4-mx bdt)₂].

than molecular and assembled structure changes which have been proposed for conventional vapochromic materials. Then, DFT calculations based on the experimentally observed crystal structures were carried out to reveal the effect of H-bond formation on the vapochromism. Calculated absorption spectra based on hypothetical crystal structures “**4-Zn·2MeOH** without 2MeOH”, where only the structural changes of the zinc complexes are considered, was almost the same as that of **4-Zn**; on the other hand, calculated absorption spectra based on the real crystal structure “**4-Zn·2MeOH**” considering the interactions with the vapor molecules through H-bonds showed a blue shift (Fig.4b). These results indicate that the origin of the vapochromism in this crystal is the intermolecular H-bond formation. In addition, from Mulliken population analysis, significant electrons transfer from the $[\text{Zn}(\text{4-mxbd})_2]^{2-}$ complex to methanol or water molecules were observed. These results reveal that the H-bond formation causes electron transfer.

To elucidate the relationship between the blue shift and the electron transfer through H-bonds, the author focused on the energy and distribution of the crystal orbitals related to the visible-light absorption. The energy diagram shows that the blue shift is caused by stronger stabilization of the crystal orbitals α and β compared with γ and δ (Fig.6c left). This comparatively strong stabilization of α and β is due to the large orbital weight on the H-bonding S atoms of α and β (Fig.6c right). Therefore, a new vapochromism mechanism based on electron transfer through H-bond formation was successfully realized in this crystal. The findings here provide important insights to expand the scope of molecular designs for vapochromic as well as other stimuli-responsive materials. In this work, the author demonstrated the d/π electronic state modulation coupled with H-bonding proton: electron-proton coupled optical functionality.

Chapter 5 General conclusion

In this Ph.D. study, the author demonstrated the first 3D H-bonded framework based on metal dithiolene complexes through the synthesis of gold catecholdithiolene complex crystals in Chapter 2, which can be the basis for novel proton-electron coupled functionalities unique to the framework structures. Then, based on this result, by exchanging the central metal from gold to nickel, the protonation/deprotonation-coupled magnetic property change (from paramagnetic to non-magnetic) through PCET in solution processes was realized in crystalline solid states in Chapter 3. Furthermore, in Chapter 4, d/π electronic states modulation based on electron transfer coupled with H-bond formation was revealed in the novel zinc-dithiolene-based vapochromic crystal, leading to the optical functionalities. This is the first vapochromic behavior caused by only the H-bond formation. Therefore, the author achieved the development of the novel metal dithiolene complex crystals exhibiting peculiar functionalities based on a coupling of H-bonding protons and d/π electrons in this Ph. D. study. These findings provide an important basis for realizing novel phenomena, where π and d electrons are coupled with the electrostatic effect of H-bonding and proton dynamics in solid state.

Reference

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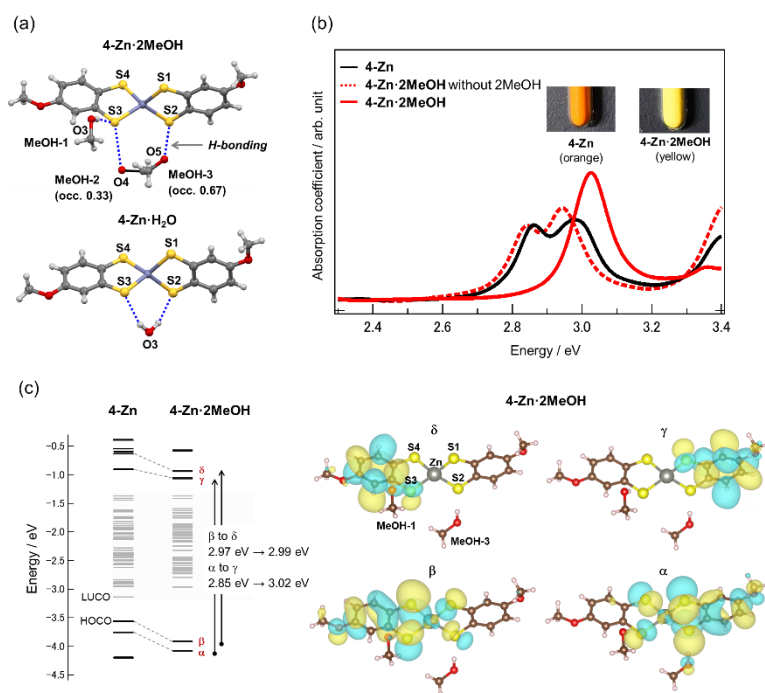


Fig.6 (a) H-bonding structures in **4-Zn·2MeOH** and **4-Zn·H₂O**. (b) The calculated absorption spectra of **4-Zn**, **4-Zn·2MeOH** and the hypothetical “**4-Zn·2MeOH** without 2MeOH” based on the experimentally observed crystal structures. The photograph of the crystalline materials. (c) (left) Crystal orbital energies of **4-Zn** and **4-Zn·2MeOH**, and (right) corresponding crystal orbitals in **4-Zn·2MeOH**.