

Study on Electrical Conductivity and Thermoelectric Properties of Redox Active Coordination Polymers

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博士論文

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Redox Active Coordination Polymers
(酸化還元活性な配位高分子の電気伝導性及び熱電特性に関する研
究)

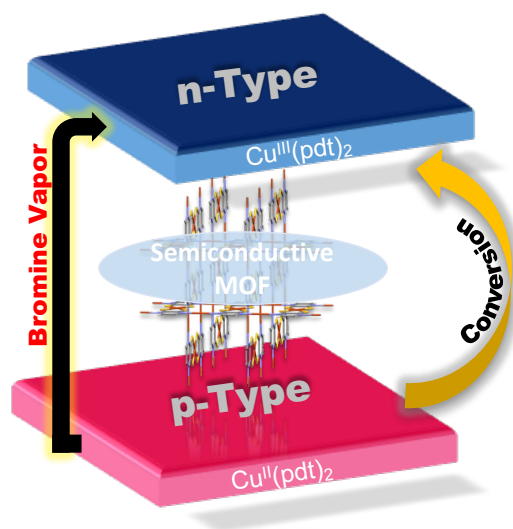
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Summary

In this work, we have reported electrically conductive coordination polymers that exhibit redox activity based on metal or ligand. Semiconducting and Thermoelectric properties were investigated. Thermoelectromotive force measurement was incorporated in order to investigate conductive carriers. Thermoelectromotive force is well-known among thermoelectric materials to investigate the electronic structure and find the efficiency of the material in converting heat into electrical energy. And it's a new concept in the field of MOF chemistry. Where, this can be used to investigate conducting carrier types in case of conductive MOF. And the study in this work shows that in the MOFs, if the metal centre is in the easily accessible reduced state, which means that charge carrier of holes can be generated thermally. This implies that the fermi energy level will be close to the valence band and hence it's a p-type semiconductor. Whereas, if the metal centre is in the easily accessible oxidized state, which means that charge carrier of electrons can be generated thermally. This implies that fermi energy level will be close to the conduction band and hence it's an n-type semiconductor. In chapter 2, we presented the extended application range of the $\text{Cu}[\text{Cu}(\text{pdt})_2]$ MOF in the field of electronics. For the first time, we reported the change in the Seebeck coefficient of MOFs via halogen doping. Conducting carrier has changed from holes to electrons after a certain fraction of halogen doping while maintaining the original structure. And halogen doping causes an appreciable amount of enhancement in the electrical conductivity. The improved conductivity and device engineering will make this material a versatile candidate for the field of MOF-based electronic devices. $\text{Cu}[\text{Cu}^{\text{II}}(\text{pdt})_2]$ possesses holes as conductive carriers and act as p-type semiconductor and upon halogen doping $[\text{Cu}^{\text{II}}(\text{pdt})_2]$ oxidizes to $[\text{Cu}^{\text{III}}(\text{pdt})_2]$. $[\text{Cu}^{\text{II}}(\text{pdt})_2]^{2-}$ can easily be oxidized to $[\text{Cu}^{\text{III}}(\text{pdt})_2]^-$, while is hardly reduced to $[\text{Cu}^{\text{I}}(\text{pdt})_2]^{3-}$, indicating that the charge carriers of hole are thermally generated, in other words, the Fermi energy

(E_F) is closer to top of the valence band than bottom of the conduction band. Which means that it is a p-type semiconductor. On the other hand, the bromine-doped compound is in the $[\text{Cu}^{\text{III}}(\text{pdt})_2]^-$ state, which can easily be reduced to $[\text{Cu}^{\text{II}}(\text{pdt})_2]^{2-}$ whereas hardly oxidized to $[\text{Cu}^{\text{IV}}(\text{pdt})_2]^0$, indicating that the charge carriers of an electron are thermally generated (n-type semiconductor).



In chapter 3 we reported neutral electrically conducting MOF $\text{Fe}^{\text{III}}_2\text{d}h\text{b}q_3$. And the MOF possess redox activity based on metal as well as ligand. It exhibited significantly high electrical conductivity of $1.2 \times 10^{-2} \text{ S cm}^{-1}$ at 300 K as a result of strong covalency between metal and ligand. The majority of charge carrier was found to be electron investigated by thermoelectromotive force measurements. In the case of $\text{Fe}^{\text{III}}_2\text{d}h\text{b}q_3$, for Fe^{III} it is easy to reduce to Fe^{II} rather than to oxidize to Fe^{IV} , (which is also supported by the cyclic voltammetry measurement), indicating that the charge carriers of electrons are thermally generated, in other words, the Fermi energy (E_F) is closer to bottom of the conduction band (n-type semiconductor). Upon fabricating the MOF as a cathode for a LIB, it showed a significantly high specific capacity (322 mA h / g) while undergoing first discharge. Such a high value of discharge capacity is the result of the many-electron uptakes which

was consistent with the result obtained by solid CV. In chapter 4, we have reported a 3-D conducting coordination polymer $\text{Na}[\text{Pt}(\text{pdt})_2] \cdot 2\text{H}_2\text{O}$ using Platinum and 2,3-pyrazine dithiol ligand. It has face-to-face stacking along *a*-axis, which results in a 3-dimensional coordination polymer. Cyclic voltammetry measurement showed that the polymer exhibited $1e^-$ reversible redox behavior based on metal. The polymer exhibited a relatively high electrical conductivity of $1.6 \times 10^{-2} \text{ Scm}^{-1}$. Such a high electrical conductivity is a result of $\pi-\pi$ interaction between the organic core along the *a*-axis. The strong $\pi-\pi$ interaction leads to a 1D π stacked column, which provides the pathway for the electron delocalization in the direction of stacking. Further charge carrier type investigation was performed using thermoelectromotive force measurement. Where the positive sign of the Seebeck coefficient indicates that holes are the majority charge carrier. For $\text{Na}[\text{Pt}(\text{pdt})_2] \cdot 2\text{H}_2\text{O}$, Since Pt is in +III oxidation state and for Pt both the oxidation state (i.e. reduced form Pt^{II} and oxidized one Pt^{IV}) are accessible as there are already reports on Pt^{II} and Pt^{IV} complexes. At this moment, we do not have idea most easily accessible oxidation state. Although, based on the results obtained from the thermoelectromotive force (as it's a p-type semiconductor), it seems that for Pt^{III} it is easier to oxidize to Pt^{IV} rather than to reduce to Pt^{II} .