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

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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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Introduction

Metal organic frameworks (MOFs) are the most studied materials in the last 3 decades because of its diverse applications in the field of nanotechnology, chemistry, physics and medicine.[1] It belongs to a new class of porous materials and because of their extraordinary features such as large surface area, permanent porosity, chemical tunability, this field have been explored a lot for a wide range of applications, such as gas storage,[2] gas separation,[3] sensing and catalysis.[4] Moreover, other than the typical use of MOF for gas storage and separation, they also have the potential to be explored as an energy storage device, capacitors, electrocatalysis, conducting materials etc.[5] However, these applications are limited by the insulating and redox inactive nature of the MOFs. In recent years, variety of strategies have been introduced including designing, synthesizing, and post synthetic modifications etc., through which the electrical conductivity can be modified. As a result of introducing these strategies, there are plenty of conductive MOFs have been reported in the last 10 years.[6] To date, they are only focusing on obtaining electrically conductive MOFs and almost no focus has been paid on their fundamental electronic properties such as investigating conducting carrier types. In this work we focus on synthesizing electrically conductive MOFs and investigated the charge carrier type by using thermoelectromotive force measurement. The positive and negative sign of Seebeck coefficient indicates that the majority of charge carrier are holes and electrons respectively. Guest-induced modification of the electronic states in metal-organic frameworks (MOFs) have brought about a new field of interdisciplinary research including host-guest chemistry and solid-state physics. Although there have been plenty of studies on guest-promoted enhancement of the electrical conductivity.[7] However, properties like structure-property relationships, stoichiometry, conductive carriers have not been studied in detail. In this study, we investigated the effect of continuous controlled halogen doping on structural, optical, semiconducting and thermoelectric properties of $Cu[Cu(pdt)_2]$ (pdt = 2,3-pyrazinedithiolate). $Cu[Cu(pdt)_2]$ is a prototype of electron conductive MOFs and possesses permanent porosity (a BET surface area of 280 $m^2\ g^{-1}$).

Results and Discussion

Structural investigation was performed using PXRD (Figure1a) and it was found that all the doped samples kept crystallinity, indicating that the MOF skeleton was maintained upon halogen doping and halogen doping does not change the intrinsic structure of the MOF. PXRD data were well fitted using Le Bail fitting (Figure 1b), and the result shows that all the samples are crystallized in a tetragonal lattice. However, the unit cell parameter *c*-axis continuously changed. Detailed electronic structure investigation using DFT calculation indicates that $[Cu^{II}(pdt)_2]^{2-}$ oxidized to $[Cu^{III}(pdt)_2]^{-}$

upon halogen doping. UV-Vis and Raman spectra also supported the aforementioned discussion. Thermoelectromotive force measurements was performed using pressed pellet samples to investigate conducting carrier and it was found that the same material could behave as both p- and n-type semiconductors while tuning the stoichiometry of the doped Br/I in $Br_x/I_x@Cu^{II}[Cu^{II}(pdt)_2]$ (Figure 1c). The pristine MOF have a seebeck coefficient of +337 μV K^{-1} and the value started decreasing as halogen fraction increases and after a certain fraction of doping sign of seebeck coefficient has changed.　Which means that conducting carrier has changed from holes in pristine MOF to electrons upon doping of certain fraction of halogen. Halogen molecules act as an oxidizing agent. Which causes the selective oxidation of $[Cu^{II}(pdt)_2]^{2-}$ in the host framework to form $[Cu^{III}(pdt)_2]^{-}$ which resulted in a redox hoping mode of charge transportation. Conductivity measurement was performed on pressed pellet sample using *I-V* characteristic. The electrical conductivity measurements indicate an enhancement of 10-fold of conductivity upon doping (Figure 1d).

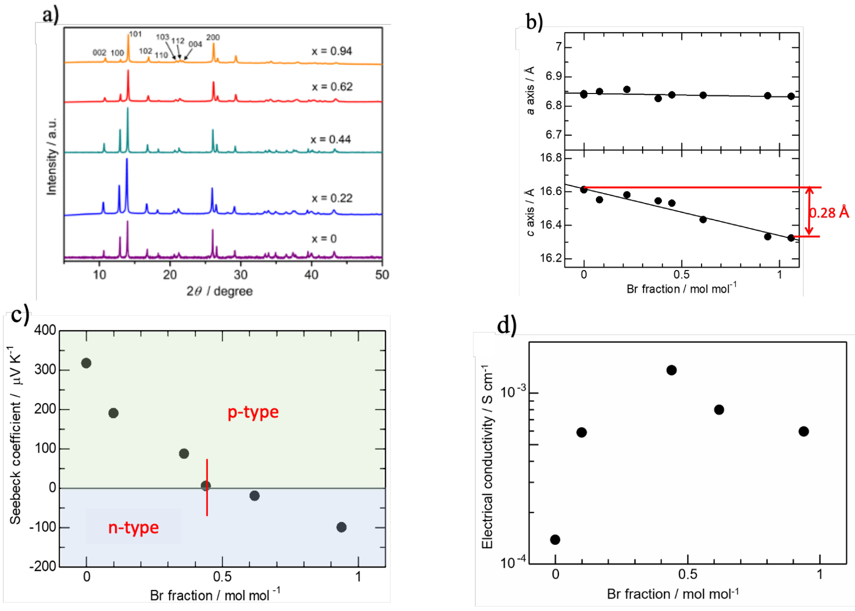

Figure 1. a) PXRD patterns of $Br_x@Cu[Cu(pdt)_2]$. b) Lattice parameters of $Br_x@Cu[Cu(pdt)_2]$. c) Seebeck coefficients as a function of Br. d) Electrical conductivity at 293 K as function of Br fraction.

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論文審査の結果の要旨

本論文は、酸化還元活性な配位高分子における伝導キャリアの種類およびその輸送特性を、結晶構造解析、UV-Vis スペクトル、量子化学計算、磁化率、電気伝導度、熱起電力測定を組み合わせることで詳細に議論している。

第一章では、配位高分子に関する紹介、および電気伝導性配位高分子の歴史、応用例などについて網羅的に述べられている。

第二章では、電気伝導性を示す多孔性配位高分子 $Cu[Cu(pdt)_2]$について、臭素蒸気暴露による $Cu(pdt)_2$ ユニットの酸化に伴う構造および電子状態の変化について粉末 X 線回折、量子化学計算、Raman スペクトルを用いて詳細に述べられている。また、同配位高分子に対する臭素ドーピングによる電気伝導性の変化、および熱起電力の測定による伝導キャリアの変化について調べ、臭素のドーピング量に応じて伝導キャリアが正孔から電子に連続的に変化する様子を明らかにしている。このように多孔性配位高分子に対してドーピング量を制御することで伝導キャリアを変革した例はこれまでなく、電気伝導性を示す多孔性配位高分子に関する研究の新たな方向性を示した点で評価できる。

第三章では、2,5-dihydroxy-1,4-benzoquinone(dhbq)配位子からなる新規多孔性配位高分子 $Fe_2(dhbq)_3$ を開発し、本錯体が高い電気伝導度を示すこと、n 型半導体であることなどを明らかにした。また、本錯体をリチウムイオン電池の正極材料として用いることで、320 mAh/g という高い電極容量を実現している。

第四章では、新規配位高分子 $Na[Pt(pdt)_2]$(pdt = 2,3-pyrazinedithiol)を開発し、本錯体が高い電気伝導度を示すこと、本錯体が p 型半導体であることを明らかにしている。

以上の内容は、論文提出者が自立して研究活動を行うために必要な高度の研究能力と学識を有することを示している。したがって、Shraddha Gupta 提出の博士論文は博士（理学）の学位論文として合格と認める。