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ナフタレンジイミドを伝導層とした多孔性配位高分子の合成と物性

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Syntheses and Physical Properties of Naphthalenediimide-based Conductive Porous Coordination Polymers

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[Introduction] Porous coordination polymers (PCPs) are organic-inorganic hybrid compounds which are formed by assembly of metal ions and organic ligands. Conductive PCPs have attracted considerable attention due to their high electrical conductivities and the potential of practical applications for making porous electrodes, capacitors, sensors, etc.^[1] Naphthalenediimides (NDIs) are large π -conjugated redox-active molecules, which can be one-electron reduced to generate stable radicals because of their electron deficient characteristic.^[2] So far, a few NDI-based conductors have been reported.^[3] Because various coordinating moieties can be introduced to the imido site, NDI is promising for the ligand of conductive PCPs.

[Experiment] In this study, *N,N'*-di(4-pyridyl)-1,4,5,8-naphthalenediimide (NDI-py₂) was chosen as the ligand. The NDI cores were reduced by electrochemical method to form radical anions, and the pyridyl groups coordinated to metal ions to construct conductive PCPs.

[Result and Discussion] As a result, five NDI-based PCPs were synthesized and confirmed by single-crystal X-ray diffraction study. All of them contained 1D π -stacked columns of NDI cores as shown in Figure 1. UV-Vis spectroscopy was performed to confirm the existence of NDI radical anions. All PCPs had absorptions over the visible light range, so they show black color. These absorptions agree with the reported UV-Vis data of NDI radicals,^[4] indicating all of the five PCPs contain NDI radicals. Thermogravimetry measurements were carried out to study the stabilities. Three PCPs are unstable in air, while [ZnI₂(NDI-py₂)₂][Zn(OH₂)₄(NDI-py₂)]·*n*NMP·*m*H₂O (**PCP-ZnI₂·NMP**) and [CdBr_x(OH₂)_{3-x}(NDI-py₂)_{1.5}]₂·*n*DMA·*m*H₂O (**PCP-CdBr₂·DMA**) are relatively stable. The electrical conductivities of these two compounds were measured. As shown in Figure 2 (a) and (b), **PCP-ZnI₂·NMP** and **PCP-CdBr₂·DMA** are semiconductors. The Activation energy (E_a) of **PCP-ZnI₂·NMP** is 167 meV in low temperature

region and 266 meV in high temperature region. The conductivity is $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The E_a is 86.6 meV and 202 meV for **PCP-CdBr₂·DMA** at low temperature and high temperature region, respectively. The conductivity is $1.2 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature. In order to confirm the existence and stability of NDI radicals, the electron spin resonance (ESR) measurement of **PCP-ZnI₂·NMP** was carried out at room temperature. In this compound, Zn²⁺ (3d¹⁰) has no spin, thus we affirm that the signal, showing in Figure 2 (c), indicates reduced NDI radicals. The g value of the NDI radical is 2.0025, which is reasonable for general organic radicals.

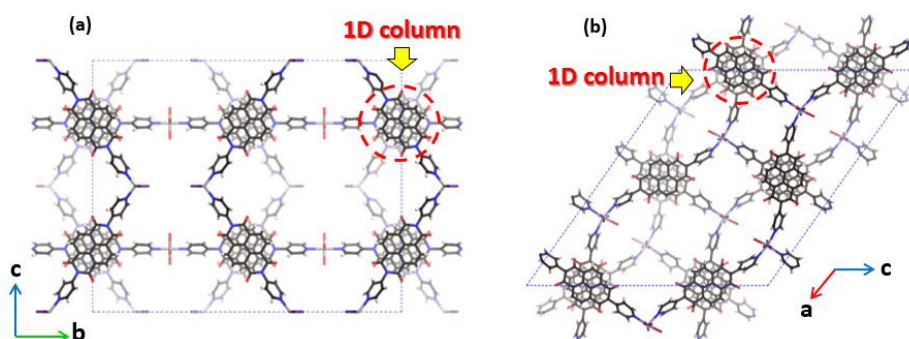


Figure 1. Crystal structure of (a) **PCP-ZnI₂·NMP** and (b) **PCP-CdBr₂·DMA**.

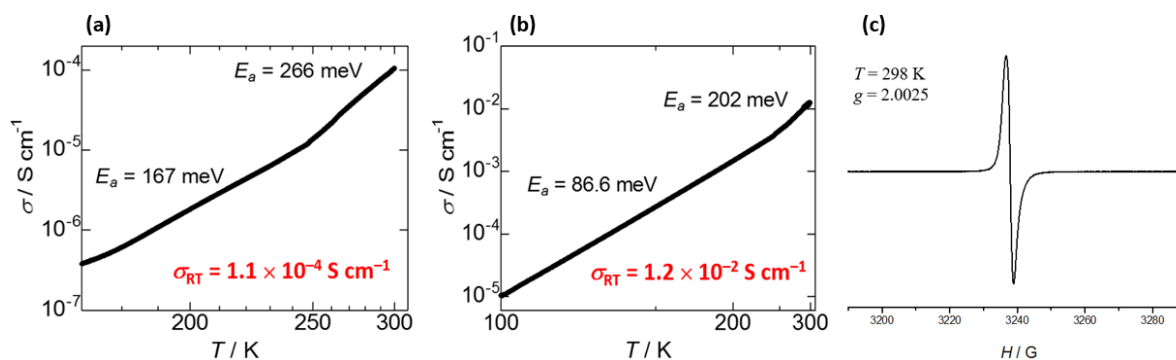


Figure 2. Conductivities of (a) **PCP-ZnI₂·NMP** and (b) **PCP-CdBr₂·DMA**; (c) ESR spectrum of **PCP-ZnI₂·NMP**.

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