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Type(English)	Summary

論文要旨

THE S I S S U M M A R Y

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要旨（英文 800 語程度）

Thesis Summary (approx. 800 English Words)

Redox-active organic molecules can play a promising role as flexible electronic elements in addition to the lineup of rigid inorganic electronic elements because the electronic state may be readily controlled by the external energy. Although various kinds of redox-active organic molecules were synthesized, the attempt to apply them to electronic devices has been limited because of lack of proper structural design. Moreover, ligand-based redox-active porous coordination networks (PCNs) have not been well explored because of the limited availability of redox-active ligands. In addition to developing new redox-active organic molecules, to design the electronic devices based on redox-active organic molecules/PCNs it is essential to understand the relationship between the molecular arrangement, electrical properties, and its redox-activity.

This thesis aims at the development of electronic devices using a redox-active organic molecule and its PCNs and highlights the importance of molecular arrangement. Redox-active organic molecule, 2,5,8-tri(4'-pyridyl)1,3-diazaphenalene (TPDAP), having a large π -plane and multi-intermolecular interactivity was utilized for developing a resistive switching memory device. Furthermore, its PCNs were synthesized to fabricate chemiresistive sensors. The electrical properties were modulated by the post-synthetic modification. Each mechanism was systematically investigated by structural determination together with well-defined control experiments. The general guideline for designing the electronic devices using redox-active organic molecules was proposed.

The TPDAP was applied to the fabrication for the resistive switching memory device. The TPDAP film showed non-volatile bistable resistance states with high on-off ratio, retention, and endurance only when the molecular orientation was anisotropic. GIWAXS and UV-vis and IR spectroscopic study of on- and off-states indicated that the resistance modulation did not result from changes in structure/electronic state/chemical bond at the bulk level. Furthermore, control experiments using an isotropic TPDAP film and a redox-inert 2,5,8-tri(4'-pyridyl)-1,3,4,6,7,9-hexaazaphenalene (TPHAP) having the same molecular shape as TPDAP verified that the anisotropic oriented layers of TPDAP via π - π stacking and its oxidation/reduction process promoted two reversible resistance states. In other words, the external voltage reversibly generated conductive oxidized layers in the local region from the non-conductive neutral layers. This study can provide general guidelines for designing resistive switching memory devices using redox-active organic molecules, highlighting the importance of molecular arrangement.

The chemiresistive humidity sensor was fabricated using the redox-active PCNs. Two kinds of redox-active PCNs composed of TPDAP and Cd^{2+} were prepared by changing the rate of solvent evaporation. $[\text{Cd}_{2.5}(\text{NO}_3)_5(\text{TPDAP})_3(\text{DMF})_3(\text{H}_2\text{O})_{7.4}]$ (PCN 1; orthorhombic *Cmma*), was synthesized by heating a DMF solution of TPDAP and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in sealed conditions at 90 °C. Reddish block shaped crystals were obtained on the bottom of the vessel, which has a π - π stacking columnar structure with a 6 Å sized diagonal channel along the [1 1 0] direction confirmed by single crystal X-ray analysis. In contrast, the higher rate of evaporation in open conditions produced reddish thin plate crystals of a completely different structure, $[\text{Cd}_{1.5}(\text{NO}_3)_{2.77}(\text{TPDAP})_{0.77}(\text{TPDAP}^-)_{0.23}(\text{DMF})_2(\text{H}_2\text{O})]$ (PCN 2; monoclinic *C2/c*). The single crystal X-ray analysis revealed that PCN 2 has a 2D slipped π - π stacking structure possessing 3D tangled pores with a window size of 7 Å. Since both PCN 1 and PCN 2 were densely crystallized on the bottom of the vessel, crystalline films of PCN 1 and PCN 2 could be obtained by replacing a glass plate with a wafer under the same condition as their single crystal growth on the Au-patterned SiO_2/Si wafer, respectively. Film 1 composed of a very densely packed layer with open channels showed a significant change in its resistivity for humidity with high sensitivity and selectivity. When wet N_2 gas was introduced to the device by passing N_2 stream through a water bath, the current significantly increased by two orders of magnitude. In contrast, when dry N_2 gas was introduced to the device, the current decreased by two orders of magnitude compared with the initial state. Single crystal X-ray analysis and IR spectroscopic measurement before/after hydration of a single crystal of PCN 1 revealed that the key mechanism of humidity sensing is the dissociation of NO_3^- from Cd ions under hydration. The locally dissociated NO_3^- made the framework positively charged, leading to an electronically deficient state in the network framework, resulting in increasing the electronic interaction between TPDAPs in the pillar.

The electrical property of redox-active PCN was controlled by the post-synthetic modification. Redox-active PCN 1 with small pores due to high π - π stacking in the columnar structure was converted into PCN 1_{open} with 1D channels by immersing the crystals in ethanol. By removing mono-dentate TPDAP ligands in PCN 1, 13 Å x 4 Å sized channels surrounded by tri-dentate TPDAPs were formed in PCN 1_{open}. Therefore, the conductive PCN 1 was changed into the insulating structure because of the absence of the π - π stacking which was a conductive pathway in PCN 1. On the other hand, the insulating PCN 1_{open} could be modulated into conductive state by intercalation of TPDAP owing to efficient oxidation of PCN1_{open}.

Redox-active organic molecule, TPDAP, was applied to electronic devices. The large π -plane and multi-intermolecular interactivity facilitated the design of targeted structures for electronic devices and the redox-activity enabled to produce the electroactive species. The external energies such as chemical environment and voltage controlled electron transfer through the π - π stacking in each device. This thesis will provide a general guideline for designing the electronic devices using redox-active organic molecules based on the understanding of relationship between molecular arrangement and electrical property.