

Elucidation of ion insertion/desertion behavior using one-dimensional lanthanoid-phthalocyaninato double-decker complexes

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Molecular crystals composed of phthalocyaninato (Pc) complexes arranged one-dimensionally have various oxidation numbers depending on the central metal and counter anion. In recent years, a neutral state of a 1-D phthalocyaninato complex (LiPc) has been reported.¹ These crystals have one-dimensional pores with diameters of about 4 Å next to the column of LiPc molecules. Researchers have focused on controlling the physical properties of these compounds by inserting gas molecules or ions into the pores.²

In our laboratory, we have reported a double-decker complex (**Figure 1**) with lanthanoid (Ln) ions sandwiched between two Pc ligands and investigated the galvanomagnetic properties of solid crystals. By using electrolytic oxidation, we have obtained a one-dimensional array crystal ([DyPc₂]_x; I = triiodide) suitable for measuring the physical properties. Since robust 1-D pores form after removing I₃[−] ions and the crystallinity and electrical conductivity are maintained under ambient conditions, we investigated the possibility of reversible ion insertion by using a chemical/electrochemical method. For these studies, a mixture of Nafion and [DyPc₂]_x was applied to the working electrode, and solid CV was performed. In cyclic voltammograms, oxidation waves were observed derived from the motion of anion (ClO₄[−]) (**Figure 2**). In addition, similar waves were observed when a single crystal was attached to the electrode surface, confirming the insertion of ions obtained from the X-ray structural analysis and SEM-EDX. In this presentation, we will report the detailed structure and the electrochemical properties related to anion doping.

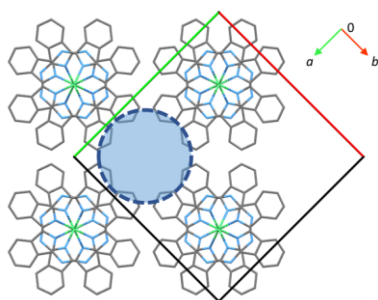


Figure 1 1-D pore of single crystal

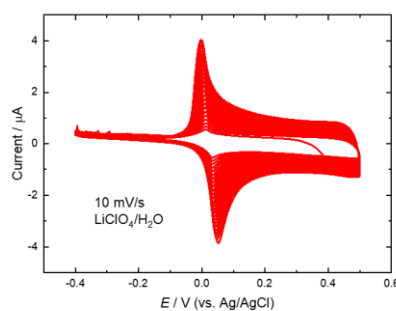


Figure 2 Cyclic voltammogram of single crystal

1) M. Nishi et al., *CrystengComm.*, **2020**, 22, 7528 2) Y. Miyoshi et al., *Chem. Commun.*, **2014**, 16, 9266