

Study and Design of Coordination Structures for Creating Functions

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論 文 内 容 の 要 旨

Self-assembly is a phenomenon where properly designed component molecules create organized structures spontaneously. Non-covalent intermolecular interactions such as hydrogen bonding, coordination bonding, hydrophobic interactions are employed to create self-assemblies. As the non-covalent bonds are flexible bonding, it enriches the variation of structure formation. That is, the possibility of creating supramolecules is infinity. By properly designing and coupling molecules based on the self-assembly, diverse structures and functions are achieved beyond those of individual molecules.

The main focus of this thesis is to create functional materials by designing the coordination structure of molecules based on supramolecular chemistry. This thesis consists of five chapters. The outline of chapter 2 and later are described below.

Chapter 2 describes the controlling of energy landscape of lipophilic cobalt coordination polymers. For the unconventional heat-set gelation of the chloroform solution of alkylated triazole cobalt complex $(C_{12}OC_3Trz)_3Co(II)Cl_2$, the gelation mechanism was elucidated based on changes in the sol-gel transition behavior derived from systematically changing the concentration of the chloroform solution and the alkyl chain length of the triazole. Also, in observation of the gelation behavior, it was found that the alkylated triazole cobalt complex $(C_{16}OC_3Trz)_3Co(II)Cl_2$ shows two different gelation behaviors of heat-set gelation and cool-set gelation in chloroform. Reentrant gel-sol-gel transition due to heating is the first discovery in the organogel and detailed investigation is studied.

Chapter 3 describes the synthesis and electrical properties of a two-dimensional metal-organic framework based on phthalocyanine (Cu-CuPc). Complexation of Cu(II) 2,3,9,10,16,17,23,24-octahydroxy-29H,31H-phthalocyanine (CuPcOH) with Cu(II) ions gives a two-dimensional (2D) metal-organic framework (MOF). This is the first report of phthalocyanine-based MOF. This 2D-MOF showed an electric conductivity of $1.6 \times 10^{-6} \text{ S cm}^{-1}$ at 80 °C. When this MOF was used as a cathode of lithium ion battery (LIB), large charge/discharge capacities of 151/128 mAh g⁻¹ were obtained. In addition, it showed good stability during 200 charge/discharge cycles. The obtained LIB performance mainly originates from the electrically conductive and redox-active framework of the phthalocyanine-based 2D MOF and its hierarchical microporous/mesoporous structure.

Chapter 4 describes the ruthenium complex functionalization of NU-1000 by solvent-assisted ligand incorporation (SALI). SALI is a useful method for the rational post-functionalization of Zr-based metal-organic frameworks since carboxylate-moieties strongly coordinate to the Zr₆ nodes. In this study, Ruthenium complex photocatalyst Ru^{II}(bpy)₂(dcbpy)(PF₆)₂ [bis(2,2'-bipyridine)-4,4'-dicarboxy-2,2'-bipyridine ruthenium(II) bis(hexafluorophosphate)] was installed into NU-1000 as a heterogeneous photocatalyst. The difference envelope density analysis was utilized to crystallographically verify the location of the inserted Ru complexes in the pores of NU-1000. Photocatalytic activity of the Ru complex functionalized NU-1000, Ru-NU-1000, was demonstrated with a basic photocatalytic reaction as a heterogeneous photocatalyst.

Chapter 5 summarizes the whole thesis work.