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Title	Structural investigation of polyoxometallates self-assembled architectures induced by crown ether supramolecular cations [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	甲第12228号
Issue Date	2016-03-24
Doc URL	https://hdl.handle.net/2115/62111
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	doctoral thesis
File Information	Jun_Xiong_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

博士 (環境科学)

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学 位 論 文 題 名

Structural investigation of polyoxometallates self-assembled architectures induced by
crown ether supramolecular cations

(クラウンエーテル超分子カチオンに誘起されるポリオキソメタレートの自己集積化構造
に関する研究)

Crystal engineering based on polyoxometallates (POMs) has intimate relationship with our daily life because of their far ranging applications, which involve catalysis, magnetism, nonlinear optics, medicine and so on. However, constructing the desirable functional architecture is difficult, and the characteristics of building blocks should be taken into account at first. POMs are discrete early transition metal-oxide cluster anions with many of structural characteristics. First, POMs have multiple hydrogen bonding sites, which promote them to construct versatile organic-inorganic hybrids architecture. Second, POMs have gigantic size, which allow them to embed large size of organic/supramolecular cation and construct multifunctional materials. Third, POMs with the large three dimensional structure and alternating short and long bond length distortion feature make them be an excellent candidate to prepare chiral materials. The structure characteristics of POMs can be matched well with the structural features of crown ethers. Carbon atoms and donor oxygen atoms in crown ether are the potential hydrogen bonding sites, which enable to construct self-assembled supramolecular structure with multiple hydrogen bonding sites POMs. Large cave of crown ethers have the ability to capture cations such as alkali metals and organic ammonium cations, and construct large size supramolecular cations, which make it possible to be filled into the large cave formed by POMs. Flexible structure of crown ethers allows them to construct diverse supramolecular structures and adjust the charge of supramolecular cations by introducing different cations. Asymmetric structural characteristics of crown ethers improve the opportunity to construct chiral crystal with POMs.

According to the structural characteristics of POMs and crown ethers, this thesis involves three aspects of investigations. (1) Building various packing structure by introducing different supramolecular cations and discovering the relationship between the packing diagram and size of supramolecular cations. (2). Constructing

supramolecular rotator by introducing supramolecular cations into POMs. (3) Designing chiral crystals by modifying POMs and crown ethers. Various supramolecular cations based on nine kinds of anilinium derivatives and three kinds of crown ethers have been constructed and were introduced into $[\text{SMo}_{12}\text{O}_{40}^{2-}]$ or $[\text{PMo}_{12}\text{O}_{40}^{3-}]$. 17 POMs self-assembled architectures based on crown ether supramolecular cations have been synthesized. This thesis includes six chapters. Chapter one, two and six are introduction, experimental and conclusions respectively.

In the chapter three, eight POMs self-assembled architectures based on different size supramolecular cations have been synthesized. The crystalline packing diagram has close relationship with the size of supramolecular cation, which is that six monovalent small size supramolecular cations encased one $[\text{SMo}_{12}\text{O}_{40}^{2-}]$ and constructed hexagonal self-assembled structure, and four divalent large size supramolecular cations surrounded one $[\text{SMo}_{12}\text{O}_{40}^{2-}]$ and formed a rectangular self-assembled structure.

In the chapter four, supramolecular cations composed of DB[18]crown-6 (DB[18]crown-6 = dibenzo[18]crown-6) and $(m\text{-XAni}^+)$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I , $\text{Ani}^+ = \text{anilinium}$) were introduced into $[\text{SMo}_{12}\text{O}_{40}^{2-}]$. Disorder of halogen atom was observed at *meta*-position of anilinium. Supramolecular rotation in terms of intermolecular interactions was investigated. Weak intermolecular interaction between $(m\text{-XAni}^+)$ cation and its adjacent ions/molecules restricted the motional freedom of the $(m\text{-XAni}^+)$ cation, which was proved by the potential energy calculation and dielectric measurements.

In the chapter five, chiral organic-inorganic hybrids based on POMs and achiral supramolecular cations have been designed through improving the asymmetric structure of the starting materials. Divalent $[\text{SMo}_{12}\text{O}_{40}^{2-}]$ and supramolecular cation based on symmetric DB[18]crown-6 molecule constructed the crystal **13**, which belonged to $P2_1/n$. Crystal **14** was obtained by introducing supramolecular cation based on asymmetric benzo[18]crown-6 (B[18]crown-6) into divalent $[\text{SMo}_{12}\text{O}_{40}^{2-}]$, and the crystal crystallized in the space group P . Crystal **15** was prepared by introducing asymmetric supramolecular cation of $[(4\text{-BrAni}^+)(\text{B}[18]\text{crown-6})]$ into trivalent $[\text{PMo}_{12}\text{O}_{40}^{3-}]$, and belonged to the chiral crystalline group space Pc . According to this method, two novel chiral POMs-based crystals **16** and **17** have been synthesized.

The research in this thesis will promote the development in the future about designing (1) diversity crystalline packing structures by introducing different size of organic cation into certain kind of inorganic building block. (2) supramolecular rotator based on crown ether and anilinium derivative by selecting suitable POMs to avoid the weak intermolecular interaction. (3) many of versatile and functional chiral organic-inorganic hybrids based on POMs and crown ether derivatives. All these results will promote the development of crystal engineering based on POMs.