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博士論文

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（選択的イオン認識のための機能性ナノ構造材料の設計と構築）

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Chapter 1. Introduction and Background

Lithium has been attracting considerable attention due to its extensive applications in various fields, such as glass and ceramics processing, lubricants and pharmaceuticals, especially in modern energy technology. Due to its high redox potential and specific heat capacity, lithium is one of the most important elements for modern energy revolution. Currently, lithium ion batteries (LIBs) are widely being used for electronic products, dominating the rechargeable battery market of cellular phones, laptop computers, cameras and cordless power tools. Today LIBs represent about 37% of the rechargeable battery world market and their use keeps steadily increasing. The use of LIBs has also recently been driven by the significant growth of electric-powered vehicles. As concerned about environmental safety and energy security, electric-powered vehicles are expected to take over the market share from the conventional internal-combustion-powered automobiles in the near future. Large LIBs will be desirable for powering these electric-powered vehicles. All these have make lithium become a very important commodity for modern life. As demand for lithium has begun to grow dramatically after the turn of the century, mining lithium in a more efficient and economically-feasible way is of great interest. Design of new functionalized nanostructured materials that exhibit selective ion recognition towards lithium will contribute to the development of new techniques for lithium resources.

Nature has been an inspiring source for the development of artificial functional materials. The extraordinary selective and efficient transport of specific ions across the cell membrane is common and essential to many of life's process. This ion-transport ability is owed to the ion channels or ion carriers with characteristic architectures and coordination geometries created by the membrane proteins. Inspired by these discoveries in biological systems, artificial nanostructured materials that are capable of recognizing specific ions efficiently have been developed. However, nanostructured materials exhibiting selective lithium ion recognizing and transport ability are still rare.

The objective of this thesis is to develop new functionalized nanostructured materials for efficient selective lithium ion recognition. Two kinds of nanostructured materials targeting selective lithium ion recognition have been designed and synthesized in this thesis. In chapter 2−4, liquid crystals consisting of lithium selective ion channels have been developed based on liquid-crystalline lithium receptors. Ion-imprinted polymeric extractants having lithium-selective recognizing blocks have been prepared in chapter 5.

Chapter 2. Design and Synthesis of Liquid-Crystalline Lithium Receptors and Effects of Molecular Structure and Lithium Salt Addition on Their Phase Behaviors

Liquid-crystalline (LC) self-assembly is a promising platform to construct nanochannels with various characteristic architectures and coordination geometries. The tunable nanostructure and functionality of LC assembly enable it to become an outstanding candidate for the design of nanostructured ion receptors or transporters. Kato and co-workers have previously developed several nanostructured lithium ion-transport materials based on LC assemblies. However, lithium ion-selective LC materials have not yet been reported to the best of our knowledge.

The aim of this chapter is to synthesize new lithium receptors with mesogenic moieties that exhibit stable LC phases and investigate the effects of molecular structure and lithium salt addition on their phase behaviors. Crown ethers (CE) are well-known ionophores and their affinity towards certain metal ions can be controlled by tuning the number of coordination sites and the cavity size. It is known that the most favourable coordination numbers for lithium cations (Li^+) are expected to be 4, 5 and 6. And 12- to 14-membered CE rings (cavity size: 1.2-1.8 Å) show the strongest affinity to Li^+ having an ionic diameter about 1.4 Å.[4] Hence, dibenzo-14-crown-4 (DB14C4) (1.8 Å) is chosen as the lithium selective ligand because of its highly matched geometry towards lithium coordination. 12-crown-4 (12C4) and benzo-12-crown-4 (B12C4) are also common and well-known lithium complexing ligands, which have been used to develop lithium-selective materials. In order to develop new LC materials for selective lithium ion recognition, wedge-shaped crown ether derivatives are designed to act as LC lithium receptors. The ionic moieties of the LC receptors consist of DB14C4, 12C4 and B12C4 as lithium ion recognizing ligands, respectively. Taking the advantages of LC self-assembly, liquid-crystalline CE derivatives could form well-defined interconnected ionic channels suitable for selective lithium ion transport. Thus, the author considered that the complexation

of the receptors with lithium salts would lead to the development of new nanostructured lithium ion-selective LC materials.

To investigate the effects of molecular structure and lithium salt (LiX) addition on the LC phase behavior of the lithium receptors, the receptors were mixed with equimolar LiX with different anions (X= ClO_4^-, $CF_3SO_3^-$ or $((CF_3SO_2)_2N^-)$ to compare their thermal behaviors. The thermal properties of the mesogenic receptors and their mixtures with lithium salts were characterized by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements. It is shown that the single component receptors exhibit only crystal and isotropic phases. However, LC mesophases can be obtained after complexation (1:1 equimolar mixture) with respective LiX depending on the molecular structure of the receptors and the added species of LiX. Liquid-crystalline columnar rectangular (Col_r) phase and columnar hexagonal (Col_h) phases were formed. It is believed that the formation of LC phases requires a delicate balance of interactions and volume between the polar and the non-polar pats in the materials, especially in the polar part. The formation of LC phase is affected by the combination effects of molecular structure, intermolecular interactions and volume balance.

Chapter 3. Selective Lithium Ion Recognition in Self-Assembly of Columnar Liquid Crystals based on Lithium Receptors

In the previous chapter, self-assembled columnar liquid crystals based on lithium receptors were obtained via the coordination interaction between the CE moiety and lithium ion. The aim of this chapter is to evaluate and study about the selective lithium ion recognition in these new nanostructured LC materials. To study about the lithium ion selectivity of the receptors, the author first carried out macroscopic observation by POM experiments in bulk state by mixing equimolar lithium and sodium perchlorate salts with the receptors, respectively. As a result, on contrary to the lithium salt mixtures, sodium perchlorate salt is immiscible with all compounds. Liquid-solid phase separations were observed above isotropization temperature under POM measurements. It is believed that sufficient coordination interactions are essential to generate stable LC phases. Thus, these results imply that the nanostructured lithium-selective ionic channels are formed within the LC assemblies by the selective interactions between Li^+ and the CE moieties.

In order to evaluate the interactions between mesogenic receptors and alkali cations (Li^+ and Na^+), the abilities of the receptors to bind lithium and sodium cations in solution were examined via multiple ^{1}H NMR spectroscopic titrations. The resulting association constants of the titrations represent the binding abilities of the receptors towards Li^+ and Na^+, respectively. As shown by the association constants, the receptors with DB14C4 and 12C4 exhibit binding preference for Li^+ over Na^+, while the receptors with B12C4 shows weak association with both cations and preferentially binds to Na^+ than Li^+. Significantly, the receptor with DB14C4 exhibits much higher binding ability and ion selectivity for Li^+ than those of the other two. The significant preference of the receptor with DB14C4 for Li^+ could be due to its larger DB14C4 cavity provides a more ideal geometry for Li^+ coordination.

Comparison of the ^{1}H NMR titration spectra of the receptor with DB14C4 treated with excess Li^+ and Na^+ implies different nature of the interactions between the receptor and the cations. The analysis of the ^{1}H NMR spectroscopic titration data reveals solution phase structural information about the cationic binding conformations of the receptor with DB14C4. The throughout and rapid downfield shift of the CE protons (reached almost maximum after about 1.0 equiv. of Li^+ addition) indicates the formation of a stable 1:1 complex of Li^+ and the receptor with DB14C4. The DB14C4 macrocycle provides an ideal coordination geometry for Li^+, in which strong coordination interactions between the lithium cation and the four ethereal oxygens occur. A different nature of the interaction between the receptor with DB14C4 and Na^+ was observed for the titrations of the receptor with DB14C4 with Na^+. The proton resonances of the receptor with DB14C4 showed not only downfield shift but also peak splittings and upfield shift for the related methylene protons. No stable 1:1 complexation of Na^+ and the receptor with DB14C4 was formed according to these results. It is known that Na^+ strongly prefers 6-fold coordination. These results imply the four binding sites of DB14C4 are not sufficient to bind larger cations with a higher coordination number. Moreover, the peak splitting demonstrated a bent conformation of the CE ring was induced by the large sodium cation with a diameter of 2.0 Å. Not only deshielding effects from the sodium-oxygen interactions, but also the shielding effects from the structural changes of the bent conformation were observed. These results suggest that the high selectivity of the receptor with DB14C4 for Li^+ results from both the preferred coordination number of four and the favoured geometry of the DB14C4 cavity.

Chapter 4. Liquid-Crystalline Assemblies of Polymerizable Lithium Selective Receptors

In chapter 2 and 3, columnar liquid crystals based on lithium selective receptors have been obtained by the complexation with lithium salts. The selective lithium ion recognition in LC assemblies of these liquid crystals has been demonstrated and evaluated. To obtain nanostructured selective membranes for lithium ion recognition, fixation of the columnar LC structures containing lithium selective ion channels to solid state polymeric films is required. This chapter describes the design and synthesis of lithium-selective LC receptors modified with polymerizable end groups. In chapter 3, it has been demonstrated that wedge-shaped CE receptors consisting of DB14C4 and 12C4 moieties as lithium coordination ligands exhibit good lithium selectivity. For the design of polymerizable LC monomers, polymerizable end groups were incorporated into the alkyl chains of these lithium selective receptors. These modified LC molecules are likely to retain the LC properties of the normal ones. After complexation with lithium salts, it is believed that well-defined lithium selective ion channels in the LC assemblies can be fixed by photopolymerization. The samples were characterized by POM, DSC and XRD measurements. Free-standing polymer films consisting of Col_h nanostructure have been obtained.

Chapter 5. Synthesis of Ion Imprinted Polymers for Selective Lithium Ion Recognition

Ion imprinted polymers are emerging polymeric materials due to their adavatnages of stability, low cost and capability of molecular recognition. Chapter 5 describes the preparation of lithium ion-imprinted polymer materials using methacrylic crown ether as ltihium selective monomer, methyl methacrylate (MMA) as binder, di(ethylene glycol) dimethacrylate (DEGDMA) as crosslinker and azobisisobutyronitrile (AIBN) as radical initiator. The as-prepared polymers were characterized by NMR, XRD and TGA measurements. After removing the imprinted lithiunm ion from the polymeric matrix, the resulting materials are expected to be used as extractants for selective lithium extraction in both liquid-liquid/solid extractions.

Chapter 6. Conclusion and Perspective

This thesis developed new functionalized nanostructured materials for efficient selective lithium ion recognition. Two kinds of nanostructured materials targeting selective lithium ion recognition have been designed and synthesized in this thesis. In chapter 2−4, LC materials

consisting of lithium selective ion channels have been developed based on wedge-shaped crown ether lithium receptors. The preparation of ion-imprinted polymeric extractants having lithium-selective recognizing sites have been described in chapter 5.

In chapter 2−4, nanostructured LC materials formed by the co-assembly of wedge-shaped CE derivatives and lithium salts have been developed. The effects of molecular structure and lithium salt addition on their phase behaviors were investigated. It is shown that the formation of LC phase is affected by the combination effects of molecular structure, intermolecular interactions and volume balance. The lithium selectivity of the compounds was characterized by ^{1}H NMR spectroscopic protocols. Remarkably, the receptor with DB14C4 moiety shows high selectivity towards lithium salts over the corresponding alkali metal salts. It is found that the high selectivity of the receptors with DB14C4 for Li$^+$ is due to the preferred coordination number of four and the ideal cavity geometry of the DB14C4 moiety. The lithium-selective LC receptors modified with polymerizable end groups have also been designed and synthesized. The LC Col$_h$ structure formed by polymerizable lithium selective receptors was fixed photopolymerization. Polymer films consisting of Col$_h$ nanostructure have been obtained. Chapter 5 reports the preparation of lithium ion-imprinted polymer materials which can be used as extractants for selective lithium extraction in both liquid-liquid/solid extractions.

The functionalized nanostructured materials described in this thesis can be applied to the fabrication of various ion-recognizing materials, and opens new pathways for the development of new techniques for efficient lithium-selective extraction.

List of Publications

Original Papers

(1) "Selective Lithium Ion Recognition in Self-Assembly of Columnar Liquid Crystals based on a Lithium Receptor", Y. Luo, N. Marets and T. Kato*, *Chem. Sci.*, 2018, **9**, 608-616.

(2) "Design of Liquid-Crystalline Lithium Receptors and Effects of Molecular Structure and Lithium Salt Addition on Their Phase Behaviors", Y. Luo, N. Marets and T. Kato*, in preparation.

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(1) "Self-Replenishing Dual Structured Superhydrophobic Coatings Prepared by Drop-Casting of an All-In-One Dispersion", A. C. C. Esteves*, Y. Luo, M. W. P. van de Put, C. C. M. Carcouet and G. de With*, *Adv. Funct. Mater.*, 2014, **24**, 986-992.