Bridge of Solution and Solid-state Chemistry through the Dynamic Nature of M6L4 Capsule

論 文 の 内 容 の 要 旨
Abstract

論文題目

Bridge of Solution and Solid-state Chemistry through the Dynamic Nature of M_6L_4 Capsule
（M_6L_4カプセルの動的性質を介した溶液化学と固相化学の架橋）

氏　　名　　寧　國宏

In the past few decades, host-guest chemistry has developed independently in solution or in solid (crystalline) state since the major environment for guest binding, major analysis methods, driving forces of guest encapsulation and dynamic behavior of hosts are completely different in the two states. Recent reports have demonstrated that clever design of common host cavities in two physical states allows us to bridge solution and solid-state chemistry. A pair of Pd_4L_4 molecular square (solution host) and Cd_4L_4 networked squares (crystalline host) was an early example. A more distinct example demonstrated that a pair of discrete and networked M_6L_4 rigid cages performed exactly the same guest binding behavior. However, there are still some problems: 1) only rigid host frameworks are employed therefore the dynamic (flexible) motion of solution hosts is not introduced into solid-state; 2) only common guest encapsulation is achieved and no further common host-guest properties are found in two states.

In this thesis, I have designed and synthesized dynamic solution and crystalline hosts with the same M_6L_4 capsule cavity. Due to the common dynamic capsule cavities, the qualitatively same host-guest chemistry was achieved in solution and in crystals. As a benefit of the bridge of solution and solid-state chemistry, I have demonstrated the applications of solution chemistry in crystals, such as quick screening suitable guest molecules and fast discovery of host-guest properties with solution capsule for crystalline capsules. Finally, as application of crystalline capsules, I have developed an idea of ‘crystalline reagent’ that can be easily and safely used during organic synthesis.

This thesis consists of 6 chapters

Chapter 1 General Introduction

Chapter 2 Construction of Dynamic Capsule Cavity in Solution

Chapter 3 Construction of Dynamic Capsule Cavity in Crystals

Chapter 4 Bridge of Solution and Solid-state Host-Guest Chemistry

Chapter 5 CH_3NCS-installed Crystalline Reagent

Chapter 6 Summary and Perspective

Chapter 1. A overview of literature examples of host-guest chemistries in solution or in the solid (crystalline) state with either rigid or flexible (dynamic) hosts that have only developed parallel and independently. The previous strategy for bridge of solution and the solid-state chemistries with a pair of rigid hosts are introduced. In addition, the overview of the thesis is discussed.

Chapter 2. A discrete Ru_6L_4 molecular capsule was newly designed and synthesized. The X-ray crystallographic analysis confirmed that it adopted capsule topology. The NMR and MS date revealed that the redox reaction of *cis*-$[Ru^{III}Cl_2(cyclen)]Cl$ occurred during the complexation. Through molecular modeling studies, a non-dissociative mechanism, which agreed with the X-ray structure evidences, was proposed and supported that the solution capsule exhibited flexible or dynamic guest encapsulation process via expansion and shrinking its aperture.

Chapter 3. A networked Co_6L_4 capsules was prepared by inspiration from the solution capsule. The X-ray crystallographic analysis confirmed that networked capsules composed of infinite capsule units and solvent accessible pores. Through the X-ray structure analysis and molecular modeling studies, a non-dissociative mechanism was proposed and supported that the networked capsules exhibited flexible or dynamic guest encapsulation and exchange process via expansion and shrinking its aperture, like solution capsule.

Chapter 4. The detailed X-ray crystallographic analysis revealed that discrete Ru_6L_4 capsule (solution host) is isostructural with repeated subunit in the networked Co_6L_4 capsules (crystalline host) and similar host-guest interaction was observed including CH-π interactions, van der Waals interactions and hydrophobic effects. With a complementary pair of solution and solid capsules, the bridge of solution and solid-state chemistries has achieved: (1) 'Cream skimming' (combination of advantages) of solution and solid-state host-guest chemistry. For

instance, I can quick screen suitable guests for crystalline capsule by NMR spectroscopy with solution capsule and precisely determine the structure of host-guest complex for solution capsules by X-ray crystallographic analysis with crystalline capsules. (2) Control of reactivity of encapsulated guest molecules (e.g. cyclopentadiene and *tetr*-butyl acrylate) has observed either in solution or in the solid-state; (3) Because of the similar dynamic behavior of solution and solid capsule, the delivery of encapsulated guests can be controlled either in solution or in the solid-state. These results revealed that common host-guest properties were also achieved in solution and in crystals with a pair of dynamic capsule hosts.

Chapter 5. Given the unique host-guest properties of capsule, I expected the networked capsules can be promising materials to deal with troublesome reagents. In Chapter 5, the networked capsules can act as crystalline host to accommodate CH_3NCS, a highly volatile reagent, in a single-crystal-to-single-crystal fashion. The X-ray crystallographic analysis revealed that four CH_3NCS guests were tightly packed within the cavity of capsule therefore installed CH_3NCS guests cannot be released from capsule even washed crystals with solvent or heated up 200 ºC. However, the introduction of aromatic amine into the crystals triggered the delivery of the CH_3NCS guests. The CH_3NCS-installed capsule network is much milder reagent than the neat CH_3NCS and the enhancement of substrate selectivity is observed in the crystalline state thiocarbamoylation.

In conclusion, this thesis have constructed common dynamic (flexible) capsule cavity in solution and in crystals. The common guest (THF) encapsulation demonstrates qualitatively same host-guest chemistry is achieved in solution and in crystals through the common dynamic M_6L_4 capsule cavity. In addition, 'cream skimming' of solution and solid-state host-guest chemistry have achieved (i.e. fruitful solution chemistries can be transferred into solid-state and these chemistries can be directly visualized by X-ray analysis) and common host-guest chemistries have been found in solution and in crystals. Finally, I have developed a 'crystalline reagent' that can be very promising for easy and safe handling troublesome reagent.