学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of ionophore hydrogen-bonded organic frameworks composed of crown ether derivatives
（クラウンエーテル誘導体で構成されるイオノフォア水素結合性有機フレームワークの開発）

Crown ethers have been one of the most important ionophores in host-guest and supramolecular chemistry because of their highly-selective recognition ability toward specific cationic and molecular species caused by preorganized oxygen atoms in the macrocycle. A number of molecular systems incorporated by crown ethers with various size have been developed, and their functionality have been intensively investigated in solution, liquid crystal, and solid states. Furthermore, if crown ethers are incorporated in crystalline porous frameworks, the resultant materials are expected to show a new functionality because of cooperativity of the precisely and periodically aligned ionophores and good accessibility of external guest molecules or analytes through the spaces of the material. However, such materials with crystalline framework have not been explored probably because of high flexibility and existence of various low-symmetric conformations of the crown ether moieties. Therefore, construction of crystalline frameworks based on crown ether building blocks remains challenging, despite attractive materials.

In this study, the author decided to construct hydrogen-bonded organic frameworks (HOFs) from crown ether building blocks. HOFs are crystalline porous molecular frameworks formed by connecting molecules through intermolecular interactions, particularly hydrogen bonds. HOFs are usually obtained as a single crystal, which is an ideal system for exploring sequential relationships between molecular conformation, H-bonded network structure and topology, and the whole structure. To construct ionophore HOFs, the author planned to incorporate crown ether and dicarboxy-*o*-terphenyl because carboxy groups and *o*-terphenyl can provide predictable hydrogen bounds with

directionality and shape persistent scaffold of the frameworks, respectively.

In **Chapter 2**, the author reported the synthetic routes of the surveyed sython, as 1CT-18C6, 2CT-18C6, 2CT-24C8, and 3CT-18C6, in detail. Besides characterizations exhibited the good purity of each compound, which show important effect through this study.

In **Chapter 3**, the author constructed various organic frameworks, **1CT-18C6-I** ($P2_1/n$), **2CT-18C6-I** (P-1), **2CT-18C6-II** (P-1) and **2CT-18C6-III** ($Cmc2_1$), based on mono- and di-benzo18-crown-6-ether derivatives, 1CT-18C6 and 2CT-18C6, respectively. In the crystals, carboxy groups form no self-complementary dimer which is often observe in hydrogen bonded frameworks composed of highly-symmetric rigid π-conjugated molecules. This result clearly indicates that flexibility and lower symmetry of the building block molecules crucially effect on a way of formation of a hydrogen bonded network in **2CT-18C6-I**, **-II**, and **-III**. However, the carboxy groups of **2CT-18C6-III** form hydrogen bonds with only water molecules to give the crystal contains no solvent but water molecules which form one-dimensional (1D) zig-zag alignment along the *c* axis. It is noteworthy that, the activation energy (*E*a) was evaluated by Arrhenius plots to be 0.14 eV, indicating that the proton jumps from H_3O^+ to the neighboring H_2O in the hydrogen-bonded network of **2CT-18C6-III**.

In **Chapter 4**, the author successfully constructed the C_3-symmetric HOF **3CT-18C6-I** as designed, which was self-assembled by an 18-crown-6-ether (18C6) derivative with three dicarboxy-*o*-terphenyl moieties. Based on the previous analysis of pristine 18C6, it is obviously that the crown macrocycle has completely different conformation in HOF **3CT-18C6-I**. The molecule **3CT-18C6** has C_3-symmetry and the macrocyclic part includes an eclipsed conformation with small dihedral angle of the non-aromatic O–C–C–O moiety, on the other hand, activation of **3CT-18C6-I** causes low-symmetrization of the framework. The resultant framework **3CT-18C6-Ia** contains crystallographically independent two molecules of **3CT-18C6**, although each of them remains to be C_3-symmetric. The eclipsed conformation observed in the non-aromatic O–C–C–O moiety of **3CT-18C6-I** has been changed into the gauche conformation, which is energetically more stable. Interestingly, the HOF has 1D channels with a shish kebab like shape and the bottle neck part of the channel is consist of eclipse-stacked 18C6 macrocycles, which can provide fundamental insight of the proton conducting pass through the narrow 18C6 channel.

In summary, the author has developed a serious of organic frameworks and hydrogen-bonded organic frameworks which provide a new strategy of development of ionophore HOFs for multifunctionality.