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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

Geometric and electrostatic effects of tectons on formation of
hydrogen-bonded organic frameworks

(水素結合性有機フレームワークの形成におけるテクトンの幾何学的および静電的な影響)

The carboxylic acid dimer has been used intensively to construct porous frameworks named hydrogen-bonded organic frameworks (HOFs). Compared with other H-bonding groups, the carboxylic acid dimer allows the researchers to design the networked structure more easily.

In some cases, two dimensional (2D) networks are capable of being constructed by design because of highly directional, and therefore, predictable H-bonding. However, the entire structure of HOFs is not easy to construct by design due to the ambiguous interactions between the low-dimensional motifs. Till now, it is still difficult to predict crystal structures of HOFs composed of flexible molecules with versatile conformations. It must be admitted that the structural hierarchy, namely, formation of two dimensional (2D) porous sheets and stacking of the sheets along the perpendicular direction to give layered HOFs, could be a simple and facile design principle to construct porous 2D HOFs using various functional π -conjugated molecules. Unfortunately, the designed 2D HOFs may show unexpected structural transformation even collapse after solvent removal during activation. For overcoming the above mentioned problems, it is useful to apply a secondary building interaction different from that working for formation of a primary 2D network.

Meanwhile, HOFs possessing interactive free sites in the pore have attracted much attention due to their potential to exhibit the site-originated specific functionalities. Although many novel HOF materials with unprecedented structures and fascinating topologies have been reported, it is rare that some H-bond donors/acceptors remain free in the frameworks. In other words, it remains to be explored how to systematically obtain HOFs with free H-bonding groups and active sites, which is a prerequisite for functionalization of HOFs.

In this thesis, the author attempted to construct tetracarboxylic acid derivatives based 2D HOFs. Two of them are HOFs based on the tectons containing the benzo[c][1,2,5]thiadiazole (BT) moiety with diisophthalic acid or dicarboxy-*m*-terphenyl (DmT) moiety. The orthogonally working two different intermolecular interactions, that are the directional H-bond between carboxy groups and slip-stacking of groups with unidirectional alignment, were applied into construction of the systems, aiming to construct two stable isostructural HOFs with rigid networks, permanent porosity, and photoconductivity. The third HOF contains less symmetric tecton possessing a less symmetric core and even arms as a phenanthroline derivative, which forms a geometrically mismatched framework with carboxy groups free from framework construction.

This thesis comprised 5 chapters. **Chapter 1** introduces the research background and development of this research field, in which the problems to be solved in this thesis are described in preceding part of this text.

In **chapter 2**, the author described a HOF, **BTIA-1**, whose building block molecule based on a BT moiety has less flexible conformation. A crystal structure of the resultant fibrous precipitates are too thin for being characterized by single crystal X-ray diffraction analysis, while are estimated by crystal structure prediction (CSP), in which carboxy groups formed complementary H-bonded dimer to give a 2D network and the BT moieties are unidirectionally slip-stacked through dipole-dipole interactions, resulting porous layered frameworks. It is noteworthy that its activated form **BTIA-1a** via a solvent exchange process showed BET surface area of $720 \text{ m}^2 \text{ g}^{-1}$ larger than that via an only heating process.

In **chapter 3**, the author successfully constructed a new HOF based on benzo[c][1,2,5]thiadiazole- (BT-) based tetracarboxylic acid **BTTA**. **BTTA-1(TCB)** crystallized into non-centrosymmetric space group *Cm*. Carboxy groups in **BTTA** form intermolecular self-complementary H-bonded dimers between the peripheral carboxy groups to give a 2D networked sheet structure possessing rhombic pores. The sheets are slip-stacked along the *c* axis to give a porous framework possessing 1D channels that have smooth surface. Interestingly, the BT moieties are unidirectionally slip-stacked. Intermolecular distance between the BT moiety is $3.45 \text{ \AA}$ and the stacked BT moiety is slipped by $1.36 \text{ \AA}$ along the direction parallel to the dipole moment. The HOF shows thermal stability up to $275 \text{ }^\circ\text{C}$, permanent porosity with moderate BET surface area of $1145 \text{ m}^2 \text{ g}^{-1}$ compared with reported HOFs composed the related tetrapotic molecules, and photoconductivity. These results suggest that the present BT-based HOFs can be a promising platform for multifunctional porous material.

In **chapter 4**, the author demonstrated that the concept of geometrical mismatch could be an effective strategy to form a H-bonded framework with the free carboxy groups directly. **CP-Phen**, a phenanthroline-based tetrapotic carboxylic acid derivative, crystallized in space group *P*-1. As expected, three of four carboxy groups in **CP-Phen** form self-complementary H-bonded dimer to form a ladder-shaped framework. One carboxy group, on the other hand, does not participate in framework formation due to geometrical mismatch, while makes a weak H-bond with a molecule of *N,N*-dimethylacetamide (DMA). The ladder-motifs are aligned in parallel manner and slip-stacked to give a layered structure. Although **CP-Phen-1** undergoes two-step structural transformation, accompanied with hydrogen-bond rearrangements, upon loss of solvent molecules, the activated framework shows good thermal stability up to $360 \text{ }^\circ\text{C}$ and selective CO_2 adsorption. These results imply that our proposed strategy is indeed effective to provide free interactive sites in porous frameworks.

Finally, the conclusions and perspectives are summarized in **chapter 5**.