学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Construction of hydrogen-bonded organic frameworks based on nitrogen-containing π-conjugated molecular systems
（窒素含有π共役分子系に基づく水素結合性有機フレームワークの構築）

Nitrogen-containing polycyclic aromatic hydrocarbons (N-PAHs) have attracted much attention as they have valuable characteristics including good electron acceptors, increased stability, luminescent properties, and attractive interactions with cationic species such as proton and metal ions. Introduction of N atoms into the π-conjugated systems is capable of fine-tuning of frontier orbital levels and improving molecular packing in crystalline states through C–H···N interactions to achieve effective charge-transport properties. However, effects of nitrogen atoms in N-PAHs on their molecular arrangements in hydrogen-bonded organic frameworks (HOFs) with permanent porosity have not fully been developed. HOFs, one of families of porous materials, are generally constructed by self-assembly of organic molecules through directional H-bonds, and have shown the advantages of high crystallinity, solution processability, easy healing and purification, due to the reversible and flexible nature of H-bonding connections. Therefore, the author has been interested in constructing N-PAHs-based HOFs (Nπ-HOFs) with permanent porosity.

In this thesis, the author planned to construct external stimuli-responsive Nπ-HOFs with multiple active sites based on new building block molecules possessing highly-symmetric N-PAH cores and peripheral carboxyphenyl groups. One of them is a HOF with hexagonally-networked structure composed of a C_3-symmetric benzotriquinoxaline derivative. Another is a HOF with rhombic networked structure composed of a C_2-symmetic pyrazinopyrazine derivative.

The thesis includes four chapters. Chapter 1 introduces general background of this study, and conclusions are summarized in chapter 4.

In chapter 2, a Nπ-HOF with hexagonally-networked structure composed of a C_3-symmetric N-PAH is presented. The author successfully synthesized a new isomer of

hexaazatrinaphthylene (**CPBTQ**), constructed a Nπ-HOF based on the compound, activated, and evaluated stability and permanent porosity. Furthermore, the author thoroughly investigated positional effects of annelated pyrazine-rings on the structure and stability of the HOF to establish design principle of Nπ-HOFs. Comparison between two kinds of Nπ-HOF composed of isomers (**CPBTQ** and **CPHATN**) possessing three pyrazine rings annelated at the different positions indicates that the positional difference of the pyrazine rings strongly effects on conformation of the peripheral phenylene groups, which then lead to different structure and stability of the Nπ-HOFs. The activated Nπ-HOF **CPBTQ-1a** is revealed to exhibit the Brunauer-Emmett-Teller (BET) surface area of 471 $m^2 g^{-1}$ and show HCl responsiveness thanks to the basic pyrazine rings annelated to the triphenylene core. The author believes that the present results can contribute not only for construction of multifunctional porous materials but also for chemistry on hetero-aromatic compounds.

In chapter 3, a Nπ-HOF with rhombic networked structure composed of a C_2-symmetic N-PAH is presented. The author constructed a novel Nπ-HOF based on pyradinopyradine (PP) which is one of the most simple and essential structural motifs of highly N-content π-conjugated molecule and described synthesis of a PP-based building block molecule with four carboxyphenyl groups (**CP-PP**), spectroscopic and electronic properties of **CP-PP** and its ester precursor, structures of **CP-PP** based HOFs, and thermal behaviors of the HOFs. Interestingly, the initial framework with H-bonded rhombic 2D network rapidly undergoes a guest release-induced three-step structural transformation into other frameworks, including a semi-opening framework with small void, through rearrangement of H-bonds. These results provide insight to design new functional Nπ-HOFs and contribute to solid-state chemistry on porous molecular crystalline material.