Structural characterization of acid-responsive hydrogen-bonded organic frameworks with permanent porosity

Hydrogen-bonded organic frameworks (HOFs) are porous molecular crystalline materials constructed through intermolecular hydrogen-bonding interactions [1]. Compared with other porous organic frameworks such as covalent organic frameworks (COFs), HOFs tend to give highly crystalline materials with a large single domain, enabling us to elucidate the structure-property relationship by single-crystalline X-ray diffraction analysis. Moreover, HOFs can show the ability to restore the original structures of frameworks by, for example, reannealing with solvents. These features originate from the reversible nature of hydrogen bond formation and destruction. However, this characteristic simultaneously results in the fragility of the frameworks and the difficulty in obtaining frameworks as designed; no rule-of-thumb for the design of rigid HOFs with permanent porosity had been established until recently.

To overcome the above-mentioned problems, we have hypothesized that building-block molecules possessing both a highly symmetric large π-conjugated planar moiety and highly directional H-bonding groups can provide predictable HOF structures with permanent porosity and rigidity. Indeed, we have demonstrated that a series of C_3-symmetric cyclic π-conjugated molecules possessing six carboxyphenyl groups in the periphery form predictable H-bonded hexagonal network (H-HexNet) structures that stack without interpenetration to give porous layered HOFs [2]. To provide further functionality to porous HOFs, we applied hexacarboxylic acid with a heteropolycyclic aromatic hydrocarbon moiety, namely, hexakis(carboxyphenyl) hexaazatrinaphthylene (CPHATN). Consequently, we demonstrated that CPHATN forms a rigid HOF exhibiting stimuli responsiveness toward strong acid species because of the nitrogen atoms incorporated in a large π-conjugated system (Fig. 1) [3,4].

The crystal structure of solvated HOF CPHATN-1(TCB), where TCB denotes 1,2,4-trichlorobenzene used as a recrystallization solvent, was characterized by single-crystalline X-ray diffraction analysis to have a layered structure of H-HexNet sheets (Fig. 2(a)). To activate the inner spaces of the frameworks, solvent molecules inside CPHATN-1(TCB) were removed by heating under a vacuum condition to give single crystals of the activated HOF CPHATN-1a, whose structure was analyzed at SPring-8 **BL38B1**.

CPHATN-1a has a very similar molecular packing to CPHATN-1(TCB), except for the conformation at one of the H-bonded carboxyphenyl dimers shown in the red square in Figs. 2(a,b). The conformational distortion causes a small shrinkage of the crystallographic cell by 200.7 Å^3 (Fig. 2(c)). The results of a N_2 sorption experiment at 77 K were used to calculate the BET surface area and pore size of the framework to be 379 m^{2}g^{-1} and 0.78 nm, respectively. Precise structural changes upon the sorption of hydrocarbons were analyzed at SPring-8 **BL02B2**. In PXRD patterns of CPHATN-1a recorded upon introducing benzene vapor (Fig. 2(d)), the 010 and 011 diffraction peaks shifted to the small-angle region upon vapor absorption, while the 001 peak remain at its original position during the sorption. Furthermore, when the benzene-filled CPHATN-1a was heated, the 010 and 011 peaks shifted to the large-angle region, indicating the shrinkage of the cell due to the release of benzene molecules (Fig. 2(e)). The observed structural changes to crystal structures of CPHATN-1(TCB) and CPHATN-1a indicate that the framework slightly changes its structure and volume of spaces upon the sorption of guest molecules.

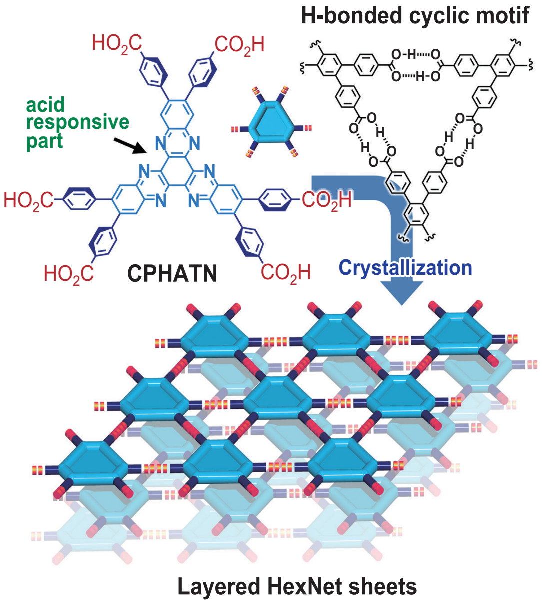
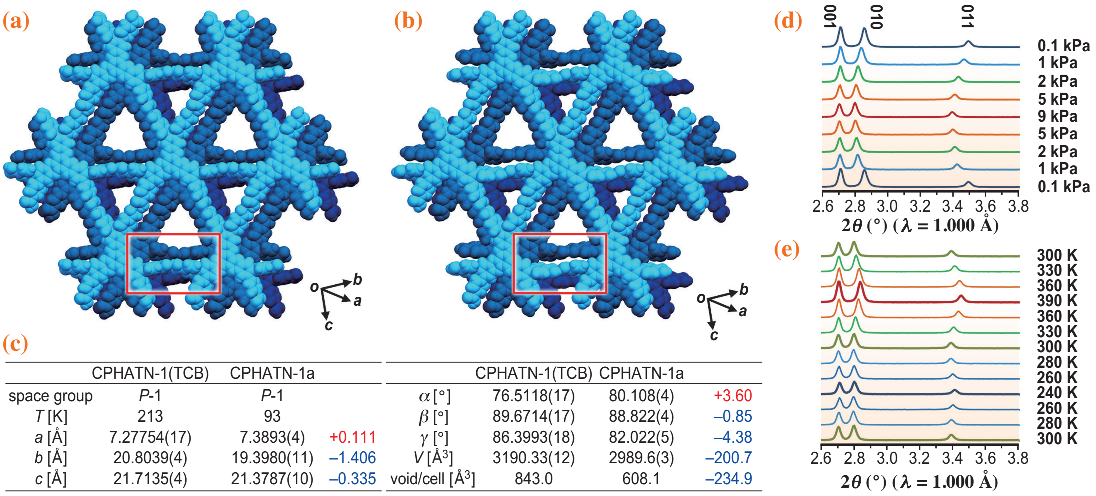


Fig. 1. Schematic representation for construction of porous HOF possessing layered HexNet structures of CPHATN. The HexNet structure is formed via a H-bonded cyclic motif.



	CPHATN-1(TCB)	CPHATN-1a			CPHATN-1(TCB)	CPHATN-1a	
space group	*P*-1	*P*-1		α [°]	76.5118(17)	80.108(4)	+3.60
T [K]	213	93		β [°]	89.6714(17)	88.822(4)	–0.85
a [Å]	7.27754(17)	7.3893(4)	+0.111	γ [°]	86.3993(18)	82.022(5)	–4.38
b [Å]	20.8039(4)	19.3980(11)	–1.406	*V* [Å^3]	3190.33(12)	2989.6(3)	–200.7
c [Å]	21.7135(4)	21.3787(10)	–0.335	void/cell [Å^3]	843.0	608.1	–234.9

Fig. 2. Selected crystal structures of the **(a)** solvated HOF CPHATN-1(TCB) and **(b)** activated HOF CPHATN-1a. **(c)** Differences in cell parameters between CPHATN-1(TCB) and CPHATN-1a. **(d)** PXRD pattern changes of CPHATN-1a upon exposure to benzene vapor. **(e)** PXRD pattern changes of benzene-filled CPHATN-1a with temperature.

It is noteworthy that CPHATN-1a shows color changes upon exposure to HCl. Yellow crystalline bulk CPHATN-1a turned reddish-brown upon exposure to HCl atmosphere, and the original color was recovered by removing HCl from the framework (Fig. 3(a)). Similarly, the green fluorescence was quenched by HCl exposure and then recovered by HCl removal (Fig. 3(b)). These observations are consistent with spectroscopic results. When exposed to HCl, a new band at 500–600 nm appeared in the absorption spectrum (Fig. 3(c)) and the emission spectrum was strongly quenched (Fig. 3(d)). These results clearly indicate the sensitivity of this HOF to acid vapors, which is explained in terms of strong interactions of the protons of acid with the core of the fundamental unit.

In conclusion, we demonstrated, for the first time, that CPHATN can be a suitable building block for constructing acid-responsive porous crystalline materials. The crystal structure of CPHATN-1a and its dynamic behavior upon the sorption of guest molecules were precisely characterized by synchrotron X-ray radiation.

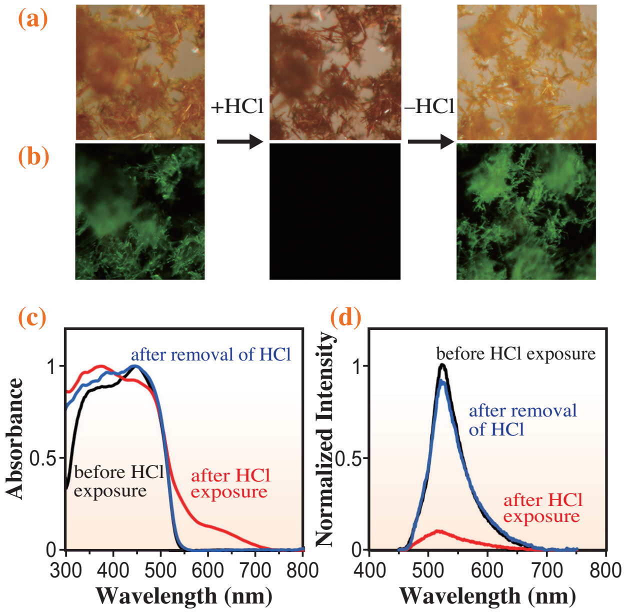


Fig. 3. HCl responsiveness of crystalline bulk of CPHATN-1a. Color changes of crystals upon exposure to HCl vapor under **(a)** ambient light and **(b)** UV light of 365 nm. **(c)** Absorption and **(d)** emission spectra of solid CPHATN-1a upon exposure to HCl atmosphere and after removal of HCl.

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