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Author(s)	Hisaki, Ichiro; Xin, Chen; Takahashi, Kiyonori et al.
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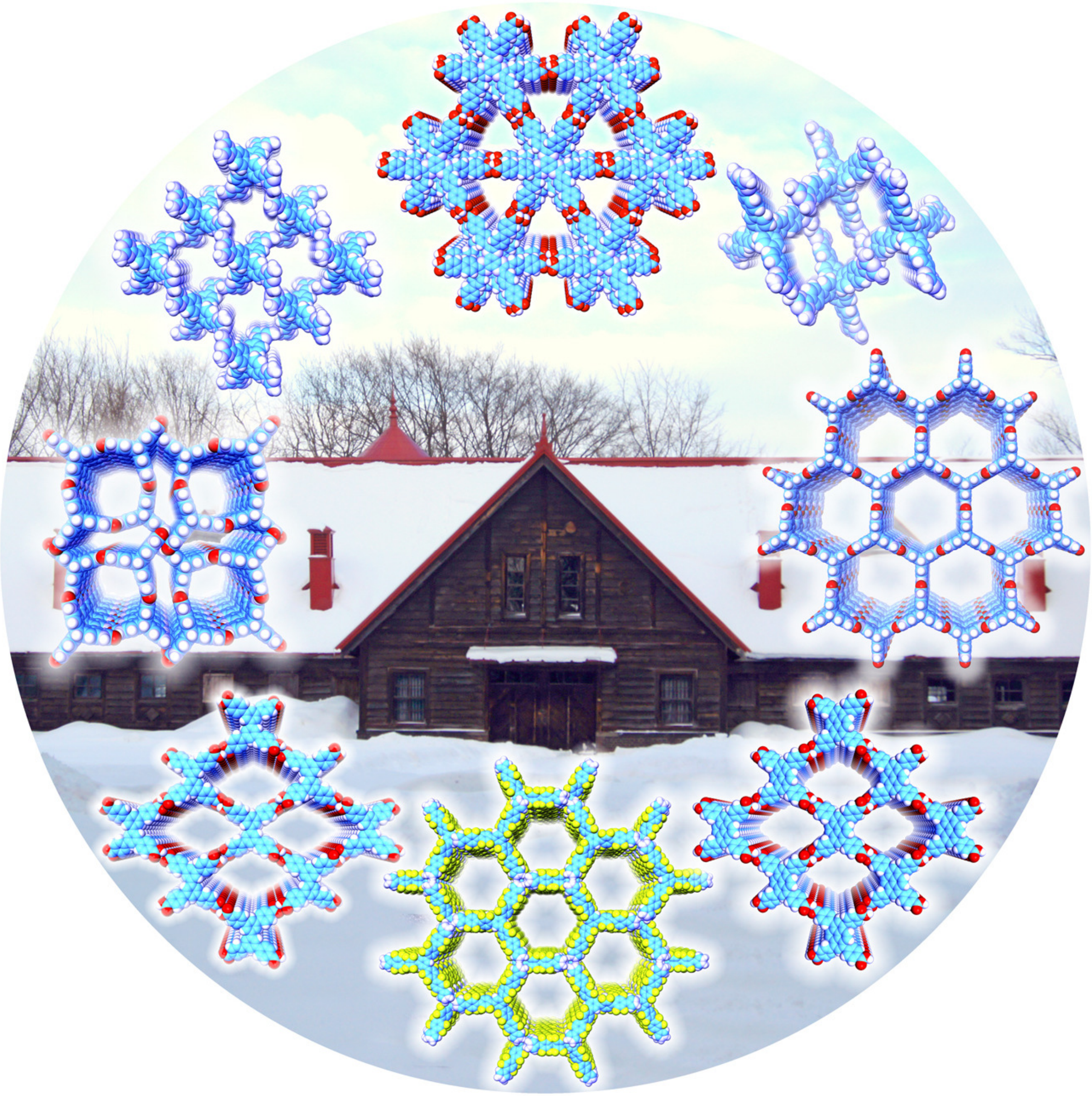
Designing Hydrogen-Bonded Organic Frameworks (HOFs) with Permanent Porosity

Ichiro Hisaki,[a],[b]* *Chen Xin,*[b] *Kiyonori Takahashi,*[a],[b] *and Takayoshi Nakamura,*[a],[b]



Abstract: Designing organic components that can be used to construct porous materials enables tailored functionalized materials. Research into porous materials has seen a resurgence in the past decade due to finding of self-standing porous molecular crystals (PMCs). Particularly, number of crystalline systems with permanent porosity that undergo self-assembly through hydrogen bonding (H-bonding) have been developed. Such systems are called hydrogen-bonded organic frameworks (HOFs). This report systematically describes H-bonding patterns (supramolecular synthons) and molecular structures (tectons) that have been used to achieve thermal and chemical durability, a large surface area, and functions such as selective gas sorption and separation, which can provide design principles for constructing HOFs with permanent porosity.

1. Introduction

During the past two decades, porous materials constructed of organic components have attracted much attention. Assembling versatile organic components into a porous framework enables functionalization such as selective gas storage/separation, catalysis, chemical sensing, and optoelectronics.[1] Porous lattice frameworks constructed from metal cations and organic ligands were initially reported by Yaghi's and Kitagawa's groups and called MOFs[2] and porous coordination polymers (PCPs),[3] respectively. In 2005, covalent organic frameworks (COFs) also were proposed.[4] The MOFs and COFs have been investigated for varied applications because of their rigid frameworks and high designability from structural and electronic aspects. There was also drawn in the field of porous molecular crystals (PMCs), which are constructed from organic molecules through reversible intermolecular interactions. Pioneering work on tris-*o*-phenylenedioxycyclotriphosphazene (TPP) crystals was reported by Comotti and Sozzani.[5]

Historically, inclusion crystals[6] and molecular zeolites[7] with void spaces capable of accommodating guest molecules (Figure 1) have been explored. However, many of these materials collapse upon removal of the guest molecules, and therefore, can be distinguished from PMCs, which have self-supporting porous structures (*i.e.*, permanent porosity). The PMCs, which involve H-bonding to form a framework with permanent porosity, were termed hydrogen-bonded organic frameworks (HOFs) by Chen.[8] Although several names and acronyms to describe PMCs constructed through H-bonding can be found in the literature, the term HOF is applied in this report whether or not this acronym was used in the articles cited.

General features of HOFs are as follows:

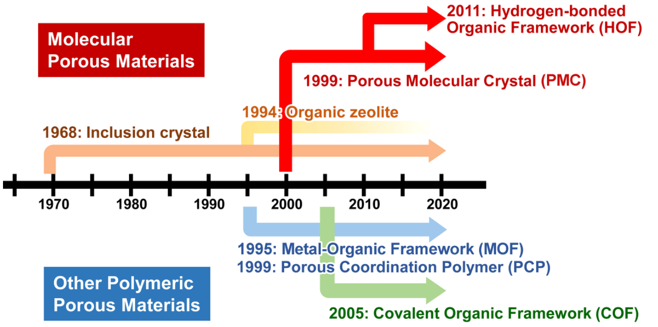


Figure 1. Representative names of porous molecular materials and related materials.

- A highly crystalline structure achieved *via* a simple solution process due to the reversible nature of H-bonding. For example, recrystallization from solution provides single crystals that can be used in single-crystal X-ray diffraction (SXRD) to provide unambiguous structural information.
- No need for a metal component, permitting construction of lightweight and environmentally friendly porous structures.
- Ability to restore crystallinity by reannealing with solvents or HCl.[9]
- Weak hydrogen bonds that can cause the collapse of the framework during solvent molecule removal from voids for activation.
- A lack of a universal design strategy compared to MOFs[10] and COFs.[11] Even when building block molecules were selected thoughtfully, the desired porous HOFs have not always been produced; instead nonporous materials result.
- A possibility that polar solvent molecules will trap the H-bonding moieties, preventing formation of networked frameworks.

Significant progress in the field has resulted in the production of HOFs with permanent porosity, thermal and chemical durability, and functionality. This review focuses on HOFs constructed with cleverly designed molecular components.

2. Supramolecular synthons and tectons for designing HOFs with permanent porosity

The term supramolecular synthon, proposed by Desiraju, is defined as "structural units within supermolecules, which can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions."[12] Thus, supramolecular synthons are a spatial arrangement of intermolecular interactions. The term "tecton" was proposed by Wuest for any molecule whose interactions are dominated by particular associative forces that induce the self-assembly of an

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[a] Dr. I. Hisaki, Dr. K. Takahashi, Prof. Dr. T. Nakamura,
Research Institute for Electronic Science (RIES), Hokkaido University, N20W10, Sapporo 001-0020, Japan
E-mail: hisaki@es.hokudai.ac.jp
[b] Dr. I. Hisaki, Chen Xin, Dr. K. Takahashi, Prof. Dr. T. Nakamura,
Graduate School of Environmental Science, Hokkaido University, N10W5, Spapporo 060-0810, Japan

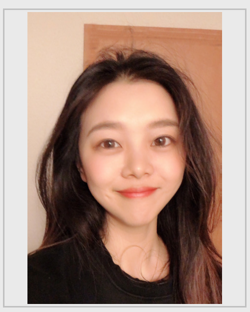
organized network with specific architectural or functional features.[13] For construction of predesigned molecular architectures, the appropriate selection of both a supramolecular synthon (directionality and multiplicity of H-bonding) and tecton (geometry, size, rigidity, planarity, symmetry, and functionality) is important. Construction of HOFs with permanent porosity requires a combination of noncovalent intermolecular interactions, such as π/π interactions, with H-bonds, because H-bonding alone is too weak to maintain low-density porous materials compared with dative and covalent bonds.[14] The next section describes supramolecular synthons and tectons reported to be useful for designing HOFs with permanent porosity.

2.1 Carboxylic acid

A carboxy group is the simplest functional group for making molecular assemblies. The carboxy dimer has been used to construct exotic molecular assemblies in natural products and in organic chemistry.[15] Because of its facile synthesis and high directionality of H-bond formation, the carboxy dimer is a suitable supramolecular synthon for design of tectons and HOFs (Figure 2).

Several breakthroughs have occurred during the history of the construction of HOFs with carboxy dimers. Marsh and Duchamp reported construction of a prototype honeycomb framework with trimesic acid in 1969.[16] The waved honeycomb sheets were interpenetrated to yield a nonporous crystal. In 1987, Herbestein and co-workers produced layered honeycomb structures with 1D inclusion channels by crystallization in the presence of long-chain template molecules.[17] This templating approach remains an important method for building porous HOFs. Expanded tectons can yield an HOF with larger pores. Tecton **1**, however, gave only nonporous DMF-solvate crystals[18] until Rowsell, Zentner, and co-workers obtained porous HOFs composed of honeycomb sheets in 2015.[19] Obtaining these HOFs required slow evaporation from alcohol solution. Even when highly polar solvents such as DMF were necessary for crystallization, network structures have been formed by slow evaporation of a mixed solvent with an apolar template solvent at high temperatures.[20] Many recently reported tectons contain carboxyphenyl groups instead of carboxy groups, probably due to three reasons: (1) Introduction of carboxyphenyl groups into π-conjugated cores improves solubility of the tecton into solvents relative to those directly bonded by carboxy groups; (2) the phenylene group acts as a spacer to generate voids; (3) metal-catalyzed cross-coupling reaction between aryl groups is commoditized, allowing facile synthesis of various tectons.

Ichiro Hisaki obtained a PhD from Osaka University under the supervision of Prof. Y. Tobe in 2005. After being a JSPS postdoctoral researcher at Kyoto University in the group of Prof. A. Osuka, he joined Osaka University in 2005 as an assistant professor in the group of Prof. M. Miyata. In 2018, he moved to Hokkaido University as an associate professor. His current research interests include developing functional crystalline materials constructed through hydrogen bonding.



Chen Xin is a PhD student in the group of Prof. Nakamura. Her current research centers on arrangement control of functional organic molecules and development of novel hydrogen-bonded organic frameworks with multifunctionality.

Kiyonori Takahashi received a PhD from Tohoku University under the supervision of Prof. T. Akutagawa in 2016. From 2016 to 2017, he was a postdoctoral fellow at the National Institute of Advanced Industrial Science and Technology, Osaka University, and Hokkaido University. He is currently an assistant professor at Hokkaido University. His current research interests include developing functional molecular materials with a molecular degree of freedom.

Takayoshi Nakamura obtained a PhD from the University of Tokyo in 1989. After working at the National Institute for Materials and Chemical Research as a senior researcher, he moved to Hokkaido University as an associate professor in 1994. He has been a full professor since 1997. His current research interests include developing novel electronic and magnetic functions of crystalline materials based on supramolecular structures.

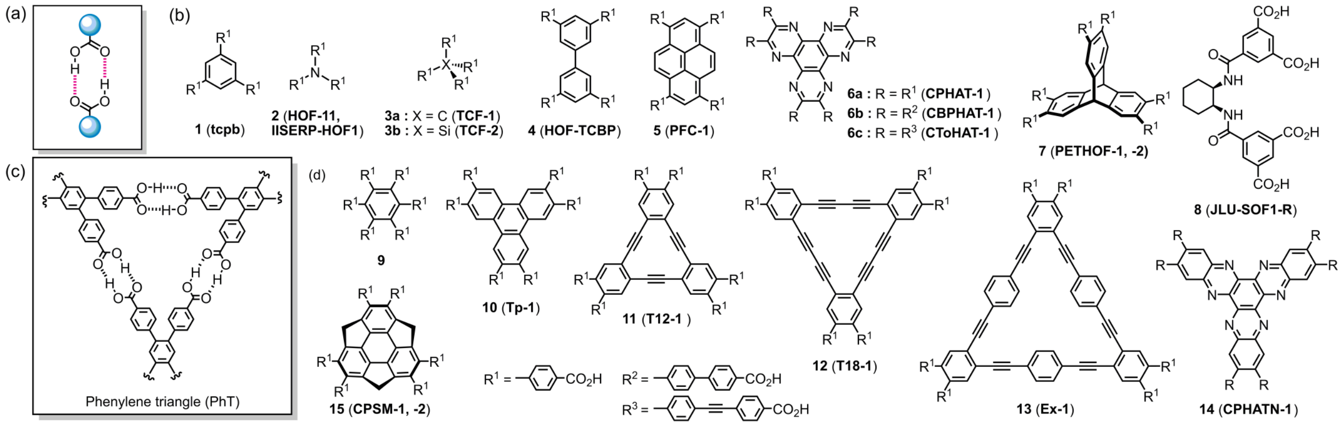


Figure 2. (a) H-bonding ways of carboxy groups. (b,d) Tectons with carboxy groups to form HOFs. (c) Cyclic H-bonded motif named phenylene triangle (PhT), which formed by C_3-symmetric tectons (d) with *o*-bis(4-carboxyphenyl)aryl moieties to give low density hexagonal sheets. Literature names for the HOFs are shown in parentheses.

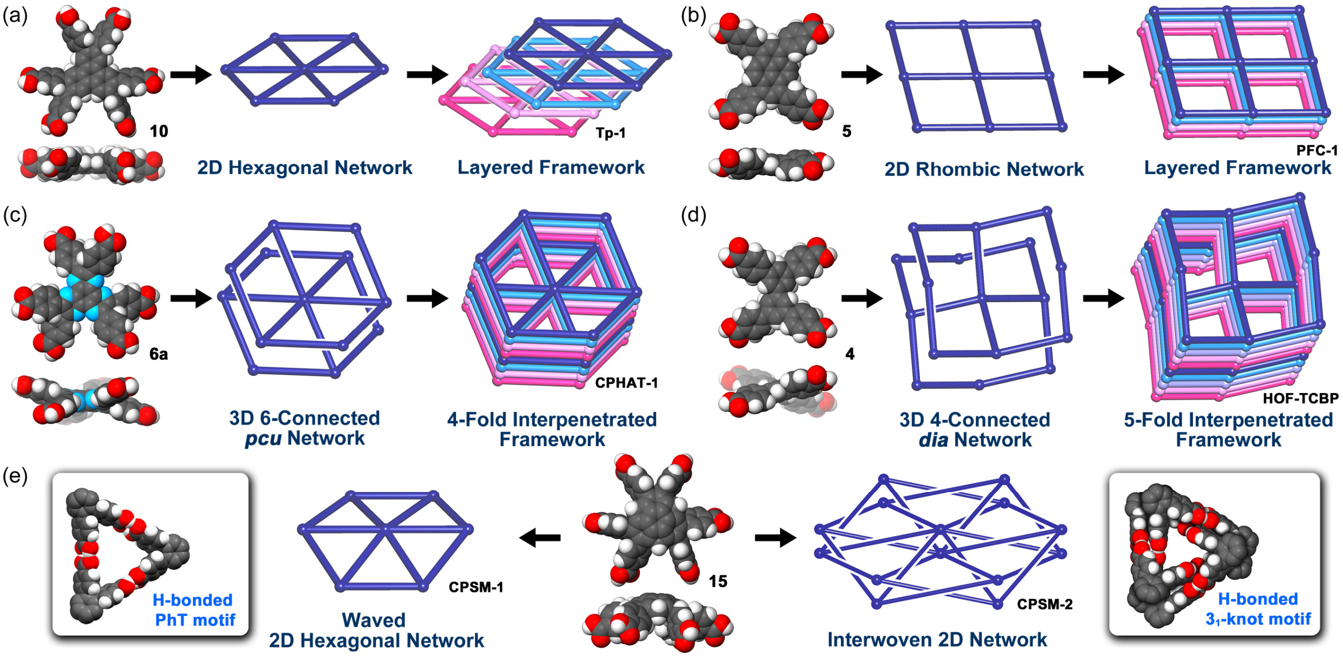


Figure 3. Representative examples of the relation between molecular conformation and network topology of HOFs. Planar (a) C_3- and (b) C_2-symmetric tectons gave layered frameworks (**Tp-1** and **PFC-1**, respectively). Twisted (c) C_3- and (d) C_2-symmetric tectons gave interpenetrated frameworks (**CPHAT-1** and **HOF-TCBP**, respectively). (e) C_3-symmetric bowl-shaped tecton yielded both waved 2D-hexagonal and 2D-interwoven networks (**CPSM-1** and **CPSM-2**, respectively) *via* H-bonded PhT or 3_1-knot motif.

Compound **1** forms porous polymorphic HOFs with 8-fold interpenetration. The activated mixture of the polymorphs (**tcpb**) possessed an Brunauer–Emmett–Teller surface area [$SA_{(BET)}$] of 1095 m^2g^{-1} and was thermally stable up to 180 °C.[19a] Furthermore, immersion of the collapsed **tcpb** into ethanol could regenerate the original framework. Tecton **2** yields an HOF with an interpenetrated (10,3)-b network (referred to as **HOF-11**[21] or **IISERP-HOF1**[22]). The activated form showed an $SA_{(BET)}$ value of 687–1025 m^2g^{-1} and were stable up to 290–300 °C. Tectons **3a**,**b** gave flexible HOFs **TCF-1** and **-2**, which involved dynamic behavior of gases such as CO_2 and Xe.[23] Tectons **4** and **5** form stable HOFs (**HOF-TCBP**[24] and **PFC-1**,[9] respectively), which possessed a large surface area with $SA_{(BET)}$ values of 2066 and 2122 m^2g^{-1}, respectively. Cao and co-workers demonstrated that photoactive **PFC-1** could encapsulate Doxorubicin, allowing synergetic chemo-photodynamic therapy.[9] Hisaki, Douhal and co-workers proposed that shape-fitted docking of twisted hexaazatriphenylene (HAT) derivatives **6a**,**b**,**c** provided robust HOFs with permanent porosity, and constructed a series of HAT-based HOFs **CPHAT-1**,[25] **CBPHAT-1**,[26] and **CTolHAT-1**[27]. Activated **CPHAT-1a** had an $SA_{(BET)}$ value of 649 m^2g^{-1} and was thermally stable up to 339 °C. The **CPHAT-1a** retained single crystallinity, enabling dynamic observation and crystallographic analysis of the inclusion behavior of iodine.[25] Similarly, activated **CBPHAT-1a** had an $SA_{(BET)}$ value of 1288 m^2g^{-1} and was stable up to 305 °C.[26] Triptycene derivative **7** remarkably yielded two types of interpenetration isomeric **PHTHOF-1** and **-2**, with different numbers of interpenetrated ***acs***-networks. Their $SA_{(BET)}$ values were 1140 m^2g^{-1} and 1690 m^2g^{-1}, respectively.[28] The **JLU-SOF-1-R** composed of the homochiral tecton **8** had an $SA_{(BET)}$ value of 460 m^2g^{-1} and selective sorption toward CO_2.[29]

Tectons **9**–**14**[30-32] formed porous layered frameworks, where an H-bonded cyclic motif, referred to as a phenylene triangle (PhT) (Figure 2c), acted as a highly ordered supramolecular synthon to yield hexagonally networked porous frameworks. Hisaki and co-workers reported that activated HOFs **Tp-apo** and **T12-apo** were stable up to 323 °C and 360 °C, respectively, and possessed permanent porosity with $SA_{(BET)}$ values of 788 m^2g^{-1} and 557 m^2g^{-1}, respectively. The **T12-apo** reversibly transformed its frameworks among four forms upon sorption of CO_2.[33] The **CPHATN-1** with thermal stability up to at least 360 °C was constructed with the relatively large π-conjugated molecule **14**. The HOF showed acid-responsive color changes due to nitrogen atoms in the conjugated π-system.[32] Bucky-Bowl **15** formed both single- and double-layered HOFs (**CPSM-1** and **-2**, respectively).[34] Although permanent porosity was not realized in these systems, the latter underwent anisotropic shrinking of 11% along the *c*-axis under high pressure (970 MPa).

The HOFs connected through simple carboxy dimers are convenient systems for exploring sequential relations among molecular conformation, H-bonded network structures and topology, and integration of the network to form whole structures of HOFs. Typical examples are shown in Figure 3. Planar rigid tectons with triphenylene and pyrene cores **10** and **5**, in which the peripheral carboxy groups lay along the same molecular plane, form 2D hexagonal and rhombic networked sheets, respectively. The 2D sheets subsequently stacked without interpenetration to form the corresponding layered HOFs (**Tp-1**[31a,b] and **PFC-1**[9]). In contrast, nonplanar tectons with HAT and biphenyl cores (**6a** and **4**) have peripheral carboxy groups out of the molecular plane (**6a** has a twisted conformation in solid state due to packing force). The nonplanar tectons form 3D networks with ***pcu*** and ***dia*** topologies, respectively, and the networks are interpenetrated to yield porous frameworks **CPAHT-1** and **HOF-TCBP**. Because of interpenetration, the frameworks composed of non-planar conformational tectons tend to be more rigid and thermally stable than nonpenetrated layered frameworks. Nonplanar bowl-shaped tecton **15** gave both a wavy 2D hexagonal sheet and a more complex interdigitated 2D sheet *via* PhT and 3_1-knot H-bonded motifs, respectively (Figure 3e).

2.2 Urea

A double H-bonded strand of urea is one of the oldest supramolecular synthons for H-bonded networked crystalline architectures. Since the discovery of a urea inclusion compound by Bengen in 1940s and publication of the structure by Smith,[35] urea and thiourea have been used as tectons of HOFs with channels. In addition, the dynamic behaviors of guest molecules accommodated in the channels have been investigated.[36] Shimizu and coworkers demonstrated stereoselective reaction in 1D channels constructed with cyclic derivatives incorporating a urea moiety.[37] Incorporation of urea moieties into a triptycene skeleton resulted in a sophisticated tecton that could be used to construct HOFs *via* 1D doublet H-bonding (Figure 4a). In 2012, Mastalerz and Oppel reported that tecton **16** formed the highly porous HOF **TTBI** with a density of 0.755 gcm^{-3}. Activated **TTBI** had a large $SA_{(BET)}$ value of 2796 m^2g^{-1}.[38] Cooper, Day, and co-workers recently introduced "energy-structure-function maps" built by combining computational crystal structure predictions and property predictions.[39] The maps describe the possible structures and properties available to a candidate molecule. Based on this methodology, multiple low-density structures, including **TTBI** (**T2-α** form), could be predicted, and three new forms (**T2-*β***, **T2-*γ***, and **T2-*δ***) were experimentally characterized (Figure 4b). Particularly, activated **T2-*γ***, whose solvate was crystallized by slow diffusion of acetone into a saturated dimethylacetamide solution of **31** and desolvated using a solvent exchange method, has an extremely low density of 0.412 gcm^{-3}, good thermal stability up to 227 °C, and a surface area with an $SA_{(BET)}$ value of 3425 m^2g^{-1}. Interestingly, structural transformations of **T2-*γ*** into **T2-α** and **T2-α** into **T2-*β*** occurred under certain conditions. Gas sorption properties of the forms also were predicted and experimentally confirmed.

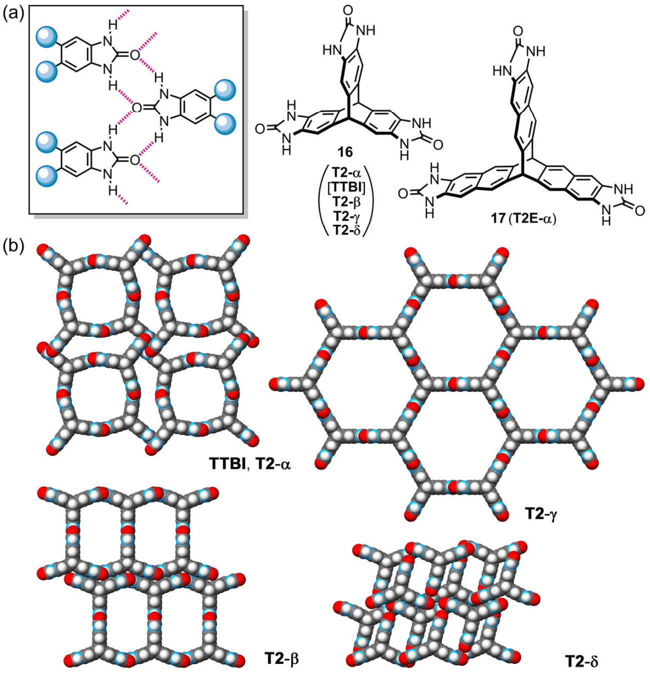


Figure 4. (a) Supramolecular synthon of cyclic urea and tectons possessing triptycene skeleton. (b) Experimentally observed polymorphic HOFs of **16**.

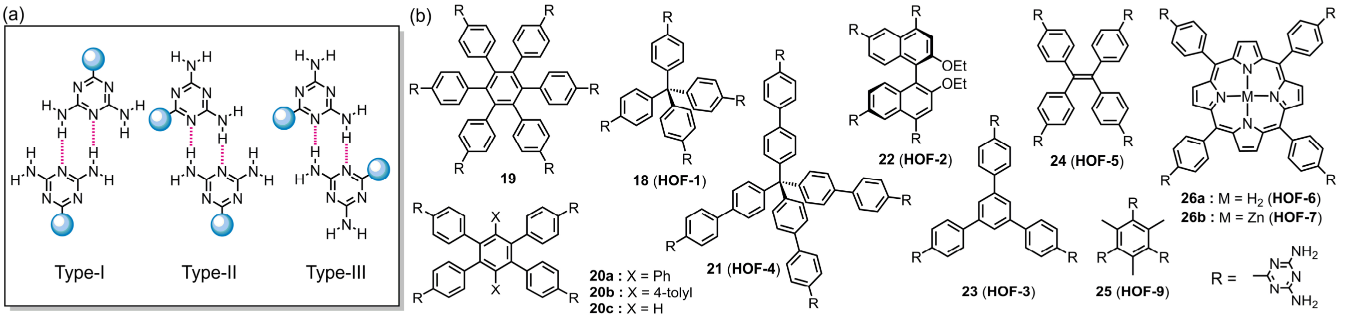


Figure 5. (a) Supramolecular synthons of DAT moieties. (b) Tectons with DTA moieties to form HOFs. Literature names for the HOFs are shown in parentheses.

2.3 Diaminotriazine (DAT)

Diaminotriazine (DAT) can form an H-bonded dimer in three ways (types-I, -II, and -III), shown in Figure 5a. The dimers have two other free amino groups, which subsequently form additional H-bonds, enabling tectons to network into 2D or 3D frameworks.[40] The first porous DTA-based HOF was constructed from **18** by Wuest and co-workers in 1997.[41] They also reported the construction of networked frameworks of a series of tetra- and hexaphenylbenzene derivatives **19** and **20a-c** using a crystal engineering approach.[42] Chen et al. demonstrated that Wuest's HOF, **HOF-1**, possessed permanent porosity, had an $SA_{(BET)}$ value of 359 m^2g^{-1}, and was thermally stable up to 420 °C.[43] They also revealed that **HOF-1** could selectively separate C_2H_2/C_2H_4 under ambient conditions. Upon applying various tectons with DAT groups, they constructed a series of HOFs (**HOF-2**,[44] **-3**,[45] **-4**,[46] **-5**,[47] **-6**,[48] **-7**,[49] **-9**[50]), with different crystal structures, H-bonded network topologies, pore shapes and sizes, and functionalities. For example, **HOF-2** with a unimodal 6-connected $\{3^3 5^5 6^6 7\}$ network topology constituted with a BINOL derivative underwent enantioselective absorption of secondary alcohols, such as 1-phenylethanol, up to 92%, as well as C_2H_2/CO_2 selective separation.[44] The **HOF-3** with 3-connected ***srs*** topology showed selective separation of C_2H_2 over CO_2 at ambient temperature and pressure.[45] The volume of flexible **HOF-5** with bimodal (4,6)-connected network shrunk by 21% upon desolvation to give porous **HOF-5a** with an $SA_{(BET)}$ value of 1101 m^2g^{-1}, which indicates significant absorption of C_2H_2 and CO_2 (102 cm^3g^{-1} and 90 cm^3g^{-1}, respectively) under ambient conditions (296 K, 1 atm).[47]

Versatile frameworks can be provided by DTA-based tectons, even when similar tectons are applied. The most representative examples are tectons **18** and **21**, both of which have similar molecular geometry but assemble into different frameworks. The **HOF-1** has a network with ***bcu***$\{4^{24}6^4\}$ topology, while **HOF-4** has a 6-fold interpenetrated framework with ***PtS*** $\{4^2 8^4\}$ topology, resulting in formation of completely different pores in the HOFs (Figure 6).

2.4 Heterocycles

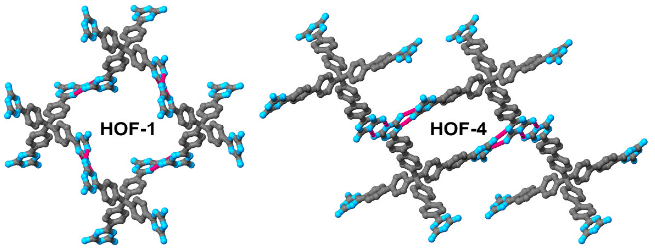


Figure 6. Structural motifs of **HOF-1** and **HOF-4** composed of tectons **18** and **21**, respectively. H-bonds are represented by pink lines. Hydrogen atoms are omitted for clarity. Color: gray (C), cyan (N).

Supramolecular synthons formed by heterocycles, such as pyridine, pyrazole, and imidazole rings, combined with a rigid skeleton possessing appropriate molecular geometries, also can provide HOFs with permanent porosity.

Miljanić and co-workers reported a series of honeycomb HOFs with $SA_{(BET)}$ values ranging from 903 m^2g^{-1} to 1821 m^2g^{-1} built from tripyrazole derivatives **27**–**29**.[51] These highly porous structures were prepared through a sophisticated combination of triangular cyclic H-bonding of three pyrazole moieties and strong π/π stacking between the electron-poor tetrafluorobenzene and relatively electron-rich pyrazole moieties. Pores covered by fluorine atoms are suitable for absorption of fluorocarbons. Tecton **30** produced a framework with 1D pores capable of accommodating C_{60}.[52] H-Bonding between pyridiyl groups and H atoms in amino or amide groups also was applied as supramolecular synthons to construct HOFs with permanent porosity. Tectons **31**[53] and **32**[54] form honeycomb type porous layers. Although permanent porosity of the former was not described, the latter (**HOF-8**) was reported to be thermally stable up to 240 °C and underwent selective sorption of CO_2 and benzene at ambient temperature and pressure.[54] Champness, Schröder, and co-workers demonstrated that tecton **33** formed a porous 3D networked HOF (**SOF-1**) with an $SA_{(BET)}$ value of 474 m^2g^{-1} and thermal stability up to 420 °C.[55] Very weak intermolecular interactions such as those between pyridyl nitrogen and aromatic protons [$N_{(pyridyl)}\cdots H–C$] governed the structural flexibility and porosity of HOFs. Aida et al. reported an example of HOFs built from **34**.[56] However, realizing these types of HOFs after designing them is difficult.

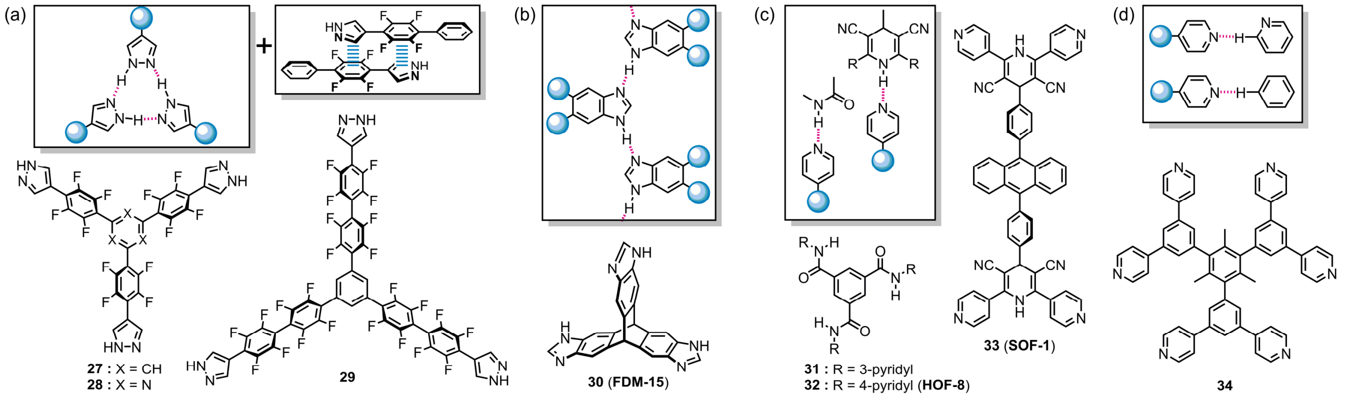


Figure 7. Supramolecular synthons and tectons with heterocycles. (a) C_3-symmetric tripyrazole derivatives that formed H-bonded trimers and π/π stacking with charge-transfer character. (b) Imidazole-substituted triptycene that formed 1D infinite H-bonds. (c) C_3-symmetric or rod-shaped tectons with pyridyl groups, which formed H-bonds with amino protons. (d) Radial-shaped tecton with terminal pyridyl groups, which formed weak H-bonds with aromatic protons.

2.5 Multi-component H-bond systems

When HOFs are constructed by combining multiple tectons, their structural versatility should increase significantly. Systematic construction of these types of HOFs was accomplished by combining pyridine and carboxylic acid derivatives.[57] Schröder and co-workers constructed HOFs with permanent porosity by combining X-shaped tetrapyridyl tectons (**35** and **36**) and tetracarboxy tectons **37**–**39** (**SOFs 7**–**10**).[58] However, in general, designing these structures is very difficult compared with mono-component systems. Combining strong acidic and basic components can be used to construct HOFs due to their robust supramolecular synthons with charge-assisted H-bonds. Wards and co-workers demonstrated that sulfonate anions and guanidium cations form two-dimensional H-bonded sheets (Figure 8b),[59] which can provide functional HOFs.[60] Similarly, Tohnai *et al*. demonstrated that a combination of sulfonate anions and ammonium cations was useful for systematic construction of HOFs.[61] Particularly, applying bulky ammonium ions, such as triphenylmethyl ammonium, formed persistent H-bonded clusters, which further assembled to form diamond-shaped porous organic salts (*d*-**POS**s) with permanent porosity.[62] A combination of amidinium with sulfonate[63] or with carboxylate also has been used.[64]

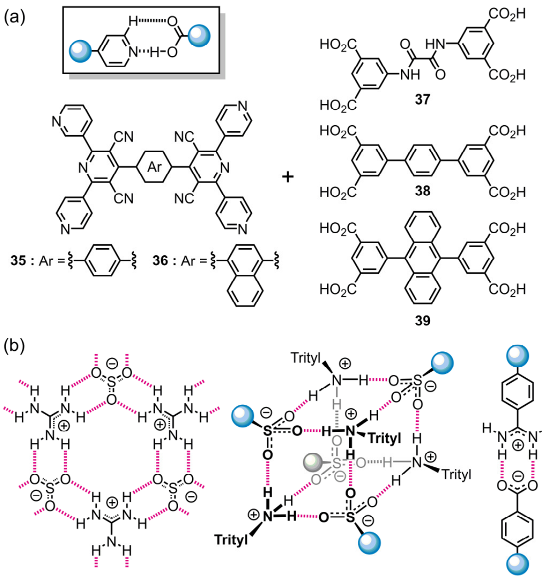


Figure 8. (a) Supramolecular synthons between acidic and basic tectons. (b) Some examples for charge assisted H-bonding patterns for construction of HOFs.

3. Isostructural frameworks

Systematic construction of isostructural porous materials can be achieved using organic units that have the same molecular geometry and bonding units but are of different sizes or lengths and can assemble into similar structures. Such isostructural frameworks have been established for MOFs and COFs, because dative and covalent bonds are strong enough to retain 3D lattice frameworks.[65] For HOFs, however, combining H-bonding with other intermolecular interactions, such as π/π stacking, is required to retain a 3D framework because of the weakness of H-bonding alone, which makes construction of isostructural porous frameworks difficult *via* preorganization (*e.g.*, **HOF-1** and **HOF-4**). Isostructural or quasi-isostructural HOFs constructed by applying highly directional supramolecular synthons have been reported recently. The simplest systems involved trimesic acid and its extended analog **1**, both of which form porous honeycomb sheets, although the assembly of the sheets was difficult to control.[17,19] Similarly, planar C_6- or C_3-symmetric π-conjugated molecules **9**–**14** were capable of forming stacked isostructural H-HexNet sheets; however, the manner of stacking depended on the interlayer interactions (*e.g.*, π/π stacking between π-conjugated cores).[20,30-32] Interestingly, tripyrazole derivatives **27**–**29** formed similar honeycomb frameworks with apertures diameters of 16.5 Å, 15.8 Å, and 26.4 Å, respectively, although **HOF-TPZ 29** possessed relatively

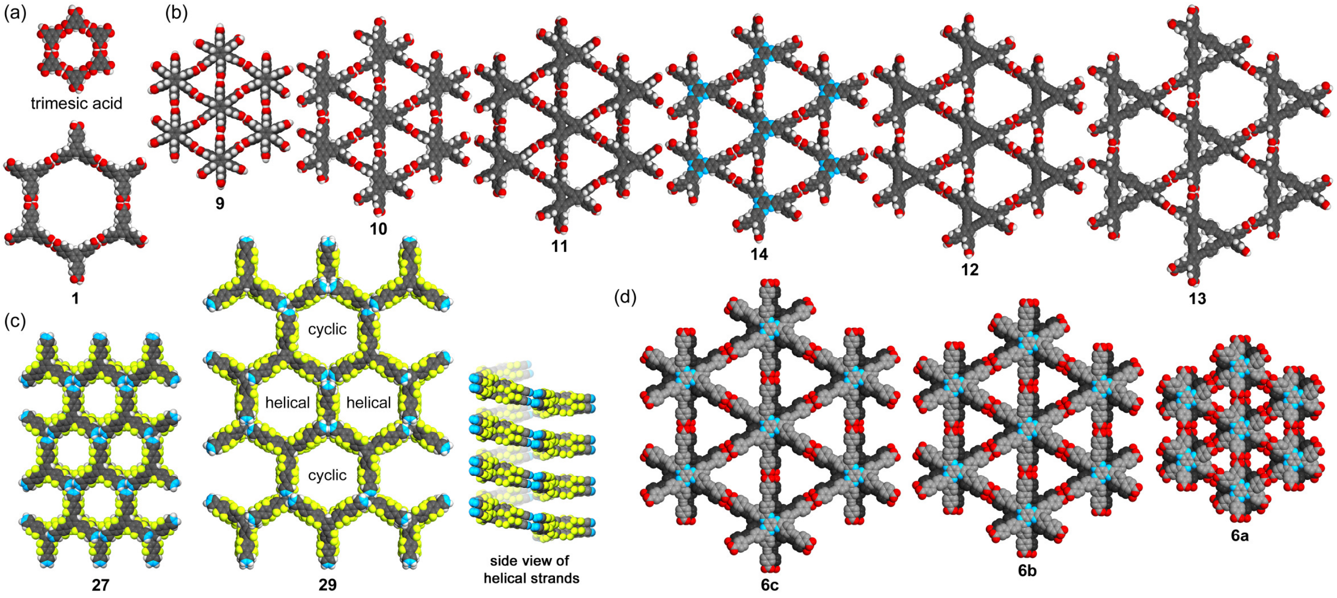


Figure 9. Selected (quasi)isostructural motifs of HOFs built from radial tectons with different arm lengths. (a) Honeycomb structures of trimesic acid and **1**. (b) A series of hexagonal sheets composed of planar C_6- or C_3-symmetric π-conjugated molecules with six carboxyphenyl groups **9**, **10**, **11**, **12**, **13**, and **14**. (c) Honeycomb frameworks composed of **27** and **29**. Compound **27** forms honeycomb sheets, which stack to yield the framework, while **29** forms complex networks involving layered and helical stacked motifs. (d) A series of hexagonal frameworks composed of armed HAT derivatives **6a**, **6b**, and **6c**, where hydrogen atoms are omitted for clarity. Color: gray and black (C), red (O), cyan (N), yellow (F), white (H).

complex H-bonded networks, including helical and planar cyclic networks.[51] In these systems, strong π/π interactions in addition to H-bonds clearly played important roles in the formation of quasi-isostructural HOFs. The HAT derivatives **6a**–**6c** yielded nearly isostructural 4-, 6-, and 8-fold interpenetrated 3D networks with different triangular aperture diameters due to the shape-fitted docking of the HAT cores.[25-27] Triptycene derivatives **16** and **17** produced isostructural HOFs,[39] and compound **17** was expected to possess an extremely large surface area with an $SA_{(BET)}$ value of 3599 $m^2g^{-1.}$

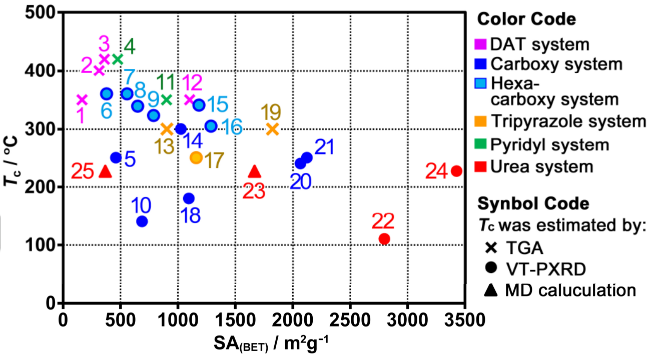


Figure 10. *Tc*-$SA_{(BET)}$ plots for selected HOFs with permanent porosity. 1: **HOF-3a** Ref [45], 2: **HOF-4a** Ref [46], 3: **HOF-1a** Ref [43], 4: **SOF-1a** Ref [55], 5: **JLU-SOF1-R** Ref [29], 6: **CPHATN-1a** Ref [32], 7: **T12-apo** Ref [31b], 8: **CPHAT-1a** Ref [25], 9: **Tp-apo** Ref [31b], 10: **HOF-11a** Ref [21], 11: **SOF-7a** Ref [58], 12: **HOF-5a** Ref [47], 13: **TPZ-28** Ref [51], 14: **IISERP-HOF1** Ref [22], 15: **PETHOF-1a** Ref[28], 16: **CBPHAT-1a** Ref [26], 17: **TPZ-27** Ref [51], 18: **tcpb** Ref [19], 19:**TPZ-29** Ref [51], 20: **HOF-TCBP** Ref [24], 21: **PFC-1** Ref [9], 22: **TTBI (T2-α)** Ref [38], 23: **T2-β** Ref [39], 24: **T2-γ** Ref [39], 25: **T2-δ** Ref [39]. For $SA_{(BET)}$ determination, N_2 sorption isotherm at 77 K was applied for 5, 6, 12, 13, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, and 25, and that at 125 K for 4, and CO_2 sorption isotherm at 195 K or 196 K was applied for 1, 2, 3, 7, 8, 9, 10, and 14, and that at 273 K for 11.

4. Permanent porosity

Enhancement of the thermal stability and enlargement of the surface area are the two main aims for constructing HOFs with permanent porosity, although other fators, such as aperture size and pore surface properties, also should be considered. Figure 10 shows the *T*c-$SA_{(BET)}$ plot of reported HOFs with permanent porosity, where T_c indicates thermal decomposition critical temperature. Interestingly many HOFs have high thermal durability at temperatures above 200 °C. In the relation between Tc and $SA_{(BET)}$, *Tc* gradually decreases with $SA_{(BET)}$. The HOFs composed of DAT derivatives have relatively small $SA_{(BET)}$ values, which allow high selectivity toward certain gas species such as CO_2 and C_2H_2. The HOFs involving pyridine derivatives also show tendencies similar to those of DAT derivatives. The HOFs composed of carboxylic acid derivatives are widely dispersed due to the tectons, shown in the plot in Figure 10. The **HOF-TCBP** and **PFC-1** showed particularly good stability and porosity with $SA_{(BET)}$ values greater than 2000 m^2g^{-1}. The C_3-symmetric π-conjugated tectons with six carboxyphenyl arms showed moderate porosity and excellent thermal stability (T_c > 300 °C). The tripyrazole systems also showed wide porosity and good thermal stability. Triptycene derivatives with urea moieties possessed extremely large surface areas, with the high thermal stability of **T2-β** (T_c greater than 200 °C) being particularly good for such low-density frameworks. Permanent porosity also allows dynamic molecular motions which allow fast molecular rotors.[61]

Summary and Outlook

This minireview introduced hydrogen-bonded organic frameworks (HOFs), which are crystalline molecular frameworks with permanent porosity assembled through H-bonding. The construction of HOFs using H-bonding and molecular structures (supramolecular synthons and tectons) also was reviewed.

For construction of pre-designed HOFs, suitable selection of supramolecular synthons and tectons is crucial. Namely, (1) H-bonding moieties that allow highly directional H-bonds with predictable manners, (2) rigid tectons exclusive degree of conformational rotation freedom, (3) secondary interacting moieties capable of well-fitted intermolecular contacts to support the H-bonded networked structures. Particularly, rational design of tectons with considering the secondary interactions is required for successful HOF formation. Another way to obtain HOFs are use of multi-bondable groups such as DAT. These groups were established empirically and indeed acted as a "magic molecular glue." The obtained structures may be unpredictable but are exactly porous. This is not predesigned but a certain way to obtain HOFs. This situation is related the early stage of MOFs; although designing secondary building units was difficult to predict, a MOF itself was successfully obtained. In addition to experimentation, computational approaches proposed by Cooper and Day can be helpful.

Once the construction methodology for HOFs was established, the properties and functionality of HOFs begin to be investigated. The authors believe that the most important merit of a HOF is its high crystalllinity. HOFs are usually obtained as single crystals by simple recrystallization. Moreover, it has become reported frequently the HOFs which retain (single) crystallinity after activation. HOFs allow precise discussion on their structures and structure-property relationship. Interactions between the surface of pore of HOFs and guest molecules such as CO_2 can be precisely estimated based on experimental results. At this moment, HOFs are suitable systems for fundamental chemistry, and are complemental systems of COFs that can provide industry-oriented polymeric materials. However, In the near future, further developments are expected on the functionality of HOFs that reflect their unique features such as high crystallinity, solution processability, and ability to be reconstituted.

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Keywords: Porous materials • Hydrogen bonds • Permanent porosity • Crystal engineering • Gas sorption

Conflict of interest

The authors declare no conflicts of interest.

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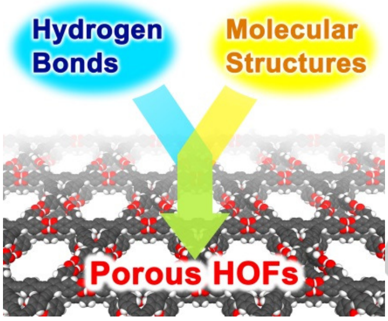
Entry for the Table of Contents

MINIREVIEW

Hydrogen-bonded organic frameworks are described systematically based on hydrogen-bonding patterns (supramolecular synthons) and molecular structures (tectons).



I. Hisaki, X. Chen, K. Takahashi, T. Nakamura*

Page No. – Page No.

Designing Hydrogen-Bonded Organic Frameworks (HOFs) with Permanent Porosity