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Communication

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A Microporous Hydrogen-Bonded Organic Framework: Exceptional Stability and Highly Selective Adsorption of Gas and Liquid

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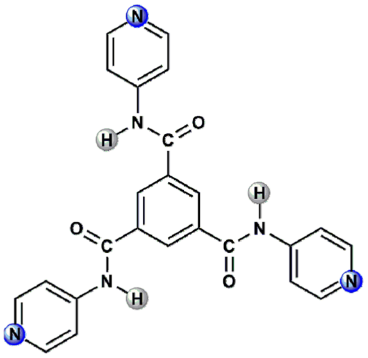
Supporting Information

ABSTRACT: An extremely stable hydrogen-bonded organic framework, **HOF-8**, was fabricated. **HOF-8** is not only thermally stable but also stable in water and common organic solvents. More interestingly, desolvated **HOF-8** exhibits high CO_2 adsorption as well as highly selective CO_2 and C_6H_6 adsorption at ambient temperature.

Recently, the syntheses and property investigations of porous materials have become one of the hottest research fields in materials science.[1] Among these porous materials, porous organic crystalline materials (POCMs), which possess lower densities than other porous materials such as zeolites and metal—organic frameworks (MOFs), have attracted more research interest in recent years.[2] Ordered POCMs usually include crystalline covalent organic frameworks (COFs) and hydrogen-bonded organic frameworks (HOFs). The former are connected by covalent bonds between atoms and show relatively high stabilities, while the latter are linked by weak non-covalent interactions such as hydrogen bonds and $\pi-\pi$ stacking interactions and exhibit relatively low stabilities. For HOFs, the solvent guests play important roles in the construction of the supermolecular network system. Once the solvent guests are removed, the supermolecular system is usually broken, and the HOFs collapse. Therefore, it is unsurprising that although thousands of HOFs have been reported in the literature during the last two decades, examples of HOFs with permanent porosity are very rare.[3] In fact, to the best of our knowledge, only three HOFs (TTBI, HOF-1, and SOF-1, reported by the groups of Mastalerz,[2a] Chen,[4a] and Schröder,[4b] respectively) show unusually high thermal stability after the removal of the guest molecules and exhibit good gas sorption properties. A common feature of these stable HOFs is that the host molecules can form strong hydrogen bonds and $\pi-\pi$ stacking interactions with each other. In this case, removal of the solvent guests has a limited influence on the stability of the supermolecular network assembled from the host molecules. Inspired by these excellent works, we synthesized the organic building block N^1,N^3,N^5-tris(pyridin-4-yl)benzene-1,3,5-tricarboxamide (TPBTC) (Scheme 1), which contains pyridine N atoms and amide H atoms as hydrogen-bond acceptors and donors, respectively, for use in HOF fabrication. Here we report **HOF-8**, an exceptionally stable HOF constructed from TPBTC that is not only thermally stable but also stable in water and common organic solvents.

Scheme 1. Molecular Structure of TPBTC



More interestingly, desolvated **HOF-8** (**HOF-8d**) exhibits highly selective CO_2 and C_6H_6 adsorption at ambient temperature. Such exceptional stability coupled with highly selective adsorption of gas and liquid has not been reported for other HOFs to date.

TPBTC was synthesized by a typical condensation amidation reaction process [Scheme S1 in the Supporting Information (SI)]. The IR, ^{13}C NMR and ^{1}H NMR spectra of TPBTC revealed the formation of a pure organic building block (Figures S1, S2, and S3a in the SI). Light-brown block single crystals of **HOF-8** were obtained by recrystallization of the TPBTC from 3:1 (v/v) chloroform/methanol (Figure S4). **HOF-8** is insoluble in water and common organic solvents such as benzene and hexane.

Single-crystal X-ray diffraction (scXRD) analysis showed that **HOF-8** crystallizes in the *C*2/*c* space group (Table S1 in the SI). As shown in Figure 1a, each TPBTC molecule connects with three other TPBTC molecules through three pairs of highly symmetric hydrogen bonds (N1···N6, N3···N2, and N5···N4), generating a two-dimensional (2D) supermolecular layer along the plane perpendicular to the *ac* plane (Figure 1b). This layer is further stacked together with adjacent two layers through $\pi\cdots\pi$ stacking interactions along the *c* axis, forming a three-dimensional (3D) microporous supermolecular structure (Figure 1c) with a pore size of 6.8 Å × 4.5 Å. The pores are filled with disordered guest molecules. A solvent-accessible volume of ~24.0% was estimated using PLATON.[5] Because of the great disorder of the guest molecules, it was difficult to

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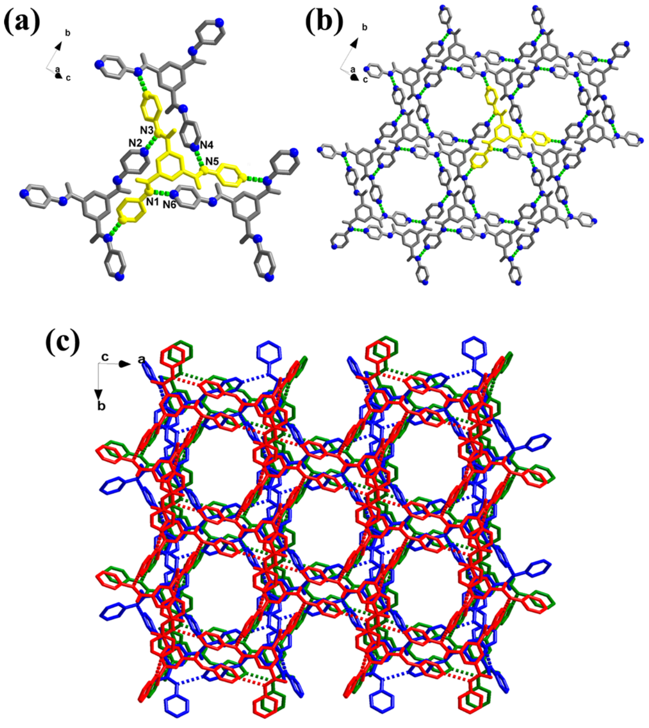

Figure 1. (a) Hydrogen-bonding interactions observed in **HOF-8**. (b) 2D supermolecular layer structure of **HOF-8**. (c) 3D supermolecular microporous structure of **HOF-8**.

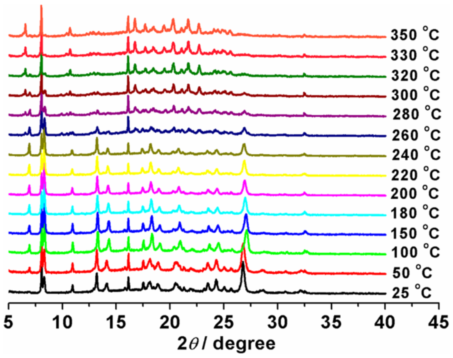

Figure 2. Variable-temperature PXRD patterns for **HOF-8** measured under N_2.

directly assign the position of the solvent guest molecules by scXRD. To determine the composition of **HOF-8**, the ^{1}H NMR spectrum of **HOF-8** dissolved in DMSO-d_6 was measured at room temperature (Figure S3b). Compared with the ^{1}H NMR spectrum of TPBTC (Figure S3a), the ^{1}H NMR spectrum of **HOF-8** contains a new peak at 8.33 ppm, which corresponds to the chemical shift of the $CHCl_3$ molecule. This result indicates that the guest molecules in the pores of **HOF-8** are $CHCl_3$ and H_2O. On the basis of the ^{1}H NMR spectrum, it was estimated that there are ~0.15 $CHCl_3$ and 3 H_2O per TPBTC molecular unit.

In the room-temperature powder XRD (PXRD) pattern (Figure S5), all of the measured peaks closely matched those in the simulated pattern generated from the scXRD data, indicating that a single phase of **HOF-8** was formed. Thermogravimetric analysis (TGA) revealed that the guest solvent molecules in **HOF-8** can be released upon heating from room temperature to 260 °C (Figure S6a); the weight loss of 13.9% corresponds to 0.15 $CHCl_3$ molecule and three H_2O molecules per TPBTC unit (calculated: 14.1%). No obvious weight loss was observed from 260 to 350 °C, after which the desolvated framework began to decompose (Figure S6b). To thoroughly understand the stability of the framework of **HOF-8**, variable-temperature PXRD data for **HOF-8** were measured from room temperature to 350 °C (Figure 2). From room temperature to 240 °C, no obvious change in the PXRD pattern was observed except that the peak at $2\theta = 27°$ shifted slightly as a result of the flexibility and shrinkage of the framework. When **HOF-8** was further heated to 260 °C, the peaks between 17° and 25° markedly changed, indicating that after the removal of the guest molecules, the framework of **HOF-8** remarkably changed. **HOF-8d** shows unbelievably good stability, as it remained stable even when heated to over 350 °C. To the best of our knowledge, no framework with as high a stability as **HOF-8d** has been observed in organic crystalline materials; even in MOF materials formed by covalent (coordinated) bonds, examples that can endure such a high temperature are very limited.[6] The high stability of **HOF-8d** may be related to the strong supermolecular system including three pairs of highly symmetric hydrogen bonds (Figure 1a).

To confirm the contribution of the hydrogen bonds to the thermal stability of **HOF-8**, we tried to replace the amide H atoms with D atoms via a deuteration reaction (see the SI). Under a nitrogen atmosphere, desolvated TPBTC was dissolved in anhydrous dimethyl sulfoxide (DMSO), to which *n*-butyllithium and heavy water were successively added; enough heavy water was added to get deuterated TPBTC powder. The ^{1}H NMR spectrum of the deuterated TPBTC powder showed that the amide H atoms were completely substituted with D atoms from heavy water (Figure S7). To obtain deuterated **HOF-8** crystals, the deuterated TPBTC was recrystallized in a mixed solvent of deuterated chloroform and deuterated methanol (see the SI). The PXRD pattern of the deuterated **HOF-8** was similar to that of **HOF-8** (Figure S8), indicating that the framework of deuterated **HOF-8** is the same as that of **HOF-8**. The deuterated **HOF-8** was further analyzed by ^{1}H NMR spectroscopy, which showed that ~42% of the amide H atoms were substituted with D atoms (Figure S9). The degree of substitution is significantly lower than that of the deuterated TPBTC powder. This may be ascribed to trace H_2O in the deuterated solvents, which led to replacement of some of the D atoms with H atoms. In addition, moisture in the air also may have induced this D → H transformation. TGA showed that from room temperature to 260 °C, the 42% deuterated **HOF-8** underwent a guest loss process similar to that of **HOF-8**, and the desolvated framework began to decompose upon further heating. This observation is different from that for desolvated **HOF-8**, which remained stable up to 350 °C (Figure 3). The TGA results indicate that the framework of deuterated **HOF-8d** shows a relatively worse thermal stability than that of **HOF-8**. The difference in thermal stabilities may be related to the substitution of the amide H atoms with D atoms, which may weaken the hydrogen-bonding system within **HOF-8**. Such a phenomenon is commonly observed in supermolecular systems of biological macromolecules.[7] Although the comparison of TGA results is based on **HOF-8** and 42% deuterated **HOF-8**, the conclusion that the hydrogen bonds within **HOF-8** contribute much to the thermal stability of **HOF-8** is undoubtedly confirmed.

To determine the permanent porosity of **HOF-8d**, N_2, H_2, and CO_2 sorption measurements under mild conditions were carried out. The results obviously showed that **HOF-8d** selectively adsorbs CO_2 rather than N_2 and H_2 (Figure 4). This highly

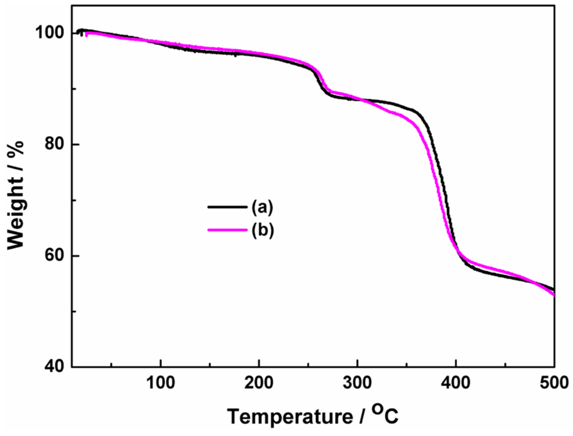

Figure 3. TGA curves of (a) **HOF-8** and (b) 42% deuterated **HOF-8**.

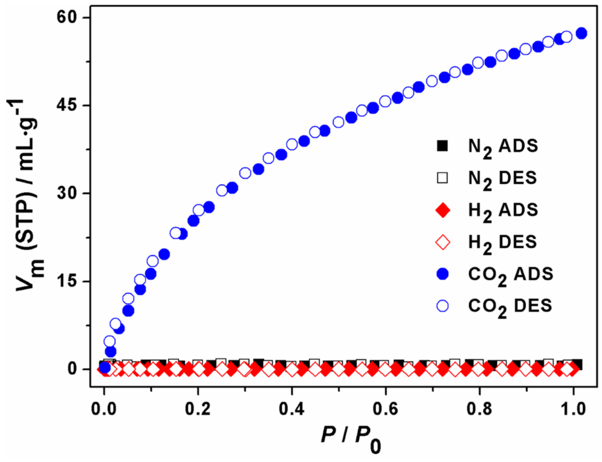

Figure 4. N_2, H_2, and CO_2 sorption isotherms for **HOF-8d** at 298 K.

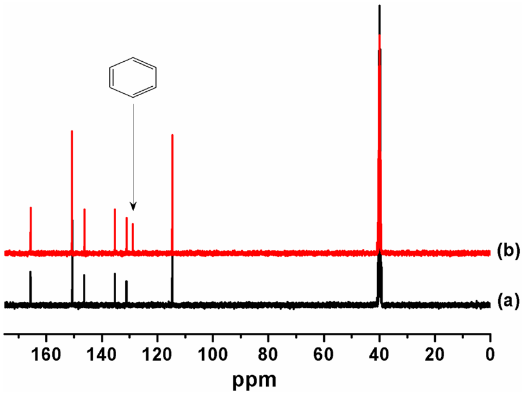

Figure 5. Partial ^{13}C NMR spectra (400 MHz, 298 K, DMSO-d_6) of (a) desolvated **HOF-8** and (b) **HOF-8d** with absorbed benzene.

selective adsorption may be ascribed to the special quadrupole moment of CO_2 (-1.4×10^{-39} C m^2).[8] It has been reported that the quadrupole moment of CO_2 can induce the framework to interact with CO_2 molecules and thus increase the CO_2 binding.[9] However, N_2 and H_2 have small quadrupole moments (4.7×10^{-40} and 2.2×10^{-40} C m^2, respectively)[10] thus cannot interact with and be adsorbed on the pore surface. The sorption isotherms of CO_2 at 298 K exhibit typical type-I behavior, with the amount of CO_2 uptake gradually increasing to 57.3 cm^3 (STP)/g at 1.0 atm. This value is higher than that of any other POCM reported in the literature[11] and those of most MOFs measured under the same conditions.[12] The large amount of CO_2 adsorption in **HOF-8d** may be ascribed to the fact that the framework is decorated with pyridyl N atoms and amide N atoms.[13]

Considering the good stability of **HOF-8** in organic solvents, experiments involving adsorption of five types of hydrocarbons by **HOF-8d** were performed (see the SI). **HOF-8d** samples adsorbed with different solvents were dissolved in DMSO-d_6 and detected by ^{13}C NMR spectroscopy. The results showed that **HOF-8d** cannot adsorb *n*-hexane, cyclohexane, toluene, or *p*-xylene (Figures S10−S14 and Table S3). However, **HOF-8d** shows adsorption of benzene. The ^{13}C resonance at 128.3 ppm, an indicator of benzene, was strongly detected in the ^{13}C NMR spectrum of **HOF-8d** with adsorbed benzene (Figure 5). The TGA curve of **HOF-8d** with adsorbed benzene showed a weight loss of 7.52% from room temperature to 355 °C (Figure S6c), corresponding to 0.31 benzene molecule absorbed per TPBTC unit. A general explanation for selective adsorption of hydrocarbons is size exclusion (steric effect). Obviously, **HOF-8d**'s selective adsorption of benzene over the other four types of hydrocarbons cannot be attributed to size exclusion because all of the tested hydrocarbons can freely enter the pores of **HOF-8d**. The different adsorption behaviors can be ascribed to the different interactions between the adsorbent (**HOF-8**) and the adsorbates (hydrocarbons). As far as benzene is concerned, the phenyl rings can strongly bind with the phenyl/pyridyl rings of **HOF-8d** through $\pi-\pi^*$ stacking interactions, leading to the adsorption of benzene by **HOF-8d**.[14] Because *n*-hexane and cyclohexane do not contain delocalized π bonds in their molecular structures, they cannot stack with the phenyl/pyridyl rings of **HOF-8d** by $\pi-\pi^*$ interactions, and thus, they cannot be adsorbed by **HOF-8d**. Although toluene and *p*-xylene can bind with **HOF-8d** through $\pi-\pi^*$ stacking interactions, the stacking interactions may be very weak because of the steric hindrance by the methyl group. When **HOF-8d** with toluene or *p*-xylene was treated at 50 °C under vacuum (see the SI), the toluene/*p*-xylene molecules easily escaped from the pores of **HOF-8d**. Therefore, no adsorption of toluene/*p*-xylene was observed either. To the best of our knowledge, although several types of porous materials (e.g., MOFs, zeolites, and nanotubes) have been developed for separation of liquid hydrocarbons,[15] the use of POCMs for liquid separation, especially for removal of benzene, has not been explored to date.[16]

In summary, we have successfully assembled an extremely stable hydrogen-bonded organic framework, **HOF-8** that is not only thermally stable but also stable in water and common organic solvents. More interestingly, desolvated **HOF-8** exhibits high CO_2 adsorption as well as highly selective CO_2 and C_6H_6 adsorption at ambient temperature. This result illustrates that **HOF-8** may have potential applications for separation and purification of gases and solvents to obtain higher-purity materials for precise analyses. These unique features of **HOF-8**, including the exceptional stability and highly selective adsorption for CO_2 and benzene, make it outstanding among the thousands of HOFs reported in the literature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and auxiliary data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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