Porous Materials

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A Rod-Packing Microporous Hydrogen-Bonded Organic Framework for Highly Selective Separation of C_2H_2/CO_2 at Room Temperature[**]

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Abstract: *Self-assembly of a trigonal building subunit with diaminotriazines (DAT) functional groups leads to a unique rod-packing 3D microporous hydrogen-bonded organic framework (HOF-3). This material shows permanent porosity and demonstrates highly selective separation of C_2H_2/CO_2 at ambient temperature and pressure.*

Development of new porous adsorbents is a very important topic for adsorption-based gas separations. For example, extensive research on porous metal–organic frameworks (MOFs) has not only led to a number of new MOF adsorbents whose separation selectivities and capacities have surpassed those traditional zeolite materials for some important CO_2/N_2, CO_2/CH_4, CO_2/H_2, and xylene isomer separations,[1,2] but also generated a few MOFs to target the very challenging C_2H_2/C_2H_4,[3] C_2H_4/C_2H_6, C_3H_6 and C_3H_8,[4,5] and CO/N_2 separations.[6]

Among diverse gas separations, C_2H_2/CO_2 is another very challenging mixture. This is because these two gas molecules have very similar shapes, dimensions (332 × 334 × 570 pm versus 318.9 × 333.9 × 536.1 pm), and boiling points (−84 °C versus −78.5 °C).[7] Since the discovery of the first MOF material for this separation,[8] several MOFs have been realized for this important gas separation, though the selectivities are quite low.[9]

Recently we, and several other groups, have realized that it is feasible to make use of hydrogen bonding interactions to construct new porous materials which we have termed as hydrogen bonded organic frameworks (HOFs),[10] providing the new approach to develop and explore new porous adsorbents for gas separations. In fact, the first, HOF-1, exhibits superior C_2H_2/C_2H_4 separation to other MOFs.[10h] Compared with MOFs, HOFs have some advantages including solution processability and characterization, easy purification, and straightforward regeneration and reusage by simple recrystallization. Because the pore surfaces within HOFs are apparently different from those within MOFs and zeolites, exploration of HOF materials might lead to some unique new adsorbents for gas separations.

Herein we report a new system, HOF-3, constructed from a new triangular organic linker containing three hydrogen-bonding motifs of 2,4-diaminotriazinyl (DAT) (Figure 1 a). Unlike those reported HOFs whose porous structures were built from discrete building units; HOF-3, to the best of our knowledge, is the first example of HOFs constructed from one-dimensional rod-packing units exhibiting the **srs** topology. More importantly, the activated HOF-3a shows superior selectivity for C_2H_2/CO_2 separation to the established MOF materials.

The triangular organic building block 3-DAT, shown in Figure 1 a, can be readily synthesized in 84 % yield by the reaction of the corresponding nitrile with dicyandiamide (Supporting Information, Scheme S1). The colorless block crystals of HOF-3 suitable for X-ray diffraction analysis were grown by slow vapor diffusion of THF into a large vial containing saturated DMSO solution of this building block for a week under room temperature. The purity of HOF-3 was confirmed by ^1H NMR and ^{13}C NMR spectroscopy, thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD; Supporting Information, Figures S1–S3). The inclusion of the solvent molecules into the framework leads to the HOF-3 whose phase is different from that of the as-synthesized 3-DAT. TGA curve indicates that the framework of HOF-3 can be stable up to 350 °C.

Single-crystal X-ray diffraction reveals that HOF-3 crystallized in the rhombohedral space group $R3$ and HOF-3 is a three-dimensional rod-packing porous material with one-dimensional hexagonal channels of about 7.0 Å in diameter

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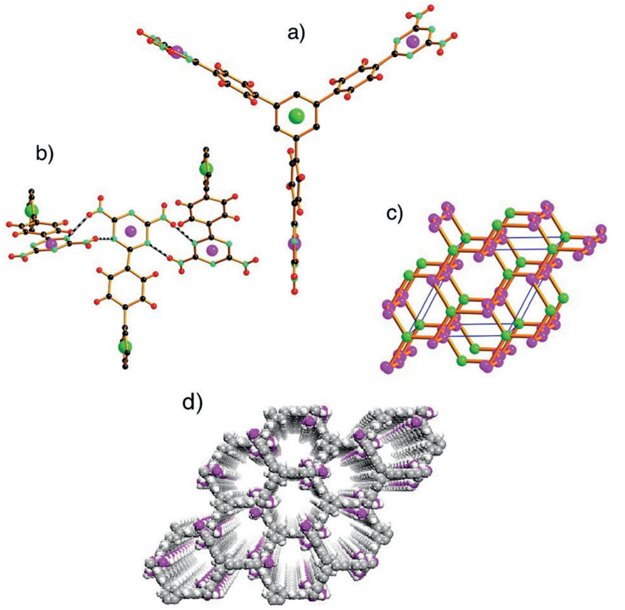

Figure 1. X-ray crystal structure of HOF-3 featuring a) the basic organic building block in which the centers of central benzene ring (green balls) and centers of three 1,3,5-triazine rings (magenta balls) act as nodes; b) The H-bonded link between DAT groups showing that each is joined to two other DAT groups; c) The net of 3-c branch points as it occurs in the crystal structure; and d) three-dimensional packing showing the 1D hexagonal channels of about 7.0 Å in diameter along the *c* axis (C gray, H white, N pink).

(Figure 1 d). The tritopic building unit has a 3-coordinated (3-c) node (A) at its center shown as a green ball in Figure 1 a. The three DAT groups shown as magenta balls (B) in the Figure 1 a are linked to two other DAT groups by H-bonds as shown in Figure 1 b, so each of these also corresponds to a 3-c node. The connectivity is A-B_3 and B-AB_2. The 3-c net is the ubiquitous **srs** (Figure 1 c), which can be described (see the Supporting Information) as parallel threefold helical rods (B) linked by additional 3-c nodes (A) into a 3-D net (Supporting Information, Figure S4). Initially, we tried to use the discrete molecule approach to rationalize the topology. However, the rationalized structure of NaCl topology apparently does not make much sense and is far away from the pore nature. It was then termed as a rod-packing topology to suitably describe the framework channels.[11] The pore spaces within the frameworks encapsulate certain amount of disordered DMSO and THF solvent molecules.

The available void space and high thermal stability of HOF-3 prompts us to examine the gas adsorption properties of HOF-3. The as-synthesized HOF-3 was exchanged with acetone several times then evacuated under dynamic vacuum to obtain desolvated HOF-3 a, which does not take up any N_2 gas molecules at 77 K. Such phenomena have been commonly observed in HOF and supramolecular organic framework (SOF) materials,[10f–h] though the exact reasons are still not clear. However, the CO_2 gas sorption isotherm of HOF-3 a at 196 K clearly indicates its microporous nature with Brunauer–Emmett–Teller (BET) surface area of 165.0 $m^2 g^{-1}$ (Supporting Information, Figure S5), which is moderate.[10] Interestingly, HOF-3 a takes up quite different amounts of C_2H_2 and CO_2 at room temperature. The C_2H_2 uptakes of 58 $cm^3 g^{-1}$ at 273 K and 47 $cm^3 g^{-1}$ at 296 K are systematically about twice higher than CO_2 uptakes of 31 $cm^3 g^{-1}$ at 273 K and 21 $cm^3 g^{-1}$ at 296 K at 1 atm (Figure 2 a; Supporting Information, Figure S6). This is unusual given the fact that these two gas molecules are comparable in terms of their dimensions and boiling points.[9]

This discovery motivated us to examine its feasibility for the industrially important C_2H_2/CO_2 separation in more details. The pure component isotherm data were fitted with the dual-Langmuir isotherm model (Supporting Information, Figure S7). To understand the binding energy at low coverage, isosteric heats of adsorption of C_2H_2 and CO_2 in HOF-3 a are calculated. Data on the loading dependence of Q_{st} in HOF-3 a are presented in the Supporting Information, Figure S8. Particularly remarkable is the relatively low value (< 20 kJ mol^{-1}) of the isosteric heat of adsorption for C_2H_2. To underscore this point, Figure 2 b presents a comparison of the heats of adsorption of C_2H_2 in various MOFs (UTSA-30a,[9a] UTSA-50a,[9b] and CuBTC).[5] We note that value of Q_{st} in HOF-3 a is significantly lower than that for MOFs. The value of Q_{st} in HOF-3 a is systematically more than twice lower than that in CuBTC with coordinately unsaturated metal sites (Figure 2 b). These data highlight that HOF-3 a is a promising material for the separation of C_2H_2/CO_2 with lower regeneration energy requirement for C_2H_2.

We further performed calculation using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[12] Figure S9 presents IAST calculations of the component loadings for C_2H_2 and CO_2 in binary equimolar mixture as a function of the total bulk gas-phase pressure at 296 K, and Figure 2 c provides a comparison of the adsorption selectivity of C_2H_2/CO_2 in equimolar mixtures in HOF-3 a and the three other MOFs at 296 K. We note that adsorption selectivity of HOF-3 a is significantly higher than that of other MOFs. Though at zero-coverage the selectivity of UTSA-50a (15) is higher than that of HOF-3 a (14), as the pressure increases to 100 kPa, the adsorption selectivity increases to 21 for HOF-3 a, while for MOF materials, the selectivity reduces significantly (lower than 6).

Preliminary studies on the breakthrough simulations for C_2H_2/CO_2 mixtures using the established methodology described in early publications of Krishna (Supporting Information, Figure S10) indicate that it is feasible for HOF-3 a to separate C_2H_2 from the C_2H_2/CO_2 mixture at room temperature (Supporting Information, Figure S11).[12b–d] That encouraged us to evaluate the actual performance of HOF-3 a through the experimental column breakthrough in which an equimolar C_2H_2/CO_2 mixture was flowed over a packed column of the HOF-3 a solid with a total flow of 5 $cm^3 min^{-1}$ at 296 K. As shown in Figure 2 d, the separation of C_2H_2/CO_2 mixture gases through a column packed with HOF-3 a solid can be efficiently achieved. To the best of our knowledge, this is the first example of porous materials whose separation for C_2H_2/CO_2 mixture has been clearly established by experimental breakthrough, enabling HOF-3 a to be a potential material for industrial acetylene purification application.

To help understand the C_2H_2/CO_2 selectivity in HOF-3 a, we performed detailed computational investigations. We first

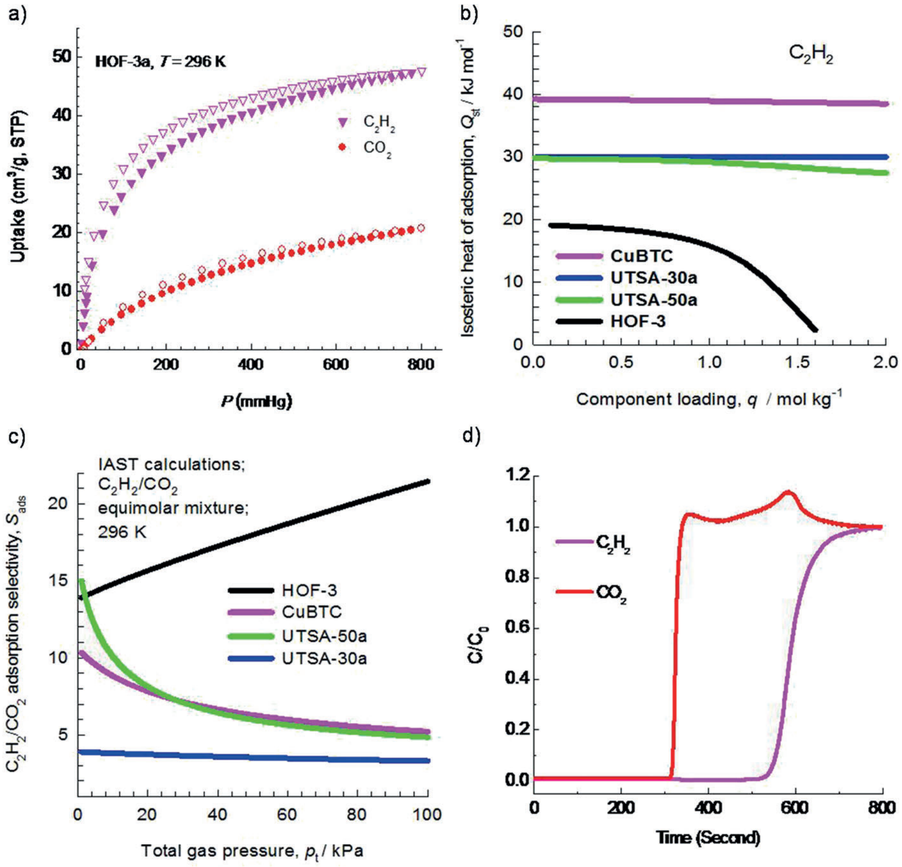

Figure 2. a) Sorption isotherms of C_2H_2 and CO_2 of HOF-3 a at 296 K; b) comparison of the heats of adsorption of C_2H_2 in HOF-3 a and various MOFs; c) IAST adsorption selectivities of C_2H_2/CO_2 in equimolar mixture in HOF-3 a and various MOFs at 296 K; and d) experimental column breakthrough curve for an equimolar C_2H_2/CO_2 mixture (296 K, 1 bar) in an adsorber bed packed with HOF-3 a.

optimized the HOF-3 a structure by first-principles DFT-D (dispersion-corrected density-functional theory) calculations,[13] and then carried out grand canonical Monte Carlo (GCMC) simulations using the classical force field method (for details, see the Supporting Information). The simulated PXRD of the optimized HOF-3 a structure matches with the experimental structure of HOF-3 a quite well (Supporting Information, Figure S3), indicating that the results from simulation studies are quite reasonable. HOF-3 a is the slightly shrunk form of HOF-3, keeping identical framework connectivity. From the probability distribution of adsorbed gas molecules generated from the simulations (Supporting Information, Figure S12), we found that for both C_2H_2 and CO_2, the adsorption takes place mainly adjacent to the "pocket" between two H-bonded DAT groups. We then introduced gas molecules at these sites, and further optimized the "HOF-3 a + gas" structures using DFT-D. We found that the gas binding is relatively weak in both cases, and of van der Waals type in nature. The derived static gas binding energies are 20.9 kJ mol^{-1} and 26.3 kJ mol^{-1} for C_2H_2 and CO_2, respectively, in qualitative agreement with the experimental Q_{st} values. Interestingly, we noticed that the relaxed, adsorbed CO_2 molecules (Supporting Information, Figure S13) are much more "localized" than C_2H_2 in terms of position and orientation, with the adsorption energy decaying rapidly if the CO_2 molecule is moved away from the optimized position. For C_2H_2, the adsorption potential surface is much "flatter" in the region adjacent to the pocket site, and more than one molecule can be accommodated on each site simultaneously with similar binding strength. This subtle difference in the gas/HOF framework interaction is likely the reason why the uptake (that is, surface coverage) of C_2H_2 is higher than CO_2 in HOF-3 a at RT.

In summary, we have targeted a three-dimensional rod-packing HOF for highly selective C_2H_2/CO_2 separation at ambient temperature and pressure. To the best of our knowledge, this is the first example of rod-packing porous hydrogen-bonded organic frameworks. More importantly, its C_2H_2/CO_2 separation selectivities are systematically higher than those found in the well-established MOF materials, highlighting the bright promise of such new porous HOF materials for gas separation. Such preferential adsorption of HOF-3 for acetylene over carbon dioxide is attributed to the unique pockets and pore surfaces within HOF-3. It is expected that extensive research endeavors on porous HOFs will facilitate the discoveries of new porous HOFs for gas separation and other important applications in the near future.

Experimental Section

Synthesis of 3-DAT: A mixture of 1,3,5-tri(4-cyanophenyl)benzene (0.90 g, 2.36 mmol), dicyandiamide (0.74 g, 8.80 mmol, Alfa), and powdered KOH (85 %, 0.12 g, 1.82 mmol, Aldrich) in 2-methoxyethanol (30 mL, Aldrich) was heated at reflux for 48 h. The resulting mixture was cooled and filtered. The solid was extracted thoroughly with hot water. The solid was then rinsed with ethanol and dried in vacuum to give the target compound as a colorless solid in 84 % yield (1.26 g, 1.99 mmol).

Crystalline material HOF-3 was generated as follows: 3-DAT (350 mg, 0.55 mmol) was dissolved in DMSO (20 mL) under heating. The resulting solution was cooled to room temperature and filtered. The filtrate was divided to 8 small disposable scintillation vials. These vials were then placed inside a large bottle containing THF as a diffusion solvent. The bottle was then closed and kept at room temperature for a week. Colorless block shaped crystals were obtained in 32 % yield. ^{1}H NMR ([D$_6$]DMSO, 300.0 MHz): $\delta = 8.38$ (d, $J = 8.4$ Hz, 6 H), 8.06 (s, 3 H), 8.01 (d, $J = 8.4$ Hz, 6 H), 6.81 ppm (s, br, 12 H); ^{13}C NMR ([D$_6$]DMSO, 75.4 MHz): $\delta = 169.63$, 167.22, 142.18, 140.98, 136.35, 128.17, 126.89, 124.80 ppm; FTIR (neat): $\tilde{\nu} =$

1632, 1578, 1533, 1449, 1433, 1396, 1255, 1227, 1016, 985, 907, 850, 808, 693, 666 cm^{-1}.

X-ray diffraction data of HOF-3 were collected at 193 K on a Bruker Apex II CCD diffractometer graphite-monochromatic enhanced ultra Cu radiation ($\lambda = 1.54178$ Å). The structure was solved by direct methods and refined by full-matrix least-squares methods with the SHELXTL program package. The solvent molecules in as-synthesized HOF-3 crystal are highly disordered. The SQUEEZE subroutine of the PLATON software suite was used to remove the scattering from the highly disordered guest molecules.

Crystal data of HOF-3: rhombohedral $R3$, $a = b = 22.5819(7)$, $c = 16.6210(8)$ Å, $V = 7340.2(7)$ Å^3, $Z = 3$, $\rho_{calcd} = 0.430\ g\,cm^{-3}$, crystal size $0.22 \times 0.20 \times 0.17\ mm^3$, $T = 193(2)$ K, $\mu = 0.228\ cm^{-1}$, 11281 reflections collected, 137 parameters, $R_1[I > 2\sigma(I)] = 0.0614$, $wR_2 = 0.1520$, GOF = 1.048. CCDC 1006896 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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