A Rod-Packing Microporous Hydrogen-Bonded Organic Framework for Highly Selective Separation of C$_2$H$_2$/CO$_2$ at Room Temperature**

Peng Li, Yabing He, Yunfeng Zhao, Linhong Weng, Hailong Wang, Rajamani Krishna, Hui Wu, Wei Zhou, Michael O’Keeffe, Yu Han, and Banglin Chen*

Abstract: Self-assembly of a trigonal building subunit with dianinotriazines (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$_2$H$_2$/CO$_2$ at ambient temperature.

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$_2$H$_2$/C$_2$H$_4,$[3] C$_2$H$_4$/C$_2$H$_6,$ C$_3$H$_6$ and C$_3$H$_8,$[4,5] and CO/N$_2$ separations.[6]

Among diverse gas separations, C$_2$H$_2$/CO$_2$ is another very challenging mixture. This is because these two gas molecules have very similar shapes, dimensions (332 x 334 x 570 pm versus 318.9 x 333.9 x 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$_2$H$_2$/C$_2$H$_4$ separation to other MOFs.[10a] Compared with MOFs, HOFs have some advantages including solution processability and characterization, easy purification, and straightforward regeneration and reuse 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 1a). 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 ssrs topology. More importantly, the activated HOF-3a shows superior selectivity for C$_2$H$_2$/CO$_2$ separation to the established MOF materials.

The triangular organic building block 3-DAT, shown in Figure 1a, 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 $^1$H 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...
to obtain desolvated HOF-3a, which does not take up any N$_2$ acetone several times then evacuated under dynamic vacuum of HOF-3. The as-synthesized HOF-3 was exchanged with DMSO and THF solvent molecules.

Interestingly, HOF-3a takes up quite different amounts of C$_2$H$_2$ (SOF) materials,[10f–h] though the exact reasons are still not clear. However, the CO$_2$ gas sorption isotherm of HOF-3a at 77 K. Such phenomena have been commonly observed in HOF and supramolecular organic framework (SOF) materials,[10d–g] though the exact reasons are still not clear. However, the CO$_2$ gas sorption isotherm of HOF-3a 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] Interactively, HOF-3a takes up quite different amounts of C$_2$H$_2$ and CO$_2$ at room temperature. The C$_2$H$_2$ 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 2a; 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$_2$H$_2$/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$_2$H$_2$ and CO$_2$ in HOF-3a are calculated. Data on the loading dependence of $Q_a$ in HOF-3a 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$_2$H$_2$. To underscore this point, Figure 2b presents a comparison of the heats of adsorption of C$_2$H$_2$ in various MOFs (UTSA-30a,[9a] UTSA-50a,[9b] and CuBTC). [5] We note that value of $Q_a$ in HOF-3a is significantly lower than that for MOFs. The value of $Q_a$ in HOF-3a is systematically more than twice lower than that in CuBTC with coordinately unsaturated metal sites (Figure 2b). These data highlight that HOF-3a is a promising material for the separation of C$_2$H$_2$/CO$_2$ with lower regeneration energy requirement for C$_2$H$_2$.

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$_2$H$_2$ and CO$_2$ in binary equimolar mixture as a function of the total bulk gas-phase pressure at 296 K, and Figure 2c provides a comparison of the adsorption selectivity of C$_2$H$_2$/CO$_2$ in equimolar mixtures in HOF-3a and the three other MOFs at 296 K. We note that adsorption selectivity of HOF-3a is significantly higher than that of other MOFs. Though at zero-coverage the selectivity of UTSA-50a (15) is higher than that of HOF-3a (14), as the pressure increases to 100 kPa, the adsorption selectivity increases to 21 for HOF-3a, while for MOF materials, the selectivity reduces significantly (lower than 6).

Preliminary studies on the breakthrough simulations for C$_2$H$_2$/CO$_2$ mixtures using the established methodology described in early publications of Krishna (Supporting Information, Figure S10) indicate that it is feasible for HOF-3a to separate C$_2$H$_2$ from the C$_2$H$_2$/CO$_2$ mixture at room temperature (Supporting Information, Figure S11).[12b–c] That encouraged us to evaluate the actual performance of HOF-3a through the experimental column breakthrough in which an equimolar C$_2$H$_2$/CO$_2$ mixture was flowed over a packed column of the HOF-3a solid with a total flow of 5 cm$^3$ min$^{-1}$ at 296 K. As shown in Figure 2d, the separation of C$_2$H$_2$/CO$_2$ mixture gases through a column packed with HOF-3a solid can be efficiently achieved. To the best of our knowledge, this is the first example of porous materials whose separation for C$_2$H$_2$/CO$_2$ mixture has been clearly established by experimental breakthrough, enabling HOF-3a to be a potential material for industrial acetylene purification application.

To help understand the C$_2$H$_2$/CO$_2$ selectivity in HOF-3a, we performed detailed computational investigations. We firstcerpted 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).
optimized the HOF-3a 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-3a structure matches with the experimental structure of HOF-3a quite well (Supporting Information, Figure S3), indicating that the results from simulation studies are quite reasonable. HOF-3a 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 C2H2 and CO2, 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-3a + 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 C2H2 and CO2, respectively, in qualitative agreement with the experimental \(Q_0\) values. Interestingly, we noticed that the relaxed, adsorbed CO2 molecules (Supporting Information, Figure S13) are much more “localized” than C2H2 in terms of position and orientation, with the adsorption energy decaying rapidly if the CO2 molecule is moved away from the optimized position. For C2H2, 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 C2H2 is higher than CO2 in HOF-3a at RT.

In summary, we have targeted a three-dimensional rod-packing HOF for highly selective C2H2/CO2 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 C2H2/CO2 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) was heated at reflux for 48 h. The resulting mixture was cooled and filtered. 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 into 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, 6H), 8.06 (s, 3H), 8.01 (d, \(J = 8.4\) Hz, 6H), 6.81 ppm (s, br, 12H); \(^13\)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): \(v = 142.18, 140.98, 136.35, 128.17, 126.89, 124.80\) ppm; FTIR (neat): \(v = 142.18, 140.98, 136.35, 128.17, 126.89, 124.80\) ppm; FTIR (neat):
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 SHEXLXTL 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 \(R3\), \(a = b = 22.5819(7)\) Å, \(c = 16.6210(8)\) Å, \(V = 7340.2(7)\) Å\(^3\), \(Z = 3\), \(\rho_{calc} = 0.430\) g cm\(^{-3}\), crystal size \(0.22 \times 0.20 \times 0.17\) mm\(^3\), \(T = 193(2)\) K, \(\mu = 0.228\) cm\(^{-1}\), 11,281 reflections collected, 137 parameters, \(R1[\text{I} > 2\sigma(\text{I})] = 0.0614\), \(wR2 = 0.1520\), 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.

Keywords: acetylene separation · adsorption · hydrogen-bonded organic frameworks · microporous materials · selectivity


