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A microporous six-fold interpenetrated hydrogen-bonded organic framework for highly selective separation of C_2H_4/C_2H_6†

Peng Li,[a] Yabing He,[a] Hadi D. Arman,[a] Rajamani Krishna,[b] Hailong Wang,[a]
Linhong Weng[c] and Banglin Chen*[ad]

A unique six-fold interpenetrated hydrogen-bonded organic framework (HOF) has been developed, for the first time, for highly selective separation of C_2H_4/C_2H_6 at room temperature and normal pressure.

As one of the most important petrochemicals, ethylene is used widely in the chemical industry and its worldwide production exceeds that of any other organic compound (140 million tons per year by 2010).[1] Thermal cracking of ethane as a feedstock in the presence of steam remains one of the most important and widely employed processes for ethylene production. Due to the similar sizes and volatilities of ethylene and ethane, the traditional cryogenic distillation technology to separate ethylene from ethane requires distillation columns with over 100 trays under the conditions of high pressure (23 bar) and low temperature (−25 °C), which has been criticized as the most energy extensive process in the petrochemical industry.[2] Therefore, tremendous efforts have been devoted to develop alternative technologies,[3] such as membrane separation,[4] liquid adsorbent separation[5] and solid adsorbent adsorption separation[6] for ethylene/ethane separation at ambient temperature and pressure with lower energy cost.

In the development of adsorption separation technologies, various porous materials, such as SiO_2,[7] zeolites,[8] molecular sieves,[9] metal–organic frameworks (MOFs),[10] nanoparticle–MOF composites,[11] porous organic polymers (POPs),[12] activated carbons,[13] and carbon nanotubes,[14] have been explored as solid adsorbents to realize olefin/paraffin separation. Two useful but distinct strategies have been proposed to achieve preferential adsorption of olefin over paraffin. One is based on reversible formation of π-complexes of olefins with transition metal cations, and the other is control of the appropriate pore size and volume for size exclusion separation. The former strategy has been successfully applied in MOFs[10a] and POPs[12a] to realize high selective adsorption for ethylene over ethane. Although this selectivity is usually very high at low pressure, it decreased significantly with increasing pressure possibly due to saturation of the preferential binding sites. The latter strategy often used in propene/propane separation,[10b,12b] however, can hardly be achieved especially for smaller ethylene and ethane molecules with tiny dimensional difference. Moreover, this strategy may result in an inevitable low adsorption capacity.[10d] Hence, finding new materials for the adsorptive separation of ethylene–ethane mixtures is very challenging and important.

Recently, we and several other groups have discovered that hydrogen-bonded organic framework (HOF) materials can be used as a new class of porous materials for a variety of applications.[15] Because HOFs have some obvious advantages such as solvent processability and straightforward regeneration by recrystallization, while they might have different pore surfaces from those of well-established porous materials, exploration of HOF materials might lead to some unique new adsorbents for gas separations. Actually, the first HOF-1 exhibits superior performance to MOFs in very challenging C_2H_2/C_2H_4 separation.[15h] Herein, we report the synthesis of a robust hydrogen-bonded organic framework (**HOF-4**), which shows a high ideal adsorbed solution theory (IAST) selectivity of 14 for ethylene/ethane separation at room temperature and normal pressure.

The new tetrahedral molecular tecton **2** (Scheme 1) has been synthesized as a building block based on the following considerations: (i) extended tecton **2** has both tetrahedral symmetry and diaminopyridine in tecton **1**, which is the basic building unit of HOF-1 and is capable of forming multiple hydrogen bonds and thus extending into the 3D framework; (ii) generally speaking, longer ligands will lead to larger voids.

The tetrahedral organic building block **2** was readily synthesized in 92% yield by the reaction of the corresponding nitrile

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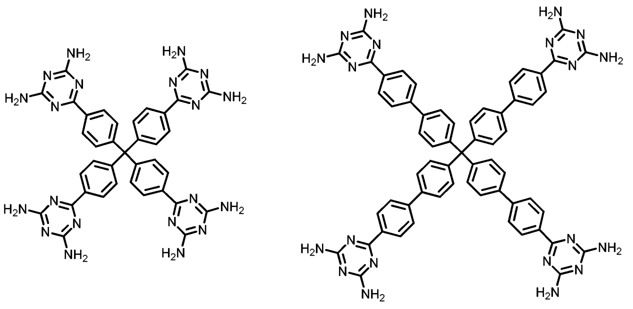
[a] *Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA. E-mail: banglin.chen@utsa.edu; Fax: +1-210-458-7428*
[b] *Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands*
[c] *Department of Chemistry, Fudan University, Shanghai, 200433, People's Republic of China*
[d] *Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 22254, Saudi Arabia*

† Electronic supplementary information (ESI) available: Synthesis and characterization of **HOF-4**, PXRD, TGA, FTIR spectra, sorption isotherms, and breakthrough simulations. CCDC 1010353. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05506c



Scheme 1 Tetrahedral building blocks.

with dicyandiamide (see Scheme S1 in the ESI†). The colorless needle-like crystals of HOF-4 were easily isolated in 79% yield by evaporating DMF solution of **2** for a week at room temperature. The purity of **HOF-4** was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy, thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD) (Fig. S1–S3, ESI†). Single crystal X-ray diffraction reveals that **HOF-4** crystallizes in the monoclinic space group *P*2/*n* and shows a 3D architecture consisting of six equivalent interwoven nets of **PtS** topology.‡ For a single net, the asymmetric unit consists of only half of the building blocks (Fig. 1a left), and each building block is connected with six neighbouring ones by 12 strong hydrogen bonds involving the 2,4-diaminotriazine (DAT) groups (Fig. 1a right, the parameters of hydrogen bonding are listed in Table S1, ESI†). There exist rhombic channels in the single net along the [101] direction with an approximate dimension of 40 Å × 30 Å along the diagonals (Fig. S4, ESI†). If one considers the tetrahedral building block to be a four-connected node in the tetrahedral geometry, and the multiple hydrogen bonding motif of DAT groups to be a four-connected node in the square planar geometry, the single net of **HOF-4** can then be rationalized as a 3D **PtS** $\{4^2 8^4\}$ network topology (Fig. 1b). Due to large void spaces, six equivalent nets interpenetrate each other *via* intermolecular $\pi \cdots \pi$ interactions between the benzene rings (Fig. 1c). This high fold net interpenetration is expected to enhance the framework stability.[16–18] The rhombic channels along the [101] direction are completely blocked due to the interpenetration, leaving a 1D rectangular channel (3.8 Å × 8.1 Å) along the *b* axis (Fig. 1d). The pore spaces within the frameworks encapsulate a few disordered DMF solvent molecules. The potential solvent accessible void space accounts for approximately 42.5% of the whole crystal volume as estimated by PLATON.

With a slit rectangular channel along the *b* axis (3.8 Å × 8.1 Å), it is reasoned that 'slim' C_2H_4 molecules (3.28 Å × 4.18 Å × 4.84 Å) can access the channel in **HOF-4a** readily, while relatively 'fat' C_2H_6 molecules (3.81 Å × 4.08 Å × 4.82 Å) can hardly get through.[19] Furthermore, the amino groups residing on the surface wall of the framework might provide stronger hydrogen bonding interactions with more acidic C_2H_4 molecules (pK_a = 44) than C_2H_6 (pK_a = 50). We speculated that the size exclusion effect and hydrogen bonding interactions can work collaboratively to make **HOF-4** an ideal material to separate C_2H_4/C_2H_6. To test our hypothesis, gas adsorption experiments were conducted.

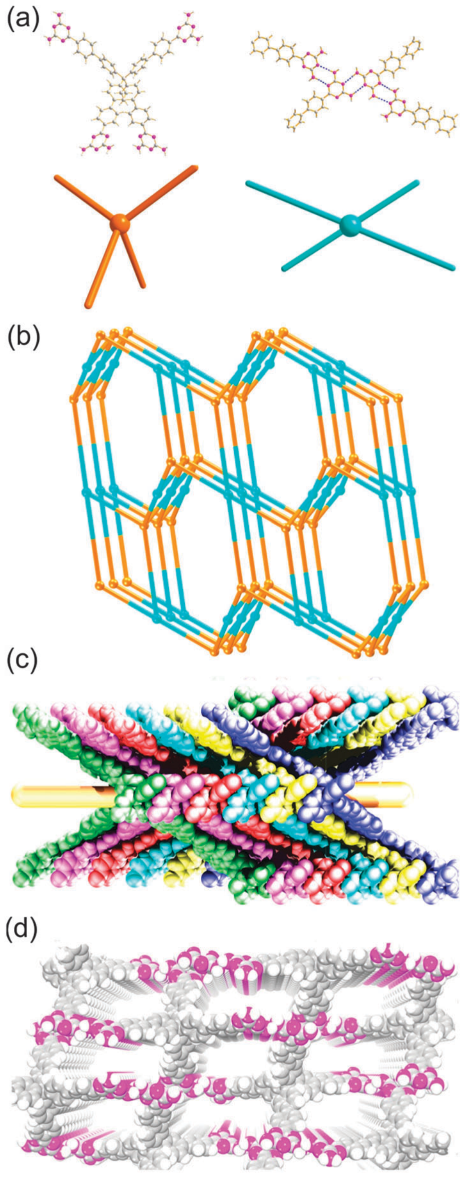


Fig. 1 X-ray structure of **HOF-4** featuring (a) the basic organic building block in which the central carbon atoms act as tetrahedral nodes (brown balls) and centres of multiple hydrogen bonding motifs act as square planar nodes (cyan balls); (b) a simplified binodal four-connected **PtS** $(4^2 8^4)$ topology; (c) six-fold interpenetrated frameworks; (d) the rectangular channels (3.8 × 8.1 Å) along the *b* axis (C, gray; H, white; N, pink).

Before examining adsorption properties, the guest solvent molecules in **HOF-4** were removed by solvent exchange with acetone and then vacuumed at 100 °C to obtain desolvated **HOF-4a** which is thermally stable up to 400 °C. The porosity of **HOF-4a** was evaluated by CO_2 gas sorption at 196 K (Fig. 2a). The type I isotherm shows a very sharp uptake at $P/P_0 < 0.1$, indicative of a microporous material. Because of the flexible nature of the HOF, there exists a small degree of sorption hysteresis. The isotherm gives an apparent Brunauer–Emmett–Teller (BET) surface area of 312 m^2 g^{-1} (Fig. S5, ESI†), which is moderate among a few examples of HOFs with permanent porosity.[15d]

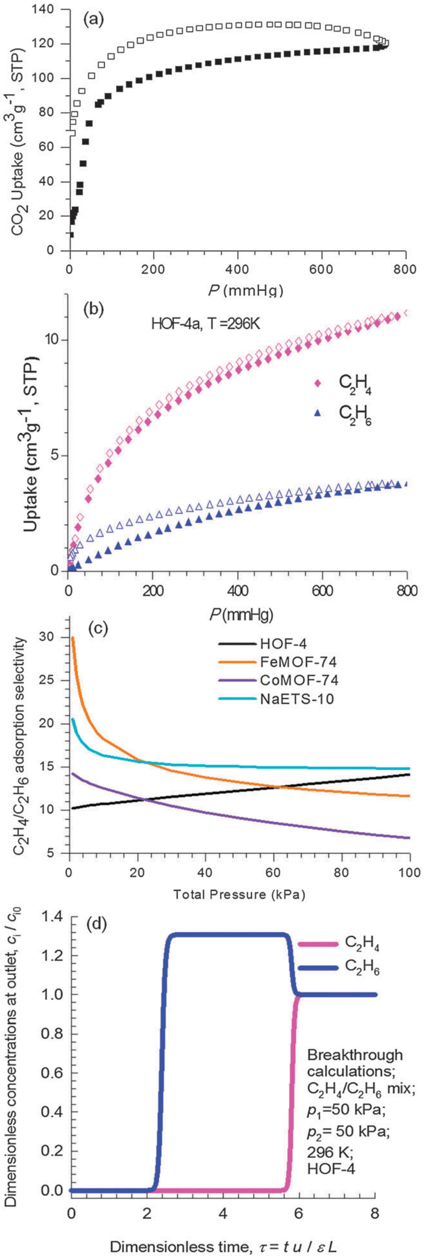


Fig. 2 (a) CO_2 sorption isotherm at 196 K; (b) single-component sorption isotherms for C_2H_4/C_2H_6 in **HOF-4a** at 296 K (solid symbol: adsorption, open symbol: desorption); (c) comparison of the IAST calculations of C_2H_4/C_2H_6 adsorption selectivities for **HOF-4**, FeMOF-74, CoMOF-74, and NaETS-10 at 296 K; (d) transient breakthrough of an equimolar C_2H_4–C_2H_6 mixture in an adsorber bed packed with **HOF-4** in the adsorption phase of a PSA operation. The inlet gas is maintained at partial pressures $p_1 = p_2 = 50$ kPa and at a temperature of 296 K.

Establishment of permanent microporosity in **HOF-4** allowed us to examine its utility as an adsorbent for industrially important C_2H_4/C_2H_6 separations. Interestingly, the C_2H_4 uptakes of 17.3 cm^3 g^{-1} at 273 K and 11.1 cm^3 g^{-1} at 296 K were systematically about three times higher than C_2H_6 uptakes of 5.1 cm^3 g^{-1} at 273 K and 3.6 cm^3 g^{-1} at 296 K at 1 atm (Fig. S6, ESI† and Fig. 2b). This discovery motivated us to examine its feasibility for the industrially important C_2H_4/C_2H_6 separation in more detail.

The pure component isotherm data were fitted with the Langmuir isotherm model (Fig. S7, ESI†). To understand the binding energy at low coverage, isosteric heats of adsorption of C_2H_4 and C_2H_6 in **HOF-4a** were calculated. Fig. S8 (ESI†) presents data on the loading dependence of Q_{st} in **HOF-4a**. The binding energy for C_2H_4 in **HOF-4a** is 44 kJ mol^{-1}, which is comparable in magnitude to those of MgMOF-74 and CoMOF-74.[10g] In contrast, the binding energy for C_2H_6 in **HOF-4a** is only about 14 kJ mol^{-1}, indicating that the **HOF-4a**–C_2H_4 interaction is much stronger than **HOF-4a**–C_2H_6 interaction at low coverage. Because **HOF-4a** is quite flexible, so its pores can be slightly enlarged to accommodate a small amount of C_2H_6 during the adsorption process.

We further performed calculations using the ideal adsorbed solution theory (IAST) of Myers and Prausnitz.[20] Fig. 2c provides a comparison of the adsorption selectivity of C_2H_4–C_2H_6 in equimolar mixtures as a function of total bulk gas phase pressure in **HOF-4a** and three well-known porous materials (MOF materials: FeMOF-74[10a] and CoMOF-74;[10g] zeolite material: NaETS-10[8c]) at 296 K. It is worthy of note that the adsorption selectivity in respect of C_2H_4/C_2H_6 for **HOF-4a** is up to 14 at 1 atm and room temperature, which not only surpasses the selectivity of the best MOF materials but is also comparable to that of the best zeolite material NaETS-10 for such an important separation, highlighting **HOF-4a** as a promising material for C_2H_4/C_2H_6 separation for industrial usage. The large pore spaces enable both FeMOF-74 and CoMOF-74 to take up much more C_2H_6 with increasing pressure; while the narrow pore sizes in **HOF-4a** limit its adsorption capacity for C_2H_6 even under increasing pressure, so **HOF-4a** is unique for C_2H_4/C_2H_6 separation: the separation selectivity increases with increasing pressure.

In order to further validate the feasibility, breakthrough simulation experiments were carried out using the established methodology described in early publications of Krishna (see the ESI† for details).[20] The simulated breakthrough curves (Fig. 2d) clearly show that **HOF-4a** can efficiently separate C_2H_4 from the C_2H_4–C_2H_6 mixture at room temperature. The more poorly adsorbed saturated C_2H_6 breaks through earlier and can be recovered in a nearly pure form (Fig. S9, ESI†). During the adsorption cycle, C_2H_6 at purities $>99\%$ can be recovered for a certain duration. Once the entire bed is in equilibrium with the partial pressures $p_1 = p_2 = 50$ kPa, the desorption, or the "blowdown" cycle is initiated, by applying a vacuum or by purging with inert gas. 99.95% of ethylene can be recovered during the time interval, which can satisfy the purity requirement for production of ethylene as a feedstock in the polymer industry.

In summary, we have prepared and characterized a unique six-fold interpenetrated **HOF-4** material with **PtS** topology by using an expanded tetrahedral tecton **2**. The high degree of interpenetration not only enhanced the structural integrity but also appropriately tuned the channel size to make **HOF-4** an ideal adsorbent for C_2H_4/C_2H_6 separation. This is the first example of a porous hydrogen-bonded organic framework for such an important industrial hydrocarbon separation, during which the channel confinement effect and hydrogen bonding interactions appear to simultaneously control the uptake of different C2 hydrocarbons. It is believed that this work could render a new strategy for designing robust HOFs with permanent porosity and promote more investigation on separation of small hydrocarbons using novel porous organic materials.

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Notes and references

‡ Crystal data for **HOF-4**: $C_{61}H_{48}N_{20}$, M = 1061.17, monoclinic, space group $P2_1/n$, a = 20.212(2) Å, b = 7.725(2) Å, c = 26.666(2) Å, β = 90.606(8)°, V = 3920.81(2) Å^3, Z = 2, D_c = 0.899 g cm^{-3}, T = 193(2) K, F(000) = 1108.0, final R_1 = 0.0976 for $I > 2\sigma(I)$, wR_2 = 0.2139 for all data, GOF = 1.133, CCDC 1010353.

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