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Flexible hydrogen-bonded organic framework to split ethane and ethylene

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Hydrogen-bonded organic frameworks represent an emerging class of porous solids that hold strong promise for industrial-relevant molecular separations. We highlight in this preview an excellent example of this type of adsorbent material that demonstrates high performance in the separation of ethylene and ethane by tuning its gating pressure.

Over the past two decades, crystalline porous materials including metal-organic frameworks (MOFs), covalent-organic frameworks (CO-Fs), and hydrogen-bonded organic frameworks (HOFs) have drawn much attention from both academia and industry for their diverse and rich chemistry as well as their potential for various applications. One of the most intriguing features of MOFs is their highly tunable pore structure and functionality, which has been well-exemplified by numerous practices of the reticular chemistry strategy.[1] Following this strategy, one can precisely tune the porosity, pore shape, pore size, and surface chemistry of an MOF. This has enabled the development of tailored adsorbents for highly efficient capture and separation of industrially important gases/vapors. For instance, several MOFs have been reported to have optimal pore aperture for complete sieving of propane and propylene, which has not been achieved by traditional adsorbent materials.[2–5]

HOFs, emerging rapidly in the past several years, have pushed the development of crystalline porous materials a step forward, particularly their potential in challenging gas separations.[6] Unlike MOFs, which involve strong coordination bonds between metal ions and organic linkers, HOFs are assembled exclusively by organic molecular building blocks through relatively weak hydrogen bonding. The absence of strong chemical bonds and inorganic building units render HOFs a series of pros and cons, such as light weight, self-healing ability, nonpolar/inert surfaces, relatively low thermal stability, and lack of tunability. Recent studies reveal HOFs may be particularly promising for the separation of light hydrocarbons, especially under industrially relevant multi-component or highly humid conditions.[7,8]

Structure flexibility and stepwise gas adsorption has been commonly observed in crystalline porous compounds, which could be greatly beneficial for challenging gas separation when the gating pressure can be suitably tuned in line with the size and shape of molecules to be separated (Figures 1A and 1B). In this preview, we highlight a particularly fascinating example of flexible HOFs published in *Nature Chemistry* by Zhang, Xiang, Chen, and coworkers.[9] The HOF material, HOF-FJU-1, is built on a tetracyano-bicarbazole organic building block, which is different from the more commonly used multi-carboxylate molecules. The bicarbazole units are connected through CN···H-C hydrogen bonds into a **dia** network, and three of such identical nets interpenetrate to form the final framework with one-dimensional (1D) microporous channels (Figure 1B). HOF-FJU-1 features permanent porosity with a Brunauer-Emmett-Teller (BET) surface area of 385 m^2/g. The optimal pore window of ~3.4 × 5.3 $Å^2$ inspired the authors to evaluate its potential for the separation of ethane and ethylene.

Ethylene and ethane adsorption isotherms in HOF-FJU-1 at different temperatures display an evident gate-opening behavior, indicating its framework flexibility (Figure 1A). It has been structurally verified that the stepwise sorption is accompanied by expansion of the pore window. By tuning the gating pressure to minimize the adsorption of ethane but retain substantial uptake of ethylene, the authors were able to achieve full separation of the two gases through a selective molecular exclusion mechanism at 333 K

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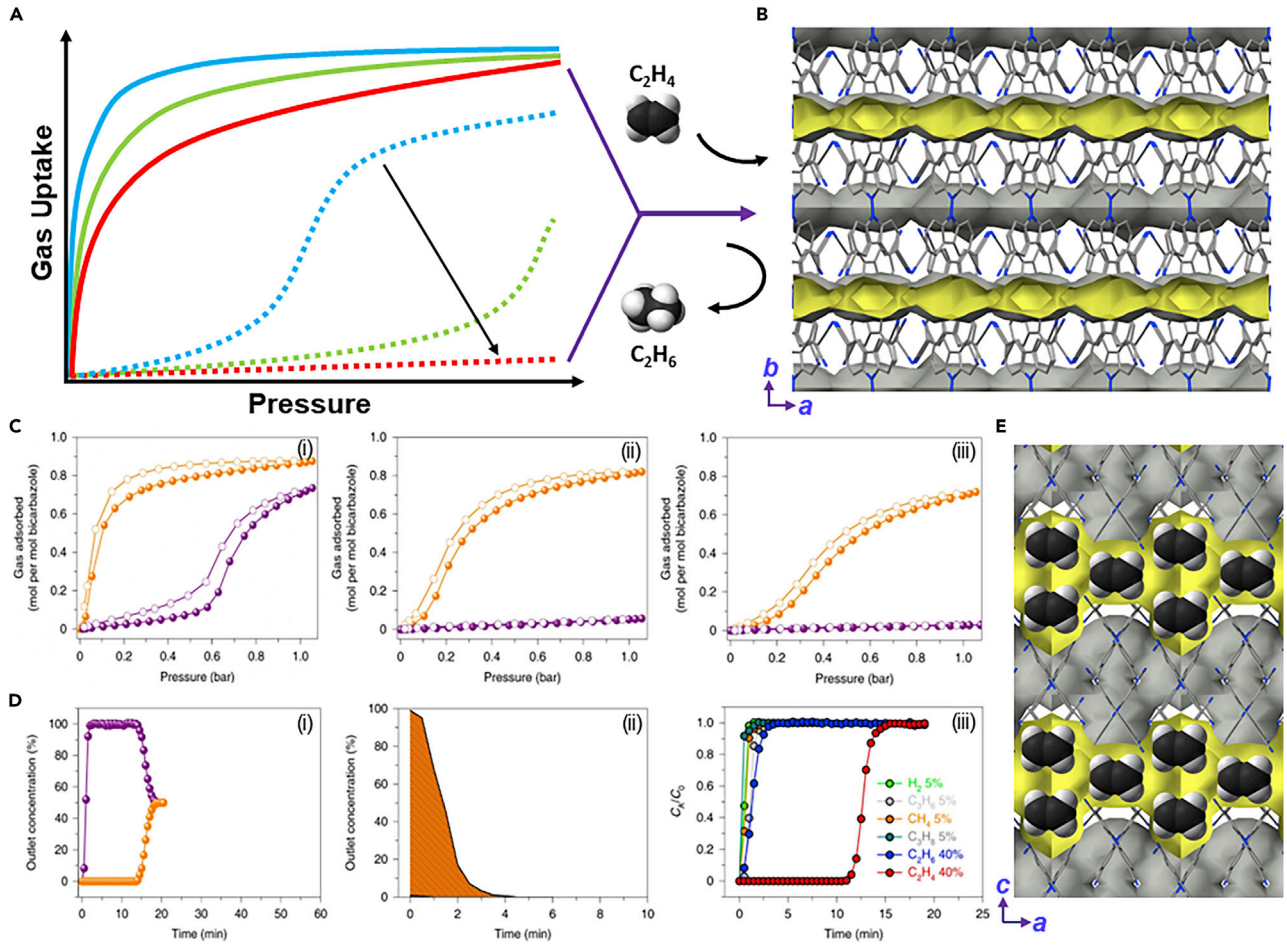

Figure 1. Gating mechanism, crystal and pore structure, adsorption, and separation of ethane and ethylene by HOF-FJU-1

(A) Schematic illustrating the size-dependent adsorption behaviors of molecules of different sizes (e.g., ethane and ethylene) via a gating mechanism.

(B) Interpenetrated framework showing pore channels along crystallographic [100] direction.

(C) Gas adsorption isotherms for C_2H_4 and C_2H_6 in HOF-FJU-1a at various temperatures: (i) 298 K; (ii) 318 K; (iii) 333 K.

(D) (i) Breakthrough curves of HOF-FJU-1a (packed in a fixed bed) for an equimolar mixture of C_2H_4/C_2H_6 (50:50, v/v) at 333 K and 1 bar; (ii) outlet concentration curve of desorbed ethylene during the regeneration process; (iii) breakthrough curves of HOF-FJU-1a for a six-component mixture $H_2/C_3H_6/CH_4/C_3H_8/C_2H_6/C_2H_4$ (5:5:5:5:40:40, v/v/v/v/v/v).

(E) View of the cross-section in the ac plane of the C_2H_4-loaded framework showing the packing pattern of the molecule.

(Figure 1C). The favored accommodation of ethylene over ethane by HOF-FJU-1 was confirmed by gas adsorption isotherms as well as column breakthrough measurements, which yielded ethylene with a purity of 99.1% from an equimolar feed with good recyclability (Figure 1D). Further evaluation revealed the material is capable of exclusively capturing ethylene from a hydrogen/propylene/methane/propane/ethane/ethylene mixture (Figure 1Diii).

The HOF structures are usually fragile and unstable, as the main forces that prop up their frameworks are weak hydrogen-bonding interactions. One observation is that the majority of HOFs would undergo structure degradation or packing transformation upon removal of organic solvents—these solvents from which the HOFs recrystallize may act as a necessary component to retain the framework. Thus, it remains a main challenge to develop robust HOFs with permanent porosity and intact structure upon activation, which also adds additional difficulty to the in-depth investigation of guest-host interactions. HOF-FJU-1 represents such a compound in that its crystal structure is perfectly preserved when it goes through activation and subsequent gas loading. This allows the authors to investigate its subtle structure variation upon solvent removal, and more importantly, to crystallographically visualize the adsorbed gases along the channel. The various binding conformations of ethylene were uncovered by gas-loaded single-crystal X-ray diffraction analysis (Figure 1E), and C-H … π interaction was found to be the primary host-guest force anchoring ethylene molecules inside the channel. This is a

precious piece of information that is unattainable for most reported HOFs that cannot retain single crystallinity upon solvent removal and gas loading.

Overall, Zhang, Xiang, Chen, and colleagues have presented a compelling study of a novel HOF across its synthesis, characterization, structure evolution, gas separation, and host-guest interactions. The work has brought several important findings and insights to researchers working in related fields. First, the separation of ethane and ethylene represents one of the most important but challenging tasks in the chemical industry. Adsorbents that are capable of complete separation of ethane and ethylene, including zeolites, MOFs, CO-Fs, and others, remain scarce with intensive research endeavors over the past decades.[10] HOF-FJU-1 is capable of splitting ethane and ethylene at industrially favorable temperature and producing high-purity ethylene with excellent recyclability in presence of various possible impurities. In addition, in contrast to the general impression that HOFs are fragile, HOF-FJU-1 is quite stable in various organic solvents, and more strikingly, in highly acidic and basic aqueous solutions, which is essential for an adsorbent to be usable for industrial separation processes where moisture or acidic/basic vapors may exist. More inspiringly, the robust framework of HOF-FJU-1 allows direct and precise evaluation of the framework flexibility and underlying gas-framework interactions at molecular level.

Unlike the ongoing MOF research, which is guided by well-established reticular chemistry, the current approaches for the synthesis of HOFs remain largely trial-and-error and lack rationale. We envision that this work by Zhang, Xiang, Chen, and coworkers would further spur the development of HOFs, with a growing focus on the judicious design of structures with high framework stability and permanent porosity and on possible strategies to tune their pore structure and functionality for desirable gas adsorption properties. Undoubtedly, an increasing number of novel HOFs with robust structures and excellent gas separation performance will be discovered in the days to come.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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