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## Efficient separation of C<sub>2</sub> hydrocarbons in a permanently porous hydrogen-bonded organic framework†

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**A highly robust porous hydrogen-bonded organic framework (HOF) constructed by 4,4',4''-benzene-1,3,5-triyl-tris(benzoic acid) not only achieves the highest uptakes of ethylene and ethane among the HOF materials, but also exhibits unusual adsorption selectivity of C<sub>2</sub>H<sub>6</sub> over other C<sub>2</sub> gases. Besides, it exhibits the second highest acetylene uptake among all the reported HOF materials.**

Hydrogen-bonded organic frameworks (HOFs), also referred to as supramolecular organic frameworks (SOFs), are promising porous organic crystalline materials that are self-assembled through multiple hydrogen bonding interactions and other non-covalent interactions like  $\pi$ - $\pi$  stacking.<sup>1</sup> Over the past few years, HOFs have attracted increasing interests due to their potential applications in several areas including hydrocarbon separation,<sup>2</sup> CO<sub>2</sub> separation,<sup>3</sup> proton conduction,<sup>4</sup> molecular capture<sup>5</sup> and sensing.<sup>6</sup> In addition, compared with other porous materials, they show inherent advantages such as solution processibility, easy purification, and reproducibility by simple recrystallization. However, the multiple non-covalent interactions generally do not guarantee the stability of a porous framework, thus it is difficult to maintain a permanent porosity upon solvent removal. Consequently, we still have witnessed a few permanently porous HOFs to date.

Carboxylic acids play an important role in directing various supramolecular structures and C<sub>3</sub>-symmetric planar carboxylic acids are of interest because they can form hexagonal networks with voids through the formation of carboxylic acid dimers.<sup>1,7</sup> In fact, Hisaki and coworkers demonstrated that hexagonal

networks prepared with various C<sub>3</sub>-symmetric planar carboxylic acids can be used as structural motifs for porous HOFs.<sup>8</sup> Similarly, Zentner and coworkers recently reported a microporous HOF of C<sub>3</sub>-symmetric 4,4',4''-benzene-1,3,5-triyl-tris(benzoic acid) (H<sub>3</sub>BTB) via a hexagonal (6,3) honeycomb structural motif (Fig. 1a) in ethanol and propanols.<sup>9</sup> The  $\pi$ - $\pi$  stacking and eight-fold interpenetration of two-dimensional (2D) hexagonal sheets in this HOF-BTB generates one-dimensional (1D) solvent channel in the framework (Fig. 1b). Meanwhile, H<sub>3</sub>BTB is also known to form nonporous DMF solvate crystals (H<sub>3</sub>BTB-DMF) in *N,N*-dimethylformamide (DMF) where the carboxylic acids are masked by DMF molecules, prohibiting the formation of carboxylic acid dimers.<sup>10</sup>

Herein, we report single-component adsorption properties of light hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) in a robust microporous hydrogen-bonded organic framework HOF-BTB prepared from the H<sub>3</sub>BTB-DMF crystals in methanol. We also report efficient selective separations of C<sub>2</sub>/CH<sub>4</sub> binary gas mixtures in HOF-BTB. In our effort to find new self-assembled H<sub>3</sub>BTB structures, we found that H<sub>3</sub>BTB-DMF crystals readily recrystallize in methanol to



**Fig. 1** (a) 2D Hexagonal sheet with a unimodal 3-c hcb (honeycomb) topology in HOF-BTB formed through carboxylic acid dimers. The yellow ball represents a one-dimensional channel with a diameter of ca. 25 nm. (b) Solvent-accessible void space of HOF-BTB calculated with the probe radius of 1.4 Å.

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Fig. 2 (a) Powder X-ray diffraction patterns and (b) TGA curves of as-prepared and activated HOF-BTB crystals.

produce clear, transparent crystals suitable for single crystal X-ray diffraction. H<sub>3</sub>BTB is practically insoluble in methanol so that it is inefficient to attempt direct crystallization of H<sub>3</sub>BTB in methanol. Instead, our finding shows that soaking H<sub>3</sub>BTB–DMF crystals in methanol at 50 °C facilitates recrystallization of H<sub>3</sub>BTB–DMF crystals and the resulting crystals were found to exhibit essentially the same structure as the previously reported HOF-BTB by Zentner.<sup>9</sup> The bulk purity of HOF-BTB crystals is examined by powder X-ray diffraction (PXRD). An observed PXRD pattern of as-prepared HOF-BTB crystals is in good agreement to the simulated PXRD pattern obtained from the reported single crystal structure (Fig. 2a). The crystals of HOF-BTB were treated under high vacuum at 120 °C for 15 hours to generate an activated sample. The PXRD pattern of activated HOF-BTB crystals is identical to that of as-prepared HOF-BTB crystals, which means that the HOF-BTB crystals are very stable even after the removal of solvent molecules. Furthermore, we also found that the immersion of the activated crystals in water for 20 days has no effect on structural stability of the activated HOF-BTB crystals (Fig. S1, ESI†). Thermogravimetric analysis (TGA) curve indicates that HOF-BTB can be stable over 300 °C, resulted from the strong hydrogen bonding interactions as well as the consecutive strong  $\pi$ – $\pi$  stacking interactions. In addition, the TGA curve of the activated HOF-BTB sample reveals that no residual solvent molecules remain in the activated HOF-BTB (Fig. 2b).

The high stability and the large solvent-accessible void space of HOF-BTB allowed us to investigate its permanent porosity. The N<sub>2</sub> adsorption isotherm of the activated sample obtained at 77 K shows rapid N<sub>2</sub> uptake at relative low pressures ( $P/P_0 < 0.1$ ), which is typical for a Type I isotherm curve and is also typical characteristic for microporous solids (Fig. S2a, ESI†). The total uptake of N<sub>2</sub> at relative pressure  $P/P_0 = 1$  is 256 cm<sup>3</sup> g<sup>−1</sup>. The BET and Langmuir surface areas are estimated to be 955 and 1128 m<sup>2</sup> g<sup>−1</sup>, respectively. The mean pore diameter and total pore volume are determined to be 16.6 Å and 0.40 cm<sup>3</sup> g<sup>−1</sup>, respectively. In addition, we calculated micropore size distribution using nonlocal density functional theory (NLDFT) method (Fig. S2b, ESI†). HOF-BTB has a very narrow micropore size distribution of 1.1 to 1.5 nm diameter and a distribution peak at



Fig. 3 (a) The adsorption isotherms of HOF-BTB for C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> at 273 K and 295 K, respectively, and (b) loading dependent isosteric heat ( $Q_{st}$ ) of adsorption. The  $Q_{st}$  values were calculated based on adsorption isotherms at 273 K and 295 K by using the Virial method.

1.2 nm. The high surface area and total pore volume of HOF-BTB indicates that HOF-BTB possesses a highly porous structure. In order to evaluate the adsorption properties for small hydrocarbons, we performed the adsorption experiments for CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> at 273 K and 295 K, respectively. Fig. 3a shows their adsorption isotherms at both temperatures. All adsorption isotherms are fully reversible in HOF-BTB, indicating pure physisorption processes and easy regeneration of HOF-BTB after gas adsorption. At 273 K, HOF-BTB is the most effective adsorbent for C<sub>2</sub>H<sub>2</sub>, taking up C<sub>2</sub>H<sub>2</sub> up to 110.3 cm<sup>3</sup> g<sup>−1</sup> (4.92 mmol g<sup>−1</sup>) at 1 bar. The uptake capacities of HOF-BTB for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are also fairly high at 273 K and 1 bar, with the values of 85.3 cm<sup>3</sup> g<sup>−1</sup> (3.80 mmol g<sup>−1</sup>) and 95.4 cm<sup>3</sup> g<sup>−1</sup> (4.25 mmol g<sup>−1</sup>), respectively. Meanwhile, at 295 K and 1 bar, HOF-BTB shows a higher C<sub>2</sub>H<sub>6</sub> uptake (69.2 cm<sup>3</sup> g<sup>−1</sup>, 3.09 mmol g<sup>−1</sup>) than C<sub>2</sub>H<sub>2</sub> (64.3 cm<sup>3</sup> g<sup>−1</sup>, 2.87 mmol g<sup>−1</sup>) and C<sub>2</sub>H<sub>4</sub> (55.7 cm<sup>3</sup> g<sup>−1</sup>, 2.48 mmol g<sup>−1</sup>) uptakes. Among the C<sub>2</sub> hydrocarbons, C<sub>2</sub>H<sub>4</sub> has the lowest adsorption capacities at both temperatures. Interestingly, at 273 K, HOF-BTB adsorbs more of C<sub>2</sub>H<sub>6</sub> than the others at lower pressures. As the pressure increases, the adsorption amount of C<sub>2</sub>H<sub>2</sub> exceeds the adsorption amount of C<sub>2</sub>H<sub>6</sub>. At 295 K, on the other hand, the adsorption amount of C<sub>2</sub>H<sub>6</sub> exceeds the adsorption amount of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in the entire pressure range. This is remarkable because selective adsorption of C<sub>2</sub>H<sub>6</sub> over C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> is rarely observed in porous materials including MOFs and zeolites.<sup>11</sup> The higher affinity for C<sub>2</sub>H<sub>6</sub>, the largest among C<sub>2</sub> hydrocarbons, might suggest that the molecular sizes (C<sub>2</sub>H<sub>2</sub>, 3.32 × 3.34 × 5.70 Å; C<sub>2</sub>H<sub>4</sub>, 3.28 × 4.18 × 4.84 Å; C<sub>2</sub>H<sub>6</sub>, 3.81 × 4.08 × 4.82 Å)<sup>2e</sup> and/or kinetic diameters (C<sub>2</sub>H<sub>2</sub>, 3.3 Å; C<sub>2</sub>H<sub>4</sub>, 4.2 Å; C<sub>2</sub>H<sub>6</sub>, 4.4 Å)<sup>12</sup> of the C<sub>2</sub> hydrocarbons are less important in the adsorption of C<sub>2</sub> hydrocarbons. It might be likely that van der Waals interactions between C<sub>2</sub> hydrocarbons and HOF-BTB are more crucial factor for C<sub>2</sub> hydrocarbons adsorption than the molecular sizes of the gases at lower pressures. The van der Waals interaction is generally stronger as the molecular

Table 1 Comparison of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> uptakes in reported HOFs

HOFs	S <sub>ABET</sub> (m <sup>2</sup> g <sup>-1</sup> )	C <sub>2</sub> H <sub>2</sub> (cm <sup>3</sup> g <sup>-1</sup> )		C <sub>2</sub> H <sub>4</sub> (cm <sup>3</sup> g <sup>-1</sup> )		C <sub>2</sub> H <sub>6</sub> (cm <sup>3</sup> g <sup>-1</sup> )		Q <sub>st</sub> (kJ mol <sup>-1</sup> )			Ref.
		273 K	295 K	273 K	295 K	273 K	295 K	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	
SOF-1a	474	61	50	—	—	—	—	36.2	—	—	2f
HOF-1a	359	63	57	8.3	3.9	—	—	58.1	31.9	—	2e
HOF-3a	165	58	47	—	—	—	—	18	—	—	2c
HOF-4a	312	—	—	17.3	11.1	5.1	3.6	—	44	14	2d
HOF-5a	1101	182	102	—	—	—	—	27.6	—	—	3c
HOF-BTB	955	110.3	64.3	85.3	55.7	95.4	69.2	24.3	22.6	25.4	This work

size increases, so it can be expected that the largest molecule C<sub>2</sub>H<sub>6</sub> is the most efficient to interact with HOF-BTB. It should be noted that HOF-BTB achieves the highest C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> uptakes among all the HOF materials reported to date (Table 1). Compared with covalent organic frameworks (COFs), C<sub>2</sub>H<sub>6</sub> uptake of HOF-BTB is comparable to most reported COFs. ZnP-CTF-500<sup>13a</sup> and T-COF<sup>13b</sup> outperform the C<sub>2</sub>H<sub>6</sub> uptake capacity of HOF-BTB (Table S1, ESI†). Furthermore, C<sub>2</sub>H<sub>4</sub> uptake capacity of HOF-BTB surpasses those of the reported COFs such as DBA-3D-COF-1<sup>13c</sup> and MCOF-1.<sup>13d</sup> It also exhibits the second highest C<sub>2</sub>H<sub>2</sub> uptake among the HOF materials reported to date. Only HOF-5a exceeds the C<sub>2</sub>H<sub>2</sub> uptake amount of HOF-BTB. In contrast to the high C<sub>2</sub> hydrocarbons uptakes, much less amount of CH<sub>4</sub>, with the values of 14.5 and 8.7 cm<sup>3</sup> g<sup>-1</sup>, is adsorbed in HOF-BTB at 273 K and 295 K, respectively. The loading dependent isosteric heats (Q<sub>st</sub>) of adsorption of C<sub>2</sub> hydrocarbons are larger than that of CH<sub>4</sub>, which indicates that the stronger interactions between the C<sub>2</sub> hydrocarbons and the pore surfaces of HOF-BTB than that of CH<sub>4</sub> and HOF-BTB (Fig. 3b). For all the hydrocarbons, the values of Q<sub>st</sub> remain relatively constant through the whole loading ranges. High affinity for C<sub>2</sub>H<sub>6</sub> is also evident in the Q<sub>st</sub> value. As shown in Fig. 3b, the Q<sub>st</sub> value of C<sub>2</sub>H<sub>6</sub> is higher than those of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. Compared with other HOF materials, zero-coverage isosteric heats of adsorption for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> are smaller than those of reported HOFs (Table 1). These lower values of Q<sub>st</sub> suggest HOF-BTB would be a promising candidate for energy-saving separation of C<sub>2</sub> hydrocarbons/CH<sub>4</sub> mixtures.

To analyse the binary gas mixture separation abilities, the pure single-component isotherms were fitted with the Langmuir-Freundlich isotherm model (Fig. S3–S6, ESI†).<sup>14</sup> Then, ideal adsorbed solution theory (IAST)<sup>15</sup> was used to predict the separation selectivity of binary gas mixtures (50:50) at 273 K and 295 K (Tables S2 and S3, ESI†). The IAST predicts that HOF-BTB would allow selective separations of C<sub>2</sub> hydrocarbons over CH<sub>4</sub>. At both temperatures, C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> gas mixture shows the highest selectivity values among the C<sub>2</sub> hydrocarbon/CH<sub>4</sub> gas mixtures. The observed C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> selectivity at 295 K (14) is comparable with the IAST-predicted C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> selectivities for N-COF (18), P-COF (12) and T-COF (10) at 298 K.<sup>13b</sup> The IAST also predicts the fairly good separation selectivities for C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> binary gas mixtures (Fig. 4a and b). Although the IAST can predict the mixture behaviours in terms of adsorption equilibrium, it cannot reflect the mixture behaviours in terms of adsorption kinetics, which cannot be ignored in real adsorption separation processes. Hence, we performed dynamic breakthrough experiments to evaluate the potential of



Fig. 4 The IAST-predicted binary gas mixture separation selectivities of HOF-BTB at (a) 273 K and (b) 295 K. The experimental breakthrough curves at three consecutive cycles for a packed-bed filled with HOF-BTB pellets at 298 K and total hydrocarbon pressures of 0.5 bar: (c) equimolar C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> mixture (20 ml min<sup>-1</sup>); (d) equimolar C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> mixture (20 ml min<sup>-1</sup>). For each run, 20 ml min<sup>-1</sup> of He flow was mixed with equimolar hydrocarbon mixture.

HOF-BTB for the adsorptive separation of C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> mixtures under dynamic flow conditions.<sup>16</sup> Unfortunately, we could not perform the dynamic breakthrough experiment for C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> mixture due to the University's safety regulations. Fig. 4c and d show the experimental breakthrough curves of C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> mixtures on a column packed with HOF-BTB pellets. In the case of C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> separation, CH<sub>4</sub> elutes first from the column, whereas C<sub>2</sub>H<sub>6</sub> is strongly retained. This indicates that under mixture flow condition, HOF-BTB primarily adsorbs C<sub>2</sub>H<sub>6</sub> rather than CH<sub>4</sub>. Similarly, the breakthrough curves for C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> mixture exhibit selective C<sub>2</sub>H<sub>4</sub> adsorption over CH<sub>4</sub>. For all cases, breakthrough curves of weaker adsorbate CH<sub>4</sub> show “roll-up” behaviours, which are normally explained as a result of the competitive adsorption between two adsorbate species. Although the weaker adsorbate molecules initially occupy the adsorption sites in the column, some of the adsorbed molecules are replaced by stronger adsorbate molecules.<sup>17</sup> These experimental breakthrough results indicate that HOF-BTB can effectively separate C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> mixtures under dynamic flow conditions. Easy regeneration of the used adsorbent is an essential consideration for practical operation of an adsorptive separation process. After performing a breakthrough experiment, we regenerated

the column by simply purging it for 10 min under a He flow of 40 ml min<sup>-1</sup> without heating the column. As displayed in Fig. 4c and d, essentially identical breakthrough curves were produced during the three consecutive cycles for both gas mixtures. This is remarkable because the regenerations were performed under mild conditions. This mild regeneration condition could be attributed to the relatively small  $Q_{st}$  values for C<sub>2</sub> hydrocarbons.

In summary, we have reported a highly robust microporous hydrogen-bonded organic framework HOF-BTB, which shows the higher adsorption capacities for C<sub>2</sub> hydrocarbons at 273 K and 295 K. The adsorption amounts of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> reach the highest values among all the reported HOFs, while C<sub>2</sub>H<sub>2</sub> uptake amount reaches the second highest values among all the HOFs. Breakthrough experiments reveal that HOF-BTB can selectively separate C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> from CH<sub>4</sub> under dynamic mixture flow conditions.

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## Conflicts of interest

There are no conflicts to declare.

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