

A highly stable metal-organic framework with well-matched pore cavity for efficient acetylene separation

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Abstract

Acetylene, an important petrochemical feedstock, is the starting chemical to produce many polymer products. Separating C₂H₂ from its by-product mixtures is still an energy-consuming process and remains challenging. Here, we present a metal-organic framework[Zn₂(bpy)(btec)], with a desirable pore geometry and highly stable framework, which demonstrated a high separation performance of C₂H₂ from simulated mixtures. With the desirable pore dimension and hydrogen bonding sites, Zn₂(bpy)(btec) shows by far the both highest C₂H₂/CO₂ and C₂H₂/CO₂ uptake ratios, very high adsorption selectivities and moderately C₂H₂ uptake of 93.5 cm³*cm⁻³ under 298 K and 1 atm. Not only straightforwardly produced high purity of C₂H₄, but also recovered high purity of C₂H₂ (>98%) in the regeneration process (>92% recovery). More notably, Zn₂(bpy)(btec) can be straightforwardly synthesized at a large scale under environmentally friendly conditions, and its good water/chemical stability, thermostability, and cyclic stability highlight the promise of this molecular sieving material for industrial C₂H₂ separation.

Introduction

Both acetylene (C₂H₂) and ethylene (C₂H₄) are widely used as basic chemical materials in the petrochemical industry. The production of C₂H₄ is from the fractional distillation of petroleum, which usually coexists with 1% C₂H₂.¹⁻³ In addition, carbon dioxide (CO₂) appears in the production of C₂H₂ by the thermal cracking process.^{4,5} Thus, selectively separation of C₂H₂ from C₂H₄/C₂H₂ or CO₂/C₂H₂ mixtures is important to meet the requirement of polymer-grade C₂H₄ and high-purity C₂H₂ in petrochemical industries.^{6,7} However, considering the small difference of molecular dimension of C₂H₂ (3.3 Å×3.3 Å×5.7 Å), C₂H₄ (3.3 Å×4.2 Å×4.8 Å) and CO₂ (3.2 Å×3.3 Å×5.4 Å), as well as their similar physical properties, it is a very challenging to separate C₂H₂ from C₂H₄ or CO₂.^{8,9} Although the cryogenic distillation for C₂H₂ separation is a very mature operation, it requires huge capital and energy input primarily due to the requirement of low temperature operation.¹⁰⁻¹² It is necessary to develop a more efficient separation process such as porous materials based adsorptive separation with relatively low energy consumption and favorable regeneration.^{13,14}

Porous materials, such as zeolites, metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs), with porous structures, huge specific surface area, and designable frameworks have received extensive attention in recent years,¹⁵⁻¹⁷ as they present great potential to revolutionize some industrial applications, especially in separation, purification, and the storage of gases.¹⁸⁻²⁰ An ideal adsorbent for C₂H₂ separation is expected to be chemically stable, be able to capture trace C₂H₂ from C₂H₄ or other feed gas mixtures, and be able to regenerate easily. In recent years, a number of porous materials have been reported for C₂H₂/C₂H₄ separation through a synergistic approach of pore tuning and functionalization.^{21,22} In 2016, Xing's group¹⁴ reported the anion-pillared hybrid porous materials SIFSIX-2-Cu-i, with the specific binding

sites and suitable pore space to effectively overcome the trade-off effect for C_2H_2 separation. In 2017, the first case of an ideal molecular sieve for C_2H_2/C_2H_4 was found called SIFSIX-14-Cu-i (UTSA-200)²³, which with the ultrafine tuning of its pore size (3.4 Å), can not only effectively block C_2H_4 but also adsorb high amounts of C_2H_2 , thus setting up the benchmarks for both C_2H_2 adsorption and C_2H_2/C_2H_4 separation. However, UTSA-200 can also take up a large amount of CO_2 or C_3H_4 at the same conditions,^{24,25} which significantly restricts its separation performance for C_2H_2/CO_2 and other multicomponent gases mixtures.

Traditional research on porous materials for gas separation mainly focused on those porous structures in the one-dimensional channel (Figure 1a) or cage type pore (Figure 1b). During our exploration of porous materials for C_2H_2 separation, we realized that one unique class of porous MOFs, which have interlayer pore cavities (Figure 1c)^{26,27} in their layered structures, had been overlooked. Compared to the traditional pore types, this kind of pore cavity has a narrow pore space, may exhibit multiple host-guest interactions with gas molecules, and thus could be utilized for selective separation of some specific gas component.

Herein, we report an ultramicroporous MOF ($Zn_2(bpy)(btec)$)^{28,29} that incorporates two-dimensional interlayer cavities, which enabled the full entrance of C_2H_2 and effectively blocked the C_2H_4 and CO_2 , thus exhibiting the benchmark C_2H_2/C_2H_4 and C_2H_2/CO_2 uptake ratios. According to the breakthrough experiments, C_2H_2 can be directly removed from C_2H_2/C_2H_4 (1/99, v/v) or C_2H_2/CO_2 (50/50, v/v) mixtures and high-purity C_2H_4 (>99.9999 %), CO_2 (>99.999 %), and C_2H_2 (>98%) can be obtained in the single separation process. More importantly, $Zn_2(bpy)(btec)$ can be straightforwardly synthesized at the kilogram scale under room temperature in an aqueous solution. Its good chemical stability, water stability, thermal stability, and cyclic stability are well satisfied requirements of industrial application.

Experimental

Synthesis of $[Zn_2(bpy)(btec)(H_2O)_2] \cdot 2H_2O$

Hydrothermal synthesis

The synthesis of the crystal sample was performed following a reported method with minor modifications.²⁸ 0.1097 g (0.6 mmol) Zinc acetate, 0.1091 g (0.5 mmol) Pyromellitic dianhydride, 0.0781 g (0.5 mmol) 4,4'-Bipyridine and 10 mL deionized water were well mixed in a 25 mL Teflon-lined autoclave. Crystallization was carried out at 180 °C for 5 days. Then the autoclaves are cooled to room temperature. The crystals were filtered off, washed with hot water/ethanol mixture (1:1) for three times, then dried in air (yield: 0.1306 g, 76.1% based on Zinc acetate).

Rapid room temperature synthesis

0.1527 g (0.7 mmol) Pyromellitic dianhydride, 0.1093 g (0.7 mmol) 4,4'-Bipyridine and 5 mL deionized water were mixed in a 20 mL sealed vial with stirring at ambient temperature for 10 min, then 200 μ L $NH_3 \cdot H_2O$ (25%) was added into the vial. After the above mixture was thoroughly mixed, a 5 mL aqueous solution of 0.2569 g (1.4 mmol) Zinc acetate was added with stirring for 10 min. Then the products were filtered off, washed with hot water/ethanol mixture (1:1) three times, then dried in air (yield: 0.3288 g, 82.1% based on 4,4'-Bipyridine).

Large-scale synthesis

Synthesis at the 1000-times scale was carried out as follows. White powder sample was obtained by mixing an aqueous solution (0.65 L) of Zinc acetate ($Zn(Ac)_2$, 1.64 mol, 0.3 kg) with an aqueous solution (1.10 L) of Pyromellitic dianhydride (0.7 mol, 0.1528 kg), 4,4'-Bipyridine (0.7 mol, 0.1094 kg) and 4 mL $NH_3 \cdot H_2O$ (25%). The crystallization was finished at ambient temperature after stirring for 30 min, the sample was filtered, washed thoroughly with water/ethanol and dried under air, with a yield of 0.3236 kg (80.9% based on 4,4'-Bipyridine).

Characterization

The crystallinity and phase purity of the materials were measured by powder X-ray diffraction (PXRD) on

a Bruker D8 ADVANCE X-ray diffractometer with Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation operated at 40 kV and 40 mA. Scanning was performed over the 2θ range of $5-50^\circ$ at $4^\circ/\text{min}$. Scanning electron microscopy (SEM) images were obtained using a Hitachi SEM (SU8010, Hitachi, Japan) equipped with a Horiba X-Max 50 EDX system. The TGA of the samples was collected on a thermal analyzer (NETZSCH, STA 449 F5) at a heating rate of $5^\circ\text{C}/\text{min}$ under air atmosphere. CO_2 adsorption/desorption isotherms were obtained using an ASAP 2460 Surface Area and Porosity Analyzer at 273 K.

Adsorption experiment

The purities of the acetylene, ethylene and carbon dioxide were higher than 99.99%. Their adsorption isotherms were collected with an Intelligent Gravimetric Analyser (IGA 001, Hiden, UK). Samples were activated under vacuum at 150°C overnight or until no further weight loss was observed. Adsorption equilibrium data was collected once a stable pressure (more than 20 adsorption points were recorded from 0 to 1 bar) and weight was maintained for at least 40 min to reach an adsorption equilibrium at each point along the isotherm.

Breakthrough tests

The breakthrough experiments for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (1/99, v/v) mixtures were carried out at a flow rate of 1.25 mL/min (298 K, 1.01 bar). In the separation experiment, $\text{Zn}_2(\text{bpy})(\text{btec})$ sample (3.0575 g) was packed into $\Phi 4 \times 275 \text{ mm}$ stainless steel column, and the column was activated under reduced pressure at 150°C overnight. The experimental set-up consisted of two fixed-bed stainless steel reactors. One reactor was loaded with the adsorbent, while the other reactor was used as a blank control group to stabilize the gas flow. The horizontal reactors were placed in a temperature-controlled environment, maintained at 298 K. The flow rates of all gas mixtures were regulated by mass flow controllers, and the effluent gas stream from the column was monitored by gas chromatography. Prior to the breakthrough experiment, we activated the sample by flushing the adsorption bed with helium gas for 2 hours at 150°C . Subsequently, the column was allowed to equilibrate at the measurement rate before we switched the gas flow.

Results and Discussion

Structure characterization

The synthesized $[\text{Zn}_2(\text{bpy})(\text{btec})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ has a two-dimensional structure, each layer is formed by Zn coordinated with bpy and btec, and H_2O molecules between layers provide multiple hydrogen bonding sites to connect the two layers²⁸. In this work, we investigated the rapid synthesis and large-scale synthesis processes of these materials, the PXRD patterns of these samples were matched well with the simulated one, and the SEM images show that the samples have relatively high crystallinity (Figure S1 and S2). After guest removal, $\text{Zn}_2(\text{bpy})(\text{btec})$ still shows porosity with the pore cavities of $3.6 \text{ \AA} \times 3.8 \text{ \AA} \times 6.6 \text{ \AA}$ (Figure 2a, b). These cavities match well with the size and shape of C_2H_2 ($3.3 \text{ \AA} \times 3.3 \text{ \AA} \times 5.7 \text{ \AA}$), suggesting a potential application for C_2H_2 separation.

The porosity in $\text{Zn}_2(\text{bpy})(\text{btec})$ was established by CO_2 sorption at 273 K. As shown in Figure S3, the CO_2 adsorption isotherms slowly increase with increasing pressure. By using the Dubinin-Radushkevich equation, the surface area of $\text{Zn}_2(\text{bpy})(\text{btec})$ was calculated to be $397 \text{ m}^2/\text{g}$, and its pore-size is around 3.6 \AA (Figure S3). The pore cavity between two layers is about $3.6 \text{ \AA} \times 3.8 \text{ \AA} \times 6.6 \text{ \AA}$, which is slightly larger than the size of C_2H_2 , CO_2 and smaller than C_2H_4 , thus could be used for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2/\text{CO}_2$ separation.

Single-gas sorption isotherm

Pure component equilibrium adsorption isotherms for C_2H_2 , C_2H_4 and CO_2 were measured at 298 K up to 1 bar, as presented in Figure 3a. The C_2H_2 uptake on $\text{Zn}_2(\text{bpy})(\text{btec})$ reached $93.5 \text{ cm}^3 \text{ cm}^{-3}$ at 298 K and 1 bar, significantly higher than that of C_2H_4 and CO_2 at the same conditions. Notably, through size sieving by the appropriate aperture, $\text{Zn}_2(\text{bpy})(\text{btec})$ presents the C_2H_2 uptake of $93.5 \text{ cm}^3 \text{ cm}^{-3}$, very low C_2H_4 uptake of $9.1 \text{ cm}^3 \text{ cm}^{-3}$ and low CO_2 uptake of $28.9 \text{ cm}^3 \text{ cm}^{-3}$ (298 K and 1 bar), giving an excellent uptake

ratio of C_2H_2 over C_2H_4 (10.31) and CO_2 (3.23), which are the highest values among the indicated MOFs (Supporting information, Table S2 and S3).

To compare the separation properties of $Zn_2(bpy)(btec)$ with other top-performing MOFs, its ideal adsorbed solution theory (IAST) selectivity of C_2H_2 over C_2H_4 and CO_2 were calculated on their single-component isotherms (Figure 3a). The gas mixtures were selected as C_2H_2/C_2H_4 (1:99, v/v) and C_2H_2/CO_2 (50:50, v/v) at a total gas pressure of 1 bar and 298 K, to mimic the composition of the industrial purification process. As seen in Figure 3b, c, $Zn_2(bpy)(btec)$ exhibits an extraordinarily high selectivity of over 107.8 for the C_2H_2/C_2H_4 mixture and 33.3 for the C_2H_2/CO_2 mixture, notably higher than the previous benchmark SIFSIX-2-Cu-i (44.54)¹⁴, M'MOF-3a (24.03)³⁰, CPL-1 (26.8)³¹ and ELM-12 (14.8)³² for C_2H_2/C_2H_4 separation, and FeNi-M'MOF (24)³³ HOF-3a (21)³⁴, UTSA-74 (9)³⁵, TIFSIX-2-Cu-i (6.5)³⁶ and for C_2H_2/CO_2 separation.

In industrial applications, energy cost in the regeneration process is also an unavoidable problem and should be taken into consideration. The interactions between the adsorbents and C_2H_2 are evaluated by calculating the isosteric heats of adsorption (Q_{st}), which is measured from the single component isotherms at different temperatures (Figure 3d). The calculated Q_{st} of $Zn_2(bpy)(btec)$ at zero coverage for C_2H_2 is 28.7 kJ/mol (Figure S4), which is much lower than those values reported in other MOFs with open metal sites such as MOF-74 series (47 kJ/mol for Fe-MOF-74).¹² Thus, the molecular sieving based adsorption not only avoided excessive temperature fluctuations during the adsorption process but also decreased the cost and energy requirement in the regeneration process, which indicates advantages of $Zn_2(bpy)(btec)$ in real industrial applications. In addition, comparing with other top-performing materials (Table S2, S3), $Zn_2(bpy)(btec)$ exhibits the lowest total C_2H_4 and CO_2 loading in normal conditions (Figure 3e), and less co-adsorption will lead to a higher C_2H_2 purity in the generation process. Besides, this material exhibits the highest C_2H_2/C_2H_4 uptake ratio (10.31) and C_2H_2/CO_2 uptake ratio (3.23), as well as extraordinarily high selectivity (107.8, 33.3) (Figure 3f), which makes it one of the most promising materials for the efficient C_2H_2 separation from C_2H_4 or CO_2 mixtures.

Breakthrough separation

Furthermore, we performed actual breakthrough experiments on $Zn_2(bpy)(btec)$ to establish the feasibility of C_2H_2/C_2H_4 and C_2H_2/CO_2 separations, in which C_2H_2/C_2H_4 (v/v, 1/99) and C_2H_2/CO_2 (v/v, 50/50) mixtures were used as feeds to mimic the industrial process conditions (Figure 4 and S6). As shown in Figure 4a, c, only after several minutes, C_2H_4 or CO_2 first eluted through the bed to yield a polymer-grade gas and the purity of C_2H_4 monitored at the outlet was >99.9999%. Then, after a long period of time (130 min for C_2H_2/C_2H_4 , 50 min for C_2H_2/CO_2), C_2H_2 broke through from the adsorption bed. During this process, C_2H_2 was clearly captured by $Zn_2(bpy)(btec)$, with the concentration of the impurities decreased to lower than 1 ppm for C_2H_4 and 10 ppm for CO_2 . Polymer-grade C_2H_4 and high purity of CO_2 were directly collected at the outlet. From the desorption curves in Figure 4b, d, it can be found that adsorbates were fully desorbed from the materials in 20 minutes. Due to the high C_2H_2/C_2H_4 and C_2H_2/CO_2 uptake ratios and selectivities, a high purity of C_2H_2 over 98.5 % (b) or 92.5 % (d) were generated, respectively.

The kinetic ad/desorption rate of C_2H_2 was also investigated in Figure S8 and S9, showing that $Zn_2(bpy)(btec)$ has a high kinetic ad/desorption rate, and therefore that C_2H_2 can be saturated or fully desorbed in about ten minutes. In addition, the desorption and recycling measurements revealed that this material can maintain its C_2H_2 capture ability and high selectivity in several repeated adsorption and separation cycles (Figure 4b, d, and S7). The breakthrough time remains almost unchanged during five cyclic breakthrough experiments, confirming the good recyclability of this material for the C_2H_2/C_2H_4 and C_2H_2/CO_2 separation.

Generally, in the real production process, the feed gas also contains some other components, which is a tremendous challenge in the recovery of C_2H_2 from such refinery gas. Therefore, we investigated the single-component adsorption isotherms of some main components of refinery gas (CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_4 , C_3H_6 and C_3H_8) and common gas components (CO_2 , H_2 , N_2 and O_2) as seen in Figure 5 a, b. Based

on the well-matched pore cavity of $\text{Zn}_2(\text{bpy})(\text{btec})$, this material selectively adsorbs C_2H_2 and blocks most other molecules to achieve an admirable sieving effect (Fig. 4a). The uptakes of most of the gases were below $10 \text{ cm}^3\text{cm}^{-3}$ at 1 bar and 298 K. Furthermore, the gas mixtures separation process was carried out on this molecular sieve material for the recovery of C_2H_2 from the simulated steam cracking mixtures. As can be seen from the breakthrough curves, most of the mixture gases eluted through the fixed bed quickly and a trace amount of C_2H_2 was totally adsorbed during the long retention time. In the generation process, the adsorbent was fully desorbed in 20 minutes and obtained high purity C_2H_2 ($> 98\%$). The multi-component separation and desorption tests show strong evidence of the efficient C_2H_2 separation ability of $\text{Zn}_2(\text{bpy})(\text{btec})$ materials, which has initiated the promise of MOF materials for this very important industrial application.

Grand canonical Monte Carlo simulations

To have a better insight into the excellent C_2H_2 separation ability of $\text{Zn}_2(\text{bpy})(\text{btec})$, GCMC simulations were performed to structurally elucidate how C_2H_2 molecules are adsorbed in this MOF.^{35,37,38} The calculated binding sites of C_2H_2 are shown in Figure 6. The C_2H_2 molecules are preferentially located in the pore cavities between the layers of $\text{Zn}_2(\text{bpy})(\text{btec})$. The $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds of each C_2H_2 molecule interacts with two oxygen molecule with a distance of $2.2\sim 2.33 \text{ \AA}$, which are much shorter than the sum of the van der Waals radii of oxygen (1.52 \AA) and hydrogen (1.20 \AA) atoms, indicating a relatively strong interaction.

Scalable synthesis and stability

In order to promote the industrialization of MOFs materials, it is the general trend to produce stable MOF materials at low costs and with simple operation processes. Therefore, a water-based and scalable synthesis was developed at room temperature for the large-scale preparation of $[\text{Zn}_2(\text{bpy})(\text{btec})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$.³⁹ As shown in Figure 7a, only by mixing the metal salt and the ligands in aqueous solution and stirring for 30 minutes, then filtering and drying, can we obtain more than 320 g of product at room temperature. TGA and DSC were tested on $[\text{Zn}_2(\text{bpy})(\text{btec})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ to explore its thermal stabilities (Figure 7b). Below 150 degC , the initial weight loss of $\sim 14\%$ was accounted for by the loss of water molecules, and then $\text{Zn}_2(\text{bpy})(\text{btec})$ can stabilize up to about 410 degC before its decomposition.

Besides, the adsorbents require relatively high thermostability to keep a long operation lifetime, The real C_2H_2 -relevant separation tasks are typically implemented under more extreme conditions, typically containing a trace amount of water and acidic gases.⁴⁰ Herein, the structural stability of $\text{Zn}_2(\text{bpy})(\text{btec})$ was examined in detail. As depicted in Figure 7c, d, the PXRD patterns of those materials treated under extreme conditions (acid, base, or boiling water) coincide with those of pristine samples, which indicates that its structure has no framework collapse and still retains its crystallinity. After such treatment, its C_2H_2 adsorption is largely maintained, comparable to the initial value (Figure S11), which demonstrated that this material is highly stable in the acidic/basic solutions ($\text{pH}=1\sim 13$), even in the water up to 120 degC . The water and thermal stability of $\text{Zn}_2(\text{bpy})(\text{btec})$ has been superior to most C_2H_2 -separated MOFs (Figure 7e). Its exceptionally high stability is due to its dense structure forming by the strong multiple hydrogen bonding interactions and offset π - π stacking interactions (Figure S12).

Conclusion

In summary, we have identified an abnormally layered MOF ($\text{Zn}_2(\text{bpy})(\text{btec})$) for the highly efficient separation of C_2H_2 from C_2H_4 and CO_2 mixtures. The interlayer pores cavity can exactly adsorb C_2H_2 and block C_2H_4 or the other C1-C3 hydrocarbons, resulting in by far both the highest $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2/\text{CO}_2$ uptake ratios (10.31, 3.23) and superior IAST selectivities (107.8, 33.3) among the rigid MOFs. Through size sieving by the appropriate aperture, this MOF achieves efficient separation of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (1/99, v/v), $\text{C}_2\text{H}_2/\text{CO}_2$ (50/50, v/v) and simulated steam cracking mixtures, finally obtaining a polymer grade of C_2H_4 (99.9999%) and a high purity of C_2H_2 (98%). Furthermore, the synthesis of this material is easily scale-up at an environmentally friendly condition and its structure can be maintained in solutions with a wide range of pH ($1\sim 13$) as well as in the boiling (373 K) water. These desirable properties of $\text{Zn}_2(\text{bpy})(\text{btec})$ demonstrated that this new MOF material is a promising adsorbent, which has great potential to be used for the practical

C₂H₂ production process.

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Conflict of interest

The authors declare no conflict of interest.

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Figure captions:

Figure 1. Schematic illustration of the representative porous structures in MOFs: (a) One-dimensional channel, (b) Cage type pore, and (c) Interlayer cavity.

Figure 2. (a, b) The crystal structures and channel shapes of Zn₂(bpy)(btec). (c) Comparison of molecular size difference of C₂H₂ and C₂H₄ (Color code: Zn, green; O, red; N, light blue; C, gray).

Figure 3. (a) Single-component sorption isotherms of C_2H_2 , C_2H_4 , and CO_2 at 298 K for $Zn_2(bpy)(btec)$. (b, c) IAST selectivities of C_2H_2/C_2H_4 (1/99) and C_2H_2/CO_2 (50/50) mixtures on some benchmark materials. (d) Adsorption isotherms of C_2H_2 for $Zn_2(bpy)(btec)$ at 288-308 K. (e) C_2H_4 and CO_2 uptakes of different MOF materials at 1 bar and 298 K. (f) Comparison of C_2H_2/C_2H_4 (1/99) and C_2H_2/CO_2 (50/50) IAST selectivities and C_2H_2 - C_2H_4 - CO_2 uptake ratios of different adsorbents at 1 bar and 298 K.

Figure 4. Experimental breakthrough (298 K, 1 bar) and desorption (333 K, 1 bar) curves for C_2H_2/C_2H_4 (1/99) (a, b) and C_2H_2/CO_2 (50/50) (c, d) mixtures on $Zn_2(bpy)(btec)$.

Figure 5. (a, b) Single-component adsorption isotherms of CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_4 , C_3H_6 , C_3H_8 , CO_2 , H_2 , O_2 , and N_2 in $Zn_2(bpy)(btec)$ at 298 K. (c, d) Multi-component breakthrough (298 K, 1 bar) and desorption (333 K, 1 bar) curves for $CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_6/C_3H_8/CO_2/H_2$ (30/1/10/25/10/10/1/13) mixtures on $Zn_2(bpy)(btec)$.

Figure 6. Calculated C_2H_2 molecule binding sites in $Zn_2(bpy)(btec)$ by GCMC simulation. Color code: Zn (green), O (red), N (light blue), C (gray), and C_2H_2 (blue).

Figure 7. (a) Scale-up synthesis of $[Zn_2(bpy)(btec)(H_2O)_2] \cdot 2H_2O$. (b) TG and DSC curves for as-synthesized $[Zn_2(bpy)(btec)(H_2O)_2] \cdot 2H_2O$. (c, d) PXRD patterns of $[Zn_2(bpy)(btec)(H_2O)_2] \cdot 2H_2O$ after different treatment. (e) Comparison of the heat and water stability of some benchmark MOF materials.

Figure 1

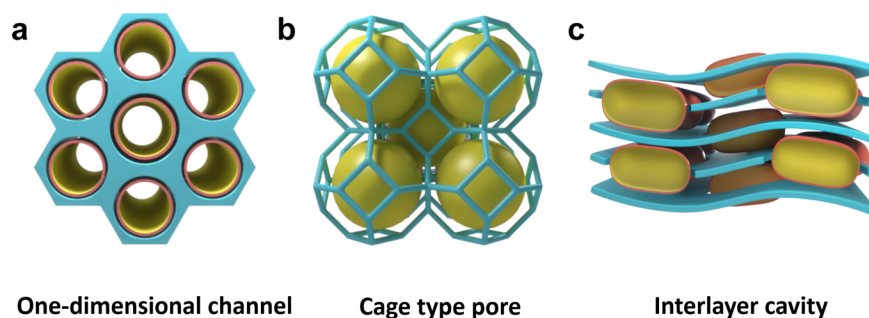


Figure 2

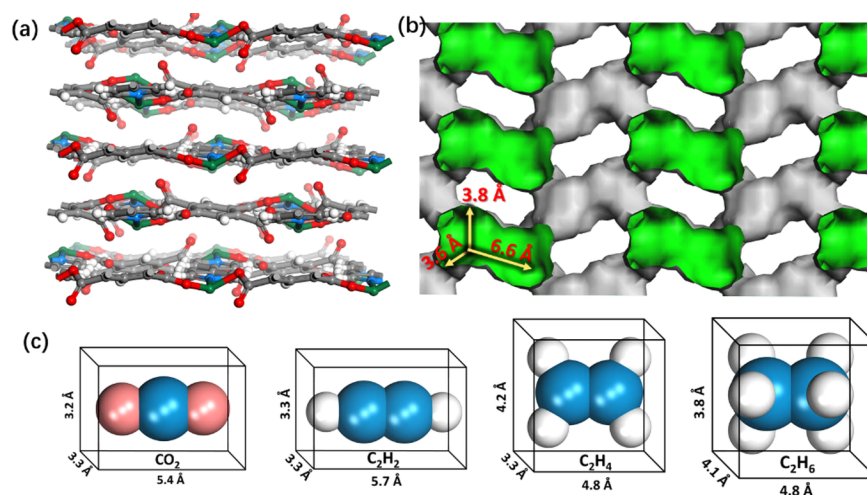


Figure 3

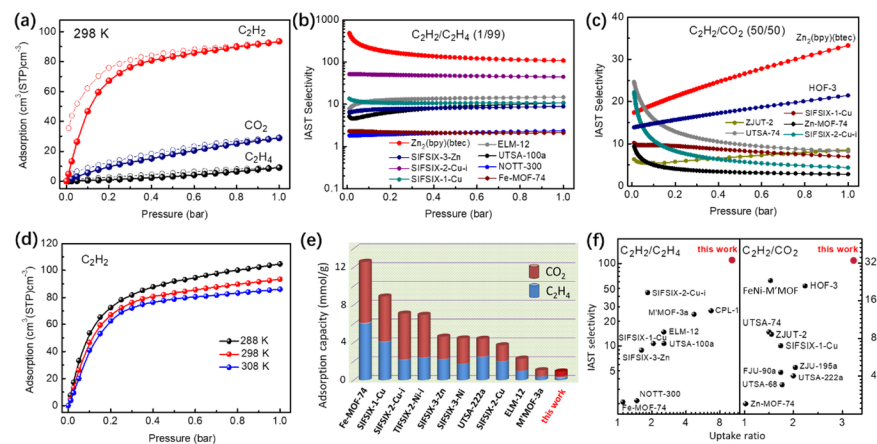


Figure 4

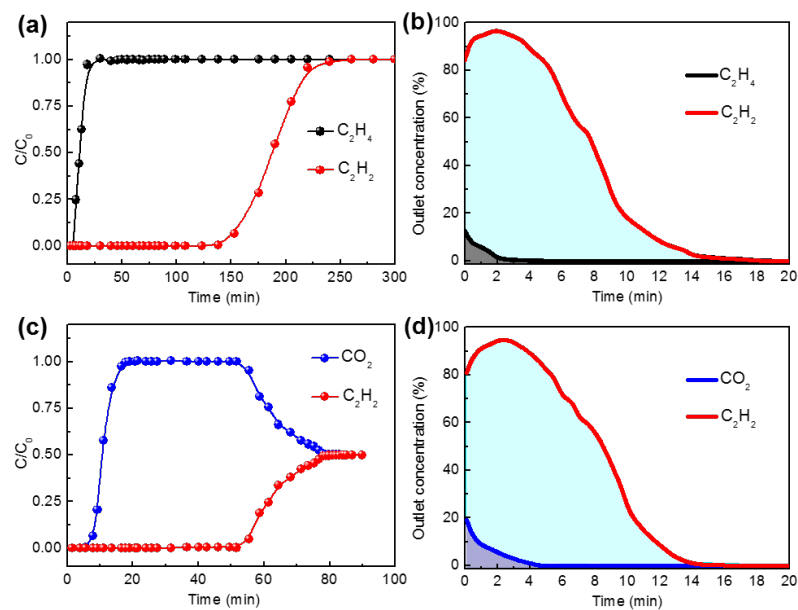


Figure 5

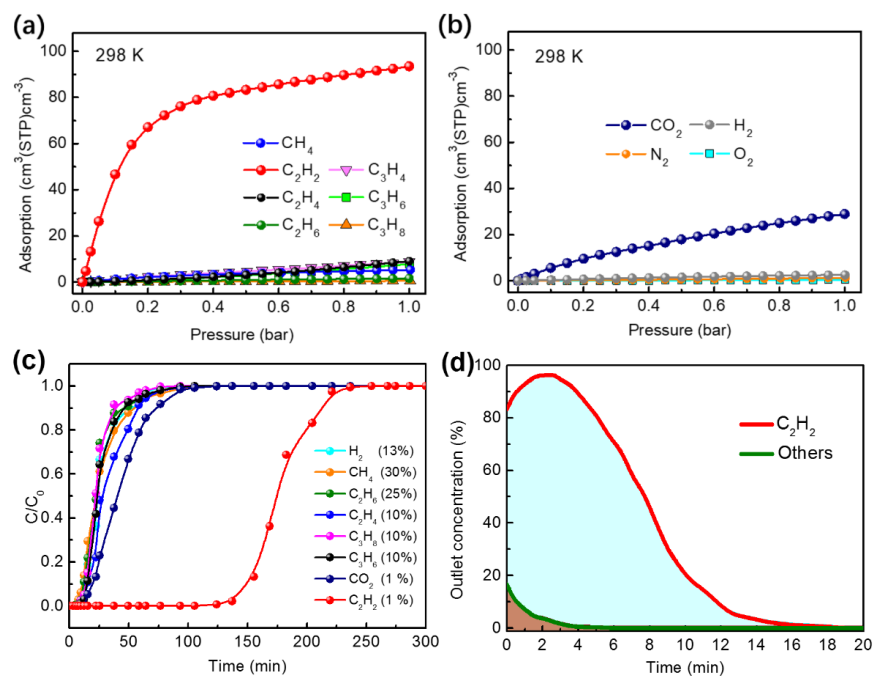


Figure 6

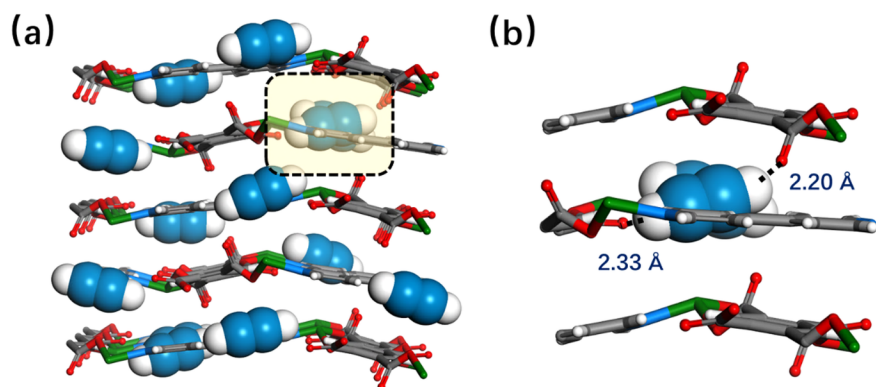
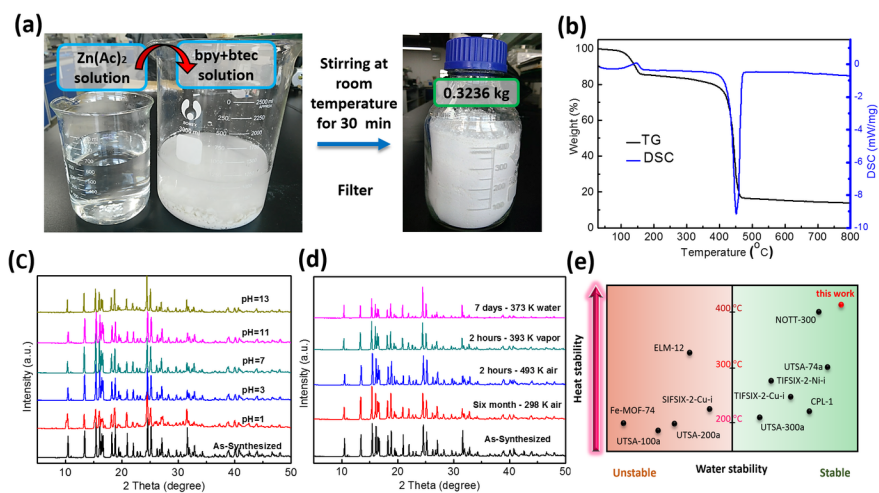


Figure 7



TOC Art

