


## RESEARCH ARTICLE

# Interpenetrated Three-Dimensional Covalent Organic Framework for Selective Adsorption of C<sub>2</sub>H<sub>2</sub> Over CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>

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**Keywords:** dynamic breakthrough | gas separation | in situ FTIR | three dimensional COFs

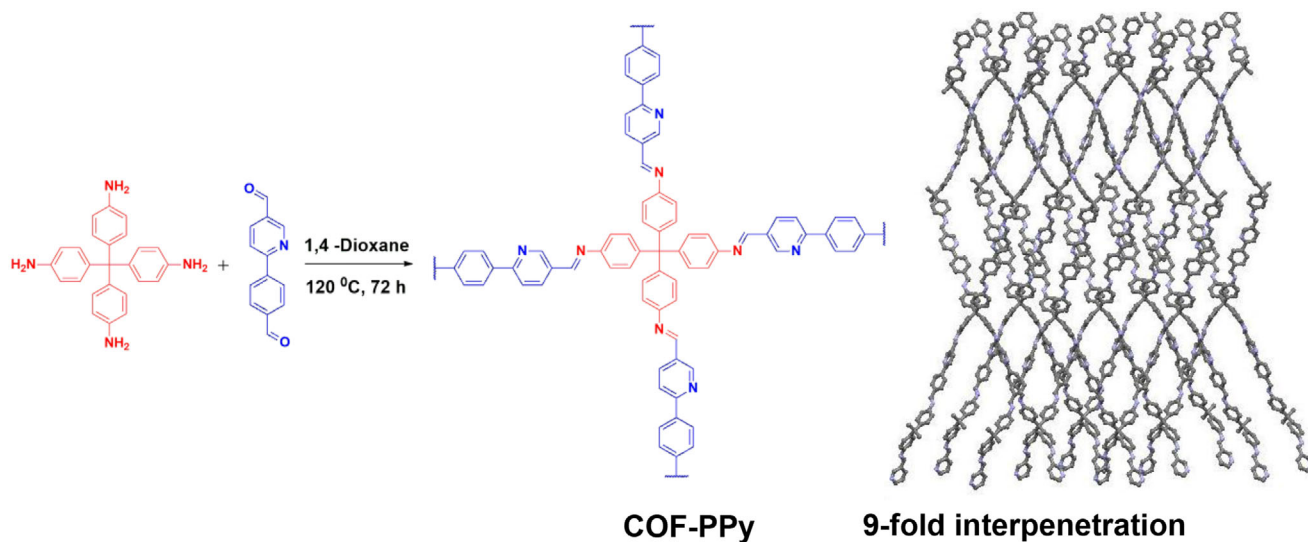
## ABSTRACT

Selective separation of acetylene (C<sub>2</sub>H<sub>2</sub>) from carbon dioxide (CO<sub>2</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>) mixtures is critical in the petrochemical industry due to their similar size and physicochemical properties. Developing three-dimensional porous covalent organic frameworks (3D COFs) remains challenging in this context. In this work, a non-symmetrical 2-phenyl pyridine based three-dimensional covalent organic framework (**COF-PPy**) has been synthesized, which features a rare dia-C9 fold interpenetrated structure as suggested by computational simulations. **COF-PPy** exhibits high acetylene (C<sub>2</sub>H<sub>2</sub>) adsorption capacity (4.5 mmol g<sup>-1</sup> at 298 K), as well as excellent separation and purification performance for C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures. The *in situ*-FTIR studies suggest that the multi-point interactions between nitrogen centers of **COF-PPy** and H-C≡CH (COF-Pyridine-N⋯H-C≡C-H and COF-imine-N⋯H-C≡CH) account for the higher affinities for C<sub>2</sub>H<sub>2</sub> over other gases. Furthermore, dynamic breakthrough studies reveal that **COF-PPy** can be employed as an effective adsorbent for the efficient separation of C<sub>2</sub>H<sub>2</sub> from CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. In addition, **COF-PPy** exhibits lower heat of adsorption (Q<sub>st</sub>) values with high adsorption capacity for C<sub>2</sub>H<sub>2</sub> as compared to previously reported C<sub>2</sub>H<sub>2</sub>-selective adsorbents, indicating less regeneration energy. Our work therefore provides some new avenues for the design and construction of 3D COFs for efficient C<sub>2</sub>H<sub>2</sub> capture and separation.

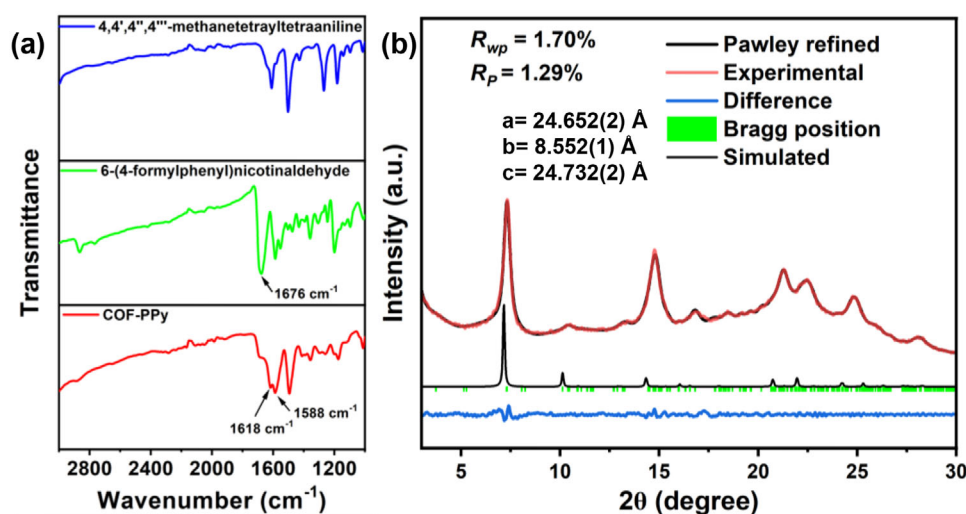
## 1 | Introduction

As an emerging class of crystalline nanoporous materials, covalent organic frameworks (COFs) have garnered a lot of interest because of their high surface areas, customizable constructions, and adaptability to a wide range of uses, including gas storage, catalysis, molecule separation, and sensing [1–3]. COFs offer attractive solutions for potential applications due to their inher-

ent designability through the selection of building blocks and functional groups [4, 5]. However, despite these advantages, most COFs feature two-dimensional (2D) structures with difficulty in pore size control to micropore and ultra-micropore thus limiting their effectiveness in gas separation applications [6, 7]. The development of three-dimensional (3D) interpenetrated COFs, which could overcome many of the structural drawbacks of non-interpenetrated 2D COFs, has been a significant advancement in



**SCHEME 1** | Synthetic scheme of COF-PPy.



**FIGURE 1** | a) FT-IR, and b) PXRD of COF-PPy.

the field [8–11]. In COFs, interpenetration is the process by which two or more networks of the framework structures spatially interconnect between the layers with one another to build a stronger, more stable network with reduced pore size beneficial for separation applications, specially the separation of acetylene ( $C_2H_2$ ) from other  $C_2$  hydrocarbon gases (ethylene ( $C_2H_4$ ), ethane ( $C_2H_6$ )) and carbon dioxide ( $CO_2$ ) gas mixtures [9, 10].

It is well known that high purity is required for  $C_2H_2$  which is among the most used organic raw materials for synthetic industrial compounds, particularly 1,4-butyndiol and derivatives of acrylic acid.  $C_2H_2$  typically occurs as a by-product of the combustion of hydrocarbons, along with  $C_2H_4$  and  $CO_2$  [12]. On the other hand, removing  $C_2H_2$  contamination from  $C_2H_4$  is also important in the petrochemical industry since  $C_2H_2$  is poisonous to the  $C_2H_4$  polymerization catalyst used in polyethylene manufacturing, resulting in significantly lower-quality polyethylene [13]. However, it is a challenging task to separate  $C_2H_2$  from  $C_2H_2/C_2H_4$  and  $C_2H_2/CO_2$  mixtures due to their similar molecular shape, kinetic diameter, boiling temperatures, and

electronegativity. The techniques most commonly employed for removing  $C_2H_2$  typically involve liquid absorbent materials or cryogenic distillation, which are cost- and energy-intensive [14]. On the other hand, alternative methods such as membrane separation or adsorption offer substitutes with relatively lower energy costs. Recently, porous materials have gained widespread attention for  $C_2H_2/CO_2$  and  $C_2H_2/C_2H_4$  separations, with metal-organic frameworks (MOFs) leading the front. However, despite their high porosities and good separation performances, they suffer from the disadvantages of stability and cyclability over long periods of time [14]. COFs on the other hand can provide superior stability for continuous operation but remain relatively less explored owing to the difficulty in pore size control for sieving applications. For example, Wang and colleagues developed a pyridine-based 5-fold interpenetrated 3D COF that showed superior one-step  $C_2H_4$  purification over a mixture of  $C_2H_6$  and  $C_2H_4$  [15]. This performance behavior was attributed to the  $-CH\cdots N$  interactions between  $C_2H_6$  and pyridine groups of the COF linkers. Another two-dimensional covalent organic framework based on boronic ester linkages was reported for effective capture

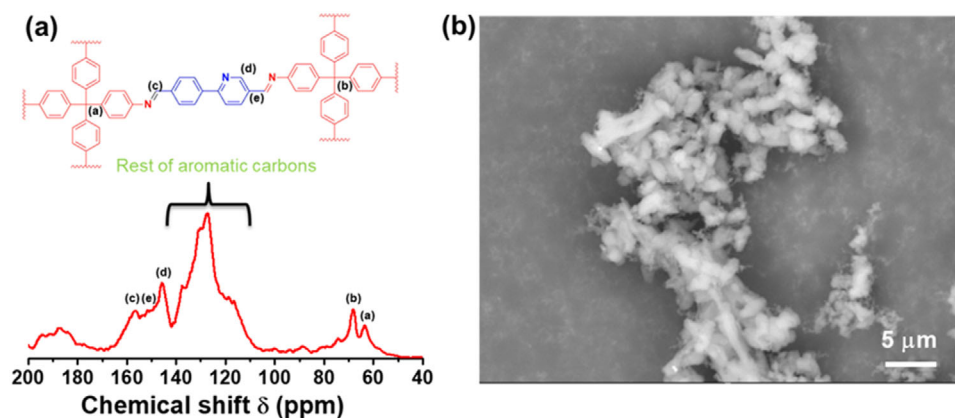


FIGURE 2 | (a) Solid-state  $^{13}\text{C}$  NMR, and (b) SEM image of COF-PPy.

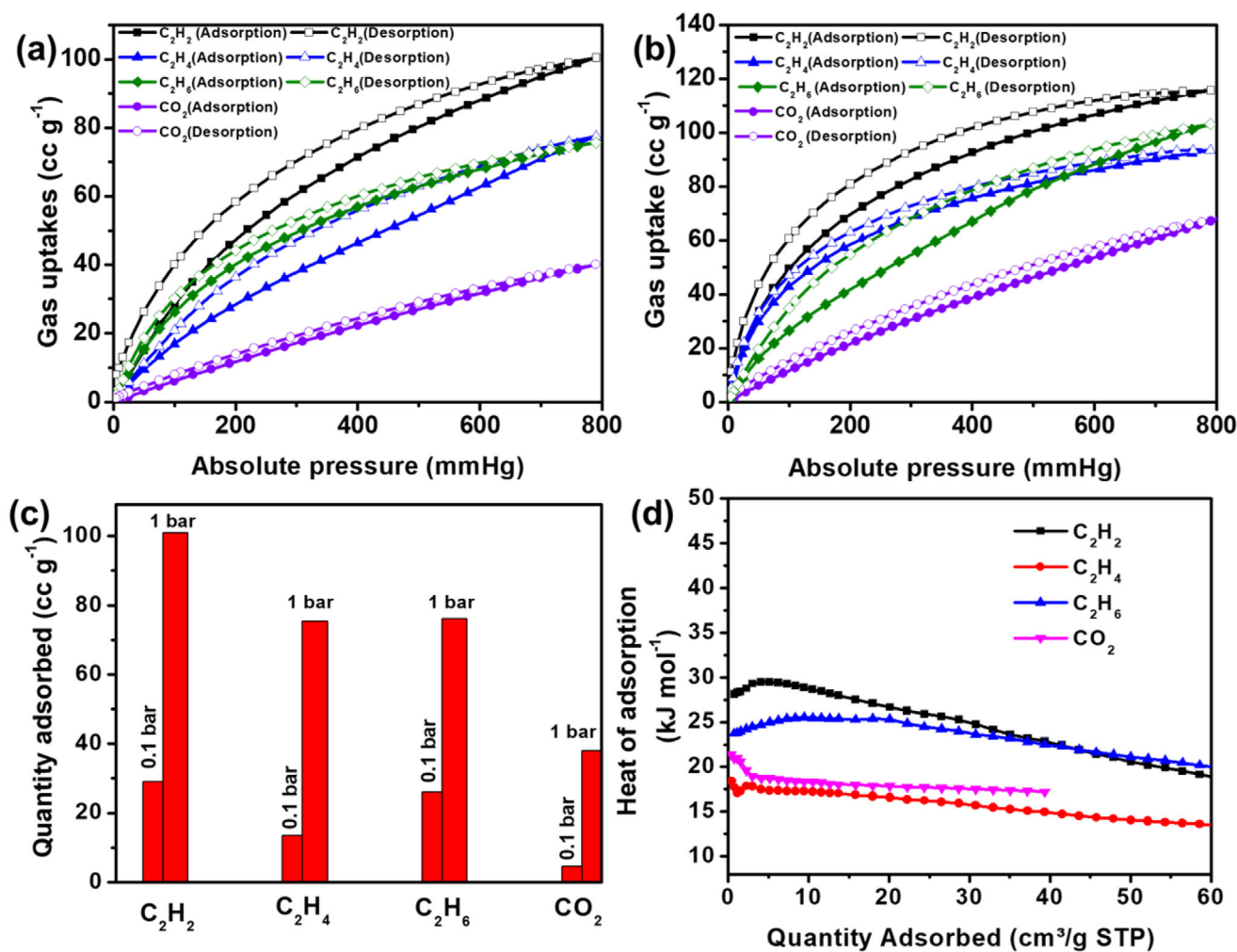
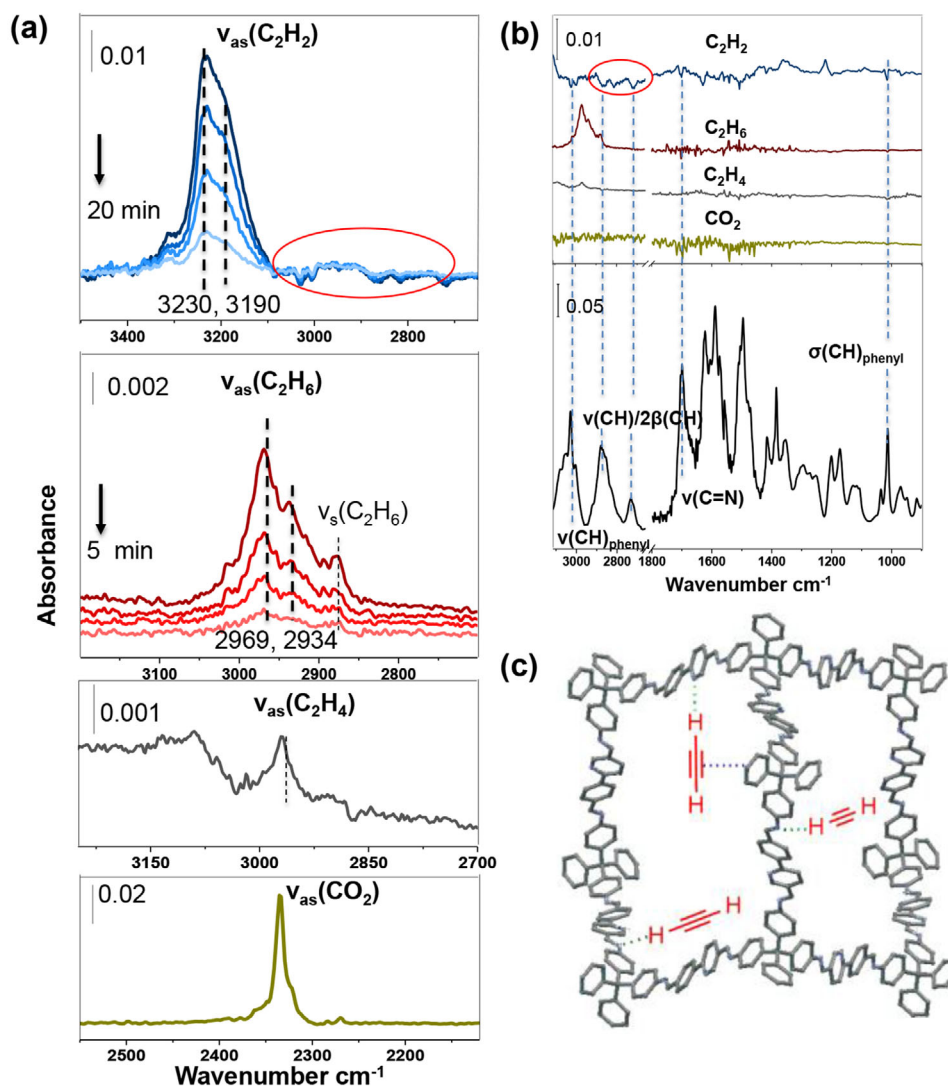


FIGURE 3 | a) Single-component  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{CO}_2$  adsorption (filled symbols) and desorption (open symbols) isotherms of COF-PPy at (a) 298 K and (b) 273 K. (c) Comparison of 298 K adsorption capacities of the four gases for COF-PPy at 0.1 and 1 bar. (d)  $Q_{\text{st}}$  plots of  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{CO}_2$  for COF-PPy.

of  $\text{C}_2\text{H}_2$  over  $\text{CO}_2$  via the  $\pi\cdots\pi$  interactions between  $\text{C}\equiv\text{C}$  and the aromatic rings of COF [16]. Sun *et al.* utilized a cobalt-unctionalized two-dimensional covalent organic frameworks for efficient  $\text{C}_2\text{H}_2/\text{CO}_2$  separation via strong host-guest interactions [17]. Zhu *et al.* developed a system of two-dimensional crystalline

polyimide porous organic framework for selective adsorption of  $\text{C}_2\text{H}_2$  over  $\text{C}_2\text{H}_4$ , and the separation performance was attributed to the strong H-bonding between the  $\text{HC}\equiv\text{CH}$  and O atoms in the COF backbone [3]. Our group also recently published work on single-molecule trapping for selective capture of  $\text{C}_2\text{H}_2$  from



**FIGURE 4** | (a) IR spectra showing the asymmetric stretching band of adsorbed  $C_2H_2$ ,  $C_2H_6$ ,  $C_2H_4$ , and  $CO_2$  inside COF upon loading  $C_2H_2$  gas at  $\approx 1$  bar and 298 K. (b) Difference spectra showing the perturbation occurring to COF structure upon loading gases; each is referenced to the bottom spectrum of activated COF in vacuum. (Notation and acronym:  $\nu$ , stretch;  $\delta$ , deformation;  $\beta$ , bending; as, asymmetric; and s, symmetric). (c) Schematic representation of interactions between the  $H-C\equiv CH$  and COF-PPy backbone.

$C_2H_4$ -rich gas mixtures using 2D-COFs [18]. Thus, it becomes imperative that for specific gas adsorption and separation from a broad spectrum of gas mixtures, it is essential to install selective groups or atoms and create interpenetrated 3D-COFs that can provide sieving behavior with suitable pores as well as resistance to external stresses and deformation.

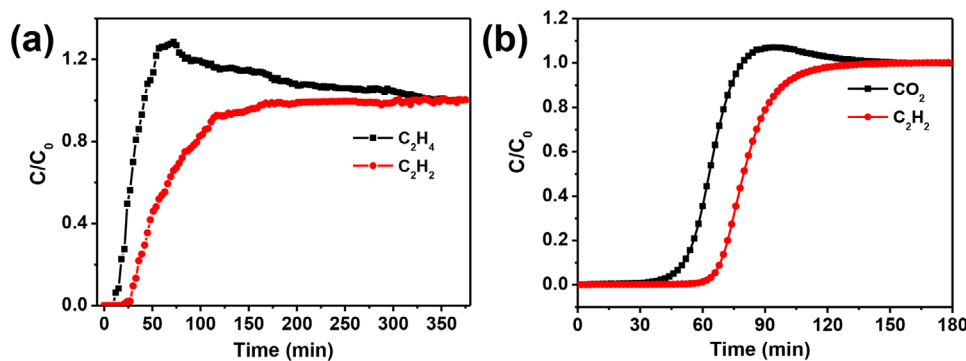
This work describes the development of a microporous three-dimensional COF (COF-PPy) based on 2-phenyl pyridine and tetrahedrally symmetric 4,4',4'',4'''-methanetetrayltetraaniline as secondary building block units (Scheme 1). The topology of COF-PPy is a rare example of nine-fold interpenetrated *dia* networks among COFs.  $C_2H_2$  is efficiently captured by COF-PPy compared to  $C_2H_4$ ,  $CO_2$ , and  $C_2H_6$ . Furthermore, dynamic breakthrough experiments showed that 3D-COF-PPy can effectively purify  $C_2H_4$  and  $CO_2$  from mixtures of  $C_2H_2/C_2H_4$  and  $C_2H_2/CO_2$  in a single step. In situ-IR studies further supported detailed evidence on the impact of the mechanism of chemisorption and physisorption processes. This is explained by the fact that

COF-PPy's more accessible pores as well as the presence of pyridine and imine groups can improve the  $C_2H_2$ -capture ability by interacting with  $C_2H_2$  to generate strong  $C-H\cdots N$  interactions. This performance is better than several other reported COFs and even at par with a few other benchmark porous materials.

## 2 | Results and Discussion

### 2.1 | Structural Characterization

The COF-PPy was obtained by heating a solution of 1,4-dioxane containing the non-symmetric 2-phenyl pyridine and the tetrahedrally symmetric 4,4',4'',4'''-methanetetrayltetraaniline in 6 M aqueous acetic acid to 120 degrees for three days in a sealed tube followed by simple filtration and washing with anhydrous 1,4-dioxane and tetrahydrofuran (THF). The resultant material was immersed in tetrahydrofuran for three days and dried under vacuum to yield COF-PPy as a fine yellow powder in 77%



**FIGURE 5** | (a) Dynamic breakthrough curves of  $C_2H_2/C_2H_4$  ( $v/v = 1:99$ ) mixture and (b)  $C_2H_2/CO_2$  ( $v/v = 1:1$ ) with a total flow rate of  $1 \text{ mL min}^{-1}$ .

yield. Several spectroscopic techniques were utilized to prove the successful construction of the 3D **COF-PPy**. FT-IR spectra of the **COF-PPy** show stretching bands at  $1618$  and  $1588 \text{ cm}^{-1}$  for imine ( $-C=N-$ ) and aromatic  $-C=C-$  bonds respectively, indicating the presence of imine linkages in **COF-PPy** [19]. The disappearance of aldehyde peaks of 2-phenyl pyridine moiety at  $\sim 1676 \text{ cm}^{-1}$  in **COF-PPy** further established the formation of imine linkages in the framework (Figure 1a). **COF-PPy** shows several sharp PXRD peaks at  $2\theta$  values of  $7.3$ ,  $10.4$ ,  $14.5$ ,  $21$ ,  $22.3$ , and  $24.6^\circ$ , suggesting the formation of a highly crystalline framework structure (Figure 1b). The experimental PXRD pattern is in a good agreement with the PXRD pattern predicted from the computational simulation. Moreover, the simulations reveal that **COF-PPy** adopts *dia* C-9 folded interpenetration topology. Pawley refinement of the PXRD patterns using this model generated unit cell parameters of:  $a = 24.652(2) \text{ \AA}$ ,  $b = 8.552(1)$ , and  $c = 24.732(2) \text{ \AA}$  ( $R_{wp} = 1.70\%$  and  $R_p = 1.29\%$ ), with a good agreement between the experimental and simulated profiles.

$^{13}\text{C}$  solid-state NMR measurements also demonstrate the formation of imine linkages and desired functionalities in **COF-PPy**. The peaks at  $158$ – $156$  ppm suggest the presence of two types of imine bonds in the 3D framework structure due to the nonsymmetrical aldehyde building block unit (Figure 2a). Apart from that, two peaks also arise at  $69$  and  $64$  ppm due to two different types of aliphatic carbons attached to the  $4,4',4'',4'''$ -methanetetrayltetraaniline unit in **COF-PPy**. The scanning electronic microscopy imaging further implies a uniform morphology with aggregates of small plate-shaped crystals of **COF-PPy** (Figure 2b). **COF-PPy** shows high thermal stability up to  $450^\circ\text{C}$  (Figure S3), after an initial loss of solvent from the pores.

## 2.2 | Surface Area Measurements

The permanent porosity, specific surface area, and pore size of the **COF-PPy** were evaluated by  $N_2$  sorption isotherms at  $77 \text{ K}$ , which demonstrate that the COF exhibits type I isotherm indicating microporosity, with a BET surface area of  $752 \text{ m}^2 \text{ g}^{-1}$  (Figure S2). The nonlocal density functional theory (NLDFT) model was used to calculate the pore size distribution of **COF-PPy**, and the results show that the average pore size is  $\approx 0.8$ – $1.1 \text{ nm}$ . These characteristics establish the formation of **COF-PPy** with high structural regularity, architectural robustness, and intrinsic porosity.

## 2.3 | Low-Pressure Gas Adsorption Measurements

In order to assess their gas adsorption capacities, we investigated the single-component  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ , and  $CO_2$  sorption isotherms of **COF-PPy** at  $298$  and  $273 \text{ K}$  (Figure 3a,b, respectively). The material shows the greatest affinity toward  $C_2H_2$  over the other gases, with the uptake reaching  $101 \text{ cm}^3 \text{ g}^{-1}$  at  $298 \text{ K}$  and  $1 \text{ bar}$ . As expected, the uptake increases to  $116 \text{ cm}^3 \text{ g}^{-1}$  at  $273 \text{ K}$  (Figure 3c). The  $C_2H_2$  adsorption capacity of **COF-PPy** at  $298 \text{ K}$  and  $1 \text{ bar}$  is significantly higher than that of other benchmark COFs (Table S1) such as NUS-71/72 ( $42.4$  and  $48 \text{ cm}^3 \text{ g}^{-1}$ ) [16], PAF-110 ( $49.95 \text{ cm}^3 \text{ g}^{-1}$ ) [3], PAF-120 ( $50.85 \text{ cm}^3 \text{ g}^{-1}$ ) [20], UPC-COF-1 ( $89.8 \text{ cm}^3 \text{ g}^{-1}$ ) [17], Py-Na COF ( $38 \text{ cm}^3 \text{ g}^{-1}$ ) [21] and HOF-FJU-100a ( $\approx 40 \text{ cm}^3 \text{ g}^{-1}$ ) [22]. Furthermore, under comparable circumstances, these values exceed some forefront MOFs such as CAU-10-H ( $89.8 \text{ cm}^3 \text{ g}^{-1}$ ), FJU-112a ( $74 \text{ cm}^3 \text{ g}^{-1}$ ), UTSA-300 ( $68.9 \text{ cm}^3 \text{ g}^{-1}$ ), and NKMOF-1-Ni ( $61 \text{ cm}^3 \text{ g}^{-1}$ ) [23–25]. Significant interactions between **3D-COF-PPy** and  $C_2H_2$  are indicated by the  $C_2H_2$  uptake capacities of **COF-PPy** in the ultralow ( $0.01 \text{ bar}$ ) and low pressure ( $0.1 \text{ bar}$ ) regimes, which are  $3.1$  and  $23 \text{ cm}^3 \text{ g}^{-1}$  at  $298 \text{ K}$ , and increase to  $8.5$  and  $43 \text{ cm}^3 \text{ g}^{-1}$  at  $273 \text{ K}$ , respectively. To the best of our knowledge, very few other COF adsorbents exhibit such large uptakes at ultralow pressures for  $C_2H_2$ . In contrast, the uptakes of  $C_2H_4$ ,  $C_2H_6$ , and  $CO_2$  for **COF-PPy** are much lower with the corresponding values of  $63$ ,  $75$ , and  $50 \text{ cm}^3 \text{ g}^{-1}$  at  $298 \text{ K}$  and  $1 \text{ bar}$ , respectively. It is interesting to note that  $C_2H_2/CO_2$  has the greatest uptake ratio of  $>2.6$  as compared to  $C_2H_2/C_2H_4$  and  $C_2H_2/C_2H_6$ .

The gas adsorption performance of **COF-PPy** thus leads us to postulate that the addition of pyridine groups to the 3D networks greatly increases the  $C_2H_2$  adsorption capacity through extra pyridine-acetylene interactions. To investigate further, the affinities of **COF-PPy** for all the gases were assessed using the Clausius-Clapeyron equation to calculate the coverage-dependent isosteric heat of adsorption ( $Q_{st}$ ). For  $C_2H_2$ , **COF-PPy** shows a  $Q_{st}$  of  $28 \text{ kJ mol}^{-1}$  at nearly zero loading, whereas for  $CO_2$  it is much lower at  $21 \text{ kJ mol}^{-1}$ .  $C_2H_2$  thus shows a stronger affinity than  $CO_2$  due to its smaller size and strong interactions with the pyridyl groups, which enables it to pack more molecules quite effectively into the same space inside the **3D COF-PPy**. The  $Q_{st}$  of  $C_2H_2$  shows a decrease with increasing  $C_2H_2$  uptake, suggesting that adsorption sites with higher interaction energy are initially occupied followed by those with lower interaction energy. On the other hand,  $C_2H_4$  has a substantially lower heat of adsorption ( $18 \text{ kJ mol}^{-1}$ ), indicating weaker binding interactions

with COF. For C<sub>2</sub>H<sub>6</sub>, the material shows a comparable Q<sub>st</sub> value ≈24 kJ mol<sup>-1</sup>. Moreover, Q<sub>st</sub> values of C<sub>2</sub>H<sub>2</sub> for **COF-PPy** are lower than several reported C<sub>2</sub>H<sub>2</sub>-selective porous adsorbents [18, 19, 21–23], making the regeneration process more energy efficient.

To evaluate the stability of the material after adsorption measurements, FT-IR and PXRD measurements on COF-PPy were carried out. The results reveal no major changes in the framework structure when compared to pristine COF (Figure S4). Thus, the material can be reutilized for subsequent measurements after washing it with acetone and THF, and activated again.

## 2.4 | Mechanistic Studies Using In Situ IR

To gain a deeper understanding of the sorption mechanism and superior performance of COF toward adsorbing C<sub>2</sub>H<sub>2</sub>, we conducted in situ infrared (IR) spectroscopy measurements on **COF-PPy** by separately loading C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and CO<sub>2</sub>, respectively at ≈1 bar and 298 K. The spectroscopic results are presented in Figure 4. Given that the spectra of the gas phase are prohibitively high, that hinders direct observation of the adsorbed species. We thus evacuated the gas phase by pumping the cell and collected the spectra immediately after ~5 sec of evacuation, i.e., the pressure drops below 500 mTorr that showing negligible gas-phase IR absorption. As shown in Figure 4a, the adsorbed molecules can be readily characterized by their asymmetric stretching mode (ν<sub>as</sub>) absorption.

Note that the symmetric stretching modes of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CO<sub>2</sub> are IR in-active. Interestingly, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> show two clearly distinguished ν<sub>as</sub> bands in contrast to C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub>, which show only one band. This points to two types of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> molecules adsorbed within the COF structure that give rise to distinct IR absorption features [26, 27], whereas only one type of C<sub>2</sub>H<sub>4</sub>, and CO<sub>2</sub> is present under the same conditions. We further examined the perturbations occurring to the vibrational bands of COF upon loading the four gases. Figure 4b shows that COF bands are most affected after loading C<sub>2</sub>H<sub>2</sub>. As shown in the difference spectra of Figure 4b, the CH-stretching/CH-bending Fermi resonance from HC = N linkage, denoted as ν(CH)/2β(CH), and C = N stretch modes [28], are clearly perturbed, indicated by the derivative-like feature; C-H stretching and in-plane deformation from phenyl ring of aldehyde linker, sensitive to the chemical environment [29, 30], show slight decrease of intensities; in addition, stretching of pyridine C–N bond at 1200 cm<sup>-1</sup> is also blue-shifted [31]. All these point to multi-point interaction of C<sub>2</sub>H<sub>2</sub> with COF structure (Figure 4c).

## 2.5 | Dynamic Breakthrough Experiments

To better understand the actual separation performance of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (v/v = 1:99) and C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> (v/v = 1:1) mixtures (Figure 5a,b) by **COF-PPy**, dynamic breakthrough experiments [32–34] were carried out under ambient conditions at a flow rate of 1 mL min<sup>-1</sup> (Figure 5a,b). The curve suggests a distinct separation between C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, whereby the C<sub>2</sub>H<sub>4</sub> first eluted from the column and reached saturation in 7 min, and then C<sub>2</sub>H<sub>2</sub> broke through with a substantially longer retention period of 27 min, indicating the effective separation performance

of the **COF-PPy** for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures. The estimated C<sub>2</sub>H<sub>4</sub> productivity in C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation is 5 mL g<sup>-1</sup>. For the C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation using **COF-PPy**, the material shows an impressive separation curve whereby CO<sub>2</sub> is passed through the columns with a short retention period of 30 min, followed by C<sub>2</sub>H<sub>2</sub> with a significantly longer retention time of 67 min. This indicates that **COF-PPy** has a good C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation performance and an exceptional capacity for C<sub>2</sub>H<sub>2</sub> adsorption over CO<sub>2</sub>.

## 3 | Conclusion

In conclusion, we have successfully designed and synthesized a pyridine functionalized microporous 9-fold interpenetrated **3D COF (COF-PPy)** that shows effective one-step CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> purification ability from C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures. The rational design of **3D COF-PPy** using non-symmetric 2-phenyl pyridine ligand exhibits significantly enhanced C<sub>2</sub>H<sub>2</sub> adsorption capacity. Multiple interaction sites for C<sub>2</sub>H<sub>2</sub> are provided by **COF-PPy**, which leads to an increase in affinity over the other gases. We have further conducted in situ FTIR and dynamic breakthrough studies to understand the mechanism and evaluate the practical separation performance. This paper provides a direction of synthesis of the higher fold of interpenetrated 3D COF, and high performance of CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> purification from C<sub>2</sub>H<sub>2</sub> mixture with high adsorption capacity. Given the encouraging uses of 3D COFs in gas separation, our research opens the door for the further development of functionalized 3D COFs for the effective separation of industrially relevant gases.

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### Conflicts of Interest

The authors declare no conflicts of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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### Supporting Information

Additional supporting information can be found online in the Supporting Information section.

**Supporting file 1:** marc202500317-sup-0001-SupMat.docx