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Isorecticular Synthesis of Ionic Covalent Organic Frameworks for Enhanced SO₂ Adsorption and Separation

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Abstract

Achieving selective SO₂ capture at low pressures is pivotal and challenging for possible flue gas desulfurization and air pollution control. In this study, we synthesized a series of ionic covalent organic frameworks (iCOFs) with β -ketoenamine linkages and sulfonic acid groups using a solvothermal method. TpPa-SO₃H and TpBD-(SO₃H)₂ show a higher SO₂ uptake of 4.46 and 5.24 mmol g⁻¹ than TpPa-1 (4.24 mmol g⁻¹) at 1 bar and 298 K, respectively, due to the combination of the good SO₂ affinity of the polar sulfonic acid groups, higher pore volumes, and the good stability of β -ketoenamine COFs. TpBD-(SO₃H)₂ captured 2.83 mmol g⁻¹ of SO₂ at 0.1 bar and 298 K, which is 1.6 times higher than TpPa-1 (1.82 mmol g⁻¹) under the same conditions. Notably, the IAST SO₂/CO₂ selectivity of TpBD-(SO₃H)₂ and TpPa-1 are 61 and 51, respectively, reflecting the impact of the incorporated SO₃H groups' higher affinity toward SO₂. Notably, the multicomponent gas mixture breakthrough experiments confirm that TpBD-(SO₃H)₂ displays longer breakthrough time than TpPa-1 (987 vs. 311 min g⁻¹). These β -ketoenamine iCOFs demonstrate nearly complete retention of crystallinity and porosity after exposure to dry or humid SO₂. This work demonstrates that iCOFs are promising adsorbents for SO₂ capture due to their high capacity, stability, and affinity for SO₂ at low pressure.

Keywords: ionic covalent organic frameworks; sulfur dioxide; carbon dioxide; adsorption

1. Introduction

Sulfur dioxide (SO₂) is a colorless, non-flammable gaseous species characterized by a pungent odor. Classified by the World Health Organization (WHO) as a highly toxic substance to human health, SO₂ can be readily absorbed via respiratory inhalation and skin contact, and exposure to concentrations exceeding 100 ppm for merely a few minutes can be fatal [1,2]. SO₂ released by the combustion of fossil fuels has caused serious impacts on human health and ecosystems [3–5]. It is challenging to selectively capture SO₂ instead of CO₂ with higher concentration (0.05–0.3% vs. 10–15 vol%) from flue gas [6]. To date, advanced flue gas desulfurization (FGD) technologies utilizing limestone scrubbing or amine scrubbing processes can remove approximately 90–95% of sulfur dioxide, but they are extremely energy-intensive [7]. Furthermore, the residual low-concentration SO₂ (<500 ppm) may still contaminate downstream carbon dioxide scrubbing units [8–10] and irreversibly poison NO_x reduction catalysts [11] and CH₄ combustion catalysts [12].



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Thus, the development of new porous adsorbents for SO₂ removal at low pressures is of great significance.

Given that SO₂ possesses a larger kinetic diameter than CO₂ (4.1 Å vs. 3.3 Å), a molecular sieving mechanism based on size exclusion is unattainable. Therefore, adsorption effect should be emphasized in the design of porous adsorbents for SO₂ capture based on the different and superior physical properties of SO₂ over CO₂: dipole moment (1.63 vs. 0 D) and polarizability (47.7×10^{-25} vs. 26.5×10^{-25} cm³). Currently, activated carbon [13] adsorbents exhibit insufficient selectivity. Metal oxides [14] and zeolites [15] are difficult to be regenerated. Metal–organic frameworks (MOFs) demonstrate excellent adsorption capacity and selectivity; nevertheless, most MOFs suffer from poor stability [16–20]. Therefore, developing porous adsorbents with high SO₂/CO₂ selectivity and good stability presents a big challenge.

Covalent organic frameworks (COFs) represent a class of porous crystalline polymers featuring ultrahigh specific surface areas and highly designable structural units [21,22]. Their well-defined ordered architectures, uniform open channels, and tunable skeletons render COFs as an ideal platform for elucidating structure–property relationships [23–25]. N-heterocyclic moieties [26–28], hydroxyl [29], and carboxylate groups [30] have been incorporated in COFs for SO₂ adsorption and separation as well as SO₂ sensing [31,32]. For example, Zhang et al. have reported an olefin-linked COF named NKCOF-12 featured with ultramicroporous structures and abundant nitrogen sites, thereby achieving high SO₂ adsorption capacity and good desulfuration performance [32]. However, anionic COFs have not been explored for SO₂ removal in this field. These iCOFs can be constructed from ionic monomers with sulfonic acid groups (–SO₃H), which should be advantageous for preferential SO₂ affinity and selective adsorption of SO₂ due to the polarization capability of –SO₃H groups. To the best of our knowledge, sulfonic acid functionalized COFs for the adsorption and separation of SO₂ has not been reported.

As a proof-of-concept study, herein, we report the isorecticular synthesis and structures of two sulfonic acid-functionalized COFs, namely TpPa-SO₃H and TpBD-(SO₃H)₂ (Figure 1a), and their performance for the selective adsorption of SO₂ over CO₂, N₂ and CH₄. We introduced the –SO₃H group into β-ketoenamine-based COFs via pre-synthetic strategy. This not only enhanced the interfacial polarity of the framework but also strengthened the interactions with SO₂ molecules, thereby improving the affinity for SO₂, especially under low-pressure conditions. Moreover, although the humid SO₂ environmental conditions are of great significance in actual desulfurization scenarios, there are relatively few studies on the structural stability assessment in the literature regarding the use of COFs for SO₂ removal. Our work demonstrated that these β-ketoenamine-based COFs exhibited good structural stability under both dry and humid SO₂ conditions.

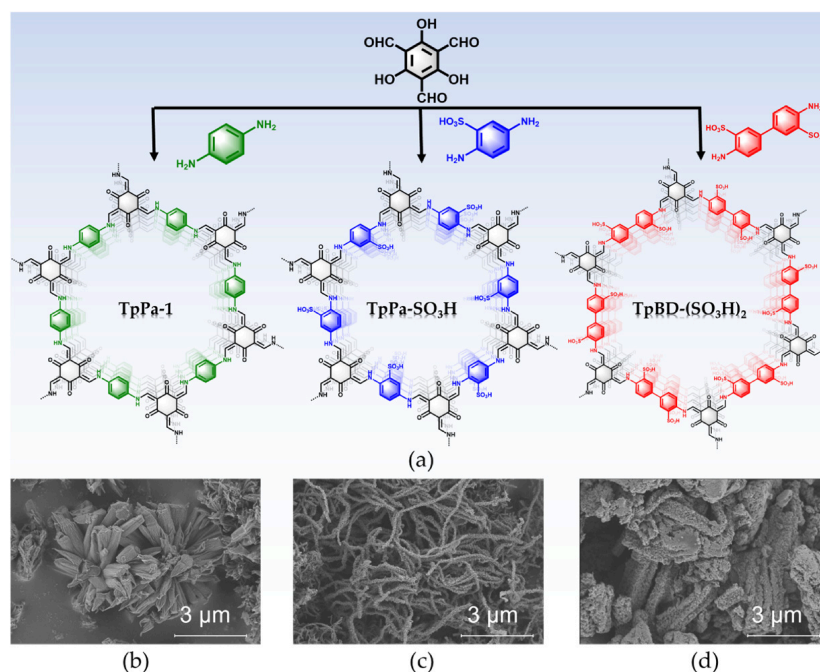


Figure 1. (a) Schematic representation of the synthesis of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ with hexagonal pores. SEM images of (b) TpPa-1, (c) TpPa-SO₃H and (d) TpBD-(SO₃H)₂.

2. Results and Discussion

The synthetic routes of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ are depicted in Figure 1a, and all of them were prepared separately under similar solvothermal reaction conditions. Scanning electron microscopy (SEM) images show that TpPa-1 displays the flower-shaped morphology resulting from the aggregation of petals with lengths in the micrometer range (1–1.5 μm) (Figure 1b). TpPa-SO₃H has nanofibrous morphology consisting of the interconnected tiny nanoparticles (Figure 1c). Moreover, TpBD-(SO₃H)₂ is composed of micrometer particles (Figure 1d).

The powder XRD pattern of TpPa-1 shows typical diffraction peaks at 2θ values of 4.7° and 8.1° (Figure 2a), which are assigned to the (100) and (2–10) planes from the A-A stacking model [33], while TpPa-SO₃H exhibits intense peaks of (100) facet at 4.9° (Figure 2b) [34]. TpBD-(SO₃H)₂ exhibits intense peaks of (100) and (200) facets at 3.7° and 7.2° (Figure 2c) [35], respectively. These results confirm the good crystallinity of the obtained three COFs. The reference XRD patterns were taken from the literature [33–35].

The Fourier transform infrared (FT-IR) spectra of TpPa-SO₃H and TpBD-(SO₃H)₂ are different from that of TpPa-1 (Figures 2d and S1–S3). The C=C and C–N stretching bands occur at 1585 and 1232–1259 cm^{−1}, respectively, which clearly corroborates the formation of the β-ketoenamine configuration in TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂. Furthermore, new bands at 1091 and 1020 cm^{−1} can be attributed to the stretching vibrations of –SO₃H in TpPa-SO₃H and TpBD-(SO₃H)₂.

To further probe the surface properties of these iCOFs with –SO₃H groups, zeta potential measurements were carried out in pure water. TpPa-1 shows a slightly positive zeta potential of 5.5 mV, whereas TpPa-SO₃H and TpBD-(SO₃H)₂ exhibit obviously negative zeta potentials of −31 mV and −36 mV, respectively (Figure S4). These results indicate that the presence of –SO₃H groups markedly changes the surface charge properties of the frameworks and increases the surface polarity of the two iCOFs. Such polar surfaces should be advantageous to provide more adsorption sites and strengthen the interactions with polar SO₂ molecules, especially under low-pressure conditions.

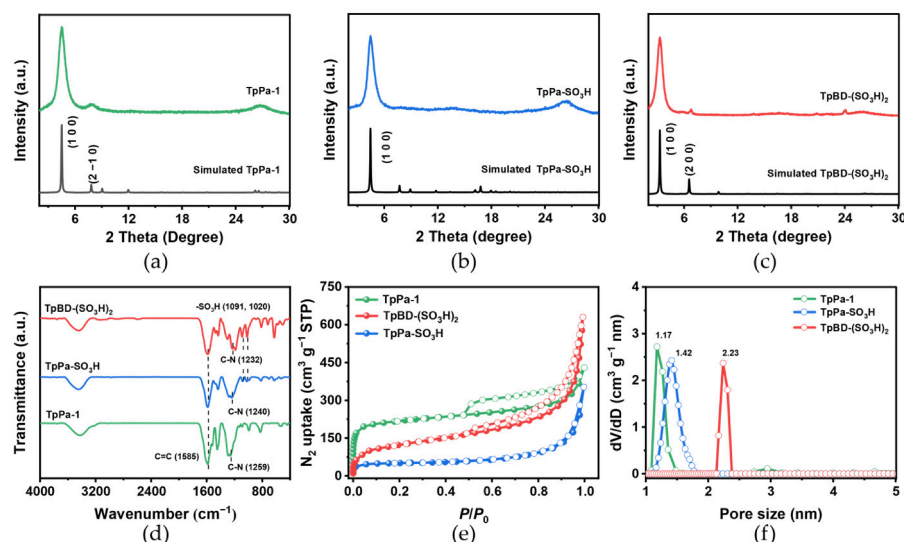


Figure 2. PXRD patterns of as-synthesized and simulated (a) TpPa-1, (b) TpPa-SO₃H and (c) TpBD-(SO₃H)₂. (d) FT-IR spectra, (e) N₂ adsorption-desorption isotherms with solid dots and white dots, respectively, and (f) pore size distributions based on nonlocal density functional theory (NLDFT) calculations for TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂.

The permanent porosities were assessed by N₂ sorption measurements at 77 K (Figure 2e). The N₂ adsorption-desorption isotherms of all samples exhibited a combination pattern of type I and type IV [36]. The Brunauer-Emmett-Teller (BET) specific surface area of TpPa-1 is calculated to be 687 m² g⁻¹. With integrated -SO₃H groups, the BET surface areas of TpPa-SO₃H and TpBD-(SO₃H)₂ are determined to be 195 and 430 m² g⁻¹ (Table 1). The pore size distribution analyses show that the dominant pores are centered at 11.7, 14.2, 22.3 Å for TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ (Figure 2f, Table 1), respectively. Thermogravimetric analysis (TGA) curves show that TpPa-1 is stable before 330 °C under N₂ atmosphere (Figure S5). Compared to TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ display a slightly higher thermal stability, remaining stable up to 400 °C.

Table 1. Porosity characteristics of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ and the results of SO₂ adsorption at 298 K.

Material	BET-Surface Area ¹ [m ² g ⁻¹]	Pore Width ² [Å]	SO ₂ Uptake (298 K) [mmol g ⁻¹] at:			SO ₂ /CO ₂ Selectivity ³ at SO ₂ /CO ₂ Molar Ratio:	
			0.01 Bar	0.1 Bar	1.0 Bar	0.1	0.5
TpPa-1	687	1.00–1.59	0.78	1.82	4.24	51	49
TpPa-SO ₃ H	195	1.12–1.81	1.19	2.25	4.46	54	54
TpBD-(SO ₃ H) ₂	430	2.13–2.38	1.27	2.83	5.24	61	70

¹ Obtained from five adsorption points in the pressure range 0.001 < P/P₀ < 0.05. ² Pore widths from pore size distribution are measured by N₂ sorption at 77 K. ³ See Section S4 in the SI for the CO₂ sorption data.

The water contact angle measurements were performed to investigate the wettability of all samples in the form of pellets (Figure S6). The results indicate that all materials possess hydrophilic surfaces. It is noticed that after the incorporation of -SO₃H groups in the two iCOFs, these frameworks become more hydrophilic than TpPa-1, probably due to the increased polarity of the two iCOFs' surfaces, which is consistent with the results of zeta potential measurements (Figure S4). These polar iCOFs are expected to show selective adsorption performance toward SO₂.

The SO₂ adsorption isotherms of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ were collected at 298 K. At 1.0 bar, the SO₂ adsorption capacities of TpPa-1, TpPa-SO₃H and TpBD-

(SO₃H)₂ were 4.24, 4.46, and 5.24 mmol g^{−1} (Figure 3a, Table 1). At 0.01 bar, TpPa-SO₃H and TpBD-(SO₃H)₂ with −SO₃H groups show significantly higher SO₂ uptake capacities than TpPa-1 (1.19 mmol g^{−1} for TpPa-SO₃H, 1.27 mmol g^{−1} for TpBD-(SO₃H)₂ and 0.78 mmol g^{−1} for TpPa-1) (Figure 3b, Table 1). Notably, the SO₂ uptake of TpBD-(SO₃H)₂ at 298 K and 0.01 bar surpasses the uptake in some well-known COFs, such as COF-701 [32] and TMT-TA [32]. As the pressure increased to 0.1 bar, the SO₂ uptake of TpBD-(SO₃H)₂ rapidly rises to 2.83 mmol g^{−1}, accounting for about 54% of the SO₂ uptake. Similarly, TpPa-SO₃H displays an adsorption capacity of 2.25 mmol g^{−1} at 0.1 bar, 50% of the total adsorption capacity. In contrast, TpPa-1 exhibits an adsorption capacity of 1.82 mmol g^{−1} at 0.1 bar, approximately 43% of the total adsorption capacity (Table 1). The observed relatively high SO₂ uptake of TpBD-(SO₃H)₂ at low pressure (<0.1 bar) meets a prerequisite of potential adsorptive flue-gas desulfurization processes. The enhanced SO₂ uptake of TpPa-SO₃H and TpBD-(SO₃H)₂ in the low-pressure region should be reasonably associated with the introduction of polar −SO₃H groups into the frameworks. This interpretation is further supported by the significantly negative zeta potentials of the sulfonated iCOFs (Figure S4). Compared with the non-sulfonated TpPa-1, the −SO₃H-functionalized iCOFs provide more polar pore surfaces, which are favorable for strengthening the interactions with the polarizable SO₂ molecules. Therefore, multiple adsorption sites (likely both carbonyl groups and sulfonate groups) might be responsible for the improved SO₂ adsorption behavior under low pressures.

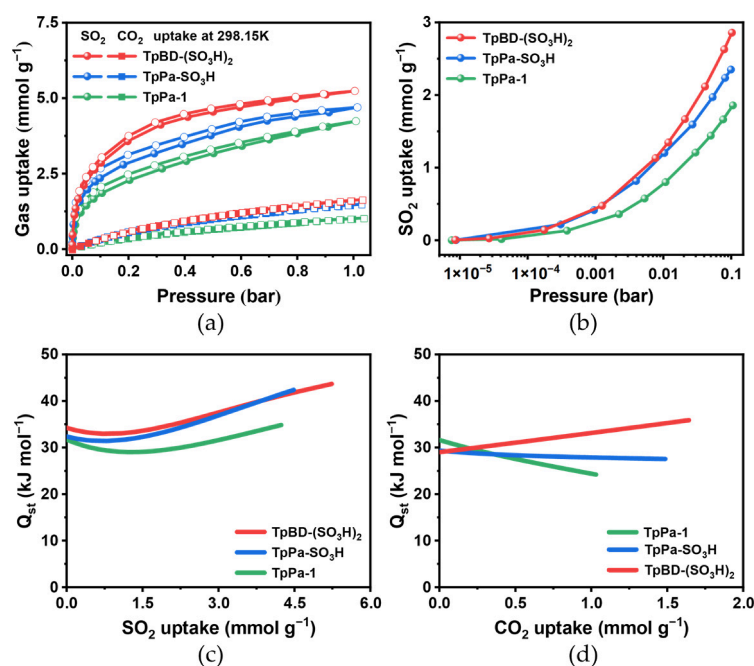


Figure 3. (a) SO₂ and CO₂ sorption isotherms of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ measured up to 1 bar at 298 K. (b) The enlarged SO₂ adsorption at low pressure of 0–0.1 bar for better clarity of the onset of steep uptake. Isosteric enthalpy of adsorption of (c) SO₂ and (d) CO₂ on TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ calculated by virial fitting of the single-component adsorption isotherms measured at 273 and 298 K, respectively (Figures S7–S10).

The SO₂ adsorption isotherms at 273 K and 298 K were used to determine the isosteric enthalpy of SO₂ adsorption ($\Delta H_{\text{ads}} = -Q_{\text{st}}$) by virial analysis (Figures S7 and S8) [37]. The $-\Delta H_{\text{ads}}$ values near zero coverage ($-\Delta H_{\text{ads}}^0$) in TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ are 31.72, 32.36 and 34.26 kJ mol^{−1}, respectively (Figure 3c). The $-\Delta H_{\text{ads}}$ values of the SO₃H-functionalized COFs are slightly higher than that of TpPa-1, suggesting efficient host-guest interactions arising from the increased polarity of the two iCOFs.

The single-component CO₂, CH₄, and N₂ adsorption isotherms for TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ were measured at 298 K (Figures S9, S11 and S12). As expected, the two iCOFs exhibit slightly improved CO₂ and CH₄ adsorption performance than TpPa-1 up to 1 bar at 298K. Nevertheless, compared to TpPa-1, less N₂ are adsorbed by TpPa-SO₃H and TpBD-(SO₃H)₂ (Table S1). Notably, the SO₂ adsorption curves of all COFs are much steeper than those of CO₂ and CH₄ probably due to the higher polarizability ($47.7 \times 10^{-25} \text{ cm}^3$) and higher dipole moment (1.63 D) of SO₂ [5]. It should be noted that the uptake amounts of CO₂ and CH₄ were much lower than the SO₂ uptake on these COFs at 1.0 bar (Table S1). Through virial analysis of CO₂ adsorption isotherms at 273 K and 298 K, the $-\Delta H_{\text{ads}}^0$ of CO₂ are determined to be 29.00, 29.32 and 31.61 kJ mol⁻¹, respectively (Figures 3d and S10). The generally higher $-\Delta H_{\text{ads}}$ values and steeper adsorption curves of SO₂ than those of CO₂ indicate the potential of these COFs for selective SO₂ adsorption from gas mixtures. Overall, both the adsorption capacity of SO₂ and isosteric heat of adsorption ($-\Delta H_{\text{ads}}$) by iCOFs are slightly increased than those of TpPa-1 under low-pressure conditions. These indicate that the introduction of the -SO₃H groups helps to enhance the polarity of the framework and providing more electron-rich adsorption sites and higher pore volumes for SO₂, thereby significantly improving the affinity and uptake amount of SO₂ by these iCOFs.

To evaluate the selectivity of SO₂ over CO₂, CH₄, and N₂, ideal adsorbed solution theory (IAST) calculations were performed for binary gas mixtures as a function of variable SO₂ molar fractions from 0.02 to 0.5 at 1 bar and 298 K. Considering the trace SO₂ amount present in the flue gas, high SO₂ selectivity over these gases is required for a realistic adsorptive gas desulfurization process. For a molar SO₂/CO₂ ratio of 10:90, the selectivity of TpPa-1 is 51, while TpPa-SO₃H and TpBD-(SO₃H)₂ display an increased selectivity of 54 and 61 (Figure 4a and Table S3). To the best of our knowledge, the IAST SO₂/CO₂ selectivity value of TpBD-(SO₃H)₂ is relatively high among all the COFs materials reported so far (Figure 4d,f and Table S4). Meanwhile, TpBD-(SO₃H)₂ also possesses a high SO₂/CH₄ and SO₂/N₂ selectivity of 124 and 621, respectively, when the SO₂/CH₄ or SO₂/N₂ ratio is 10:90 (Figure 4b,c). Furthermore, at a CO₂/N₂ ratio of 10:90, the CO₂/N₂ selectivity of TpBD-(SO₃H)₂ and TpPa-SO₃H are 70 and 355, respectively (Figure S13 and Table S3). Therefore, the experimental results have demonstrated the superiority of these iCOFs with SO₃H groups over neutral TpPa-1 for enhanced selective SO₂ capture in flue gas containing SO₂, CO₂ and N₂. TpPa-SO₃H and TpBD-(SO₃H)₂ also show enhanced selective CO₂ capture performance than TpPa-1 (Figure S13).

For porous materials, it is reported that BET surface area and the pore volume are the main factors contributing to high SO₂ adsorption capacity at high pressure. However, unlike high-pressure SO₂ adsorption, the uptake at low pressure correlates with the affinity between SO₂ and the adsorbent pore surface [18]. In our work, TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ show moderate surface areas and an increased pore volume of 0.42, 0.51, and 0.96 cm³ g⁻¹, which explains their moderate and enhanced SO₂ uptake capacity at 1 bar and 298 K (Figure 4e). Moreover, the incorporation of SO₃H in these iCOFs efficiently enhanced the SO₂ uptake at low pressure range (<0.1 bar) by providing polar surfaces, leading to improved SO₂/CO₂ selectivities, which are even higher than some COFs with higher BET surface areas (Figure 4f).

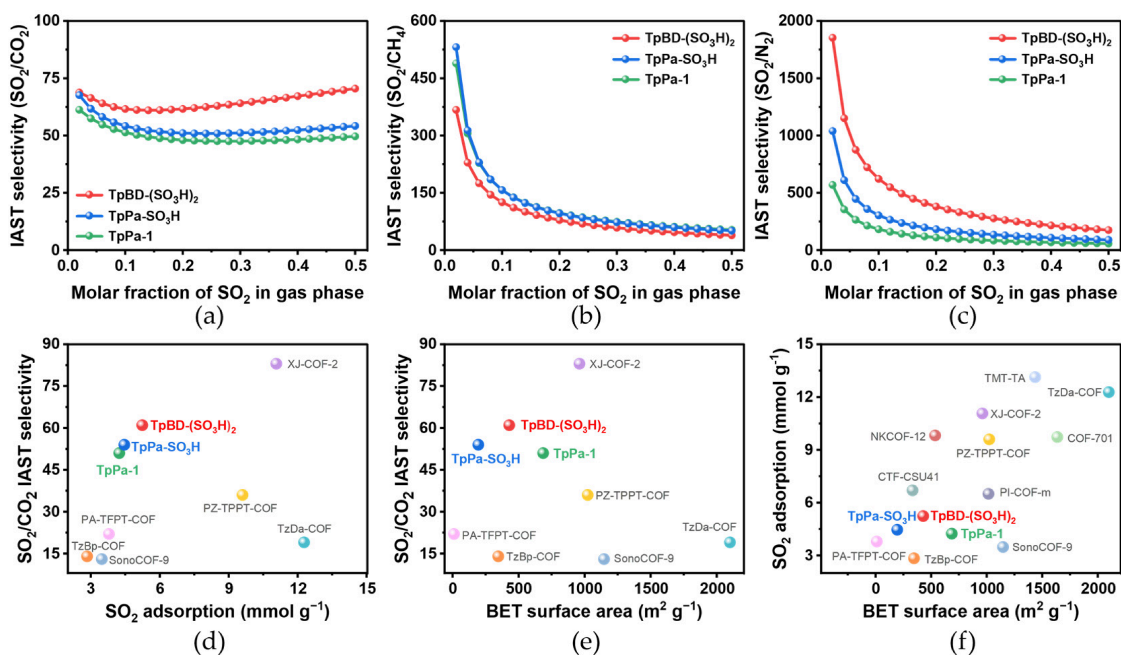


Figure 4. IAST selectivity of (a) SO_2/CO_2 , (b) SO_2/CH_4 and (c) SO_2/N_2 for TpPa-1, TpPa- SO_3H and TpBD- $(\text{SO}_3\text{H})_2$ series as a function of SO_2 molar fractions (0.02–0.5) at 1 bar and 298 K. Comparison of SO_2 adsorption performance of TpPa-1, TpPa- SO_3H , TpBD- $(\text{SO}_3\text{H})_2$ and representative COFs. (d) Plot of SO_2/CO_2 selectivity against SO_2 adsorption capacity at 1.0 bar. (e) Plot of SO_2 adsorption capacity against BET surface area. (f) Plot of SO_2/CO_2 selectivity against BET surface area. Temperature for TpPa-1, TpPa- SO_3H , TpBD- $(\text{SO}_3\text{H})_2$ is at 298 K (Table S4).

To investigate the structural stability of TpPa-1, TpPa- SO_3H and TpBD- $(\text{SO}_3\text{H})_2$ towards SO_2 , all activated materials were exposed to dry SO_2 and to humid SO_2 for 6 h. The humid SO_2 condition corresponds to a sealed air atmosphere containing 35 ppm SO_2 and 75% RH (please see Section S5 and Figure S14 for details). The XRD patterns of all materials after dry and humid SO_2 exposure remained, suggesting the retention of crystallinity without noticeable phase transformation (Figure S15). After all the materials were exposed to dry and humid SO_2 environments, the FT-IR spectra showed very little change. This indicates that their structures were maintained and no obvious covalent bond breakage occurred (Figure S16). Interestingly, a new peak at $1350\sim 1326\text{ cm}^{-1}$ in TpPa-1, TpPa- SO_3H , and TpBD- $(\text{SO}_3\text{H})_2$ after humid SO_2 exposure is observed, which might be assigned to the asymmetric stretching vibrations of residual SO_2 molecules [38,39]. The symmetric stretch of adsorbed SO_2 (around 1144 cm^{-1}) are not observed due to overlap with the strong vibration bands of TpBD- $(\text{SO}_3\text{H})_2$ [40]. The BET surface areas of TpPa-1, TpPa- SO_3H , and TpBD- $(\text{SO}_3\text{H})_2$ after exposure to dry and humid SO_2 remained 98%, 97% and 95% of the pristine COFs after dry and humid SO_2 adsorption (Figures S17 and S18). To further evaluate the structural robustness, the materials were also exposed to humid SO_2 for extended durations of 24 h and 72 h. No significant changes can be observed in the XRD patterns (Figure S15), FT-IR spectra (Figure S16), and BET surface areas (Figures S17 and S18). These results indicate that the frameworks can maintain their crystallinity, chemical integrity, and porosity under prolonged humid SO_2 conditions, suggesting their potential for stable adsorption performance.

Furthermore, the selective capture of SO_2 from mixed gases is of great importance for practical applications. To further evaluate the separation performance under competitive conditions, dynamic breakthrough experiments were conducted. A typical gas mixture of $\text{SO}_2/\text{CO}_2/\text{N}_2$ (2000 ppm of SO_2 + 14.8% CO_2 + 85% N_2) was purged into a COF-packed column with an inlet flow rate of 8 mL min^{-1} at 298 K and 1 bar. As shown

in Figure 5, N_2 and CO_2 broke through the column rapidly, while SO_2 was retained in the adsorption bed for a significantly longer time, indicating the preferential adsorption of SO_2 . TpPa-1 exhibited an SO_2 breakthrough time of $\sim 311 \text{ min g}^{-1}$ with a saturated breakthrough capacity of 0.31 mmol g^{-1} (Figure 5a). Notably, TpBD- $(SO_3H)_2$ displayed a much longer breakthrough time of 987 min g^{-1} and a higher saturated breakthrough capacity of 0.80 mmol g^{-1} (Figure 5b). Compared to the microporous neutral TpPa-1, the significantly enhanced breakthrough performance of TpBD- $(SO_3H)_2$ can be ascribed to the presence of $-SO_3H$ groups and higher pore volumes under competitive conditions. Moreover, TpBD- $(SO_3H)_2$ compares favorably with representative SO_2 adsorbents reported in the literature (Figure 5c, Table S5). These results are consistent with the selectivity trend predicted from the IAST analysis.

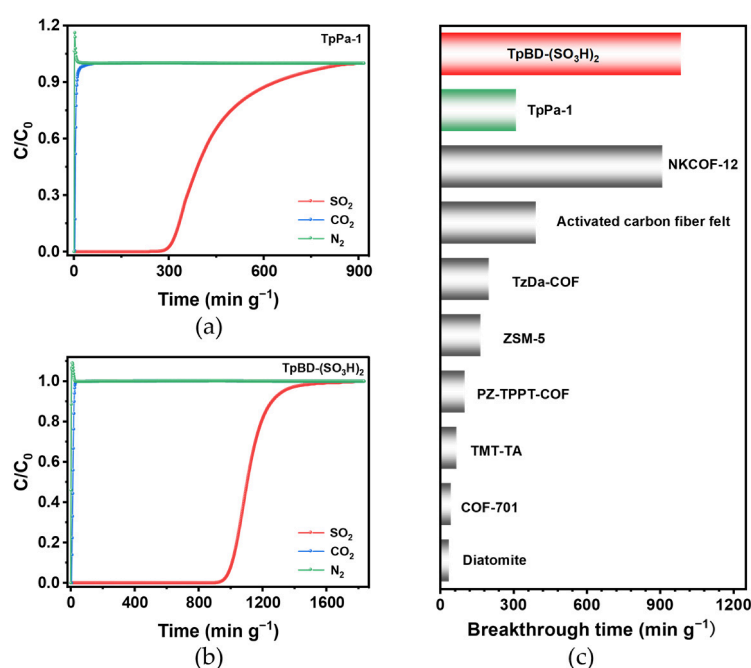


Figure 5. Experimental breakthrough curves of mixture gas $SO_2/CO_2/N_2$ (2000 ppm + 14.8% + 85%) for (a) TpPa-1 and (b) TpBD- $(SO_3H)_2$. (c) The breakthrough time of TpPa-1, TpBD- $(SO_3H)_2$ and representative adsorbents.

3. Materials and Methods

3.1. Instrumentation

Powder X-ray diffraction (PXRD) patterns were collected on an X-ray diffractometer (Cu $K\alpha$ radiation source, Miniflex600, Rigaku, Tokyo, Japan). Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets using a Bruker TENSOR 27 (Bruker Corporation, Karlsruhe, Germany) spectrometer. The surface charge characteristics of the samples were characterized using the SURPASS 3 type Zeta potential analyzer (Anton Paar GmbH, Shanghai, China). Nitrogen adsorption and desorption isotherms were measured at 77 K using a surface area and porosity analyzer (JW-BK200, Jingwei Gaobo Instrument Co., Ltd., Beijing, China). The samples were degassed at 120°C for 10 h before the measurements. Specific surface areas were calculated from the adsorption data using the Brunauer–Emmett–Teller (BET) equation. The pore size distributions were obtained using nonlocal density functional theory (NLDFT) calculations with an “ N_2 -Tarazona, cylinder” model. Thermogravimetric analysis (TGA) was carried out on a TG209F1 Libra instrument (NETZSCH Group, Bayern, Germany) by heating the samples from 30°C to 800°C in a dynamic nitrogen atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$. The water contact angle

was observed using a water contact angle analyzer (DSA100, KRÜSS, Hamburg, Germany). Scanning electron microscopy (SEM) images were obtained on a MIRA LMS microscope (Tescan Group a.s., Bohunice, Czech Republic) operated at an accelerating voltage of 3.0 kV. The humid SO₂ atmosphere was monitored using a portable SO₂ detector (GT903-SO₂-B, Kornuo Electronic Technology Co., Ltd., Shenzhen, China).

Comparative SO₂, CO₂, CH₄ and N₂ gas adsorption experiments at 273 and 298 K:

Before each experiment, samples were activated for 12 h and at a minimum of 393 K under a vacuum $< 5 \times 10^{-3}$ mbar. SO₂, and CH₄ sorption experiments were measured at 273 and 298 K on an advanced corrosive gas adsorption and micropore analyzer (BSD-660MC, Beishide Instrument Technology Co., Ltd., Beijing, China) instrument within a pressure range of 1×10^{-3} to 1.0 bar. CO₂, and N₂ sorption experiments were measured at 273 and 298 K on an advanced measurement instrument (JW-BK330C, Jingwei Gaobo Instrument Co., Ltd., Beijing, China) within a pressure range of 1×10^{-3} to 1.0 bar. The breakthrough separation experiments were conducted in a multi-constituent adsorption breakthrough curve analyzer (BSD-MAB, Beishide Instrument Technology Co., Ltd., Beijing, China) under ambient conditions (298 K, 1 bar) using a gas mixture of 2000 ppm SO₂ + 14.8% CO₂ + 85% N₂. All used gases were of ultra-high purity (99.999%) and supplied by Sizhiqiti, Tianjin, China.

3.2. Chemicals

The 2,4,6-Triformylphloroglucinol (Tp) (98%), *p*-Phenylenediamine (Pa) (99%), 2,5-Diaminobenzenesulfonic acid (Pa-SO₃H) (98%) and 4,4'-diamino-3,3'-biphenyl-disulfonic acid (BD-(SO₃H)₂) (97%) were obtained from the commercial supplier Adamas-beta (China), and were used without further purification. All solvents were purchased from commercial suppliers with a minimum purity of 99.8%.

3.3. Synthesis of TpPa-1

TpPa-1 was synthesized according to the modified literature procedures [33]. Tp (63.00 mg, 0.30 mmol), Pa (48.70 mg, 0.45 mmol), 1.5 mL of mesitylene and 1.5 mL of 1,4-dioxane were successively added to a Pyrex tube. This mixture was dispersed by ultrasonication for 10 min to get homogenous dispersion. Subsequently, 0.5 mL of CH₃CO₂H (3 mol L⁻¹) was added to the tube. After the mixture was sonicated for 10 min, the tube was frozen under liquid N₂ bath, and air was removed through three-pump-thaw cycles. Then, the tube was sealed off and put in an oven at 120 °C for 72 h. Reddish-brown powder was obtained by filtration after the mixture cooling down to room temperature. The powder was washed with tetrahydrofuran (THF), and further purified by Soxhlet extraction with THF over 24 h. The resultant reddish-brown solid was dried in a vacuum oven at 60 °C for 24 h.

3.4. Synthesis of TpPa-SO₃H

TpPa-SO₃H was synthesized according to the modified literature procedures [34]. Tp (63.00 mg, 0.30 mmol), Pa-SO₃H (84.70 mg, 0.45 mmol), 2.7 mL of mesitylene and 0.3 mL of 1,4-dioxane were successively added to a Pyrex tube. This mixture was dispersed by ultrasonication for 10 min to get homogenous dispersion. Subsequently, 0.3 mL of CH₃CO₂H (6 mol L⁻¹) was added to the tube. After the mixture was sonicated for 10 min, the tube was frozen under liquid N₂ bath, and air was removed through three-pump-thaw cycles. Then, the tube was sealed off and put in an oven at 120 °C for 72 h. Reddish-brown powder was obtained by filtration after the mixture cooled down to room temperature. The powder was washed with acetone, and further purified by Soxhlet extraction with acetone over 24 h. The resultant reddish-brown solid was dried in a vacuum oven at 60 °C for 24 h.

3.5. Synthesis of TpBD-(SO₃H)₂

TpBD-(SO₃H)₂ was synthesized according to the modified literature procedures [35]. Tp (63.00 mg, 0.30 mmol), BD-(SO₃H)₂ (155.00 mg, 0.45 mmol), 2.4 mL of mesitylene and 0.6 mL of 1,4-dioxane were successively added to a Pyrex tube. This mixture was dispersed by ultrasonication for 10 min to get homogenous dispersion. Subsequently, 0.5 mL of CH₃CO₂H (6 mol L^{−1}) was added to the tube. After the mixture was sonicated for 10 min, the tube was frozen under liquid N₂ bath, and air was removed through three-pump-thaw cycles. Then, the tube was sealed off and put in an oven at 120 °C for 72 h. Reddish brown powder was obtained by filtration after the mixture cooling down to room temperature. The powder was washed with acetone, and further purified by Soxhlet extraction with acetone over 24 h. The resultant reddish-brown solid was dried in a vacuum oven at 60 °C for 24 h.

4. Conclusions

We have synthesized two β -ketoenamine-based ionic COFs with high thermal and chemical stability for the demanding selective SO₂ capture at low pressures. Compared to the neutral COF without sulfonic acid group, it is found that the incorporation of sulfonic acid groups in these iCOFs could provide more polar surfaces for SO₂ adsorption, and achieve higher SO₂ affinity, higher SO₂ uptake capacity (5.24 mmol g^{−1}, 298 K, 1 bar) and improved SO₂/CO₂ selectivity (61, 298 K) in TpBD-(SO₃H)₂. The iCOFs also display enhanced SO₂ capture performance than the neutral counterpart COF at low pressures of 0.001–0.01 bar. Additionally, all β -ketoenamine COFs exhibit excellent structural stability toward both dry and humid SO₂. Considering the synthetic scalability, excellent stability and tunability of β -ketoenamine COFs [41], we believe that more ionic COFs can be developed for SO₂ capture.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules31091445/s1>, Section S1: Isothermic enthalpy of adsorption; Section S2: Ideal adsorbed solution theory (IAST) Selectivity; Section S3: Characterization and analysis; Section S4: SO₂, CO₂, CH₄ and N₂ gas adsorption experiments; Section S5: Stability of crystallinity and porosity after dry and humid SO₂ exposure; Section S6: Breakthrough performance; Section S7: References [26–32,37,42]; Figure S1: FT-IR spectra of Tp, Pa and TpPa-1; Figure S2: FT-IR spectra of Tp, Pa-SO₃H and TpPa-SO₃H; Figure S3: FT-IR spectra of Tp, BD-(SO₃H)₂ and TpBD-(SO₃H)₂; Figure S4: Zeta potential of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂; Figure S5: TGA curves of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ under N₂ atmosphere; Figure S6: Photographs demonstrating the hydrophilicity of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ with a water contact angle of 40°, 35°, 31°, respectively; Figure S7: SO₂ sorption isotherms of (a) TpPa-1, (b) TpPa-SO₃H and (c) TpBD-(SO₃H)₂ at 273 K and 298 K. Filled and open symbols indicate the adsorption and desorption, respectively; Figure S8: Virial analysis for SO₂ adsorption isotherms of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ at 273 and 298 K with the fitting parameters (virial coefficients) a_i and b_j . The virial coefficients a_i have the unit [K·mol^{−1}]; Figure S9: CO₂ sorption isotherms of (a) TpPa-1, (b) TpPa-SO₃H and (c) TpBD-(SO₃H)₂ at 273 and 298 K. Filled and open symbols indicate the adsorption and desorption isotherms, respectively; Figure S10: Virial analysis for CO₂ adsorption isotherms of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ at 273 and 298 K with the fitting parameters (virial coefficients) a_i and b_j . The virial coefficients a_i have the unit [K·mol^{−1}]; Figure S11: CH₄ sorption isotherms of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ at 298 K. Filled and open symbols indicate the adsorption and desorption isotherms, respectively; Figure S12: N₂ sorption isotherms of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ at 298 K. Filled and open symbols indicate the adsorption and desorption isotherms, respectively; Figure S13: IAST selectivity for CO₂/N₂ mixtures with varying CO₂ molar fractions in the gas phase at 298 K and 1 bar; Figure S14: Setup for humid SO₂ exposure experiments. Note: a, SO₂ sensor and hygrometer; b, N₂ flowmeter; c, sodium metabisulfite solution

(Na₂S₂O₅); d, sodium chloride solution; e, sample; f, NaOH aqueous solution; Figure S15: Comparison of PXRD patterns of (a) TpPa-1, (b) TpPa-SO₃H and (c) TpBD-(SO₃H)₂ before and after exposure to dry or humid SO₂ for different durations; Figure S16: Comparison of FT-IR patterns of (a) TpPa-1, (b) TpPa-SO₃H and (c) TpBD-(SO₃H)₂ before and after exposure to dry or humid SO₂ for different durations; Figure S17: Comparison of N₂ adsorption isotherms of (a) TpPa-1, (b) TpPa-SO₃H and (c) TpBD-(SO₃H)₂ before and after exposure to dry or humid SO₂ for different durations; Figure S18: The retained BET surface area percentages of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ after exposure to dry or humid SO₂ for different durations relative to corresponding pristine COFs; Table S1: CO₂, CH₄ and N₂ uptakes at different partial pressures and isosteric enthalpies of adsorption on TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ at 298 K; Table S2: Parameters of DSLAI Sips model fitted adsorption isotherms; Table S3: The result of IAST selectivity of TpPa-1, TpPa-SO₃H and TpBD-(SO₃H)₂ at 298 K at 1 bar; Table S4: Comparison of SO₂ sorption data in this work with reported COFs; Table S5: The breakthrough time of TpPa-1, TpBD-(SO₃H)₂ and representative adsorbents.

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