Synthesis of triphenylamine-based nanoporous organic polymers for highly efficient capture of SO₂ and CO₂†

Jun Yan, Ya Tan, Sihan Tong, Jiangli Zhu and Zefeng Wang*

The fabrication of nanoporous organic polymers (NOPs) for the highly efficient capture of sulfur dioxide (SO₂) and carbon dioxide (CO₂) through the self-polymerization of AB₂ monomers presents significant challenges. In this study, two triphenylamine-based NOPs (ANOP-3 and ANOP-4) were synthesized via the self-condensation of 4-(N,N-diphenylamino)benzaldehyde and 4’-(diphenylamino) biphenyl-4-carbaldehyde. The resultant polymers exhibited a large BET surface area of up to 1016 m² g⁻¹ and a small pore size of <0.7 nm. ANOP-4 demonstrated an SO₂ adsorption uptake of 21.9 mmol g⁻¹ at 273 K and 100 kPa. At 298 K and 100 kPa, ANOP-3 and ANOP-4 exhibited remarkable SO₂/CO₂ selectivities of up to 64.7 and 50.5, respectively, when applying the ideal adsorbed solution theory (IAST). The exceptional adsorption and separation performance of the ANOPs can be attributed to the ultramicroporous structure and the strong affinity between the adsorbents and polymers. This robust affinity has been revealed by theoretical simulations. This study presents a novel building block for the development of highly efficient SO₂ sorbents.

Introduction

Sulfur dioxide (SO₂) is a highly corrosive molecule, and is produced in large quantities through the combustion of fossil fuels. It can cause respiratory diseases in humans and affect the environment by contributing to the formation of acid rain.¹ About 87% of the global sulfur dioxide (SO₂) originates from flue gas, with a SO₂ concentration exceeding 500 ppm.² This implies that the partial pressure of SO₂ ranges from approximately 0.001 to 0.05 bar. Studies have investigated several strategies to reduce SO₂ emissions.³–⁵ However, an alternative approach is to collect and purify the produced SO₂ for further utilization in the industrial production of sulfuric acid (H₂SO₄). Various conventional methods, which employ sodium hydroxide (NaOH), alkaline lime slurry, and dilute H₂SO₄, have been effective at addressing the toxic effects of SO₂. However, these techniques have certain inherent drawbacks, such as inefficient capture, complex procedures, and safety hazards. Therefore, there is an urgent need to develop environmentally friendly and economically efficient adsorbents specifically designed for the capture of SO₂. This requirement has become both essential and pressing within the field.

Compared to conventional absorption processes, physisorption is known to be a powerful strategy for the convenient and energy-efficient capture of SO₂ and involves the use of various porous adsorbents, such as porous carbon,⁶–¹¹ metal–organic frameworks (MOFs),¹²–²¹ and nanoporous organic polymers (NOPs),²²–²⁷ which serve as major adsorbents for physisorption. Among these materials, NOPs have been regarded as promising candidates for SO₂ capture due to their wide range of reactions, high surface area, and excellent chemical and thermal stabilities. Park et al. introduced a modulator called 4-[(dimethylamino)methyl]aniline into an imide-linked covalent organic framework (COF). The amine-functionalized PI-COF-m10 with an SO₂ uptake of 6.30 mmol g⁻¹ demonstrates exceptional sorption capacity.²⁷ Farha et al. conducted post-synthesis modifications on the archetypal PIM-1 by functionalizing it with amidoxime groups. This resulted in an increased SO₂ adsorption capacity from 5.89 to 7.32 mmol g⁻¹.²³ Ma et al. successfully synthesized a three-dimensional (3D) ultramicroporous organic framework (TAM-POF) by condensing 2,4,6-triformylphloroglucinol aldehyde and tetra-4-aminophenol...
The ultramicroporous structure of TAM-POF enables it to exhibit a high SO₂ uptake of 9.45 mmol g⁻¹. Yan and coworkers conducted a study on the synthesis of two nanoporous semi-cycloaliphatic polyaminal networks (sPANs) by utilizing cycloaliphatic piperazine and aromatic tetrakis-functionalized aldehyde monomers. The sPANs demonstrated an impressive SO₂ uptake of up to 9.36 mmol g⁻¹ (at 273 K and 100 kPa), along with an exceptional selectivity for SO₂ over CO₂ (50.2, at 298 K and 100 kPa). The abovementioned studies have demonstrated the potential of adjusting the pore chemistry of NOPs through heteroatom nitrogen (N) substitution to create a rich microporous structure for improved SO₂ adsorption behavior. However, these studies typically involve the synthesis of NOPs through two-component co-condensation with different functional groups or complex post-modification methods. Additionally, the preparation of nitrogen-containing MOPs involves controlling the proportion of monomers and selecting specific synthetic conditions (e.g., solvent, temperature, reaction time, and concentration), leading to a complicated synthesis process. To address this complexity and simplify nitrogen-containing NOP synthesis for SO₂ capture, we have previously proposed the use of AB₂ monomers. Nevertheless, very few investigations have looked further in this direction.

In this study, two triphenylamine-based NOPs were synthesized through the self-condensation of two AB₂ monomers, namely 4-(N,N-diphenylamino)benzaldehyde (DPAB) and 4′-(diphenylamino)biphenyl-4-carbaldehyde (DPABC). The length–diameter ratios of DPAB and DPABC differ significantly, which is speculated to impact the topological structure of the network struts. Consequently, we investigated the influence of the building blocks on the porosity parameters and the SO₂ and CO₂ adsorption/separation capabilities of the resulting polymers.

Experimental section

Materials

4-(N,N-Diphenylamino)benzaldehyde (DPAB, 98%), and 4′-(diphenylamino)biphenyl-4-carbaldehyde (DPABC, 98%) were obtained from Zhengzhou Alfa Chemical Co., Ltd, China. p-Toluenesulfonic acid monohydrate (TsOH·H₂O, 99%), anhydrous o-dichlorobenzene (o-DCB, 99%), anhydrous N,N-dimethylformamide (DMF, 99%), anhydrous tetrahydrofuran (THF), anhydrous dichloromethane (DCM, 99%), and anhydrous dimethyl sulfoxide (DMSO, 99%) were acquired from J&K Chemical Co., Ltd, China.

Synthesis of triphenylamine-based nanoporous organic polymers

Synthesis of ANOP-3. Under an argon (Ar) atmosphere, a dry 50 mL Schlenk flask was charged with DPAB (0.82 g; 3.0 mmol), TsOH·H₂O (0.63 g; 3.3 mmol), and o-DCB (16.4 mL). The reaction mixture was heated and stirred at 180 °C for 24 hours. The resultant black precipitate formed was isolated through filtration and washed with o-DCB, DMF, and DCM. The obtained solid was then subjected to extraction with THF for 3 days and subsequently vacuum-dried at 120 °C for 48 hours. The yield of the final product was found to be 98%.

Synthesis of ANOP-4. The preparation of the ANOP-4 polymer followed the same method described above for ANOP-3, involving the use of DPABC (1.05 g; 3.0 mmol), TsOH·H₂O (0.63 g; 3.3 mmol), and 21.0 mL of o-DCB. The resulting yield was determined to be 97%.

Material characterization

Thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), field-emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FTIR) spectroscopy, solid-state ¹³C cross-polarization (CP)/total suppression of spinning side bands (TOSS) nuclear magnetic resonance (NMR) spectrometry, and elemental analysis (EA) were performed using the same methodology and equipment as in our previous studies. Adsorption measurements for SO₂ and CO₂ were performed using a gas adsorption analyzer (BSD-PMC, BeiShiDe Instrument Co. Ltd, China). The N₂ sorption isotherms (77 K) of the as-synthesized ANOPs were analyzed using an Autosorb iQ gas sorption analyzer (QuanTachrome Instruments).

Results and discussion

Preparation and characterization of polymers

In this work, both ANOP-3 and ANOP-4 were synthesized through a self-condensation reaction using the AB₂ monomers DPAB and DPABC, as illustrated in Scheme 1. The polymerization was carried out under an inert atmosphere in a dry solvent. The resulting polymers were characterized using various techniques, including TGA, WAXD, FE-SEM, FTIR, CP/TOSS NMR, and EA. The N₂ sorption isotherms of the as-synthesized ANOPs were analyzed using an Autosorb iQ gas sorption analyzer (QuanTachrome Instruments).
ations were carried out in o-DCB at 180 °C. The ANOPs were found to be insoluble in commonly used organic solvents such as o-DCB, DMF, DMSO, THF, and DCM. This characteristic can be ascribed to their highly cross-linked structure, developed through the aforementioned self-condensation. The thermal stability of the two polymers was assessed through thermogravimetric analysis (TGA) conducted under a nitrogen atmosphere (Fig. S1†). The weight losses associated with the skeletal decomposition were observed at temperatures exceeding 500 °C, whereas the char yields at 700 °C were found to be 67.2 wt% and 75.8 wt% for ANOP-3 and ANOP-4, respectively. The amorphous nature of both ANOPs was verified by powder X-ray diffraction (PXRD; Fig. S2†). The FE-SEM images revealed the morphologies of the ANOPs, indicating a highly interconnected polymer network (Fig. S3(a) and (b)†). This characteristic was consistent with the findings of previous studies on NOPs.30–32 Characterization techniques such as FTIR spectroscopy, solid-state $^{13}$C CP/TOSS NMR, and EA were utilized to validate the chemical structure and composition of ANOP-3 and ANOP-4. The FTIR spectra indicated the presence of the characteristic methylene group stretching bands in the range of 2800–3000 cm$^{-1}$ (Fig. S4†). Additionally, the spectra revealed distinct phenyl ring vibrations for both polymers, corresponding to the $\equiv$C–H and C$\equiv$C groups, at 3032, 1601, and 1497 cm$^{-1}$. Moreover, a noticeable C–N stretching in the two ANOPs was identified at 1264 cm$^{-1}$. Furthermore, a noticeable decrease in the peak intensity at 1700 cm$^{-1}$ indicated a reduction in the aldehyde functional groups. The $^{13}$C NMR spectra of ANOP-3, DPAB, ANOP-4, and DPABC are depicted in Fig. 1(a) and (b). The chemical shifts of the methylene-linkage in ANOP-3 and ANOP-4 were centered around 55 and 62 ppm, respectively. The ANOPs exhibited aromatic ring structure carbon signals within the chemical shift range of 110–160 ppm, which is consistent with the FTIR spectroscopy results. Moreover, ANOP-3 did not exhibit an aldehyde group characteristic peak, indicating the completion of its reaction. Conversely, in the case of ANOP-4, residual aldehyde groups were detected, suggesting an incomplete reaction due to the strong rigidity of DPABC and premature precipitation during the polymerization process. It is worth mentioning that discrepancies were observed between the experimental findings and the theoretical values of the ANOP chemical compositions (Table S1†). These disparities can be attributed to the presence of adsorbed moisture, CO$_2$, and unreacted functional groups during the experiments. Based on the aforementioned analysis, our expectations regarding the formation of the ANOPs through the self-condensation of AB$_2$ monomers were validated.

Porosity analysis

The permanent porosity structures and parameters of the obtained ANOPs were analyzed by examining the N$_2$ adsorption isotherms at 77 K (Fig. 2(a) and Table 1). For both polymers, the isotherms exhibited a rapid increase for low relative pressure ($P/P_0 < 0.01$), indicating the existence of permanent micropores, followed by a relatively gradual increase with increasing relative pressure. The $S_{BET}$ values for ANOP-3 and ANOP-4 were 287 and 1016 m$^2$ g$^{-1}$, respectively. The higher $S_{BET}$ value of ANOP-4 than that of ANOP-3 aligned with previous studies on porous materials.33 The $S_{BET}$ values measured for ANOP-4 were similar to those reported for other NOPs, such as PAN-1 (925 m$^2$ g$^{-1}$),34 PCN-TCP (751 m$^2$ g$^{-1}$),35 POPTrB-4F (776 m$^2$ g$^{-1}$),36 and CPOP1-V2 (1150 m$^2$ g$^{-1}$).37 Additionally, the total pore volumes for ANOP-3 and ANOP-4 were determined, from the N$_2$ sorption isotherms at $P/P_0 = 0.99$, to be 0.186 and 0.789 cm$^3$ g$^{-1}$, respectively. The microporous surface area and volumes, evaluated using the t-plot method, were found to be 217 m$^2$ g$^{-1}$ and 0.109 cm$^3$ g$^{-1}$, respectively, for ANOP-3, and 792 m$^2$ g$^{-1}$ and 0.392 cm$^3$ g$^{-1}$, respectively, for ANOP-4. The pore size distribution curves for both polymers were determined by analyzing the N$_2$ adsorption isotherms using the non-local density functional theory (NLDFT; Fig. 2(b)). The pore size for both polymers was < 2 nm, concentrated in the microporous region. The results aligned with the N$_2$ adsorption isotherms observed at 77 K. The pore size of ANOP-3 (0.49–0.60 nm) was smaller than that of ANOP-4 (0.66 nm). It was speculated that due to the higher length–diameter ratio of DPABC than that of DPAB, after the

![Fig. 1](image1)

Fig. 1 $^{13}$C NMR spectra of (a) ANOP-3 and DPAB, and (b) ANOP-4 and DPABC.

![Fig. 2](image2)

Fig. 2 (a) N$_2$ adsorption (filled) and desorption (empty) isotherms at 77 K for ANOP-3 and ANOP-4; (b) pore size distribution curves of ANOP-3 and ANOP-4.
cross-linking reaction, the longer struts support the framework and generate larger pores in comparison with those in ANOP-3.

SO₂ and CO₂ adsorption/separation

On account of the high BET specific surface area and numerous triphenylamine units of the ANOPs, we employed a gas adsorption analyzer to evaluate the SO₂ and CO₂ adsorption isotherms at 273 and 298 K (Fig. 3(a) and (b)). Both polymers exhibited a higher uptake of SO₂ and CO₂ at 273 K than that at 298 K, suggesting that the adsorption of these gases onto the polymers is primarily physical in nature. Moreover, the adsorption uptake of SO₂ was greater than that of CO₂ for both polymers, a discrepancy that arises from the distinct physicochemical characteristics of the two gases. The polarizability, dipole moment, and critical temperature of SO₂ (37.2–42.8 × 10²⁵ cm³, 1.63 × 10¹⁸ esu × cm, and 430.8 K, respectively) significantly surpass those of CO₂ (29.11 × 10²⁵ cm³, 0 esu × cm, and 304.1 K, respectively). Consequently, the triphenylamine skeleton within the polymers is more likely to induce polarization in the SO₂ molecule, resulting in an enhanced affinity towards the polymers and a higher uptake.³⁸ Table 2 presents a summary of the SO₂ and CO₂ adsorption uptake of ANOP-3 and ANOP-4 at 100 kPa. Although ANOP-3 has a high nitrogen content, its adsorption capacity for SO₂ and CO₂ is lower than

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO₂ (mmol g⁻¹)</th>
<th>CO₂ (mmol g⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>ANOP-3</td>
<td>12.5 7.7</td>
<td>1.8 1.1</td>
</tr>
<tr>
<td>ANOP-4</td>
<td>21.9 10.9</td>
<td>2.4 1.3</td>
</tr>
</tbody>
</table>

Table 2 The capacity of adsorption for SO₂ and CO₂ in ANOPs

³⁸ Uptake at 100 kPa.
that of ANOP-4. This effect can be attributed to the larger microporous surface area and volume of the latter, resulting in a higher number of available adsorption sites. The findings of this study emphasize the significance of a high microporous surface area and volume. Additionally, to assess the cycling stability of the ANOPs during the adsorption of SO$_2$ and CO$_2$, five adsorption experiments were performed at 273 K and 100 kPa (Fig. 3(c)). After five cycles of adsorption, we observed a decrease in the quantity of SO$_2$ adsorbed, while the amount of carbon dioxide adsorption remained constant. Furthermore, the FTIR spectra of the polymers before and after the five adsorption tests were identical (Fig. S5†), suggesting only weak interactions between the ANOPs and SO$_2$. The polymers could be reused by decreasing the pressure or increasing the temperature.

It is well-known that SO$_2$ is primarily emitted from flue gas, where the partial pressure of SO$_2$ is very low. Therefore, it is essential to capture sulfur dioxide at low partial pressure. The SO$_2$ uptakes of ANOP-4 were estimated to be 6.4 mmol g$^{-1}$ at 273 K and 3.5 mmol g$^{-1}$ at 298 K, respectively, under a pressure of 10 kPa. The value of 3.5 mmol g$^{-1}$ can compete with those of the reported porous materials under the same conditions, such as BIDC-3-800 (4.57 mmol g$^{-1}$),$^6$ TAM-POF (4.52 mmol g$^{-1}$),$^{25}$ HNIP-TMBM-1 (3.39–3.54 mmol g$^{-1}$),$^{39}$ ECUT-100 (3.3 mmol g$^{-1}$),$^{14}$ ECUT-Th-60 (2.5 mmol g$^{-1}$),$^{16}$ ELM-12 (1.95 mmol g$^{-1}$),$^{12}$ sPAN-2 (1.9 mmol g$^{-1}$),$^{26}$ HNIP-DCX-1 (1.57 mmol g$^{-1}$),$^{39}$ and ECUT-77 (0.48 mmol g$^{-1}$).$^{13}$ Surprisingly, ANOP-4 demonstrates a notable uptake of 21.9 mmol g$^{-1}$ SO$_2$ at 273 K and 100 kPa (Table 2), surpassing the performance of several previously reported porous materials, such as TAM-POF (about 13.0 mmol g$^{-1}$),$^{25}$ viologen-POF (about 18.3 mmol g$^{-1}$),$^{24}$ DUTs (about 10.3–10.6 mmol g$^{-1}$),$^{17}$ sPANs (8.45–9.36 mmol g$^{-1}$),$^{26}$ and

Fig. 4  Experimental adsorption isotherms and dual-site Langmuir–Freundlich fitting curves for SO$_2$ and CO$_2$ in ANOP-3 (a) and ANOP-4 (b) at 298 K; (c) SO$_2$/CO$_2$ selectivities of ANOP-3 and ANOP-4 at 298 K; (d) comparison of the SO$_2$/CO$_2$ selectivities of ANOPs and the previously reported materials.
CTFs (4.4–6.7 mmol g\(^{-1}\)).\(^{22}\) Additionally, when the measurement temperature was increased from 273 K to 298 K, the SO\(_2\) adsorption capacities of both ANOPs decreased slightly due to their physiosorption characteristics. However, at 298 K and 100 kPa, ANOP-3 and ANOP-4 demonstrated significant SO\(_2\) uptakes, reaching up to 7.7 and 10.9 mmol g\(^{-1}\), respectively. These values exceeded/competed with those of other previously reported nitrogen-containing NOPs, such as TAM-POF (9.45 mmol g\(^{-1}\)),\(^{25}\) XJCOPs (8.4–9.6 mmol g\(^{-1}\)),\(^{46}\) ICTF-SCN (9.22 mmol g\(^{-1}\)),\(^{41}\) sPANs (5.56–5.64 mmol g\(^{-1}\)),\(^{26}\) PI-COF-m (6.5 mmol g\(^{-1}\)),\(^{27}\) PIMs (5.53–7.32 mmol g\(^{-1}\)),\(^{23}\) POPs (3.8–12.2 mmol g\(^{-1}\)),\(^{32}\) and MOFs, such as MFM-601 (12.3 mmol g\(^{-1}\)),\(^{43}\) SIFSIX-1-Cu (11.01 mmol g\(^{-1}\)),\(^{44}\) DUTs (9.1–9.3 mmol g\(^{-1}\)),\(^{17}\) and ECUTs (4.95–11.6 mmol g\(^{-1}\))\(^{14},^{15}\) as well as porous carbons, such as BIDC-2-700 (10.25 mmol g\(^{-1}\))\(^{6}\), NPCs (1.22–1.80 mmol g\(^{-1}\)),\(^{7}\) GU-1 (7.60 mmol g\(^{-1}\)),\(^{29}\) 296.2 K),\(^{6}\) and GC-2 (10.2 mmol g\(^{-1}\))\(^{29}\). Comparison of the previously reported porous materials at 298 K and 100 kPa (Fig. 3(d) and Table S2†) with ANOPs reveals the latter's superior SO\(_2\) adsorption capacity. This is due to the combination of two factors: (i) high microporosity, which provides more space for SO\(_2\) adsorption, and (ii) a large number of triphenylamine structures, which offer more sites for SO\(_2\) adsorption. Additionally, the ANOPs also exhibited good CO\(_2\) uptake (ANOP-4: 1.3 mmol g\(^{-1}\) and ANOP-3: 1.1 mmol g\(^{-1}\)) at 298 K and 100 kPa). These values were comparable with those of the previously reported NOPs, such as TAM-POF (1.40 mmol g\(^{-1}\)),\(^{25}\) HCP-PNs (0.86–1.31 mmol g\(^{-1}\)),\(^{45}\) sPANs (0.94–1.09 mmol g\(^{-1}\)),\(^{26}\) ANOP-1 (0.95 mmol g\(^{-1}\)),\(^{32}\) and PAN-5F (0.88 mmol g\(^{-1}\)).\(^{46}\)

The isosteric enthalpies of adsorption (Q\(_{\text{st}}\)) between the ANOPs and the two gases, namely SO\(_2\) and CO\(_2\), were determined using the Clausius–Clapeyron equation (Fig. S6†),\(^{37}\) based on the measured SO\(_2\) and CO\(_2\) adsorption isotherms at 273 and 298 K. Fig. 3(a) and (b) show the SO\(_2\) and CO\(_2\) adsorption uptakes of the ANOPs at different pressures. With increasing gas adsorption, the Q\(_{\text{st}}\) values of the polymers consistently decreased. This suggests that, rather than forming clusters, the gases preferentially adsorb onto the network structures of the pore walls. Moreover, the order of the Q\(_{\text{st}}\) values obtained for the two gases at a specific adsorption quantity was Q\(_{\text{st}}\) (SO\(_2\)) > Q\(_{\text{st}}\) (CO\(_2\)), indicating that the polymers can remove SO\(_2\) from exhaust flue gas. The Q\(_{\text{st}}\) (SO\(_2\)) of ANOP-3 was higher than that of ANOP-4 due to its smaller pore size. Therefore, ANOP-3 exhibited a pronounced interaction with the polar SO\(_2\) gas through a pore-trapping effect. However, the isosteric enthalpies of adsorption exhibit distinct behavior for CO\(_2\) gas. This effect can be attributed to the ANOP-4 polymer having more space and offering a larger number of adsorption sites, leading to an intensified interaction with CO\(_2\).

To evaluate the SO\(_2\)/CO\(_2\) selectivities of both the ANOPs, we measured the single-component adsorption isotherms for both gases at 298 K, which fitted well with the dual-site Langmuir–Freundlich curves of the corresponding gases (Fig. 4(a) and (b)). The fitted parameter is summarized in Table S3.† Comparative analysis revealed that the SO\(_2\) uptake of each polymer was significantly higher than that of CO\(_2\) within the measured pressure range, suggesting that the triphenylamine skeleton has a preferential affinity for SO\(_2\) compared to CO\(_2\) under environmental conditions. Using the ideal adsorbed solution theory (IAST), we calculated the SO\(_2\)/CO\(_2\) selectivity under ambient conditions for binary gas mixtures with a molar ratio of 10:90. Fig. 4(c) illustrates the relationship between the SO\(_2\)/CO\(_2\) selectivities and the pressure. The selectivity of ANOP-3 for SO\(_2\) over CO\(_2\) was higher than that of ANOP-4, due to the smaller pore size of ANOP-3 and the stronger interactions of the polymer skeleton with SO\(_2\). Moreover, ANOP-3 and ANOP-4 exhibited a remarkable SO\(_2\)/CO\(_2\) selectivity of up to 64.7 and 50.5, respectively, at 298 K and 100 kPa. These values compete with and also surpass those reported for other (i) nitrogen-containing NOPs, such as sPANs (37.6–50.3),\(^{26}\) POPs (17.8–31.0),\(^{12}\) XJCOPs (39.0–42.0),\(^{40}\) HNIP-TBMB-2 (50.0),\(^{39}\) and TAM-POF (61.0),\(^{25}\) and (ii) porous materials, such as CPL-1 (8.7),\(^{48}\) ECUT-TH-60 (27.0),\(^{16}\) DUTs (33.0–37.0),\(^{17}\) Fe-soc-MOF (32.0),\(^{49}\) ELM-12 (30.0),\(^{12}\) BC-X-650 (21.0–32.0),\(^{10}\) and GU-1 (15.9 at 296.2 K).\(^{8}\) The comparison of the data for porous materials reported at 298 K and 100 kPa (Fig. 4(d) and Table S2†) revealed the superior adsorption selectivity of the ANOPs for SO\(_2\) compared to that for CO\(_2\). This can again be attributed to the presence of extensive polar...
triphenylamine structures in these polymers, which provide numerous adsorption sites for SO₂ due to dipole–dipole interactions, surpassing those available for CO₂.

To investigate the disparity in adsorption performance between SO₂ and CO₂ in the ANOPs, we employed dispersion-corrected density functional theory to examine the affinities between the polymer fragments and adsorbates using optimized configurations. Fig. 5 illustrates the calculated static binding energies ($ΔE_{ads}$) between the gas and the adsorbent, revealing that $ΔE_{ads}(SO₂) > ΔE_{ads}(CO₂)$. This finding aligned with their respective adsorption capacities and $Q_a$ values. These results further confirmed that the synthesized ANOPs could be used to remove the corrosive SO₂ from exhaust flue gas. Additionally, we observed that the difference in the binding affinity between SO₂ and CO₂ ($|ΔE_{ads}(SO₂) - ΔE_{ads}(CO₂)|$) was higher for ANOP-3 (10.6 kJ mol⁻¹) than that for ANOP-4 (9.5 kJ mol⁻¹), further verifying the higher affinity of the former for SO₂. To summarize, extreme ultramicroporosity and polar triphenylamine moieties in the ANOP networks enable the differentiation of the two gas components and facilitate the selective capture of SO₂ from exhaust flue gas containing CO₂.

Conclusions

In this work, we have successfully synthesized ANOP-3 and ANOP-4 polymers through the self-condensation of two AB₃ triphenylamine-based monomers, i.e., DPABC and DPAB, respectively. The ANOPs exhibit specific surface areas ranging from 287 to 1016 m² g⁻¹, with pore size < 0.70 nm. ANOP-4 demonstrates an excellent SO₂ uptake of 21.9 mmol g⁻¹ at 273 K and 100 kPa. Furthermore, ANOP-3 and ANOP-4 show impressive SO₂/CO₂ selectivity of up to 64.7 and 50.5, respectively, at 298 K and 100 kPa. These findings suggest that a highly ultramicroporous polymer network incorporated with extended triphenylamine moieties exhibits enhanced SO₂ uptake. This investigation aims to provide valuable guidance for the development of novel NOPs and expand the applications of triphenylamine-based NOPs, particularly in corrosive SO₂ removal.

Author contributions

Jun Yan: methodology, investigation, supervision, project administration, validation, funding acquisition, writing – review & editing. Yan Tan: methodology, investigation, software, data curation, writing – original draft. Sihan Tong: investigation, software, data curation, writing – original draft. Jiangli Zhu: methodology, investigation, data curation. Zefeng Wang: funding acquisition, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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