Microporous Materials

Directing the Structural Features of N₂-Phobic Nanoporous Covalent Organic Polymers for CO₂ Capture and Separation


Abstract: A family of azo-bridged covalent organic polymers (azo-COPs) was synthesized through a catalyst-free direct coupling of aromatic nitro and amine compounds under basic conditions. The azo-COPs formed 3D nanoporous networks and exhibited surface areas up to 729.6 m² g⁻¹, with a CO₂-uptake capacity as high as 2.55 mmol g⁻¹ at 273 K and 1 bar. Azo-COPs showed remarkable CO₂/N₂ selectivities (95.6–165.2) at 298 K and 1 bar. Unlike any other porous material, CO₂/N₂ selectivities of azo-COPs increase with rising temperature. It was found that azo-COPs show less than expected affinity towards N₂ gas, thus making the framework “N₂-phobic”, in relative terms. Our theoretical simulations indicate that the origin of this unusual behavior is associated with the larger entropic loss of N₂ gas molecules upon their interaction with azo-groups. The effect of fused aromatic rings on the CO₂/N₂ selectivity in azo-COPs is also demonstrated. Increasing the π-surface area resulted in an increase in the CO₂-philic nature of the framework, thus allowing us to reach a CO₂/N₂ selectivity value of 307.7 at 323 K and 1 bar, which is the highest value reported to date. Hence, it is possible to combine the concepts of “CO₂-philicity” and “N₂-phobicity” for efficient CO₂ capture and separation. Isosteric heats of CO₂ adsorption for azo-COPs range from 24.8–32.1 kJ mol⁻¹ at ambient pressure. Azo-COPs are stable up to 350 °C in air and boiling water for a week. A promising cis/trans isomerization of azo-COPs for switchable porosity is also demonstrated, making way for a gated CO₂ uptake.

Introduction

Carbon dioxide (CO₂) emissions into the atmosphere account for the majority of energy and environmental challenges, and its global impact in the form of climate change is well-documented.[1] The unprecedented increase in the atmospheric presence of CO₂ also endangers the ecosystem by ocean acidification and other, yet unknown, direct interferences to the life on Earth.[2] The threat becomes more imminent as the time passes because no viable solution to effectively capture and store CO₂ is available. In the case of capture and separation, CO₂ scrubbing by ethanolic aqueous amines is yet to be challenged.[3] Nanoporous materials (pore sizes under 100 nm) have been studied extensively for CO₂ capture and separation on account of their modular nature, chemical and thermal stability, and large accessible surface area.[4] Most existing porous materials, however, suffer from water instability (e.g., metal-organic frameworks, MOFs)[2,5] or the difficulty to tune their structures (e.g., zeolites, activated carbon) or the lack of sustainable synthesis, owing to the use of rare earth catalysts (e.g., conjugated microporous polymers).[6]

There are several examples of crystalline or amorphous nanoporous polymers reported in the literature,[7] namely, polymers with intrinsic microporosity (PIM),[8] hypercross-linked and conjugated microporous polymers (HCP and CMP),[8b,9] organic cages,[10] benzimidazole-linked polymers (BILP),[11] covalent triazine frameworks (CTF),[12] porous aromatic frameworks (PAF),[13] porous polymer networks (PPN),[14] covalent organic frameworks (COF),[15] porous organic frameworks (POF),[16] covalent organic polymers (COP),[17] carbazole-based porous organic polymer (CPOP),[18] elemental-organic frameworks (EOFs),[19] porous cross-linked polymers (PCPs),[20] porous organic polymers (POPs),[21] tetrazine-based organic frameworks (TzFs),[22] porous polymer frameworks (PPF),[23] Schiff base networks (SNW),[24] and others.[25] Although CO₂-philic sorbents that are decorated with amines have been well-documented,[26,40] their energy intensive regeneration on account of their high isosteric heats of adsorption (Q > 40 kJ mol⁻¹) and low thermal and chemical stability due to the oxidation of amino groups limit their application in CO₂ capture and separation. For example, polyamine-tethered PPNs showed CO₂ capacity of 4.3 mmol g⁻¹ and CO₂/N₂ selectivity as much as 442 at 295 K and 1 bar,[26] however, amine functionalities were prone to oxidative degradation and decomposed below 200 °C in air. This observation is in line with the concept that physisorption of CO₂ is more...
preferred over the chemisorption one due to the fact that there are no chemical bonds formed or broken during adsorption and regeneration cycles. One proof for the latter is a report by El-Kaderi et al.\textsuperscript{27} in which BILPs are shown to have exceptional CO\textsubscript{2}/N\textsubscript{2} capture capacities up to 5.34 mmol g\textsuperscript{-1} at 273 K and 1 bar. Another example is the recent report on PPFs by Zhu et al.\textsuperscript{28} in which CO\textsubscript{2} capacities of up to 6 mmol g\textsuperscript{-1} were reported with imine-linked nanoporous amorphous polymers at 273 K and 1 bar. All these examples showed exceptional CO\textsubscript{2} capacities with moderate-to-low CO\textsubscript{2}/N\textsubscript{2} selectivity, which decrease with rising temperature, an important limitation for their application in the temperature range (>40 °C) for the post-combustion CO\textsubscript{2} capture.\textsuperscript{16} We have recently reported a new class of nanoporous polymers called azo-bridged covalent organic polymers (azo-COPs), synthesized by catalyst-free coupling of aromatic nitro and amine compounds under basic conditions.\textsuperscript{28} Azo-COPs revealed an increase in CO\textsubscript{2}/N\textsubscript{2} selectivity with rising temperature due to the fact that azo (–N–N–) functionalities showed less than expected affinity towards N\textsubscript{2} gas, thus making the framework “N\textsubscript{2}-phobic”, in relative terms. Azo-COP-2 showed moderate CO\textsubscript{2}/N\textsubscript{2} selectivity of 130.6 at 298 K, which is increased to the then highest value (288.1, at 323 K and 1 bar) with rising temperature. Our previously reported\textsuperscript{28} theoretical simulations suggested that the origin of N\textsubscript{2}-phobicity is due to the entropic loss of N\textsubscript{2} gas molecules upon their interaction with the azo-groups, although the binding process is enthalpically favorable.

Herein, we have described the synthesis of a family of azo-COPs that show remarkable CO\textsubscript{2}/N\textsubscript{2} selectivities at warm temperatures. To understand the scope of azo-coupling, we have used a series of monomers with varying steric hindrance, rigidity, and π-surface area and investigated their effect on the CO\textsubscript{2} and N\textsubscript{2} gas sorption characteristics. We have also demonstrated that the increasing π-surface area by using fused aromatic rings resulted in a significant increase in the CO\textsubscript{2}/N\textsubscript{2} selectivity. Our simulations indicate that CO\textsubscript{2} has a higher affinity towards aromatic units when compared with N\textsubscript{2} gas molecules, thus increasing the π-surface area increases the CO\textsubscript{2}-philicity of the framework. These results indicate that it is possible to combine the concepts of CO\textsubscript{2}-philicity with N\textsubscript{2}-phobicity to improve CO\textsubscript{2}/N\textsubscript{2} selectivity and also CO\textsubscript{2}-uptake capacity. The formation of azo-COPs and their structural stability were confirmed by using a series of analytical techniques. We have also investigated the switching of azo-COPs and its effect on the surface area. Azo-COPs are shown to be extremely stable up to 350 °C in air and also in boiling water for a week.

**Results and Discussion**

Aromatic azo compounds are generally prepared from oxidation of aromatic amines in the presence of metal-based catalysts.\textsuperscript{29} In the search for an environmentally benign process, we have recently demonstrated\textsuperscript{28} the catalyst-free direct coupling of aromatic amines and nitro compounds under basic conditions to prepare azo-COPs. A family of azo-COPs were synthesized by the direct coupling of tetrakis(4-nitrophenyl)ethane with various aromatic amines, including 4,4',4''-methanetetrayl tetraaniline (azo-COP-1), p-phenylenediamine (azo-COP-2), benzidine (azo-COP-3), 2,3,5,6-tetramethyl-1,4-phenylenediamine (azo-COP-4), 2,5-dimethyl-1,4-phenylenediamine (azo-COP-5), 1,3-phenylenediamine (azo-COP-6), 3,3'-dimethylbenzidine (azo-COP-7), 4,4'-methylenedianiline (azo-COP-8), 4,4'-oxydianiline (azo-COP-9), 1,5-diaminonaphthalene (azo-COP-10), and tris(4-aminophenyl)methanol (azo-COP-11), resulting in a series of azo-COPs with different structural geometries and properties (Figure 1).

To verify the formation of azo-COPs, we have carried out a set of analyses, including Fourier transform infrared spectroscopy (FTIR), elemental analysis, cross-polarization magic-angle spinning (CP/MAS) $^{13}$C NMR spectroscopy, and thermogravimetric analysis (TGA). The FTIR spectra confirmed the formation of azo (–N–N–) linkages as shown by the stretching bands at 1447 and 1403 cm\textsuperscript{-1} (Figure S1 in the Supporting Information). Other noticeable bands were observed at 3400 (s, N–H), 3200 (s, N–H), 1610 (s, C–C aromatic), 1447 and 1403 (s, N–N), 1520 and 1340 (s, N–O), and 1280 cm\textsuperscript{-1} (s, C–N). The high oxygen content of azo-COPs in the elemental analysis could be attributed (Table S1 in the Supporting Information) to the presence of terminal nitro groups along with moisture trapped in the framework. Moreover, the ICP-MS analyses of azo-COPs show that the potassium content varies in the range from undetectable to 0.036% (w/w; Table S2 in the Supporting Information), confirming that higher oxygen content is associated with terminal nitro groups and moisture. Moreover, the stretching band located at 3600–3000 cm\textsuperscript{-1} also indicates the presence of terminal amino groups. The chemical shifts in the CP/MAS $^{13}$C NMR spectra of azo-COPs, namely, azo-COP-1 to azo-COP-11, located at $\delta = 150.2, 144.7, 129.5, 123.4, and 54.9$ ppm confirmed the formation of the azo-linked aromatic polymers (Figure S2 in the Supporting Information). The signal at $\delta = 115$ ppm, which is attributed to the carbon atom incorporating the terminal –NH\textsubscript{2} moiety, is clearly visible in all samples, confirming the presence of amine end-groups. The chemical shifts of aromatic moieties are merged in the region $\delta = 120–155$ ppm.

Thermogravimetric analysis (TGA) performed on azo-COPs up to 800 °C with a heating rate of 10 °C min\textsuperscript{-1}. Azo-COPs exhibited remarkable thermal stability up to 350 °C in air (Figure S3 in the Supporting Information). The TGA patterns showed a single-step mass-loss, which is attributed to the degradation of organic frameworks. Interestingly, when we carried out the TGA experiment under an N\textsubscript{2} atmosphere, azo-COPs decomposed at lower temperatures (e.g., 300 °C) when compared with the one under air. We believe that although the low molecular weight residual impurities in azo-COPs induced the decomposition at elevated temperatures under an N\textsubscript{2} atmosphere, those impurities are just oxidized in the presence of O\textsubscript{2} without affecting the network structure. To confirm this behavior, we have synthesized a model azo compound (see the Supporting Information) and studied its thermal stability. The model azo compound showed (Figure S4 in the Supporting Information) identical weight loss both in N\textsubscript{2} and in air, confirming that the early mass loss of azo-COPs under N\textsubscript{2} atmosphere is due to the decomposition of low molecular weight residual...
impurities. To investigate the water stability of azo-COPs, we kept the polymers in boiling water for a week and measured their surface areas. Azo-COPs did not show any noticeable loss of surface area (Figure S5 in the Supporting Information), indicating that their network structures are highly robust.

To investigate the permanent nanoporous nature of azo-COPs, \( \text{N}_2 \) adsorption–desorption experiments were conducted at 77 K (Figure 2). All samples were degassed at 150 °C for 5 h under vacuum prior to the measurement. Azo-COPs showed typical type I reversible sorption isotherms with Brunauer–Emmett–Teller (BET) surface areas ranging from 11.1–729.6 m\(^2\) g\(^{-1}\), verifying the porous nature of the synthesized materials (Table 1). The BET surface areas were calculated from the slope within 0.01–0.25 relative pressures (Figure S6 in the Supporting Information). The Langmuir surface area of azo-COPs is varied from 13.4 to 949.8 m\(^2\) g\(^{-1}\) (Table 1). Azo-COPs contain mesoporous network along with microporosity as evident from the hysteresis at the low pressure region that is ascribed to the pore network effects, wherein mesopores accessible only through micropores.\(^{[30]}\) The shape of nitrogen isotherm for azo-COP-6 differs at the higher relative pressure range, that is, more than 0.9, indicating an adsorption on the outer surface of small particles. The increase in the \( \text{N}_2 \) sorption may arise in part from inter-particulate voids coupled with the meso and macrostructures.\(^{[31]}\) In addition to the fact that the enhancement in BET surface area may not be the deciding factor for gas sorption behavior (especially for \( \text{CO}_2 \) gas sorption in which nitrogen, electron-rich moieties perform better), a moderate porosity (e.g. surface areas of 100 m\(^2\) g\(^{-1}\) or less) could lead to complete access to \( \text{CO}_2 \)-philic nitrogen-rich functionalities in the framework.\(^{[9]}\)

Figure 1. Building blocks of azo-bridged covalent organic polymers (azo-COPs), azo-COPs-1 to -11. Direct coupling of aromatic nitro with amines under basic conditions at 150 °C resulted in the formation of azo-COPs as bright-orange powders on a multigram scale. Azo-COP-1, -2, and -3 are discussed\(^{[28]}\) for comparison with other azo-COPs.

Figure 2. \( \text{N}_2 \) adsorption–desorption isotherms of azo-COPs-1 to -11 carried out at 77 K and the gas uptake and release are indicated by solid and open symbols, respectively. The BET surface areas of azo-COP-1 to -3 (measured by Ar adsorption–desorption at 87 K) have been reported\(^{[42]}\) and were used for comparison. The \( \text{N}_2 \) adsorption-desorption isotherms of azo-COPs-1 to -3 are given as Figure S12 (in the Supporting Information).
ticular case with azo aromatics, however, we see two competi-
linkers yield considerable losses in overall porosity. In this par-
This result is rather contrary to the common belief that flexible
rigid azo-COP-3, both structures showed similar surface areas.
bridges between biphenylic linkers. When compared to the
decrease, however, could be attributed to short monomer dis-
alignment, resulting in a relatively high surface area. The small

doubled the linker length (R 2 unit in Figure 1), a common strat-
egy in the construction of hybrid porous materials. Azo-COP-
(2) is expected for CO 2 adsorption–desorption
processes, because azo-COP-1 is the third spacious
area. Tetrahedral linkers of both
azo-COP-1 and 11 are expected to produce the highest degree of
porosity, as shown previously in porous boronic esters, that is,
COF-102. This is, however, not

Table 1. BET and Langmuir surface areas, CO 2 and N 2 capture capacities, CO 2/N 2 selectivities and isostructural heats of adsorption (Q a) for azo-COPs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BET [m 2 g −1]</th>
<th>Langmuir [m 2 g −1]</th>
<th>CO 2 adsorption (mmol g −1) at 273 K</th>
<th>CO 2 adsorption (mmol g −1) at 298 K</th>
<th>N 2 adsorption (mmol g −1) at 273 K</th>
<th>N 2 adsorption (mmol g −1) at 298 K</th>
<th>CO 2/N 2 (15:85) at 1 bar</th>
<th>Q a [kJ mol −1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>azo-COP-1</td>
<td>635.8</td>
<td>800.7</td>
<td>2.44</td>
<td>1.48</td>
<td>0.11</td>
<td>0.04</td>
<td>63.7</td>
<td>96.6</td>
</tr>
<tr>
<td>azo-COP-2</td>
<td>729.6</td>
<td>949.8</td>
<td>2.55</td>
<td>1.53</td>
<td>0.06</td>
<td>0.03</td>
<td>109.6</td>
<td>130.6</td>
</tr>
<tr>
<td>azo-COP-3</td>
<td>493.1</td>
<td>632.4</td>
<td>1.93</td>
<td>1.22</td>
<td>0.07</td>
<td>0.03</td>
<td>78.6</td>
<td>95.6</td>
</tr>
<tr>
<td>azo-COP-4</td>
<td>11.1</td>
<td>13.4</td>
<td>1.75</td>
<td>1.12</td>
<td>0.13</td>
<td>0.05</td>
<td>79.3</td>
<td>138.5</td>
</tr>
<tr>
<td>azo-COP-5</td>
<td>127.6</td>
<td>169.4</td>
<td>2.04</td>
<td>1.24</td>
<td>0.16</td>
<td>0.05</td>
<td>73.8</td>
<td>144.6</td>
</tr>
<tr>
<td>azo-COP-6</td>
<td>679.1</td>
<td>887.2</td>
<td>2.22</td>
<td>1.31</td>
<td>0.17</td>
<td>0.06</td>
<td>72.7</td>
<td>114.8</td>
</tr>
<tr>
<td>azo-COP-7</td>
<td>241.6</td>
<td>315.3</td>
<td>1.91</td>
<td>1.16</td>
<td>0.16</td>
<td>0.06</td>
<td>68.5</td>
<td>115.3</td>
</tr>
<tr>
<td>azo-COP-8</td>
<td>472.1</td>
<td>612.7</td>
<td>2.02</td>
<td>1.22</td>
<td>0.16</td>
<td>0.07</td>
<td>70.3</td>
<td>103.4</td>
</tr>
<tr>
<td>azo-COP-9</td>
<td>592.6</td>
<td>649.5</td>
<td>2.05</td>
<td>1.23</td>
<td>0.17</td>
<td>0.07</td>
<td>69.6</td>
<td>102.8</td>
</tr>
<tr>
<td>azo-COP-10</td>
<td>156.8</td>
<td>200.2</td>
<td>1.91</td>
<td>1.15</td>
<td>0.15</td>
<td>0.06</td>
<td>69.6</td>
<td>165.2</td>
</tr>
<tr>
<td>azo-COP-11</td>
<td>259.2</td>
<td>336.1</td>
<td>2.13</td>
<td>1.26</td>
<td>0.15</td>
<td>0.06</td>
<td>77.8</td>
<td>128.4</td>
</tr>
</tbody>
</table>

Accessible surfaces can be directed by the structural fea-
tures, despite the challenge of lacking order in azo-COP
frameworks. In an attempt to increase pore-size diameter, we
doubled the linker length (R 2 unit in Figure 1), a common strat-
egy in the construction of hybrid porous materials. Azo-COP-
3 (with double linker-length than that of azo-COP-2) showed a
55% increase in pore size (from 0.58 to 0.9 nm) though with a
loss of 32% in BET surface area (from 729.6 to 493.1 m 2 g −1).

Bulky groups are introduced to the ortho positions of the
linker in azo-COP-2, leading to azo-COPs incorporating tetra-
methyl (azo-COP-4) and dimethyl (azo-COP-5) groups, to
investigate the effect of steric hindrance. Surface areas are considerably reduced (> 80%), owing to the inability of in-plane exten-
sion of the monomers, a preferable alignment for azo-aromat-
ics. In the simplest terms, methyl groups force the N–N–
double bond to move outer plane, to at least a tilted geometry
with respect to the aromatic phenyls. The biphenyl linker in
azo-COP-3 also shows a similar loss of surface area (51%) when
ortho-methyl groups are attached on both ends (see azo-
COP-7). The lesser decrease in the latter can be attributed to the
already tilted geometry of biphenyl moieties. Tetramethyl-
yl substituents in azo-COP-4 are also responsible for the diffi-
culty in the formation of a porous network structure.

The best measure for the effect of kinks and tilts, perhaps,
would be forcing the linker to have a non-linear connectivity.
We chose a 1,3-diaminobenzene as a linker (azo-COP-6) to
check against azo-COP-2 incorporating 1,4-diaminobenzene as
a linker. To our surprise, the reduction in the surface area was
only 7%. This result might be associated with the uninterrupted
in-plane π-connectivity of azo units with the aromatic rings.
The trans configuration of azo groups also allows a zigzag
alignment, resulting in a relatively high surface area. The small
decrease, however, could be attributed to short monomer dis-
tances with a contracted spring-like monomer extension.

In azo-COP-8 and 9, we assessed the effect of flexible
bridges between biphenylic linkers. When compared to the
rigid azo-COP-3, both structures showed similar surface areas.
This result is rather contrary to the common belief that flexible
linkers yield considerable losses in overall porosity. In this par-
cular case with azo aromatics, however, we see two competi-
tive acts. Whereas the flexibility brings free rotation and conse-
quent contraction in framework construction, it also eliminates
the restriction on the in-plane alignment of biphenylic azo
units. As a result, the more con-
jugated, semi-rigid oxygen bridge shows an enhanced sur-
face area, whereas the methyl-
ene bridge reports a reduced area. Tetrahedral linkers of both
azo-COP-1 and 11 are expected to produce the highest degree of
porosity, as shown previously in porous boronic esters, that is, 
COF-102.

Given the variation of azo-COPs in their surface area, micro-
porosity, and structural geometry, it is anticipated that each
azo-COP would reveal a different gas sorption behavior. The
gas adsorption and desorption measurements for CO 2 and N 2
were obtained for all azo-COPs using a volumetric gas analyzer
at 273 and 298 K (Figure 3). All azo-COPs were degassed at
150 °C over 5 h to remove the adsorbed water and residual sol-
vent molecules from the nanopores of the framework. The shapes of the CO 2 isotherms are somewhat different at the
two temperatures. At 273 K, the CO 2 adsorption amount in
azo-COPs increased rapidly at the lower pressure range before
approaching saturation, and consequently showed a higher
CO 2 adsorption capacity when compared with the value found
at 298 K. Because both the high porosity and nitrogen content
contribute to the CO 2-philicity of the framework, azo-COP-2
showed the highest CO 2 sorption capacity of 2.55 and
1.53 mmol g −1 at 273 and 298 K, respectively. Other azo-COPs
demonstrated CO 2 adsorption capacity in the range of 1.75–
2.44 and 1.12–1.48 mmol g −1 at 273 and 298 K, respectively.
Most likely, at low pressures, the nitrogen-rich sites of the azo-
COPs have much higher binding affinity for CO 2 because of its
large quadrupolar moment and when the pressure is increased
these binding sites become saturated and therefore less avail-
able for CO 2 molecules.

There is a negligible hysteresis in CO 2 adsorption–desorption
isotherms at 273 and 298 K (Figure S7 in the Supporting Infor-
mation), confirming the complete regeneration without any
need for an external heat treatment. This property is highly des-
irable in post-combustion CO 2 capture because it eliminates
excessive energy consumption during adsorbent regeneration.

The CO 2 scrubbing by well-established industrial processes
that use aqueous amine solutions (e.g., 30% monoethanolamine) require significant amounts of heat for regeneration, resulting in a high-energy penalty, not to mention the accelerated corrosion.[1a] Azo-COPs adsorb relatively small amount of N$_2$ resulting in a high-energy penalty, not to mention the acceleration of regeneration, required significant amounts of heat for regeneration, and is not typically used in aqueous amine solutions (e.g., 30% monoethanolamine) due to the high-energy penalty and accelerated corrosion. Unlike any porous material, azo-COPs reveal an increase in selectivity with rising temperature. This unusual behavior is associated with the unfavorable interactions between N$_2$ gas molecules and azo-linkages in azo-COPs, allowing us to coin the term “N$_2$-phobicity” for this new concept. The CO$_2$/N$_2$ (0.15:0.85) selectivities of azo-COP-10 is superior to azo-COP-2 in its CO$_2$/N$_2$ selectivity. The fact that azo-COP-10 is superior to azo-COP-2 in its CO$_2$/N$_2$ selectivity, prompted us to investigate these two structures specifically. Since both structures only differ in the linkers, that use aqueous amine solutions (e.g., 30% monoethanolamine) require significant amounts of heat for regeneration, resulting in a high-energy penalty, not to mention the accelerated corrosion. Unlike any porous material, azo-COPs reveal an increase in selectivity with rising temperature. This unusual behavior is associated with the unfavorable interactions between N$_2$ gas molecules and azo-linkages in azo-COPs, allowing us to coin the term “N$_2$-phobicity” for this new concept. The CO$_2$/N$_2$ (0.15:0.85) selectivities of azo-COP-10 is superior to azo-COP-2 in its CO$_2$/N$_2$ selectivity. The fact that azo-COP-10 is superior to azo-COP-2 in its CO$_2$/N$_2$ selectivity, prompted us to investigate these two structures specifically. Since both structures only differ in the linkers, benzene (azo-COP-2) versus naphthalene (azo-COP-10), we chose to compare the respective model constructs. The optimized geometries and binding energies (Figure S8 in the Supporting Information) show an even higher CO$_2$/N$_2$ selectivity of 307.7, which is the highest value reported to date at 323 K and 1 bar (Figure S9 in the Supporting Information). The IAST selectivity is higher at low pressure region and subsequently decreased with the increasing pressure (Figure 4). We also determined the isosteric heats of adsorption (Q$_s$) by using the Clausius–Clapeyron method from the CO$_2$ isotherms collected at 273 and 298 K (Figure 4).[36] At zero coverage, the Q$_s$ values of CO$_2$ for azo-COPs were found to be 7.0–34.1 kJ mol$^{-1}$, which were decreased with higher loadings to 24.8–27.9 kJ mol$^{-1}$. These Q$_s$ values are very common in nitrogen-rich nanoporous polymers and facilitate pressure swing desorption (< 40 kJ mol$^{-1}$) from the porous networks without needing a successive thermal treatment.[25a, 37]

In a typical theoretical assessment, the quantum-chemical calculations using Perdew–Burke–Ernzerhof exchange-correlation functional[38] with dispersion correction[39] in Q-Chem[40] were performed to understand the changes in Q$_s$ and the selectivity with different models of azo-COPs. The fragment azo-models that are considered in this paper are illustrated along with the optimized geometries and binding energies (Figure S10 in the Supporting Information). The binding energies (BEs) of these modeled azo-COP fragments for CO$_2$ adsorption range between 14 and 17 kJ mol$^{-1}$ at the B3LYP-D2/aug-cc-pVTZ level. A more-or-less uniform underestimation of the calculated BEs with respect to the experimental Q$_s$ by about 10 kJ mol$^{-1}$ (with the correct trend) is perhaps due to the removal and simplification of the amorphous polymer network surroundings in our model calculations. The multiple interactions with more than one functional group are possible in amorphous polymers due to the interpenetration of the framework, which leads to an increase in the observed binding energies (Figure S11 in the Supporting Information).

The fact that azo-COP-10 is superior to azo-COP-2 in its CO$_2$/N$_2$ selectivity, prompted us to investigate these two structures more closely. Since both structures only differ in the linkers, benzene (azo-COP-2) versus naphthalene (azo-COP-10), we chose to compare the respective model constructs. The optimized geometries of CO$_2$ and N$_2$ binding with the bare benzene and naphthalene molecules as well as the same molecular structures were used to calculate CO$_2$/N$_2$ selectivity for a gas mixture of 0.15:0.85. Although breakthrough studies with mixture of gases are ultimately needed for absolute selectivity values, it is well-known[16, 28] that competitive adsorptions at limited sorption sites favor even higher selectivities than pure component IAST calculations. The absolute component loadings were fitted with a single-site Langmuir model for N$_2$ isotherms and dual-site Langmuir model for CO$_2$ isotherms (Figure S8 in the Supporting Information). The saturation loading and parameter in the pure component Langmuir adsorption isotherms were obtained from the fitting curves and were used to calculate CO$_2$/N$_2$ selectivity for a gas mixture of 0.15:0.85.

The CO$_2$/N$_2$ selectivities of the azo-COPs range from 63.7–109.6 at 273 K and become 95.6–165.2 at 298 K, which is higher than those previously reported[44] (Table S3 in the Supporting Information). At more industrially relevant temperatures (> 40°C), CO$_2$/N$_2$ selectivity of azo-COP-2 is 288.1 at 323 K and 1 bar[28] whereas azo-COP-10 shows an even higher CO$_2$/N$_2$ selectivity of 307.7, which is the highest value reported to date at 323 K and 1 bar (Figure S9 in the Supporting Information). The IAST selectivity is higher at low pressure region and subsequently decreased with the increasing pressure (Figure 4). We also determined the isosteric heats of adsorption (Q$_s$) by using the Clausius–Clapeyron method from the CO$_2$ isotherms collected at 273 and 298 K (Figure 4).[36] At zero coverage, the Q$_s$ values of CO$_2$ for azo-COPs were found to be 7.0–34.1 kJ mol$^{-1}$, which were decreased with higher loadings to 24.8–27.9 kJ mol$^{-1}$. These Q$_s$ values are very common in nitrogen-rich nanoporous polymers and facilitate pressure swing desorption (< 40 kJ mol$^{-1}$) from the porous networks without needing a successive thermal treatment.[25a, 37]
lar moieties with azo extensions are shown in Figure 5. The BE values of CO$_2$ and N$_2$ for bare benzene are 10.1 and 6.7 kJ mol$^{-1}$, respectively, and these values are increased to 11.6 and 7.4 kJ mol$^{-1}$ for bare naphthalene. When there are azo-groups, however, the preferential CO$_2$ adsorption compared with N$_2$ adsorption is noticeably increased to 14.5 (CO$_2$) versus 6.0 kJ mol$^{-1}$ (N$_2$) for azo-benzene, and 15.5 (CO$_2$) and 7.5 kJ mol$^{-1}$ (N$_2$) for azo-naphthalene. In other words, although the N$_2$ binding with and without the azo group is almost the same (from 6.7–7.4 to 6.0–7.5 kJ mol$^{-1}$), the azo group significantly enhanced the CO$_2$ binding (from 10.1–11.6 to 14.5–15.5 kJ mol$^{-1}$), thereby increasing the selectivity. One interesting observation in these experiments was the change in $Q_s$ as well as the selectivity that occurred by the modification of the benzene linker (azo-COP-2) with naphthalene (azo-COP-10). The increase (3.1 kJ mol$^{-1}$) in $Q_s$ of CO$_2$ for azo-COP-10 (naphthalene) compared with azo-COP-2 (benzene) is qualitatively consistent with the calculated binding energy difference (1.0 kJ mol$^{-1}$) shown in Figure 5. The selectivity at low temperature can be predicted by the difference in calculated binding energies of CO$_2$ versus N$_2$. The BE difference between CO$_2$ and N$_2$ for azo-COP-2 (benzene) is 8.5 and 8.0 kJ mol$^{-1}$, which means that the selectivity would be marginally higher for azo-COP-2 at low temperature as is observed in experiments. However, the large temperature-dependent selectivity increase in azo-COP-10 compared with azo-COP-2 seems to have its origin in the relative entropy difference between the CO$_2$ and N$_2$ binding configurations. Qualitatively, this phenomenon may be due to the larger spatial distribution of the CO$_2$-bound configurations around naphthalene compared with benzene because naphthalene has a larger π-surface area that can interact with CO$_2$.

We have also investigated the trans→cis isomerization of the azo-COPs by irradiating the samples with UV light to alter the pore characteristics (on–off porosities) of their network structure. The absorbance maxima, $\lambda_{\text{max}}$, recorded around 360 nm for all the azo-COPs represent the π–π* transition of the relatively stable trans form (Figure S12 in the Supporting Information). Specifically, we have recorded the solid-state UV/Vis spectra of powder azo-COPs after irradiating with UV light (light source: 365 nm; 8 W) overnight and measured the change in surface area. We did not observe a significant change in the peak located at 360 nm for azo-COPs, except for azo-COP-2 and -9, after exposing the samples to UV light for 24 h. It is known that the trans-to-cis isomerization of azo-benzines is hampered severely in restricted environments. Azo-COP-2 and azo-COP-9 showed the formation of a new broad peak located at 440 nm, which can be attributed to an n–π* transition of cis-azobenzene. This result prompted us to investigate further alterations in its surface area with respect to UV irradiation. Azo-COP-2 and azo-COP-9 were irradiated by UV light for 24 h, followed by degassing for 3 h at 298 K, in which low-temperature activation is preferred to minimize thermal relaxation of cis-azobenzene back to its trans configuration. The surface area measurement was then carried out under identical conditions to those for azo-COP-2 and azo-COP-9 with and without UV irradiation (Figure 6). The BET surface area is reduced from 594.8 to 568.8 and 343.7 to 325.9 m$^2$ g$^{-1}$ for azo-COP-2 and azo-COP-9, respectively, suggesting that a structural change in the network has occurred after UV irradiation. Azo-COP-2 and azo-COP-9 were irradiated by UV light for 24 h, followed by degassing for 3 h at 298 K, in which low-temperature activation is preferred to minimize thermal relaxation of cis-azobenzene back to its trans configuration. The BET surface area is reduced from 594.8 to 568.8 and 343.7 to 325.9 m$^2$ g$^{-1}$ for azo-COP-2 and azo-COP-9, respectively, suggesting that a structural change in the network has occurred after UV irradiation. As expected, these BET surface areas are lower than those measured after degassing at 150 °C for 5 h. Although we observed a relatively small change in the porosity of the material, these findings could lead to the development of porous polymers with tunable pore size and chemical nature.

Figure 4. CO$_2$/N$_2$ selectivity of azo-COPs measured by IAST technique for CO$_2$/N$_2$ gas mixture of 15:85 at: a) 273 K, and b) 298 K. c) Isosteric heats of adsorption $(Q_s)$ for CO$_2$ calculated from the isotherms measured at 273 and 298 K for azo-COPs.
Conclusion

We have prepared a family of nanoporous azo-COPs by using a catalyst-free chemical route and show that their azo groups significantly disfavor N₂ by exhibiting an anomalous trend in which CO₂/N₂ selectivity is increased with a rise in temperature. The CO₂/N₂ selectivity of azo-COP-10 (165.2 at 298 K) exceeds previously reported values for azo-COPs. Azo-COP-2 shows the highest CO₂ uptake capacity of 2.55 mmol g⁻¹ and surface area of 729.6 m² g⁻¹, among other azo-COPs studied here. The moderate Qˢᵗ and negligible hysteresis for CO₂ adsorption isotherms are suggesting energy efficient recyclability. We have also demonstrated the scope of azo-coupling and contribution of π-surfaces to the CO₂/N₂ selectivity. Considering the higher affinity of CO₂ towards the azo-naphthalene moiety over the azo-benzene one, we have proven that the concepts of CO₂-philicity and N₂-phobicity can co-exist, thus creating myriad of possibilities to combine N₂-phobic azo-groups with CO₂-philic functionalities. When coupled with porosity engineering, for example, tuning surface area and pore size, the new chemical insights that our study brings may lead to custom-designed architectures for efficient CO₂ capture and separation. In particular, the unique ability of azo-COPs to retain high CO₂/N₂ selectivity at elevated temperatures, combined with their chemical stability, makes them ideal candidates for post-combustion CO₂ capture. We believe that the tailoring of structural features in azo-COPs with control over both the functionality and surface area will further contribute to the development of superior CO₂ sorbents and also to the fight against global warming and ocean acidification.

Experimental Section

General synthetic procedure for azo-COPs

All organic solvents and materials used for synthesis were of reagent grade and used without further purification. In an typical reaction, tetrakis(4-nitrophenyl)methane (0.5 mmol, 250 mg) was treated with the aromatic amines, namely, 4,4′,4′',4''-methanetetratrayltaetraaniline (190 mg), p-phenylenediamine (108 mg), benzidine (184 mg), 2,3,5,6-Tetramethyl-1,4-phenylenediamine (164 mg), 2,5-dimethyl-1,4-phenylenediamine (136 mg), 1,3-phenylenediamine (108 mg), 3,3′-dimethylbenzidine (212 mg), 4,4′-methyleneedianiline (198 mg), 4,4′-oxydianiline (200 mg), tris(4-aminophenyl)methanol (214 mg), and 1,5-diaminonaphthalene (158 mg), in N,N-dimethylformamide (25 mL) in the presence of potassium hydroxide (5 mmol, 281 mg) under N₂ atmosphere at 150 °C for 24 h. The reaction mixture was cooled to room temperature and stirred in an excess of distilled water for 1 h. The precipitate was filtered off and...
washed with warm distilled water (×3), followed by washing with Me6CO (×3) and THF (×2). Subsequently, an orange precipitate was dried at 110 °C under vacuum for 4 h. All azo-COPs were isolated as orange powders and were reproducible on at least three separate batches and on multigran scales.

Measurements

FTIR spectra were recorded on KBr pellets using a PerkinElmer FTIR spectrometer. Solid-state cross polarization magic angle spinning (CP/MAS) 13C NMR spectra of azo-COPs were collected by a Bruker Avance III 400 WB NMR spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH-TG 209 F3 instrument by heating the samples to 800 °C at a rate of 10 °C·min⁻¹ under an air atmosphere. The absorbance of azo-COPs samples was measured on a UV/Vis spectrophotometer, in which the powder samples were sandwiched between two quartz glasses and irradiated by a 365 nm (8 W; 230 V; ≈ 50/60 Hz from Vilbert Lourmat, France) UV lamp. To evaluate the porosity of azo-COPs, N₂ adsorption isotherms were obtained to give the pore parameters, including BET \( (P/P_0 = 0.01–0.25) \) and Langmuir \( (P/P_0 = 0.1–0.35) \) surface area, and pore volume. The pore volume of azo-COPs was calculated at \( P/P_0 = 0.95 \). The low pressure CO₂ and N₂ adsorption–desorption isotherms for azo-COPs were measured at 273 and 298 K by using a static volumetric system (ASAP 2020, Micromeritics Inc.). The temperature during adsorption and desorption was kept constant by using a circulator. Prior to the adsorption measurements, the samples were dried at 110 °C for 24 h. The samples were further activated in situ by increasing the temperature at a heating rate of 1 K·min⁻¹ up to 423 K under vacuum (5 × 10⁻³ mm Hg) and the temperature and vacuum was maintained for 5 h before taking the sorption measurements. All the adsorption–desorption experiments were carried out twice to ensure the reproducibility. There were no noticeable differences in the isotherm points obtained from both experiments.

The IAST selectivities for the CO₂/N₂ (0.15:0.85) gas mixtures were calculated by using following Equation (3):

\[
S = \frac{q_1 / q_2}{p_1 / p_2}
\]

(3)

in which \( S \) is the selectivity factor, \( q_1 \) and \( q_2 \) represent the quantity adsorbed of components 1 and 2, and \( p_1 \) and \( p_2 \) represents the partial pressure of components 1 and 2, respectively. Isothermic heats of adsorption were calculated from the adsorption data by using the Clausius–Clapeyron Equation (4):

\[
\Delta_{ads} H = R \left[ \frac{\partial \ln P}{\partial (1/T)} \right]_{ads}
\]

(4)

in which \( R \) is the universal gas constant, whereas \( \theta \) is the fraction of the adsorbed sites at a pressure \( P \) and temperature \( T \).

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