

Microporous Materials

Directing the Structural Features of N₂-Phobic Nanoporous Covalent Organic Polymers for CO₂ Capture and SeparationHasmukh A. Patel,^[a] Sang Hyun Je,^[a] Joonho Park,^[a] Yousung Jung,^[a] Ali Coskun,^{*,[a, b]} and Cafer T. Yavuz^{*,[a]}

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. Iso-steric 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-or-

ganic 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),^[6b,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,^[2,4b] 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

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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.^[27] in which BILPs are shown to have exceptional CO₂-capture capacities up to 5.34 mmol g⁻¹ at 273 K and 1 bar. Another example is the recent report on PPFs by Zhu et al.^[23] in which CO₂ capacities of up to 6 mmol g⁻¹ were reported with imine-linked nanoporous amorphous polymers at 273 K and 1 bar. All these examples showed exceptional CO₂ capacities with moderate-to-low CO₂/N₂ selectivity, which decrease with rising temperature, an important limitation for their application in the temperature range (> 40 °C) for the post-combustion CO₂ capture.^[1a] 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.^[28] Azo-COPs revealed an increase in CO₂/N₂ selectivity with rising temperature due to the fact that azo (–N=N–) functionalities showed less than expected affinity towards N₂ gas, thus making the framework “N₂-phobic”, in relative terms. Azo-COP-2 showed moderate CO₂/N₂ 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^[28] theoretical simulations suggested that the origin of N₂-phobicity is due to the entropic loss of N₂-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 CO₂/N₂ 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 CO₂ and N₂ 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 CO₂/N₂ selectivity. Our simulations indicate that CO₂ has a higher affinity towards aromatic units when compared with N₂ gas molecules, thus increasing the π -surface area increases the CO₂-philicity of the framework. These results indicate that it is possible to combine the concepts of CO₂-philicity with N₂-phobicity to improve CO₂/N₂ selectivity and also CO₂-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.^[29] In the search for an environmentally benign process, we have recently demonstrated^[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)-methane with various aromatic amines, including 4,4',4'',4'''-

methanetetrayltetraaniline (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) ¹³C 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⁻¹ (Figure S1 in the Supporting Information). Other noticeable bands were observed at 3400 (s, free N–H), 3200 (s, hydrogen-bonded N–H), 1610 (s, C=C aromatic), 1447 and 1403 (s, N=N), 1520 and 1340 (s, N–O), and 1280 cm⁻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⁻¹ also indicates the presence of terminal amino groups. The chemical shifts in the CP/MAS ¹³C NMR spectra of azo-COPs, namely, azo-COP-1 to azo-COP-11, located at δ = 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 δ = 115 ppm, which is attributed to the carbon atom incorporating the terminal –NH₂ 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 δ = 120–155 ppm.

Thermogravimetric analysis (TGA) performed on azo-COPs up to 800 °C with a heating rate of 10 °C min⁻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 N₂ 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 N₂ atmosphere, those impurities are just oxidized in the presence of O₂ 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 N₂ and in air, confirming that the early mass loss of azo-COPs under N₂ atmosphere is due to the decomposition of low molecular weight residual

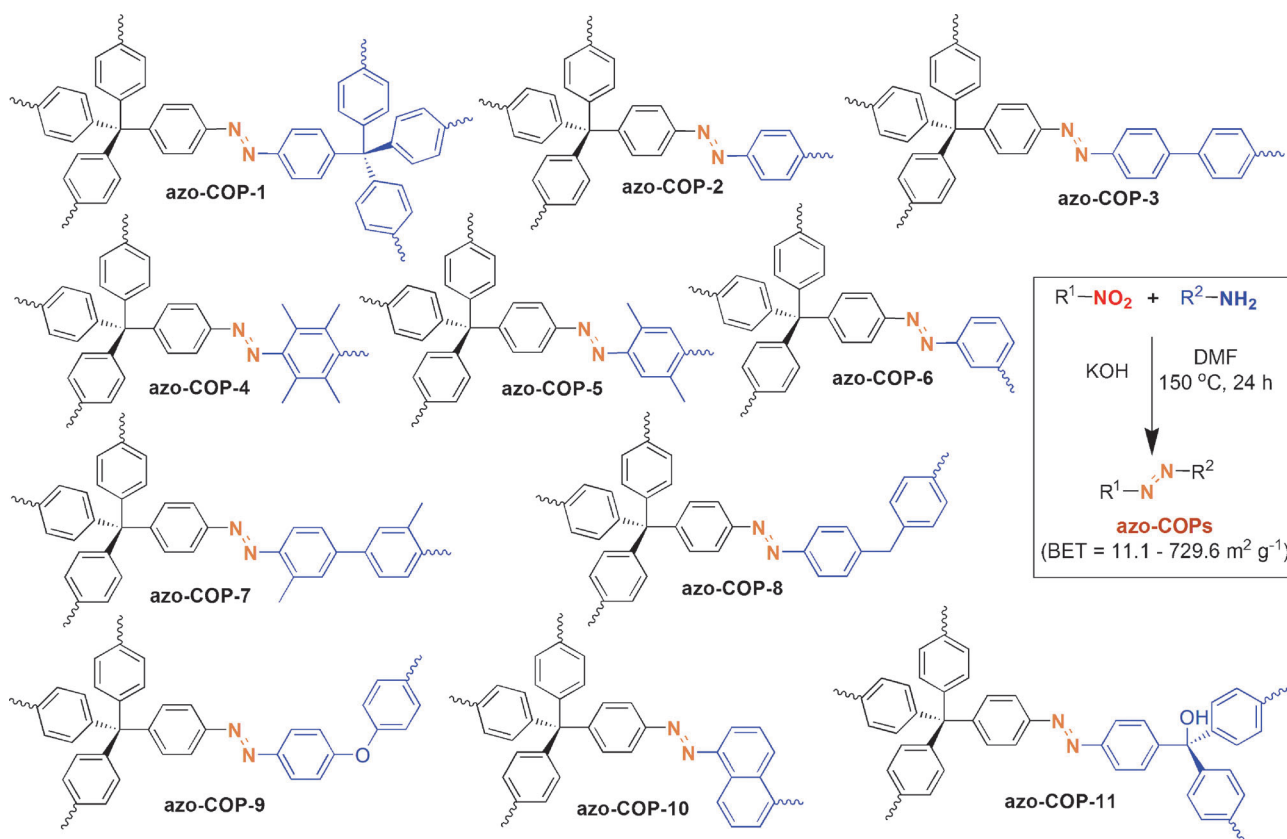


Figure 1. Building blocks of azo-bridged covalent organic polymers (azo-COPs), azo-COPs-1 to -11. Direct coupling of aromatic nitro with amines under basic conditions at 150 °C resulted in the formation of azo-COPs as bright-orange powders on a multigram scale. Azo-COP-1, -2, and -3 are discussed^[28]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

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, N₂ 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 m² 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 m² 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 N₂ 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

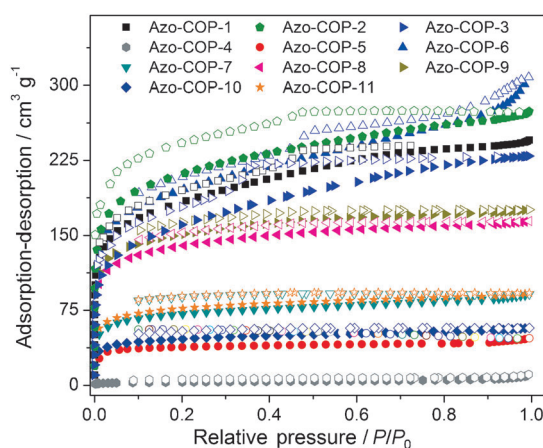


Figure 2. N₂ adsorption-desorption isotherms of azo-COPs-1 to -11 carried out at 77 K and the gas uptake and release are indicated by solid and open symbols, respectively. The BET surface areas of azo-COP-1 to -3 (measured by Ar adsorption-desorption at 87 K) have been reported^[42] and were used for comparison. The N₂ adsorption-desorption isotherms of azo-COPs-1 to -3 are given as Figure S12 (in the Supporting Information).

factor for gas sorption behavior (especially for CO₂ gas sorption in which nitrogen, electron-rich moieties perform better), a moderate porosity (e.g. surface areas of 100 m² g⁻¹ or less) could lead to complete access to CO₂-philic nitrogen-rich functionalities in the framework.^[9]

Table 1. BET and Langmuir surface areas, CO₂ and N₂ capture capacities, CO₂/N₂ selectivities and isosteric heats of adsorption (Q_{st}) for azo-COPs.

Compound	BET [m ² g ⁻¹]	Langmuir [m ² g ⁻¹]	CO ₂ adsorption [mmol g ⁻¹]		N ₂ adsorption [mmol g ⁻¹]		CO ₂ /N ₂ (15:85) at 1 bar		Q_{st} [kJ mol ⁻¹]
			273 K	298 K	273 K	298 K	273 K	298 K	
azo-COP-1	635.8	800.7	2.44	1.48	0.11	0.04	63.7	96.6	29.3
azo-COP-2	729.6	949.8	2.55	1.53	0.06	0.03	109.6	130.6	24.8
azo-COP-3	493.1	632.4	1.93	1.22	0.07	0.03	78.6	95.6	32.1
azo-COP-4	11.1	13.4	1.75	1.12	0.13	0.05	79.3	138.5	26.8
azo-COP-5	127.6	169.4	2.04	1.24	0.16	0.05	73.8	144.6	27.3
azo-COP-6	679.1	887.2	2.22	1.31	0.17	0.06	72.7	114.8	25.8
azo-COP-7	241.6	315.3	1.91	1.16	0.16	0.06	68.5	115.3	26.1
azo-COP-8	472.1	612.7	2.02	1.22	0.16	0.07	70.3	103.4	25.3
azo-COP-9	509.6	649.5	2.05	1.23	0.17	0.07	69.6	102.8	25.3
azo-COP-10	156.8	200.2	1.91	1.15	0.15	0.04	69.6	165.2	27.9
azo-COP-11	259.2	336.1	2.13	1.26	0.15	0.06	77.8	128.4	27.4

Accessible surfaces can be directed by the structural features,^[32] despite the challenge of lacking order in azo-COP frameworks. In an attempt to increase pore-size diameter, we doubled the linker length (R² unit in Figure 1), a common strategy in the construction of hybrid porous materials.^[33] 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 m² g⁻¹).

Bulky groups are introduced to the *ortho* positions of the linker in azo-COP-2, leading to azo-COPs incorporating tetramethyl (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 extension of the monomers, a preferable alignment for azo-aromatics. 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 substituents in azo-COP-4 are also responsible for the difficulty 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 distances 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 particular case with azo aromatics, however, we see two competi-

tive acts. Whereas the flexibility brings free rotation and consequent contraction in framework construction, it also eliminates the restriction on the in-plane alignment of biphenylic azo units. As a result, the more conjugated, semi-rigid oxygen bridge shows an enhanced surface area, whereas the methylene 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.^[34] This is, however, not

the case for azo-COPs, because azo-COP-1 is the third spacious among the 11 azo-COPs reported here. Azo-COP-11 also features a reactive alcohol at the tetrahedral center, presumably leading to side redox reactions under highly basic conditions. The redox effect is most evident in a failed azo-COP architecture (see the Supporting Information), in which a biphenylic linker with a sulfone (–SO₂–) bridge is used. The reductive coupling of nitro and amino groups are altered substantially with the interference of the sulfone functionality of the linker.

Given the variation of azo-COPs in their surface area, microporosity, and structural geometry, it is anticipated that each azo-COP would reveal a different gas sorption behavior. The gas adsorption and desorption measurements for CO₂ and N₂ 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 solvent molecules from the nanopores of the framework. The shapes of the CO₂ isotherms are somewhat different at the two temperatures. At 273 K, the CO₂ adsorption amount in azo-COPs increased rapidly at the lower pressure range before approaching saturation, and consequently showed a higher CO₂ adsorption capacity when compared with the value found at 298 K. Because both the high porosity and nitrogen content contribute to the CO₂-philicity of the framework, azo-COP-2 showed the highest CO₂ sorption capacity of 2.55 and 1.53 mmol g⁻¹ at 273 and 298 K, respectively. Other azo-COPs demonstrated CO₂ 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 CO₂ because of its large quadrupolar moment and when the pressure is increased these binding sites become saturated and therefore less available for CO₂ molecules.

There is a negligible hysteresis in CO₂ adsorption–desorption isotherms at 273 and 298 K (Figure S7 in the Supporting Information), confirming the complete regeneration without any need for an external heat treatment. This property is highly desirable in post-combustion CO₂ capture because it eliminates excessive energy consumption during adsorbent regeneration. The CO₂ scrubbing by well-established industrial processes

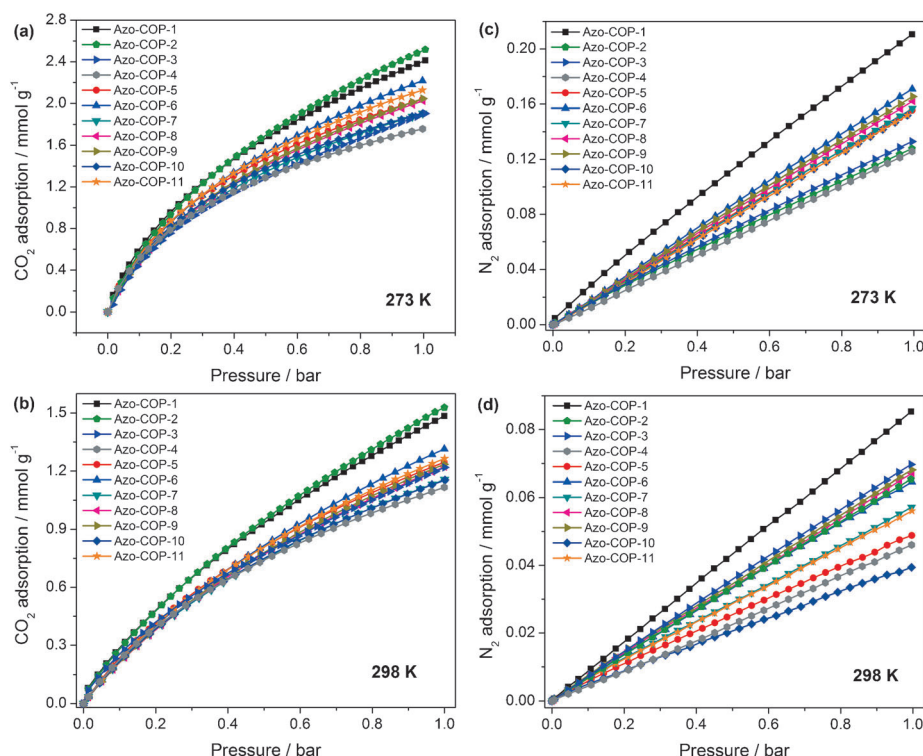


Figure 3. Low-pressure: a,b) CO_2 , and c,d) N_2 adsorption isotherms for azo-COPs-1 to -11 at 273 and 298 K. When the temperature was increased from 273 to 298 K, the CO_2 -uptake capacity loss was about 40%, whereas it is approximately 70% for N_2 . We believe that this higher loss for N_2 is because of the lack of dispersion forces and also electron–electron repulsion between N_2 gas and azo groups.

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 and exhibit excellent CO_2/N_2 selectivity. 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-COPs were obtained from ideal adsorbed solution theory (IAST) at 273 and 298 K (Table 1) for a CO_2/N_2 gas mixture. The IAST method predicts the adsorption selectivity for gas mixtures based on pure component gas isotherms and has been used to investigate several adsorbents.^[26,35] Although breakthrough studies with mixture of gases are ultimately needed for absolute selectivity values, it is well-known^[1b,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^[4e] (Table S3 in the Supporting Information). At more industrially relevant temperatures ($> 40^\circ\text{C}$), 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_{st}) 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_{st} values of CO_2 for azo-COPs were found to be 27.0–34.1 kJ mol^{-1} , which were decreased with higher loadings to 24.8–27.9 kJ mol^{-1} . These Q_{st} values are very common in nitrogen-rich nanoporous polymers and facilitate

pressure swing desorption ($< 40 \text{ kJ mol}^{-1}$) 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_{st} 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 PBE-D2/aug-cc-pVTZ level. A more-or-less uniform underestimation of the calculated BE's with respect to the experimental Q_{st} 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 molecu-

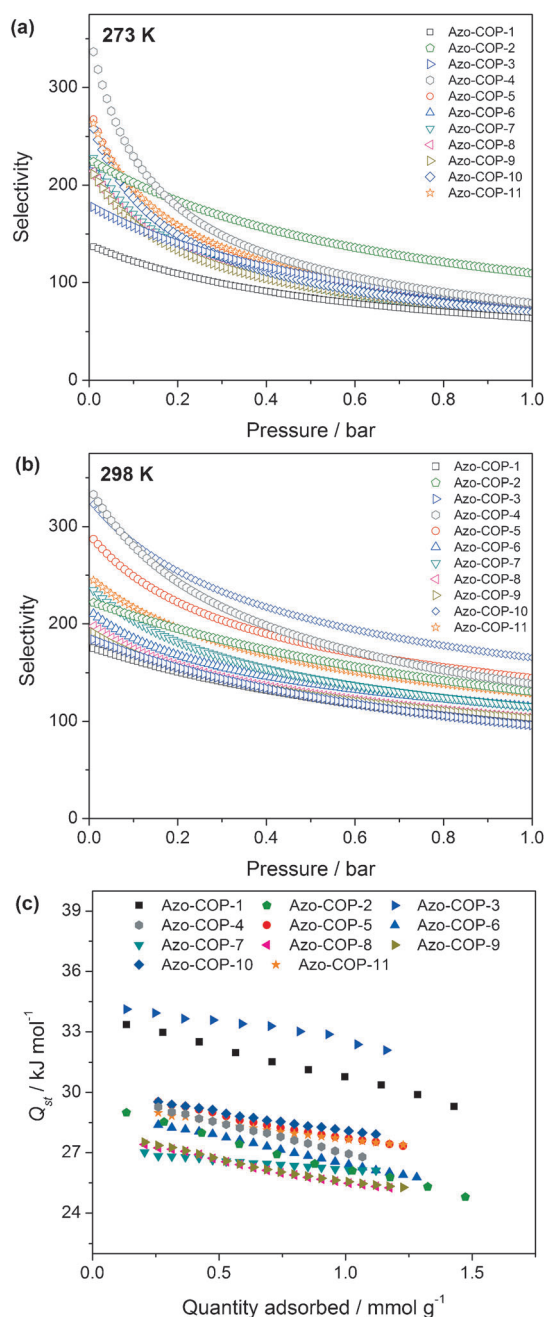


Figure 4. CO₂/N₂ selectivity of azo-COPs measured by IAST technique for CO₂/N₂ gas mixture of 15:85 at: a) 273 K, and b) 298 K. c) Isothermic heats of adsorption (Q_{st}) for CO₂ calculated from the isotherms measured at 273 and 298 K for azo-COPs.

lar moieties with azo extensions are shown in Figure 5. The BE values of CO₂ and N₂ 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 CO₂ adsorption compared with N₂ adsorption is noticeably increased to 14.5 (CO₂) versus 6.0 kJ mol⁻¹ (N₂) for azo-benzene, and 15.5 (CO₂) and 7.5 kJ mol⁻¹ (N₂) for azo-naphthalene. In other words, although the N₂ 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 CO₂ 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_{st} 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_{st} of CO₂ 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 CO₂ versus N₂. The BE difference between CO₂ and N₂ for azo-COP-2 (Figure 5c) and azo-COP-10 (Figure 5d) were 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 CO₂ and N₂ binding configurations.^[28] Qualitatively, this phenomenon may be due to the larger spatial distribution of the CO₂-bound configurations around naphthalene compared with benzene because naphthalene has a larger π -surface area that can interact with CO₂.

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)^[41] of their network structure. The absorbance maxima, λ_{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^[42] that the *trans*-to-*cis* isomerization of azobenzenes 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 m² 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.

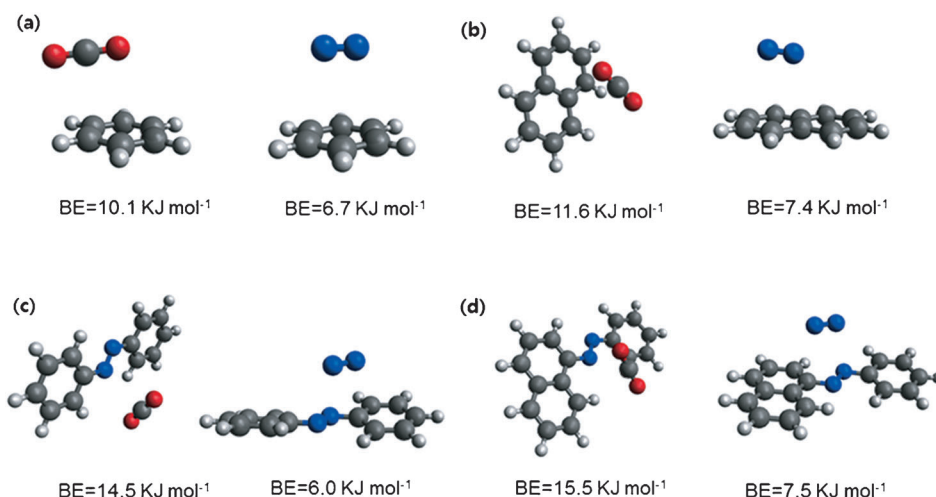


Figure 5. The optimized structures and binding energies using PBE+D2 in Q-Chem for: a) benzene, b) naphthalene, c) azo-benzene (core functionality of azo-COP-2), and d) azo-naphthalene (core functionality of azo-COP-10).

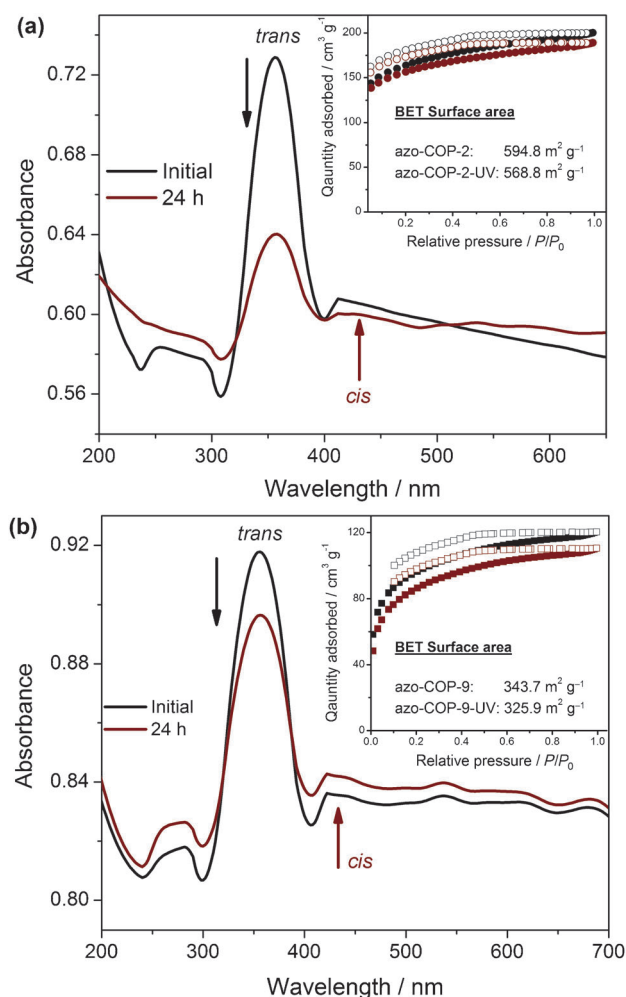


Figure 6. UV/Visible spectra showing the *trans*-*cis* transition of azo-benzene units while irradiating the solid samples with UV light (365 nm; 8 W) for 24 h. A significant decrease in the *trans* azo-benzene peak ($\lambda_{\max} = 360$ nm) and the formation of a new broad *cis* azo-benzene peak at 440 nm points to a *trans*-*cis* switching of azo-benzene units. Inset: alteration of surface area with UV irradiation. N_2 adsorption-desorption isotherms for azo-COP-2 and -9 measured at 77 K of azo-COP-2, -9, and azo-COP-2-UV, -9-UV (azo-COP-2, -9 were irradiated with UV light for 24 h).

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 N_2 by exhibiting an anomalous trend in which CO_2/N_2 selectivity is increased with a rise in temperature. The CO_2/N_2 selectivity of azo-COP-10 (165.2 at 298 K) exceeds previously reported values for azo-COPs. Azo-COP-2 shows the highest CO_2 uptake capacity of 2.55 mmol g^{-1} and surface area of $729.6 \text{ m}^2 \text{ g}^{-1}$, among other azo-COPs studied here. The moderate Q_{st} and negligible hysteresis for CO_2 adsorption isotherms are suggesting energy efficient recyclability. We have also demonstrated the scope of azo-coupling and contribution of π -surfaces to the CO_2/N_2 selectivity. Considering the higher affinity of CO_2 towards the azo-naphthalene moiety over the azo-benzene one, we have proven that the concepts of CO_2 -philicity and N_2 -phobicity can co-exist, thus creating myriad of possibilities to combine N_2 -phobic azo-groups with CO_2 -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 CO_2 capture and separation. In particular, the unique ability of azo-COPs to retain high CO_2/N_2 selectivity at elevated temperatures, combined with their chemical stability, makes them ideal candidates for post-combustion CO_2 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 CO_2 sorbents and also to the fight against global warming and ocean acidification.

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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 a typical reaction, tetrakis(4-nitrophenyl)methane (0.5 mmol, 250 mg) was treated with the aromatic amines, namely, 4,4',4''-methanetetrayltetraaniline (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'-methylenedianiline (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 N_2 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 ($\times 3$), followed by washing with Me_2CO ($\times 3$) and THF ($\times 2$). 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 multigram scales.

Measurements

FTIR spectra were recorded on KBr pellets using a PerkinElmer FTIR spectrometer. Solid-state cross polarization magic angle spinning (CP/MAS) ^{13}C 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°Cmin^{-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; $\approx 50/60$ Hz from Vilbert Lourmat, France) UV lamp. To evaluate the porosity of azo-COPs, N_2 adsorption isotherms were obtained with a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer at 77 K, after the samples had been degassed at 150°C for 5 h under vacuum. The adsorption-desorption 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 CO_2 and N_2 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 Kmin^{-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.

CO_2/N_2 Selectivity and isosteric heat of adsorption

Ideal adsorbed solution theory (IAST) data were calculated using OriginPro v8.5. The calculations for IAST can be derived from the fitting adsorption isotherms with an appropriate Langmuir model. The absolute component loadings were fitted with either a single-site Langmuir model or a dual-site Langmuir model. The single-site Langmuir model was applied when there were no noticeable isotherm inflections. These models were fitted purely on the basis of giving the best fit with adjusted R^2 values exceeding 0.98. The OriginPro 8.5 was used to solve and calculating following equations. The single-site Langmuir model can be defined as:

$$q = \frac{q_{\text{sat}} b p}{1 + b p} \quad (1)$$

The dual-site Langmuir model can be defined as:

$$q = q_A + q_B = \frac{q_{\text{sat},A} b_A p}{1 + b_A p} + \frac{q_{\text{sat},B} b_B p}{1 + b_B p} \quad (2)$$

in which q is molar loading of adsorbate; q_{sat} is the saturation loading; b is parameter in the pure component Langmuir adsorption isotherm, whereas A and B refer to two different sites.

The IAST selectivities for the CO_2/N_2 (0.15:0.85) gas mixtures were calculated by using following Equation (3):

$$S = \frac{q_1/q_2}{p_1/p_2} \quad (3)$$

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.

Isosteric heats of adsorption were calculated from the adsorption data by using the Clausius-Clapeyron Equation (4):

$$\Delta_{\text{ad}} H^\circ = R \left[\frac{\partial \ln P}{\partial (1/T)} \right]_\theta \quad (4)$$

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

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