



Tuning Pore Size in Square-Lattice Coordination Networks for Size-Selective Sieving of CO₂

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Abstract: Porous materials capable of selectively capturing CO₂ from flue-gases or natural gas are of interest in terms of rising atmospheric CO₂ levels and methane purification. Size-exclusive sieving of CO₂ over CH₄ and N₂ has rarely been achieved. Herein we show that a crystal engineering approach to tuning of pore-size in a coordination network, [Cu(quinoline-5-carboxylate)₂]_n (**Qc-5-Cu**) enables ultra-high selectivity for CO₂ over N₂ ($S_{\text{CN}} \approx 40\,000$) and CH₄ ($S_{\text{CM}} \approx 3300$). **Qc-5-Cu-sql-β**, a narrow pore polymorph of the square lattice (**sql**) coordination network **Qc-5-Cu-sql-α**, adsorbs CO₂ while excluding both CH₄ and N₂. Experimental measurements and molecular modeling validate and explain the performance. **Qc-5-Cu-sql-β** is stable to moisture and its separation performance is unaffected by humidity.

Carbon dioxide (CO₂) is a greenhouse gas and an undesirable impurity that is a component of several industrially relevant gas mixtures. The concentration of CO₂ in the atmosphere surpassed 400 ppm for the first time in 2013^[1] highlighting an urgent need for new solutions to CO₂ emissions. Moreover, the use of natural gas and biogas as cleaner alternatives to traditional fossil fuels is also increasing.^[2] Natural gas upgrading and biogas sweetening require removal of CO₂ and other impurities. The current state-of-the-art with respect to carbon capture employs liquid amine chemisorbents such as primary and secondary alkyl amines. However, chemisorbents typically require energy-intensive regeneration processes and are often corrosive. Physisorbents also offer a potential solution since they can offer faster kinetics and more facile regeneration. Molecular sieving represents a third option for carbon capture but requires rigid

networks with pore apertures intermediate between the kinetic diameters of the species to be separated. Metal-organic materials (MOMs),^[3] also known as porous coordination polymers^[4] or metal-organic frameworks (MOFs),^[5] can enable exquisite control over pore-size and pore-chemistry thanks to their inherent modularity, especially if prototypical for families of closely related MOMs.

Crystal engineering^[6] or reticular chemistry^[7] approaches to the generation of families of MOMs can offer control over pore dimensions and chemistry in a manner that is difficult to achieve in existing classes of porous materials. Indeed, new selectivity benchmarks for polarizable sorbates (e.g. CO₂) have been realized by adjusting pore-size to around that of the sorbate and through the use of inorganic linkers that offer strong electrostatics.^[8] Control over pore-size in these hybrid ultra-microporous (<0.7 nm) materials can be achieved through short organic linkers or interpenetration.^[8a,9]

Molecular sieving can enable ultra-high selectivity by excluding species with kinetic diameters larger than the pore (e.g. N₂ = 3.64 Å; CH₄ = 3.8 Å) while allowing passage of smaller guests (e.g. CO₂ = 3.3 Å). Unfortunately, molecular sieving has rarely been achieved,^[10] largely because it is difficult to control pore-size within the 3–4 Å range that is most relevant for gas molecule separations.^[11] Further, defining a material to be a molecular sieve after observing a large uptake difference for two adsorbates at low temperatures (e.g. 195 K CO₂ vs. 77 K N₂) could be an artifact of pore contraction, slower gas diffusion rates or reduced thermal motion. Indeed, dynamics are unwanted in sieving materials as they could induce a gate-opening effect and lost sieving ability. To our knowledge, there are only a handful of molecular sieves for CO₂ over CH₄ and/or N₂ at or near ambient conditions.^[12] In addition, as yet uncharacterized activated structures can account for the observed molecular sieving in several of these examples. We also note that coordination networks invariably exhibit preference towards CO₂ over N₂ and/or CH₄ because of weak adsorbate-adsorbent interactions. CO₂/N₂ selectivity, S_{CN} , rarely exceeds 100 in such materials.

Herein, we report that fine-tuning of pore-size enables molecular sieving of CO₂ thanks to supramolecular isomerism, that is, the generation of networks with the same chemical composition, but different topology.^[6,13] Five coordination networks of formula [M(quinoline-5-carboxylate)₂]_n, **Qc-5-M-dia** (M = Co, Ni, Zn and Cu, **dia** = 2-fold, 3D diamondoid network) and **Qc-5-Cu-sql-α** (**sql** = 2D square lattice network), were synthesized solvothermally from HQc (quinoline-5-carboxylic acid) and the respective metal salts

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(see Supporting Information). **Qc-5-Cu-dia** and **Qc-5-Cu-sql- α** are supramolecular isomers. These materials were studied by single-component gas sorption, dynamic breakthrough of gas mixtures, temperature-programmed desorption (TPD), and molecular modeling. In the process we observed that **Qc-5-Cu-sql- α** undergoes an irreversible phase change upon desolvation to **Qc-5-Cu-sql- β** , a more stable polymorph of **Qc-5-Cu-sql- α** . The β -phase does not revert back to the α -phase even after attempted re-solvation (see Figure 2), heating or soaking in water for 21 days. Interestingly, **Qc-5-Cu-sql- β** adsorbs moderate quantities of CO_2 at 293 K and 1 atm, but little CH_4 or N_2 under the same conditions, suggesting a sieving effect.

Qc-5-M-dia crystallizes as 2-fold interpenetrated **dia** networks in tetragonal space groups whereas **Qc-5-Cu-sql- α** crystallizes in the monoclinic space group $P2_1/c$ (Figure 1, Table S1). The coordination geometry around the metal cations is distorted octahedral: each metal is coordinated to four oxygen atoms (from two carboxylate groups) and two nitrogen atoms (from two quinoline rings). Different orien-

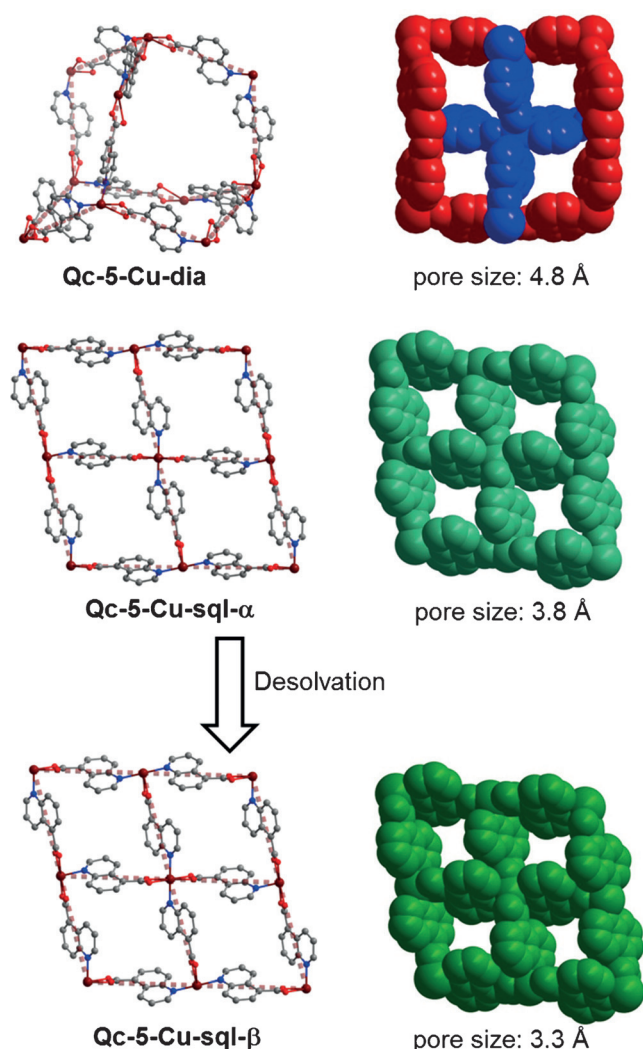


Figure 1. Pore-size tuning from supramolecular isomerism in diamondoid (**dia**, above) and square lattice (**sql**, below) polymorphs of $[\text{Cu}(\text{Qc})_2]_n$.^[23] C (gray), Cu (maroon), O (red), N (blue), H (white).

tations of the linker ligand (Table S2 in the Supporting Information) enables supramolecular isomerism to occur in **Qc-5-Cu**. **Qc-5-Cu-dia** and **Qc-5-Cu-sql- α** exhibit 1D channels with diameters of 4.8 Å and 3.8 Å, respectively, and network void spaces of 34.7% and 23.5%, respectively, as calculated by Platon.^[14] The purity of as-synthesized and activated bulk samples was validated by powder X-ray diffraction (PXRD; Figure 2 and Figures S5–S8). Thermog-

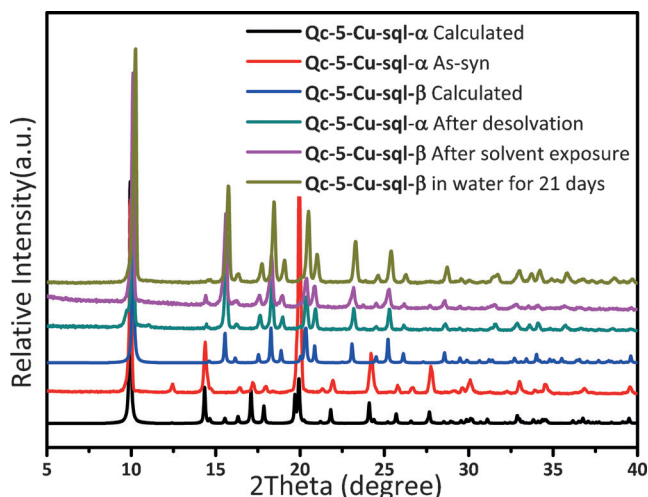


Figure 2. Calculated and experimentally measured PXRD patterns of **Qc-5-Cu-sql- α** and **Qc-5-Cu-sql- β** after exposure to solvent and water.

ravimetric analysis (TGA) measurements reveal that solvent molecules are released well before network decomposition occurs at approximately 240 °C and 280 °C, respectively, for **Qc-5-Cu-dia** and **Qc-5-Cu-sql- α** (Figure S12). **Qc-5-Co-dia** and **Qc-5-Zn-dia** both undergo structural changes to unknown amorphous phases; as such, neither compound was subjected to further study. For **Qc-5-Cu-sql- α** , we noted that PXRD patterns collected before and after desolvation at 130 °C suggest a phase transformation. Single-crystal X-ray diffraction data collected on a desolvated crystal of **Qc-5-Cu-sql- α** , that is, **Qc-5-Cu-sql- β** , reveal that space group and topology are retained. However, the *a*- and *c*-axes contract, along with the cell volume (1004.1 ± 0.1 to 908.0 ± 0.1 Å³), calculated void space (23.5% to 17.2%) and pore-size (3.8 to 3.3 Å). The stacking of **sql** networks in **Qc-5-Cu-sql- β** is controlled by π - π interactions between quinoline moieties from adjacent layers and interlayer quinoline to carboxylate C-H...O interactions. The torsion angle of the quinoline ring with respect to the square plane of the metal centers in **Qc-5-Cu-sql- β** is bigger than that of **Qc-5-Cu-sql- α** , consistent with the observed pore-size contraction. Concomitantly, C-H...O distances in **Qc-5-Cu-sql- β** are shorter than those of **Qc-5-Cu-sql- α** (Figure S2). The pore-size in **Qc-5-Cu-sql- β** is approximately that of the kinetic diameter of CO_2 and therefore smaller than those of N_2 and CH_4 . N_2 and CO_2 sorption isotherms were measured at 77 and 195 K, respectively, to determine if **Qc-5-Cu-sql- β** exhibits a sieving effect consistent with its pore-size. Very low uptake of N_2 ($4.3 \text{ cm}^3 \text{ g}^{-1}$) was observed at 77 K and 1 bar, which is consistent with surface

adsorption. CO₂ uptake of 59 cm³ g⁻¹ at 195 K and 1 bar equates to an apparent BET surface area of 222 m² g⁻¹. CO₂, N₂, and CH₄ sorption experiments were conducted at 273, 283, and 293 K for **Qc-Ni-dia**, **Qc-5-Cu-dia** and **Qc-5-Cu-sql-β**. **Qc-5-Ni-dia** and **Qc-5-Cu-dia** exhibit 293 K and 1 bar uptakes of N₂ (7.1 and 5.8 cm³ g⁻¹) and CH₄ (25.6 and 24.6 cm³ g⁻¹) that are much larger than those of **Qc-5-Cu-sql-β** (N₂: 0.3 cm³ g⁻¹, CH₄: 1.3 cm³ g⁻¹; Figure 3). Conversely, **Qc-5-Cu-sql-β** exhib-

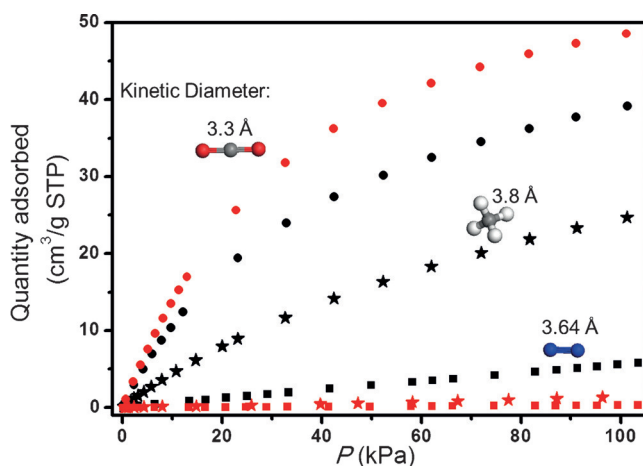


Figure 3. CO₂ (circle), CH₄ (star), and N₂ (square) sorption data at 293 K for **Qc-5-Cu-dia** (black) and **Qc-5-Cu-sql-β** (red).

its a higher CO₂ uptake than even **Qc-5-Cu-dia** at 293 K and 1 bar. CO₂/N₂ (*S*_{CN}) and CO₂/CH₄ (*S*_{CM}) selectivities were calculated in two ways: ratio of uptakes determined from single-component isotherms; ideal adsorbed solution theory (IAST).^[15] The very different sorption behavior that results from pore-size tuning means that *S*_{CN} (40 000) and *S*_{CM} (3300) are much higher than **Qc-5-Cu-dia** (19 and 3), **Qc-5-Ni-dia** (36 and 7) and, more importantly, the vast majority of porous materials studied to date (Table 1, Table S3).^[16] Details about sorption isotherm fitting and selectivity calculations are given in Figures S29–S39. CO₂ isotherms measured at 273, 283, and 293 K were fitted using the virial equation (Figures S23, S25 and S27), and the isosteric heat of adsorption (*Q*_{st}) was calculated using the Clausius–Clapeyron equation. **Qc-5-Cu-sql-β** exhibits a higher *Q*_{st} (36 kJ mol⁻¹) than **Qc-5-Ni-dia** (32 kJ mol⁻¹) and **Qc-5-Cu-dia** (34 kJ mol⁻¹). Such values are

comparable to porous materials with polar functional moieties or unsaturated metal sites, such as NJU-Bai8 (38 kJ mol⁻¹),^[12c] HKUST-1 (35 kJ mol⁻¹),^[17] Bio-MOF-1 (35 kJ mol⁻¹)^[18] and PCN-6 (35 kJ mol⁻¹).^[19] However, these values are lower than benchmark hybrid ultra-microporous materials (40–55 kJ mol⁻¹).^[8]

To further understand the sorption behavior in **Qc-5-Ni-dia**, **Qc-5-Cu-dia**, and **Qc-5-Cu-sql-β**, molecular simulations of their CO₂ adsorption were performed. These studies reveal that closest interactions between CO₂ molecules and pore walls are from CO₂ oxygen atoms and the nearby H atoms of the Qc linkers. Indeed, the adsorbed CO₂ molecules are oriented such that the negatively charged CO₂ oxygen atoms can interact with the positively charged H atoms of the linkers. When comparing the modeled CO₂-loaded structure for **Qc-5-Cu-sql-β** with that for **Qc-5-M-dia**, the former was found to exhibit a better close-fitting interaction between CO₂ molecules and the pore walls (Figure 4 and Figure S48–S57). This is indicated by the significantly shorter O(CO₂)...H distances in **Qc-5-Cu-sql-β** relative to **Qc-5-Ni-dia** and **Qc-5-Cu-dia**. The distances between the CO₂ oxygen atoms and the H atoms of the Qc linkers is under 2.5 Å in **Qc-5-Cu-sql-β** and over 3.0 Å in **Qc-5-Ni-dia** and **Qc-5-Cu-dia** (Figure 4 and Figure S55).

Retention of structural integrity after exposure to water or water vapor is a requirement of any material that might be

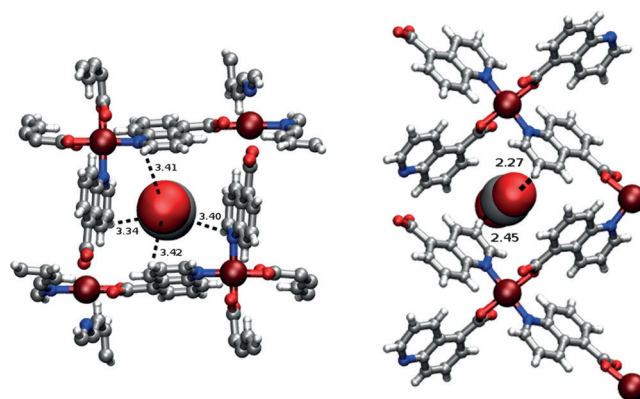


Figure 4. The modelled binding site in the CO₂-loaded structures of **Qc-5-Cu-dia** (left) and **Qc-5-Cu-sql-β** (right) within a unit cell and a 1×2×1 system cell, respectively. C (gray), Cu (maroon), O (red), N (blue), H (white).

Table 1: Summary of structural information and sorption data.

Compounds	Topo logy	Pore size [Å]	BET surface area [m ² g ⁻¹]	CO ₂ uptake [cm ³ g ⁻¹] ^[d]	CH ₄ uptake [cm ³ g ⁻¹] ^[d]	N ₂ uptake [cm ³ g ⁻¹] ^[d]	<i>Q</i> _{st} of CO ₂ [kJ mol ⁻¹] ^[e]	CO ₂ /H ₂ O captured ^[f]	<i>S</i> _{CM} ^[g]	<i>S</i> _{CN} ^[h]
Qc-5-Ni-dia	dia	4.8	664 ^b	58.9	25.6	7.1	32	0.13	7/3	36/26
Qc-5-Cu-dia	dia	4.8	488 ^c	39.2	24.6	5.8	34	0.53	3/2	19/16
Qc-5-Cu-sql^a	sql	3.3	222 ^c	48.4	1.3	0.3	36	1.35	3300/68	40000/463

[a] the desolvated phase of **Qc-5-sql**; [b] calculated from 77 K CO₂ isotherm; [c] calculated from 195 K CO₂ isotherm; [d] at 293 K and 1 bar; [e] *Q*_{st} at low loading; [f] the ratio of amounts of CO₂ and H₂O captured from wet flue gas mixture/(0.15/0.025); [g] left value: selectivity from IAST theory, right value: selectivity from CO₂ uptake at 0.5 bar/CH₄ uptake at 0.5 bar; [h] left value: selectivity from IAST theory, right value: selectivity from CO₂ uptake at (0.15 bar/N₂ uptake at 0.85 bar)/(0.15/0.85).

considered for industrial applications. Recently, we introduced “accelerated stability” pharmaceutical industry methods to evaluate the performance and stability of MOMs after exposure to water vapor.^[20] **Qc-5-Cu-dia**, **Qc-5-Ni-dia**, and **Qc-5-Cu-sql- α** , **Qc-5-Cu-sql- β** were subjected to these methods and exposed to 75 % humidity at 40 °C for 1, 7, and 14 days. After 1 day, **Qc-5-Cu-dia** exhibits a different PXRD pattern and a change in color from blue to purple (Figure S9) whereas **Qc-5-Ni-dia** transforms between 1 and 14 days (Figure S10). In contrast, **Qc-5-Cu-sql- α** and **Qc-5-Cu-sql- β** maintain structural integrity for the duration of stability test (Figure S11) and **Qc-5-Cu-sql- β** remains unchanged after being soaked in water for 21 days (Figure 2). We observed negligible weight increase after **Qc-5-Cu-sql- β** was exposed to a moist N₂ stream during gravimetric experiments (Figure S47). CO₂ sorption experiments verified that the sorption performance of **Qc-5-Cu-sql- β** is unaffected by the stability tests (Figure S22). Such stability to water and water vapor contrasts with many well-known MOFs that are subject to degradation under similar conditions.^[21] We attribute such good hydrolytic stability to the coordinatively saturated Cu²⁺ cations in **Qc-5-Cu-sql- β** (Figure S4).

Water vapor can negatively impact uptake and long-term performance of physisorbents.^[22] Temperature-programmed desorption (TPD) experiments were conducted to gauge the performance of **Qc-5-Cu-sql- β** under equilibrium conditions after exposure to a simulated flue-gas mixture containing water vapor, CO₂, and N₂. The TPD studies suggest that the performance of **Qc-5-Cu-sql- β** is unaffected by the introduction of moisture to the flue-gas stream since a minimal amount of water adsorbed. Based on the amounts of adsorbed CO₂ and H₂O and the initial ratio of CO₂ and H₂O in the inlet gas mixture, the CO₂/H₂O selectivity (S_{CW}) was calculated to be 1.35 after exposing the sample to a simulated flue-gas mixture for 1 h (Figure S44–S46). This is much higher than several benchmark materials (0.17 for MgDOBDC, 0.02 for HKUST-1, 0.27 for SIFSIX-3-Ni and 0.05 for Zeolite 13X) studied under the same conditions.^[19]

Real-time dynamic breakthrough experiments were conducted using CO₂/N₂ (wet and dry) and CO₂/CH₄ gas mixtures. Gas mixtures that simulate flue-gas streams (15 % CO₂/ 85 % N₂, or 50 % CO₂/ 50 % CH₄) were passed through a fixed-bed reactor (8 mm $\varnothing$) filled with **Qc-5-Cu-sql- β** . The sample was pre-treated by heating to 100 °C in a flow of helium gas to release atmospheric impurities and then cooled to room temperature. Evolved gas components were continuously monitored using mass spectrometry (MS, see Supporting Information). CO₂ breakthrough occurs at 121, 112, and 51 min, for dry CO₂/N₂, wet CO₂/N₂, and dry CO₂/CH₄, respectively. Conversely, N₂ and CH₄ pass through the sample bed rapidly (Figure 5). The adsorption capacity of **Qc-5-Cu-sql- β** for CO₂ was calculated to be 44.4, 41.4, and 46.5 cm³ g^{−1}, for the three gas mixtures, respectively, correlating well with CO₂ uptake (48.4 cm³ g^{−1} at 293 K, 1 bar) from single-component isotherms. These data indicate that the carbon capture capacity is independent of the gas mixture composition.

To conclude, sieving of CO₂ from gas mixtures was achieved in the 2D coordination network **Qc-5-Cu-sql- β**

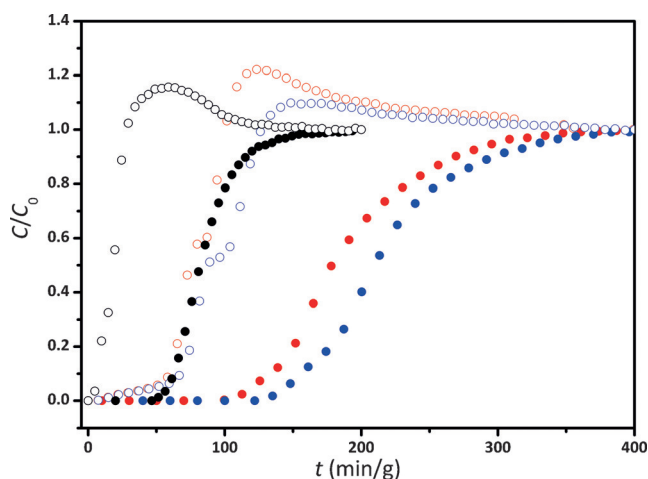


Figure 5. Breakthrough curves for **Qc-5-Cu-sql- β** in a fixed-bed under flow (2 cm³ min^{−1}) of CO₂/CH₄ (50:50, black) and CO₂/N₂ (15:85) gas mixtures under dry (blue) and wet (red) conditions (75 % humidity). filled symbols = CO₂, open symbols = CH₄ or N₂.

thanks to its 3.3 Å channels. This facile to prepare material is moisture-stable and its performance is largely unaffected by the presence of water vapor. This sweet spot in terms of pore-size and pore-chemistry was achieved by exploiting the phenomenon of supramolecular isomerism, which to our knowledge has not yet been exploited to control pore size. Molecular sieving, while difficult to achieve, offers great promise in terms of extremely high selectivity if membranes can be developed. Future work will focus on creating membranes^[10d] from **Qc-5-Cu-sql- β** , for which 2D networks should be predisposed.^[23]

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Keywords: CO₂ separation · gas sorption · molecular sieving effect · stability · supramolecular isomerism

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