

Engineering of an Isoreticular Series of CALF-20 Metal–Organic Frameworks for CO₂ Capture

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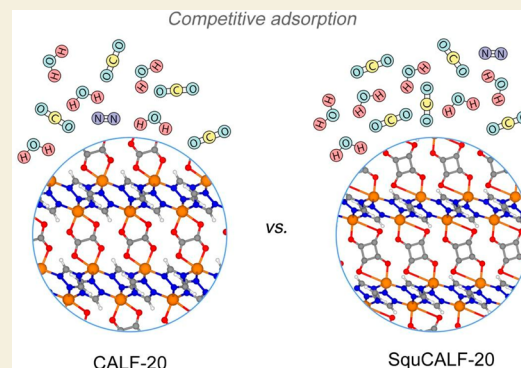
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Supporting Information

ABSTRACT: A series of linker-substituted ultramicroporous CALF-20 metal–organic frameworks (MOFs) were built in silico, and their CO₂ capture performances over N₂ in flue gas conditions were systematically computationally explored. Among the various linker substitutions explored, squarate-linker-incorporated CALF-20 (SquCALF-20) was demonstrated to show a larger CO₂ uptake at 0.15 bar (3.6 mmol/g) and higher CO₂/N₂ selectivity (500) in dry conditions compared to pristine CALF-20. Interestingly, this MOF was shown to maintain a high level of CO₂ capture performance even in the presence of humidity, although it starts to adsorb H₂O at lower relative humidity compared to CALF-20. Because squaric acid is a semiconductor industry feedstock and the few-already published squarate-based MOFs are chemically robust, this engineered SquCALF-20 offers a promising avenue for cost-effective CO₂ capture via physisorption, with potential applications in addressing environmental concerns associated with CO₂ emissions.

KEYWORDS: CALF-20, MOF, *in silico* structure engineering, CO₂ capture, flue gas, molecular simulations



INTRODUCTION

CO₂ emissions into the atmosphere warm the planet, causing climate change and serious related health issues.¹ Aqueous amine-based CO₂ absorption technology is mature for postcombustion capture of CO₂ emitted from power plant exhaust gases; however, it raises concerns in terms of toxicity and implies a high energy-cost regeneration process.² Physisorption-based processes using porous sorbents are a valuable alternative strategy to achieve energetically effective CO₂ capture.³ Beyond the emblematic porous sorbents, including activated carbons,⁴ mesoporous silica,⁵ and zeolites,⁶ metal–organic frameworks (MOFs),⁷ one of the most recent classes of porous crystalline solids, have attracted tremendous interest for diverse adsorption/separation applications due to their unprecedented chemical versatility and high tunability of their pore size/shape. A myriad of MOFs has been proposed over the last 2 decades with promising performance for CO₂ capture^{7–12} that paves the way toward alternative solutions to the standard CO₂ zeolite sorbents.⁶ The ultramicroporous SIFSIX-3-M (M = Zn and Cu) is one of the first prominent CO₂ sorbent MOFs exhibiting very high CO₂/N₂ selectivity, i.e., SIFSIX-3-Cu (10500) and SIFSIX-3-Zn (7250) associated with relatively large CO₂ uptakes (1.24 and 0.13 mmol/g, respectively) at 400 ppm and 298 K.¹³ The hydrolytically stable fluorinated MOF NbOFFIVE-1-Ni (KAUST-7) derived from the same MOF platform was further demonstrated to be an excellent candidate for CO₂ capture directly from air (direct

air capture) combining high CO₂ amount adsorbed at traces (1.3 mmol/g at 400 ppm and 298 K) and reasonable regeneration energy cost.¹⁴ Long et al. reported the N,N-dimethylethylenediamine-functionalized Mg₂(dobpdc) MOF structure for CO₂ capture from air/flue gas (CO₂, N₂, and O₂).¹⁵ This MOF was demonstrated to show very high CO₂ uptake of 2.0 mmol/g at 0.00039 bar and 298.15 K (air capture) and 3.1 mmol/g at 0.15 bar and 313.15 K (flue gas) associated with very high CO₂/N₂ selectivity of up to 49000.

However, some of these potential CO₂ sorbent MOFs suffer from competitive adsorption of H₂O, which leads to a substantial drop of CO₂ sorption capacity under the operating humidity conditions and/or a costly regeneration process with the use of relatively high-temperature treatment and still some issues in terms of long-term stability.^{16–18} To overcome these shortcomings, Shimizu et al.¹⁹ recently proposed a highly thermal and chemically robust zinc triazolate MOF made of 1,2,4-triazolate-bridged zinc(II) layers pillared by the oxalate ligand [Zn₂(1,2,4-triazolate)₂(oxalate)], namely, CALF-20 (CALF stands for Calgary Framework), seen as the current

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benchmark MOF sorbent for CO₂ capture from cement flue gas. This material encompasses an excellent CO₂/N₂ selectivity of 230 and large CO₂ uptake in postcombustion conditions (2.8 mmol/g at 0.15 bar and 293 K) combined with high durability and relatively easy scalability.¹⁹ Interestingly, this level of performance was demonstrated to be maintained in the presence of moisture up to 25% relative humidity (RH) once the MOF is shaped with a polysulfone binder. The shaping of this MOF has also been recently computationally explored.⁴⁵ More generally, the promise of zinc triazolate-based MOFs for CO₂ capture has been widely discussed in the literature, including Zn₂(Atz)₂(ox) (Atz = 3-amino-1,2,4-triazole; ox = oxalate).²⁰ A series of zinc triazolatedicarboxylate pillar-layered MOFs has been constructed with dicarboxylate linkers of different lengths and functional groups.²¹ Recently, Li et al. systematically engineered the pillaring of zinc triazolate layers with benzenedicarboxylate linkers and their ortho functionalized derivatives, e.g., Bdc-F, Bdc-Cl, Bdc-NH₂, Bdc-NO₂, and Bdc-CH₃, to tune the CO₂ sorption uptake of the resulting MOFs at 1 bar,²² while Wang et al. proposed cobalt triazolate-based MOFs with biphenyldicarboxylate linker units for the same target.²³

Inspired by these findings, herein, we deliberately expand the CALF-20 platform by envisioning an isorecticular series of MOFs with substitution of the oxalate ligand of the parent CALF-20 by alternative small linkers, including squarate (Squ), fumarate (Fum), benzenedicarboxylate (Bdc), thieno[3,2-*b*]thiophene-2,5-dicarboxylate (Ttdc), and cubanedicarboxylate (Cub). Note that these linkers have already been used as building units to synthesize many MOFs. Their CO₂ capture performance over N₂ under dry and humid conditions was further computationally assessed to predict alternative MOFs with even better performances than CALF-20 to further guide experimental efforts toward their synthesis and testing. SquCALF-20 was identified as the best candidate, combining high CO₂ uptake at 0.15 bar (3.6 mmol/g) and very high CO₂/N₂ selectivity (500), exceeding the performance of pristine CALF-20 while maintaining this attractive level of CO₂ adsorption performance under moderate moisture.

■ COMPUTATIONAL METHODS

Density Functional Theory (DFT) Calculations

The crystal structures of pristine CALF-20 and its engineered derivatives constructed by substituting the pristine oxalate linker with Squ, Fum, Bdc, Ttdc, and Cub were fully geometry-optimized (atomic positions and cell parameters relaxed) at the periodic DFT level without imposing any constraints in terms of topology/geometry. These calculations were performed using the *Quickstep* module²⁴ of the CP2K program²⁵ with the Gaussian plane-wave formalism. The Perdew–Burke–Ernzerhof²⁶ functional combined with Grimme's DFT-D3 semiempirical dispersion corrections was used for all calculations.^{27,28} All atoms except Zn were modeled via triple- ζ plus valence-polarized Gaussian-type basis sets (TZVP-MOLOPT), while for Zn, double- ζ plus valence polarization functions (DZVP-MOLOPT) were employed.²⁹ Core electron–valence shell interactions were described by the norm-conserving pseudopotentials proposed by Goedecker, Teter, and Hutter.^{30–32} The energy cutoff for the plane-wave basis set was set to 500 Ry. The atomic partial charges for each MOF were calculated using the repeating electrostatic potential extracted atomic (REPEAT) charge³³ method for further Monte Carlo (MC) and molecular dynamics (MD) simulations.

Grand Canonical Monte Carlo (GCMC) Simulations

CO₂ single-component and CO₂/N₂ (15:85) binary mixture adsorption isotherms were simulated for all MOFs at 293 K using GCMC calculations, as implemented in the Complex Adsorption and Diffusion Simulation Suite (CADSS) code.³⁴ For pristine CALF-20 and the derivatives showing the best CO₂ sorption performance, H₂O single-component and CO₂/N₂/H₂O ternary mixture adsorption isotherms were further computed. Several types of Monte Carlo moves were considered: translation move, rotation move, and insertion/deletion move. The frequencies of these moves were 0.3, 0.3, 0.2, and 0.2, respectively. In the case of a mixture, a molecular exchange move was additionally considered. A simulation box consisting of 27 unit cells (3 × 3 × 3) was considered for all MOFs, and the atomic positions of the MOFs were held fixed during the simulations. The host–guest nonbonded interactions were treated as the sum of a van der Waals interaction term and a Coulombic contribution. The Lennard–Jones (LJ) interactions were computed with a cutoff of 12.0 Å, while the electrostatic interactions were calculated using the Ewald summation³⁵ technique with an accuracy of 1 × 10^{−6}. The parameters for all MOF atoms were taken from the DREIDING³⁶ force field, and their atomic partial charges were DFT-derived using the REPEAT scheme.³³ CO₂ was described by a three-site charged LJ model as defined by Garcia-Sánchez et al.,³⁷ and N₂ was represented by a three-site charged model, with two LJ sites located at the N atoms while a third site present at its center of mass only involves electrostatic interactions.³⁸ H₂O was modeled as a four-site TIP4P_Ew model.³⁹ Table S1 provides the LJ parameters and atomic partial charges for all atoms. The LJ cross-term parameters were obtained by applying the Lorentz–Berthelot mixing rules.⁴⁰ For each pressure point, 2 × 10⁷ and 2 × 10⁸ Monte Carlo production steps following 10⁷ and 10⁸ Monte Carlo equilibration steps were considered for the CO₂ single component/binary mixture and the H₂O single component/ternary mixture, respectively. The Peng–Robinson equation of state was used to determine the gas-phase fugacity.⁴¹ The simulated single-component water adsorption isotherm for CALF-20 was first compared to both previous calculations and the corresponding experimental data.¹⁹ This comparison is reported in Figure S1. One can observe that our simulations reproduce very well the experimental S-shaped adsorption isotherm up to 20% RH, while they overestimate the amount adsorbed between 30% and 80% RH and match the experimental saturation uptake. Notably, these simulations led to a better agreement with the experimental data compared to the previous simulation work using a different force field to describe the H₂O/CALF-20 interactions.¹⁹ This overall agreement between the simulated and experimental water adsorption isotherms enabled evidence that the selected force field for both H₂O and CALF-20 atoms along the MOF partial charges achieve a fair description of the host/guest interactions in this system.

The radial distribution functions (RDFs) for all MOF/guest atom pairs were averaged over the Monte Carlo steps at different pressure ranges. The adsorption enthalpies for CO₂ and N₂ were calculated for all MOFs at infinite dilution $\Delta H_{\text{ads},\theta=0}$ using the Widom insertion method,⁴² while the corresponding values for H₂O were calculated only for CALF-20 and SquCALF-20. The adsorption enthalpy for CO₂ was also calculated by GCMC simulations as a function of the CO₂ uptake.

MD Simulations

Single-component CO₂ diffusion was investigated in CALF-20 and its best CO₂-sorbent derivatives at 293 K for a typical loading of 1 CO₂ molecule/unit cell. These MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)⁴³ simulation package. In the MD simulations, CALF-20 and the best CO₂-sorbent framework moieties were treated as flexible. In these calculations, the parameters for the intramolecular bonding, bending, and dihedral terms of the MOFs were taken from the UFF force field⁴⁴ since it was successfully applied to describe the flexibility of the pristine CALF-20 structure,⁴⁵ while the DREIDING³⁶ parameters were selected to define the nonbonded LJ

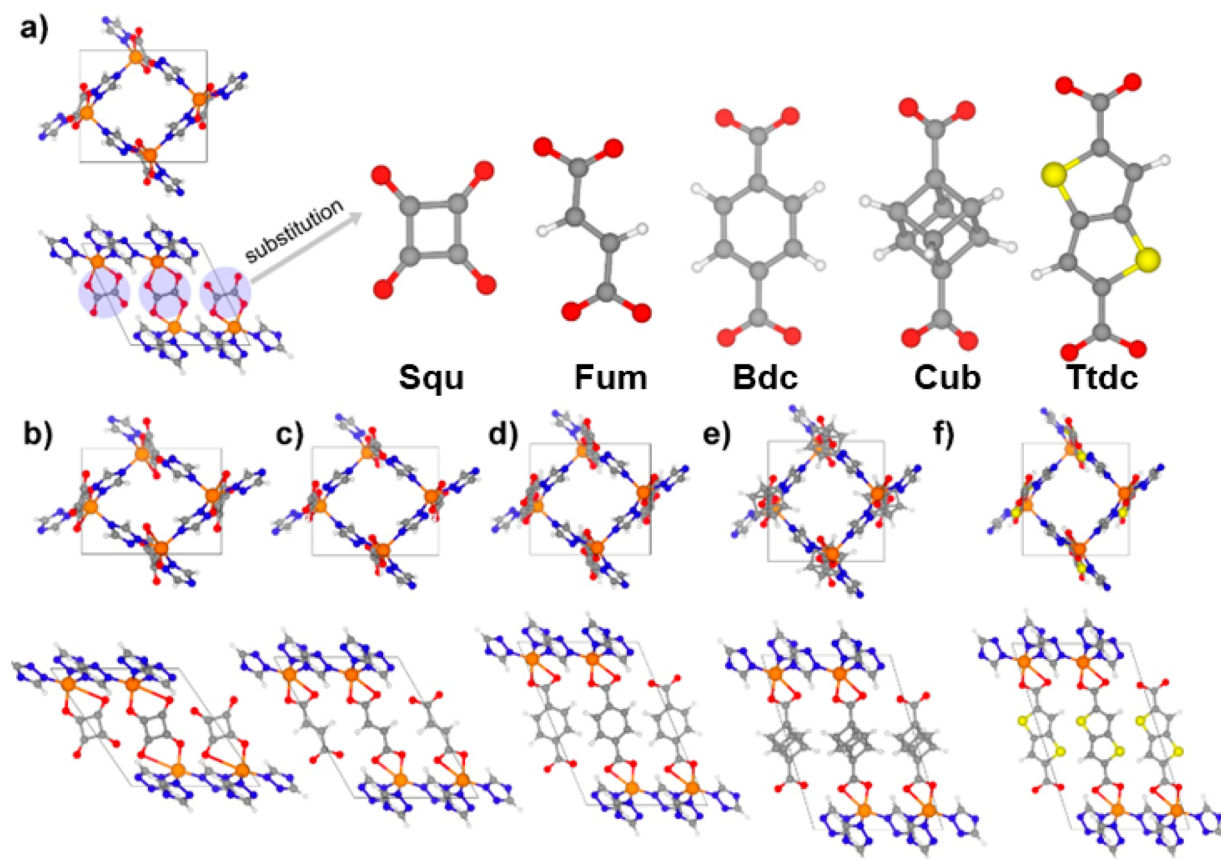


Figure 1. Illustration of the DFT-optimized structures of CALF-20 (a) and its derivatives SquCALF-20 (b), FumCALF-20 (c), BdcCALF-20 (c), TtdcCALF-20 (d), and CubCALF-20 (e). The resulting cell parameters are provided for all MOFs in Table S2. Color code: red, O; gray, C; white, H; yellow, S; orange, Zn.

potentials in a manner similar to that of the GCMC simulations. All of these simulations were performed in the NVT ensemble for 200 ns production runs following 20 ns equilibration and a time step of 1 fs. The Nosé–Hoover thermostat⁴⁶ was employed to maintain the temperature with a coupling constant time of 0.5 ps. The self-diffusion coefficients (D_s) of CO₂ averaged over three MD trajectories were calculated by applying Einstein's diffusion relationship to the linear region of the MSD versus time plot.

RESULTS AND DISCUSSION

Figure 1 illustrates the DFT-optimized crystal structures of CALF-20 and its derivatives, SquCALF-20, FumCALF-20, BdcCALF-20, TtdcCALF-20, and CubCALF-20. The structural information and textural properties of this isoreticular series of MOFs, including the pore volume (PV), void fraction (ϕ), largest cavity diameter, and pore-limiting diameter (PLD) assessed by using the Zeo++ software,⁴⁷ are tabulated in Table S2. PLD ranges from 2.7 Å (CubCALF-20) to 3.0 Å (FumCALF-20), while PV varies from 0.32 cm³/g (CALF-20) to 0.49 cm³/g (BdcCALF-20). As shown in Figure 1b–f, the organic ligand with incremental length increases the 1D channel pore dimension of the pristine CALF-20 (see also Table S2).

Single-Component CO₂ Adsorption

We further validated the selected force-field parameters and atomic partial charges of the MOFs alongside the models used for CO₂ by an excellent agreement between the CO₂ adsorption isotherm simulated for CALF-20 at 293 K with

the corresponding experimental data reported previously¹⁹ in the pressure domain of 0–1 bar (Figure 2a).

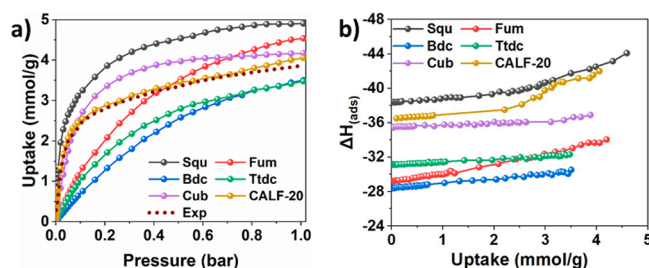


Figure 2. GCMC-predicted (a) single-component CO₂ adsorption isotherms and (b) adsorption enthalpy for CALF-20 and its derivatives in the pressure range of 0–1 bar at 293 K. The experimental data from ref¹⁹ are incorporated in part a for comparison.

The CO₂ adsorption isotherms further simulated for all CALF-20 derivatives evidenced that the choice of the linker enables to tune the CO₂ sorption uptake in the overall range of pressure explored, as shown in Figure 2a. Typically, at 1 bar the sequence BdcCALF-20 ~ TtdcCALF-20 (3.5 mmol/g) < CALF-20 (4.1 mmol/g) < CubCALF-20 (4.2 mmol/g) < FumCALF-20 (4.5 mmol/g) < SquCALF-20 (4.9 mmol/g) is revealed, while at 0.15 bar, SquCALF-20 (3.6 mmol/g) and to a lesser extent CubCALF-20 (3.1 mmol/g) still outperform CALF-20 (2.8 mmol/g). Analysis of the CO₂ distribution

(Figure S2) in the pores of SquCALF-20 (PLD = 2.9 Å; PV = 0.35 cm³/g) evidenced that a tiny expansion of its pore size/pore volume compared to CALF-20 (PLD = 2.8 Å; PV = 0.32 cm³/g) favors the adsorption of a large concentration of CO₂ in the low domain of pressure (Figure 2a). This is in line with a slightly higher simulated adsorption enthalpy at low coverage for SquCALF-20 (−38.4 kJ/mol) compared with CALF-20 (−36.5 kJ/mol) and other MOF derivatives (Figure 2b). Enhancement of the adsorption enthalpy with CO₂ uptake is attributed to an increase of the CO₂/CO₂ interaction energy contribution, as highlighted in Figure S3. Analysis of the RDF calculated for the most significant CO₂/MOF atom pairs (Figure S4a,b) for both SquCALF-20 and CALF-20 at 0.15 bar pressure revealed that while CO₂ interacts similarly with both the O atoms of the oxalate groups and the H atoms of the triazolate linkers [almost similar mean separating O_{oxalate}–C_{CO₂} (3.3 Å) and H_{triazolate}–C_{CO₂} (3.7 Å) distances and the same peak intensities] in CALF-20, the situation differs for SquCALF-20, where CO₂ preferentially interacts with the O atoms of the squarate group (mean separating O_{squarate}–C_{CO₂} distance of 3.0 Å) and to a lesser extent with the atoms of the triazolate linkers. Figure 3 illustrates the adsorption config-

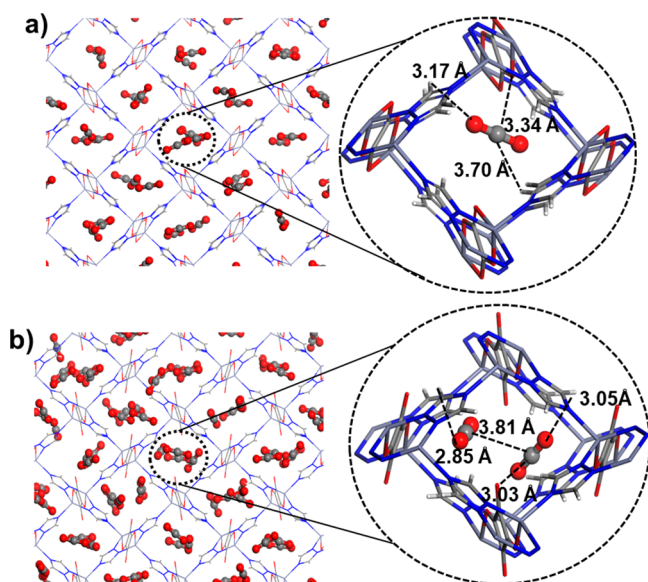


Figure 3. Illustration of the preferential sittings of CO₂ obtained from the single-component Monte Carlo simulations at 0.15 bar along their characteristic interacting distances in (a) CALF-20 and (b) SquCALF-20. For a better view, a single unit cell of each MOF structure is presented as an inset, with CALF-20 and SquCALF-20 adsorbing 1 CO₂ molecule/unit cell and 2 CO₂ molecules/unit cell at this pressure, respectively.

urations for CO₂ in both CALF-20 materials, evidence that the preferential interactions of CO₂ with the squarate O atoms in SquCALF-20 is made possible by the fact these adsorption sites are pointing toward the pore center and they are therefore more accessible for the guest molecules.

This favors a more effective packing of CO₂ in the pores of SquCALF-20, and hence combined with a slightly higher PV of this MOF compared to CALF-20, this leads to an enhancement of the CO₂ loading at a given pressure, e.g., 1 and 2 CO₂ molecules/unit cell for CALF-20 and SquCALF-20 at 0.15 bar, respectively. This is illustrated in the Monte Carlo snapshots

provided in Figure S5a,b. The RDF plots calculated for the C_{CO₂}–C_{CO₂} pairs in CALF-20 and SquCALF-20 (Figure S5c,d) exhibit similar profiles, with a first peak in the range of 3.4–3.6 Å in line with the high confinement of CO₂ in the MOF pores.

Binary CO₂/N₂ Mixture Adsorption

CO₂/N₂ (15:85) binary mixture GCMC simulations were performed for the full series of isoreticular CALF-20 MOFs to further assess their promises for CO₂ capture from flue gases. Figure 4a reports the corresponding adsorption isotherms, while Table S3 summarizes the CO₂ uptakes calculated at different total pressures for the mixture compared to the scenario of the CO₂ single component.

These simulated data evidence that SquCALF-20 still adsorbs the largest amount of CO₂ at low pressure in mixture. This, combined with a very low N₂ adsorbed amount (Figures 4a and S6), translates into a CO₂/N₂ selectivity at 1 bar above 500, substantially higher than the value simulated for CALF-20 (180) and all other derivatives including CubCALF-20 (78), as shown in Figure 4b. This behavior is in line with the highest simulated adsorption enthalpy at low coverage difference obtained between CO₂ and N₂ for SquCALF-20 compared to the other MOFs (Table S4 and Figure S7), with the calculated adsorption enthalpy at low coverage difference between CO₂ and N₂ evolving as follows: −17.8 kJ/mol (SquCALF-20) > −15.4 kJ/mol (CALF-20) > −15.0 kJ/mol (CubCALF-20) > −13.0 kJ/mol (TtdcCALF-20) > −12.9 kJ/mol (FumCALF-20) > −12.2 kJ/mol (BdcCALF-20). Figure 4c shows that the CO₂ molecules are distributed in mixture conditions in a manner similar to that of a single component with only a minor concentration of N₂ molecules adsorbed. Analysis of the RDFs calculated for the most significant CO₂/MOF atom pairs (Figure S6a,b) for both SquCALF-20 and CALF-20 for the binary mixture at a total pressure of 1 bar revealed that CO₂ adopts the same adsorption mode as that in the single-component scenario (Figure S4a,b), with a preferential sitting of CO₂ toward the O atoms of the squarate groups for SquCALF-20 leading to a better packing of CO₂ in its pore and an optimum CO₂ selectivity over N₂.

CO₂/N₂ Separation Performance in the Presence of Humidity

As a further step, we explored the ternary adsorption of the CO₂/N₂/H₂O ternary mixture in CALF-20 and SquCALF-20 at 293 K as well as the single-component H₂O adsorption in these two MOFs for comparison. These calculations were performed using a representative CO₂/N₂/H₂O ternary mixture composition of 0.199995324:0.799981296:0.00023380 for 1% RH, while a total pressure of 1 bar was applied (see Table S5 for the ternary mixture molar fraction for each % RH). The corresponding data are reported in Figure 5a,b. The calculated single-component H₂O distribution snapshots at different RHs and the corresponding RDF plots for water–MOF and water–water pairs in CALF-20 and SquCALF-20 are shown in Figures S8 and S9, respectively. This analysis shows that the H₂O adsorption mechanism is similar in both the SquCALF-20 MOF and pristine CALF-20.

SquCALF-20 is found to be more hydrophilic than CALF-20 starting to adsorb H₂O at lower RH (Figure 5a,b) in line with a slightly higher calculated adsorption enthalpy for H₂O at low coverage (−38.7 vs −33.4 kJ/mol, respectively). Analysis of the snapshots evidences that CO₂ preferentially adsorbs in the center of the MOF cavities while H₂O molecules are closer to

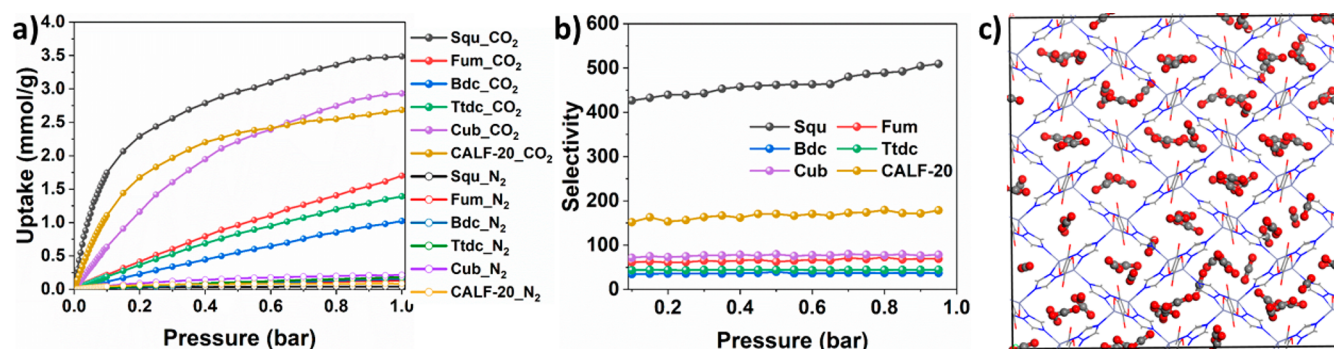


Figure 4. GCMC-simulated CO_2/N_2 (15:85 composition) mixture (a) adsorption isotherms and (b) selectivity in the pressure range from 0 to 1 bar at 293 K [the selectivity for CO_2 over a N_2 gas molecule is calculated using the expression $S\left(\frac{\text{CO}_2}{\text{N}_2}\right) = \left(\frac{X_{\text{CO}_2}}{X_{\text{N}_2}}\right)\left(\frac{Y_{\text{CO}_2}}{Y_{\text{N}_2}}\right)$, where X_{CO_2} and X_{N_2} are the molar fractions of CO_2 and N_2 gas molecules in the adsorbed phase, while Y_{CO_2} and Y_{N_2} are the molar fractions of CO_2 and N_2 molecules in the bulk phase, respectively]. (c) Simulated snapshot of a CO_2/N_2 mixture in SquCALF-20 at a total pressure of 1 bar (viewed along the MOF 1D channel pore).

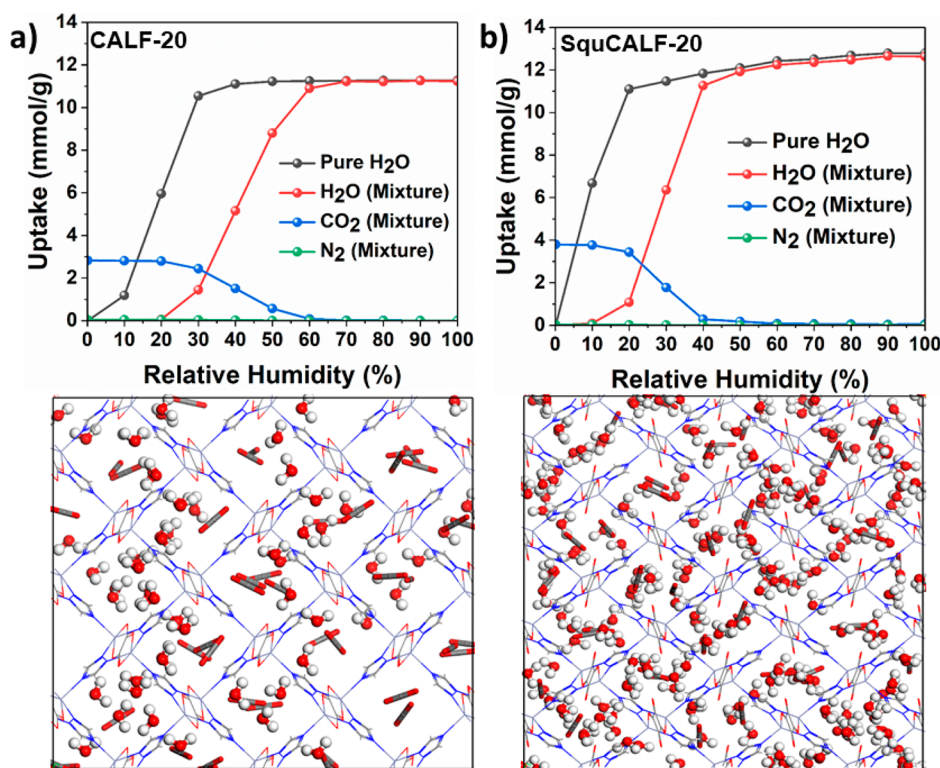


Figure 5. GCMC-simulated $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ ternary mixture (see Table S5 for the ternary mixture mole fraction for each % RH with a total applied pressure of 1 bar) adsorption isotherms at 293 K along with illustrative snapshots calculated under RHs of 30% and total pressures of the system kept at 1 bar for (a) CALF-20 and (b) SquCALF-20. CO_2 is represented as rodlike molecules, and H_2O is shown as ball–stick representations.

the pore wall (Figure 5a). Indeed, because the affinity of SquCALF-20 for H_2O is very similar to that for CO_2 (−38.4 kJ/mol), adsorption of CO_2 is still favored at low RH in the same location as in the scenario of the single component. Decisively, SquCALF-20 maintains its larger CO_2 sorption capacity of 3.4 mmol/g (vs 2.7 mmol/g for CALF-20) up to RH = 20% and shows a decrease above with a sorption uptake of 1.8 mmol/g at RH = 30%. At this RH = 30% and above, H_2O molecules preferentially adsorb in the vicinity of the O atom of squarate ($\text{O}_{\text{squarate}}$), with the formation of relatively strong hydrogen bonds associated with a separating distance of 1.7 Å (see the corresponding RDF in Figure S10a,b) while forming an extended strong hydrogen-bond network (Figure

S10c) at higher RH associated with a high-intensity peak for the $\text{H}_{\text{water}}-\text{O}_{\text{water}}$ pair at 1.8 Å. A similar hydrogen-bond network (from water cluster multimers to wired hydrogen-bond network structures) was reported for CALF-20 recently by Magnin et al.⁴⁸ This water organization constrains CO_2 molecules to occupy only the pore center of SquCALF-20 in a manner similar to that in the scenario of CALF-20 (see the snapshot in Figure 5a,b) and therefore leads to a gradual reduction of the CO_2 uptake for RH > 30%. A similar adsorption mechanism of CO_2 under water humidity (with the ranges of % RH) in pristine CALF-20 was also reported recently.^{48–50} These studies evidenced (i) the association of H_2O in the vicinity of the CALF-20 pore wall through

hydrogen bonds with the MOF atoms and (ii) the formation of water–water hydrogen bonds that repels CO₂ molecules in the middle of the confined pore of CALF-20.^{48–50}

Single-Component CO₂ Diffusion and MOF Formation Energy

MD simulations were further performed to assess D_s of CO₂ in CALF-20 and SquCALF-20 at 293 K in the NVT ensemble. These calculations revealed that D_s (CO₂) is similar in both MOFs (4.05×10^{-11} and 3.32×10^{-11} m²/s for CALF-20 and SquCALF-20, respectively; Figure S11), suggesting that the adsorption/desorption kinetics is expected to proceed within the same time scale in both cases. The formation energy of SquCALF-20 and pristine CALF-20 MOFs was further calculated by using DFT calculations to anticipate the stability/synthesizability of the newly engineered MOF. Their resulting calculated formation energies are quite similar, −0.58 and −0.43 eV/atom, respectively. For comparison, Hasan et al. reported an even lower formation energy (−0.18 eV/atom) for the functionalized ZIF8-IR820 that has been successfully synthesized.⁵¹ Therefore, because the formation energy of SquCALF-20 is only slightly lower than that of pristine CALF-20 and much higher than that reported for ZIF8-IR820, this supports that this engineered MOF is synthetically feasible.

CONCLUSIONS

A series of novel ligand-substituted CALF-20 structures were in silico constructed and their CO₂ capture performances were systematically predicted. A SquCALF-20 derivative was demonstrated to show larger CO₂ uptake at 0.15 bar (3.6 mmol/g) and higher CO₂/N₂ selectivity (500) compared to pristine CALF-20. Interestingly, this MOF was shown to maintain a high level of CO₂ performance in the presence of H₂O, although it starts to adsorb H₂O at lower RH compared to CALF-20, while the CO₂ kinetics is expected to be similar to that obtained for CALF-20. It is well documented that squarate-based microporous MOFs are chemically and thermally stable due to the strong bonds formed between squarate O and metal ion,⁵² and squaric acid is a semiconductor and laser industry feedstock. This paves the way toward the synthesis of a robust and cost-effective novel ultramicroporous SquCALF-20 highly attractive for CO₂ capture.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaelm.3c00622>.

MOF atoms and guest molecules force fields (Table S1), lattice parameters and texture properties of studied MOF systems (Table S2), comparison table of CO₂ uptake in a single component and ternary mixture (Table S3), comparison table of the CO₂/N₂ binary mixture heat of adsorption enthalpy (Table S4), ternary mixture CO₂/N₂/H₂O mole fraction composition (Table S5), experimental and simulation comparison graph of single-component H₂O adsorption isotherms (Figure S1), simulation snapshots of CO₂ in CALF-20, SquCALF-20, and CubCALF-20 (Figure S2), different host/guest and guest/guest contributions to the adsorption enthalpies for CO₂ as a single component in CALF-20 and SquCALF-20 (Figure S3), calculated

RDF graph of single-component CO₂ in CALF-20 and SquCALF-20 (Figure S4), CO₂ single-component simulation snapshots and CO₂–CO₂ RDFs in CALF-20 and SquCALF-20 at 0.15 and 1 bar (Figure S5a,d), CO₂/N₂ binary mixture simulation snapshots and RDFs in CALF-20 and SquCALF-20 (Figure S6), CO₂/N₂ binary mixture adsorption enthalpy (Figure S7), single-component H₂O adsorption snapshots and RDF in CALF-20 (Figure S8), single-component H₂O adsorption snapshots and RDF in SquCALF-20 (Figure S9), calculated RDF graph of H₂O–SquCALF-20, water–water interaction, and hydrogen-bond formation calculated at 30% RH from a CO₂/N₂/H₂O mixture (Figure S10), calculated CO₂ MSD graph with fitted parameters for CALF-20 and SquCALF-20 structures (Figure S11), and computational input files (PDF)

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Notes

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