Temperature-Dependent Nitrous Oxide/Carbon Dioxide Preferential Adsorption in a Thiazolium-Functionalized NU-1000 Metal–Organic Framework

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ABSTRACT: Solvent-assisted ligand incorporation (SALI) of the ditopic linker 5-carboxy-3-(4-carboxybenzyl)thiazolium bromide [(H2PhTz)Br] into the zirconium metal–organic framework NU-1000 [Zr6O4(OH)8(H2O)4(TBAPy)2, where NU = Northwestern University and H4TBAPy = 1,3,6,8-tetrakis(p-benzoic-acid)-pyrene], led to the SALIed NU-1000-PhTz material of minimal formula [Zr6O4(OH)6(H2O)2(TBAPy)2(PhTz)]Br. NU-1000-PhTz has been thoroughly characterized in the solid state. As confirmed by powder X-ray diffraction, this material keeps the same three-dimensional architecture of NU-1000 and the dicarboxylic extra linker bridges adjacent [Zr6] nodes ca. 8 Å far apart along the crystallographic c-axis. The functionalized MOF has a BET specific surface area of 1560 m²/g, and it is featured by a slightly higher thermal stability than its parent material (Tdec = 820 vs. 800 K, respectively). NU-1000-PhTz has been exploited for the capture and separation of two pollutant gases: carbon dioxide (CO2) and nitrous oxide (N2O). The high thermodynamic affinity for both gases [isosteric heat of adsorption (Qst) = 25 and 27 kJ mol⁻¹ for CO2 and N2O, respectively] reasonably stems from the strong interactions between these (polar) “stick-like” molecules and the ionic framework. Intriguingly, NU-1000-PhTz shows an unprecedented temperature-dependent adsorption capacity, loading more N2O in the 298 K ≤ T ≤ 313 K range but more CO2 at temperatures falling out of this range. Grand canonical Monte Carlo simulations of the adsorption isotherms confirmed that the preferential adsorption sites of both gases are the triangular channels (micropores) in close proximity to the polar pillar. While CO2 interacts with the thiazolium ring in an “end-on” fashion through its O atoms, N2O adopts a “side-on” configuration through its three atoms simultaneously. These findings open new horizons in the discovery of functional materials that may discriminate between polluting gases through selective adsorption at different temperatures.

KEYWORDS: metal–organic frameworks (MOFs), porous materials, zirconium(IV), thiazolium salts, carbon dioxide adsorption, nitrous oxide adsorption, powder X-ray diffraction (PXRD), grand canonical Monte Carlo (GCMC) simulations, molecular dynamics (MD) simulations

INTRODUCTION

The synthetic tools available for the preparation of metal–organic frameworks (MOFs) have progressively increased in number in more recent years. MOFs are crystalline materials composed of inorganic nodes coordinated via multitopic organic linkers, with a wide structural variety coming from the virtually infinite “Tinkertoy” combinations of their constituting building units.1–4 Initially, the solvothermal/hydrothermal approach (i.e., mixing metal salts and polytopic linkers in a high-boiling polar solvent and treating the mixture at high temperature under autogenous pressure in sealed autoclaves) was the most popular synthetic methodology to prepare new MOFs. After the serendipitous discovery of the ability of zirconium MOFs to participate in linker exchange or inclusion reactions while keeping their crystal structure intact, new perspectives on MOF synthesis have come up ahead. Indeed, this has led to the so-called solvent-assisted ligand exchange5–7 and solvent-assisted ligand incorporation (SALI) postsynthetic methodologies.8–11 The former is now highly exploited to prepare mixed-ligand MOFs through partial exchange of the pre-existing linker with new ones dissolved in a solution in contact with a suspended MOF powder at a high temperature. The latter approach stems from the existence, in some [Zr6]}
octahedral nodes, of monodentate hydroxo/aquo ligands that are prone to react with the COOH groups of the incoming carboxylate-based linkers that eventually replace them on the metallic node through a simple condensation reaction (and concomitant water elimination). Thus, SALI is a powerful synthetic tool to insert new species in pre-existing MOFs with the aim of creating new materials with enhanced properties. One of the most iconic zirconium MOFs is NU-1000 (NU = Northwestern University) with its \([\text{Zr}_6(\mu_3-\text{OH})_4(\mu_3-\text{O})_4(\text{OH})_4(\text{H}_2\text{O})_4]^{8+}\) nodes and tetratopic pyrene-based linkers [\(\text{H}_4\text{TBAPy} = 1,3,6,8\)-tetrakis(\(p\)-benzoic acid)pyrene]. NU-1000 is particularly suitable for SALI because the hydroxo/aquo ligands dangling from the eight-connected \([\text{Zr}_6]\) nodes are oriented toward both the 30 Å wide hexagonal channels (along the crystallographic \(a\)-axis and \(b\)-axis) and the smaller 8 Å cavities (along the crystallographic \(c\)-axis). Consequently, after \(-\text{OH}/-\text{OH}_2\) ligand replacement, up to four additional carboxylate groups may be added to the metallic nodes to complete the \(\text{Zr}^{IV}\) coordination sphere and form a 12-connected \([\text{Zr}_6]\) cluster, with a concomitant topology change. The resulting NU-1000-FG material (FG = functional group) is featured by new chemophysical properties that depend on those of the extra linker added and on the SALI extent. Previous works have already shown the great potentiality of the technique in this context.11,13–15 Following the research line of our group on the synthesis of MOF materials containing polar heterocyclic linkers for enhanced polluting gas capture and separation,16–18 we exploited SALI to prepare a new NU-1000-FG derivative suitable for both carbon dioxide (\(\text{CO}_2\)) and nitrous oxide (\(\text{N}_2\text{O}\)) adsorption. While some of these compounds have shown excellent performances in carbon dioxide storage\(^8,19\) with high absolute uptake under ambient temperature and pressure conditions and enhanced thermodynamic affinity compared to the parent NU-1000,\(^{11,15,20}\) to the best of our knowledge, no examples of NU-1000-FG MOFs exploited for nitrous oxide storage are known to date. \(\text{N}_2\text{O}\) occurs in ever-increasing amounts in the atmosphere due to the industrial anthropogenic activity (nitric acid and adipic acid production), and it has been found to be a major scavenger of stratospheric ozone with the same degradative effect as that of chlorofluorocarbons. Being the third most important long-lived greenhouse gas after methane (\(\text{CH}_4\)) and \(\text{CO}_2\), nitrous oxide substantially contributes to global warming with an extent comparable to that of \(\text{CO}_2\), albeit being present in much smaller concentration in the Earth atmosphere. On a per-molecule basis, nitrous oxide has ca. 300 times the atmospheric heat-trapping ability of carbon dioxide. Thus, it is important to design chemical sponges that capture \(\text{N}_2\text{O}\) efficiently. From a chemical viewpoint, the two molecules are isoelectronic, share the same “stick-like” linear shape, and possess the same molecular weight (44 amu). On the other hand, \(\text{N}_2\text{O}\) is not thermodynamically stable versus the...
elements; moreover, while CO$_2$ is quadrupolar, N$_2$O shows a small dipole moment (0.166 D), the anisotropic distribution of its electronic density being further enhanced by the existence of two resonance forms with integer charges: [$N\equiv N^+ – O$] $\leftrightarrow$ [$N≡N\equiv O$]. More in general, they show similarities and differences at the chemophysical$^{21}$ and biological$^{22}$ levels. The inclusion of polar linkers within NU-1000 should be beneficial for N$_2$O uptake, as observed for CO$_2$. Following this idea and our previous experience on the design of thiazole-containing polytopic carboxylates for MOF synthesis,$^{23–28}$ we have prepared the ditopic thiazolium carboxylate salt 5-carboxy-3-(4-carboxybenzyl)thiazolium bromide (H$_2$PhTz)$\cdot$Br (Scheme 1). This flexible dicarboxylic acid has been anchored to the NU-1000 nodes via SALL in a bridging fashion between adjacent [Zr$_6$]$_n$ clusters ca. 8 Å far apart. The resulting NU-1000-PhTz MOF (Figure 1) has been characterized in the solid state and exploited for CO$_2$ and N$_2$O capture, showing an unexpected temperature-dependent N$_2$O/CO$_2$ preferential adsorption.

## EXPERIMENTAL SECTION

### Materials and Methods

All the chemicals and reagents employed were purchased from commercial suppliers and used as received without further purification. NU-1000 was prepared according to the published procedure.$^{29}$ For organic syntheses, solvents were purified through standard distillation techniques. Deuterated solvents (Sigma-Aldrich) were stored over 4 Å molecular sieves and degassed by three freeze–pump–thaw cycles before use. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. $^1$H and $^{13}$C{$_1$H} NMR chemical shifts are reported in the deuterated solvent. FT-IR spectra (KBr pellets) were recorded on a Nicolet iS50 spectrometer (Thermo, San Jose, CA). The instrument was equipped with a PERT PRO diode array detector (antiscatter slit aperture: 7.5 mm). X-ray fluorescence (XRF) qualitative elemental analysis was performed by fluorescence (XRF) qualitative elemental analysis was performed by PERT PRO diode array detector (antiscatter slit aperture: 7.5 mm). X-ray tube (Cu K$_{\alpha}$) and the diode detector head was set at a distance of 0.2 m from the sample. X-ray powder diffractometry (XRD) qualitative measurements were carried out with a Cu K$_{\alpha}$ radiation source (Bruker AXS D8 ADVANCE). The single-crystal X-ray crystallographic data collection was carried out by means of a Bruker Nonius Kappa crystallographic diffractometer equipped with a 2θ/θ scan method. The data were processed and refined using the SHELXTL package.$^{30}$

### Synthesis of 5-Carboxy-3-(4-carboxybenzyl)thiazolium Bromide ([H$_2$PhTz]$\cdot$Br)

A stirred solution of thiazole-5-carboxylic acid (FW = 129.13 g/mol, 0.4 g, 3.1 mmol) and 4-bromomethyl benzoic acid (FW = 215.04 g/mol, 0.8 g, 3.7 mmol, 1.2 equiv) in acetonitrile (25 mL) was kept at 353 K for 48 h. During this time, an off-white solid formed and precipitated out of the solution. Afterward, the mixture was cooled down to ambient temperature, and acetonitrile was removed under vacuum. The remaining solid was washed with acetone (3 × 10 mL) to remove any impurities or unreacted starting material. Finally, the solid was dried in vacuo to give pure ([H$_2$PhTz]$\cdot$Br as an off-white powder (yield: 0.9 g, 84% based on thiazole-5-carboxylic acid). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 10.54 (s, 1H, H$_3^+$), 9.21 (s, 1H, H$_2$), 7.99 (d, $\delta$$_{1H} = 8.25$ Hz, 2H, H$_3^-$), 7.63 (d, $\delta$$_{1H} = 8.25$ Hz, 2H, H$_2^-$), 5.87 (s, 2H, H), 3.13 (C$_4^+$) NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 167.49 (C$_4$), 164.25 (C$_1$), 155.16 (C$_{12}$), 141.42 (C$_3$), 138.86 (C$_8$), 136.31 (C$_7$), 132.05 (C$_6$), 130.51 (C$_{10}$), 129.49 (C$_9$), 129.49 (C$_8$), 128.00 (C$_{11}$), 1182 (w), 1148 (w), 1106 (w), 784 (m), 716 (m), 659 (m).

### Experimental PXRD

Synthesis of [Zr$_6$O$_{18}$(OH)$_4$(H$_2$O)$_2$(TBAPy)$_2$(PhTz)$_2$Br$_2$H$_2$O] (NU-1000-PhTz). According to the general SALL procedure reported by Hupp, Farha et al.,$^{11,15}$ the thiazolium bromide dicarboxylate salt (H$_2$PhTz)$\cdot$Br (0.127 g, 0.370 mmol, 10 equiv) was added to a suspension of benzene-free NU-1000 (0.080 g, 0.037 mmol) in a dry and degassed polar solvent mixture (total volume, 37 mL; acetonitrile/dimethylsulfoxide = 90:10 v/v). The reaction mixture was heated at 353 K for 24 h with occasional gentle swirling. After this time, the mixture was brought back to room temperature, and the precipitate was filtered over a 0.2 μm PTFE filter. The bright yellow solid residue of NU-1000-PhTz was sequentially washed with hot acetonitrile, acetone, and dichloromethane (3 × 20 mL each) and finally dried in air. Yield: 90 mg (94%, based on zirconium). The extent of thiazolium salt incorporation (one PhTz$^+$ per [Zr$_6$]$_n$) was determined through both the structural characterization from PXRD (vide infra) and signal integration of the $^1$H NMR spectrum of the solution obtained after digesting the sample in a D$_2$SO$_4$/D$_2$O mixture and heating to 363 K for 2 h (see the Supporting Information and Figure S3). IR (KBr pellet, cm$^{-1}$): $\nu$ = 1676 (sh), 1604 (m), 1542 (m) ($\nu$(C=O)), 1419 (s), 1384 (s), 1275 (m), 1261 (s), 1182 (w), 1148 (w), 1106 (w), 784 (m), 716 (m), 659 (m).
PXR D Structural Characterization. A powdered sample (~50 mg) of NU-1000-PhTz was inserted in the cavity of a silicon-free background sample holder 0.2 mm deep (Asseg Srl, Monterotondo, Italy) and analyzed by means of PXR D using a Bruker AXS D8 Advance vertical-scan θ/2θ diffractometer, equipped with a sealed X-ray tube (Cu Kα, λ = 1.5418 Å), a Bruker LynxEye linear position-sensitive detector, a Ni filter in the diffracted beam, and the following optical components: primary beam Soller slits (2.5°), fixed divergence slit (0.5°), and anticrystal slit (8 mm). The generator was operated at 40 kV and 40 mA. A preliminary PXR D acquisition to check the purity and crystallinity of the sample was carried out in the 2θ range 2.0−35.0°, with steps of 0.02° and time per step of 1 s. The PXR D acquisition for the crystal structure assessment was then performed overnight in the 2θ range 2.0−105.0°, with steps of 0.02° and an overall scan time of about 12 h. As witnessed by a visual comparison among the PXR D patterns, NU-1000-PhTz shares the same 3D architecture of NU-100031 and of other already known NU-1000-FG MOFs.32,33 This suggestion was confirmed by performing an independent indexing procedure consisting in a standard peak search, allowing for the estimation of the first 2θ low-to-medium angle peak maximum positions that were then processed with the software TOPAS-R V3.0.34 through the singular value decomposition algorithm,35 yielding approximate unit cell parameters. The space group was assigned on the basis of the observed systematic absences. The crystallographically independent portion of the pyrene-based ligand and the thiazolium-based ligand was described using rigid constraints. The background was modeled by using a Chebyshev-polynomial function. A unique isotropic thermal factor [Biso(M)] was refined for the Zr4+ cluster constituents (i.e., Zr4+, O2−, H2O, and OH−) and the pyrene-based ligand was positioned according to the crystal structure of NU-1000-NDC (H2NDC = naphthalene-2,6-dicarboxylic acid).32 The thiazolium-based ligand, the bromide anion, and a number of oxygen atoms with variable site occupancy factor modeling smeared electron density in the triangular channels and in the cavities containing PtTz− were located using the simulated annealing approach36 implemented in TOPAS-R V3. During the structure refinement stages, carried out with the Rietveld method, rotations about the single bonds of the pyrene-based and the thiazolium-based ligands were allowed, and the position of the metal cluster constituents was refined according to the symmetry constraints. The background was modeled by using a Chebyshev-type polynomial function. A unique isotopic thermal factor [Biso(M)] was refined for the Zr4+ ions; the isotropic thermal factor of the other atoms was calculated as Biso(L) = Biso(M) + 2.0 (Å2). The peak profile was modeled through the fundamental parameters approach.35 The final Rietveld refinement plot is shown in Figure S4 of the Supporting Information.

Crystallographic data for NU-1000-PhTz: hexagonal, P6/mmm, a = 39.602(2) Å, c = 16.440(1) Å, V = 22.329(2) Å3, Z = 24, Z′ = 3, ρp = 0.567 g cm−3, F(000) = 3778, Rexp = 0.014, Rσ = 0.053, and Rexp = 0.075, for 5151 data and 45 parameters in the 2.0−105.0° (2θ) range. CCDC no. 2085493.

Variable-Temperature PXR D. The thermal behavior of NU-1000-PhTz was studied in situ by means of variable-temperature PXR D, depositing a powdered sample (~20 mg) on an aluminum sample holder and heating it through a custom-made sample heater (Officina Elettrotecnica di Tenno, Ponte Arche, Italy) in the temperature range 303−763 K, with steps of 20 K. A PXR D pattern was acquired under isothermal conditions at each step, in the 2θ range 4.0−20.0°, with steps of 0.02° and a time per step of 1 s. A parametric whole powder pattern refinement carried out with the Le Bail approach allowed to unveil the relative variations of the unit cell parameters in the investigated thermal range.

Ex Situ Heating under N2 Flow. To retrieve information about the chemical identity of the solid residue after thermal decomposition, ~20 mg of NU-1000-PhTz was placed in an oven and heated at 1023 K for 15 min under N2 flow. After cooling down to room temperature, a PXR D pattern was acquired with the Bruker AXS diffractometer described above in the 2θ range 5.0−105.0°, with steps of 0.02° and a time per step of 1 s. A qualitative analysis was carried out based on the

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Powder Diffraction File database release 2001 (ICDD—International Centre for Diffraction Data) and confirmed by means of a whole powder pattern refinement carried out with the Le Bail method.

Gas Adsorption. NU-1000-PhTz (~40 mg) was activated at 393 K under a high vacuum (10−6 Torr) for 12 h before each measurement. The textural properties were evaluated through volumetric N2 adsorption isotherms recorded at 77 K on an ASAP 2020 Micromeritics instrument. For the Brunauer–Emmett–Teller (BET) specific surface area calculation, the 0.01−0.1 p/p0 pressure range of the isotherm was used to fit the data. Within this range, all the Rouquerol consistency criteria are satisfied.38,39 The total pore volume was estimated at p/p0 = 0.98. The micro- and mesopore sizes were evaluated through NLDFT methods (Tarazona model for cylindrical pores). CO2 and N2O adsorption isotherms were recorded at 213, 253, 273, 298, 313, and 323 K at a maximum pressure of 1.2 bar. The isosteric heat of adsorption (Qis) values of both gases were calculated from the six isotherms according to the differential form of the Clausius–Clapeyron equation:40,41

$$\frac{d(\ln p)}{d(1/T_0)} = -\frac{Q_{is}}{R} \frac{\rho}{\rho_0}$$

(1)

where R is the gas constant (8.314 J K−1 mol−1). The IAST A/B adsorption selectivity (A = CO2, N2O, or N2) of binary mixtures at a total pressure of 1 bar42 and at T = 298 and 323 K was determined as the ratio of the adsorbed molar fractions of the two gases divided by the ratio of the gas-phase initial molar fractions.43

$\chi_{A/B} = \left(\frac{\Delta \rho_A}{\Delta \rho_B}\right)_{ads} \left(\frac{\Delta \rho_A}{\Delta \rho_B}\right)_{gas}$

(2)

The (\chi_A)ads and (\chi_B)ads values were derived from the application of the free software pyIAST (https://github.com/CorySimon/pyIAST) to the experimental single-component isotherms collected at the chosen temperature. The initial compositions (%) for the calculation were the following: [15:85] for the [CO2/N2] and [N2O/N2] pairs and [50:50] for the [N2O/CO2] pair. These ratios were selected to mimic the general feed composition of the landfill and flue gases, respectively.44 The Henry model was employed for the isotherm fitting. For a detailed explanation of these models and the related parameters, see the pyIAST Web page and documentation.

Computational Details. The adsorption of CO2 and N2O was simulated by Grand Canonical Monte Carlo (GCMC) methods using the RASPA software package.45 The framework was assumed to be rigid (i.e., atoms were frozen in the position assessed by crystal structure determination), and part of the point charges of the framework were distributed according to the QEq method using the code of Wells et al.46 Dispersive and electrostatic interactions between the framework and the adsorbed molecules were taken into consideration during the simulations. The Lennard-Jones (LJ) equation was used to describe dispersive interactions, and its parameters were calculated by the Lorentz–Berthelot mixed rule. For the framework, the LJ parameters of the metal atoms were taken from the UFF force field,47 while those of the other elements were taken from the DREIDING force field.48 This combination of force field parameters has already been successfully used to simulate gas adsorption in porous materials.49,50 A rigid three-point charged LJ linear model was used for CO2 and N2O. The energy parameters of CO2 were taken from the EPM2 force field,51 and the C−O bond length was set at 1.149 Å. The energy parameters of N2O were adopted from the work of Chen et al.,52 with the N−N and N−O bond lengths of 1.1282 and 1.1842 Å, respectively. The number of MOF unit cells in the simulation box was 1 X 1 X 2 to ensure that the simulation unit was extended to be at least 28.0 Å along each dimension. Periodic boundary conditions were applied. The dispersive interactions were calculated using a long-range correction with a spherical cutoff radius of 14.0 Å, while the Ewald sum was used.
to consider the electrostatic interactions. The Peng–Robinson equation of state was used to convert the fugacity. 50 000 cycles of simulations were performed, including 25 000 equilibrium cycles and 25 000 ensemble average cycles. In each cycle, the adsorbed molecules underwent three types of trials: translation, rotation, and regeneration. Further increasing the number of cycles had no significant effect on the adsorption results. Molecular dynamics (MD) simulations were performed according to the experimental conditions. One molecule was inserted into the unit cell of each MOF using a canonical (NVT) ensemble to study the diffusion behavior of CO$_2$ and N$_2$.O. Constant temperature conditions were maintained using a Nose–Hoover chain (NHC) thermostat. The velocity Verlet algorithm was used to integrate Newton’s equation of motion. The simulation steps and the time per step of each MD simulation were 6 ns cycles and 1 fs, respectively, preceded by an equilibration of 3 ns. Finally, the slope of the molecular mean-square displacement (MSD) versus time plot (in its initial time interval, where a satisfactorily linear trend can be observed) was used to calculate the molecular self-diffusion coefficient ($D_m$), averaging over 10 independent trajectories.

**RESULTS AND DISCUSSION**

**Synthesis and Solid-State Characterization of NU-1000-PhTz.** Thiazolium bromide dicarboxylic acid (H$_2$PhTz)$_n$Br is prepared through a simple thiazole N-quantization reaction starting from the commercially available thiazole-5-carboxylic acid and 4-bromomethyl benzoic acid (Scheme 1). The salt is sparingly soluble in acetonitrile; it precipitates out the MOF in its doubly deprotonated (PhTz$^{2-}$) form. Molecular dynamics (MD) simulations were performed according to the experimental conditions. One molecule was inserted into the unit cell of each MOF using a canonical (NVT) ensemble to study the diffusion behavior of CO$_2$ and N$_2$.O. Constant temperature conditions were maintained using a Nose–Hoover chain (NHC) thermostat. The velocity Verlet algorithm was used to integrate Newton’s equation of motion. The simulation steps and the time per step of each MD simulation were 6 ns cycles and 1 fs, respectively, preceded by an equilibration of 3 ns. In the crystal structure of NU-1000-PhTz, the thiazole carboxylic group is deprotonated (≈ COO$^-$), while the benzoic moiety is in its protonated (≈ COOH) form. The carboxylic–carboxylate hydrogen-bonding interactions, combined with the π−π stacking of the aromatic rings, generate dimers (Figure S2). These dimeric units are further assembled through an intricate net of hydrogen-bonding interactions involving the oxygen atoms of the carboxylic and carboxylate groups, the sulfur atoms, and the two crystallization water molecules, generating a 3D supramolecular architecture. Inclusion of (H$_2$PhTz)$_n$Br into NU-1000 was achieved following the same experimental conditions successfully employed for a similar benzothiazolium carboxylic acid and bromine-free form (HPhTz$^-$) after HBr elimination (Scheme S1).

In the crystal structure of HPhTz, the thiazole carboxylic group is deprotonated (≈ COO$^-$), while the benzoic moiety is in its protonated (≈ COOH) form. The carboxylic–carboxylate hydrogen-bonding interactions, combined with the π−π stacking of the aromatic rings, generate dimers (Figure S2). These dimeric units are further assembled through an intricate net of hydrogen-bonding interactions involving the oxygen atoms of the carboxylic and carboxylate groups, the sulfur atoms, and the two crystallization water molecules, generating a 3D supramolecular architecture. Inclusion of (H$_2$PhTz)$_n$Br into NU-1000 was achieved following the same experimental conditions successfully employed for a similar benzothiazolium carboxylic acid and bromine-free form (HPhTz$^-$) after HBr elimination (Scheme S1).
The flexible nature of PhTz− induced by the methylenic −CH2− bridge connecting the two aromatic rings together with a certain framework flexibility shown by the NU-1000-type architecture (Table S2) allowed for the successful insertion of the extra ligand in such a narrow space. Smearred residual electron density was detected in both the triangular cavities and the ∼8 Å cavities and modeled using oxygen atoms for the sake of simplicity. Neglecting the smearred electron density, the empty volume estimated with the software PLATON62 is ∼69%, which is lower than that of NU-1000 and NU-1000-NDC-HCl (showing a bridging linear pillar in the triangular channels) but comparable to that of F-BA-NU-1000, where the extra ligands dangle from the [Zr6] nodes in the triangular cavity (Table S2). At odds with what was observed with NU-1000-BzTz,23 TGA (Figure 2a) showed that the thermal stability of NU-1000-PhTz is slightly higher than that of NU-1000 (Tdec = 820 vs. 800 K, respectively). An initial weight loss of ca. 19 wt % (in line with the stoichiometric 1:1 [Zr6]/PhTz− ratio) can be reasonably ascribed to PhTz− decomposition. Indeed, the DTG peak found in this range falls at T = 580 K, a value that is close to that found for the decomposition of isolated (H2PhTz)Br, occurring at T = 545 K (Figure S12). Further proof of evidence is provided by the MS analysis of the volatiles (Figure 2b), where a peak at m/z = 85 amu, typical of thiazole, appears in the same temperature range. MOF decomposition at 820 K is witnessed by the presence in the MS spectra of the volatiles of peaks at m/z = 77, 78, and 79 amu, typical of phenyl rings. After the decomposition, nanocrystalline ZrO2 is formed, as unveiled by the PXRD pattern of the solid recovered after heating ex situ at 1023 K for 15 min under N2 flow (Figure S13).

The variable-temperature PXRD experiment carried out on NU-1000-PhTz evidenced that the material maintains its crystallinity at least up to 763 K, as depicted in Figure 3a. In the 303−583 K temperature range, the unit cell parameters variation is less than 1.4% (volumetric thermal expansion coefficient αV ∼−0.2 × 10−6 K−1), which is evidence of the structural rigidity of the MOF in this temperature range. Starting from ∼583 K, a significant decrease of the c-axis is observed (∼6.9% in the temperature range 583−643 K; linear thermal expansion coefficient, αc ∼−2.4 × 10−6 K−1) (Figure 3b) and tentatively associated to PhTz− loss, as highlighted by TGA and MS (vide supra). Indeed, by applying the so-called Kempster−Lipson rule63 that assigns to each nonhydrogen atom a volume of ∼18 Å3, the volume occupied by PhTz− amounts to ∼324 Å3, which is consistent with the volume shrinkage of 4.5% estimated in the temperature range 303−643 K (resulting in a decrease of ∼336 Å3 per formula unit). Worthy of note, the notable shrinkage of the c-axis upon
PhTz− loss is an additional proof of the existence and location of a tetra-coordinated pillar as a bridge between two nodes in the ~8 Å cavities.

The porosity of NU-1000-PhTz was evaluated through volumetric N2 adsorption at 77 K on preactivated samples (Figure 4a). The isotherm shape of Type IV is the same as that of NU-1000, but the mesopore step typical of this MOF family is smaller than that found in NU-1000. This is an additional proof of evidence of the partial mesopore filling. The BET surface area is lower than that of pristine NU-1000 (1560 vs. 2140 m²/g, respectively), with a total pore volume of 0.93 versus 1.53 (NU-1000) cm³/g. The same behavior was observed in NU-1000-BzTz, with a monodentate dangling group protruding into the NU-1000 mesopores.23 Likewise, the BET specific surface area of NU-1000-NDC, with excess NDC mono-grafted linkers dangling into the mesopores, is 1720 m²/g, versus 2030 m²/g of NU-1000-NDC-HCl, where the mono-grafted linkers were removed by HCl(aq) treatment.32 Analogously, for the R-BA-NU-1000 series (R = −NH2, −OCH3, −CH3, −H, −F, and −NO2) with mono-grafted para-R-benzoate linkers dangling into the microporous channels, the BET SSA ranges from 1660 to 1900 m²/g.31

Despite the thiazolium pillar insertion in the microporous cavities, the micropore size (Figure 4b) remains practically unchanged when passing from NU-1000 (12.4 Å) to NU-1000-PhTz (11.6 Å). This behavior was already observed in NU-1000-NDC-HCl32 and in the R-BA-NU-1000 series. On the other hand, the mesopores are smaller in NU-1000-PhTz, passing from w = 33 to 29 Å, respectively (Figure 4b). This is not unexpected, given the presence of the bromide counter ions in the hexagonal mesopores. In addition, the mesopore step occurs at a lower relative pressure than in NU-1000. All these data taken together prove that SALI involves both micropores and (to a lesser extent) mesopores, at odds with what was found for NU-1000-BzTz,23 NU-1000-NDC-HCl,32 and some other NU-1000-FG derivatives of the literature.11,15,20

CO2 and N2O Adsorption on NU-1000-PhTz. The activated material has been tested in CO2 and N2O adsorption at Pmax = 1.2 bar and at variable temperatures between T = 213 and 298 K. As found in NU-1000-BzTz,23 NU-1000-PhTz showed an increased affinity for carbon dioxide when compared with its parent MOF. The total CO2 uptake at PCO2 = 1 bar and T = 298 and 273 K is 6.2 wt % (1.4 mmol/g) and 9.5 wt % (2.2 mmol/g), respectively (Figure 5a). The absolute gas uptake at ambient temperature is comparable to

Figure 4. (a) Comparison of N2 adsorption isotherms of NU-1000 (red diamonds) and NU-1000-PhTz (blue diamonds). The desorption branch is depicted with empty symbols. (b) Comparison of NLDFT (Tarazona model for cylindrical pores) pore size distribution plots for NU-1000 (red circles) and NU-1000-PhTz (blue circles).

Figure 5. Comparison between experimental (purple and green symbols) and simulated (magenta and orange lines + symbols) CO2 (a) and N2O (b) adsorption isotherms of NU-1000-PhTz at T = 323 K (diamonds), 313 K (stars), 298 K (hexagons), 273 K (triangles), 253 K (pentagons), and 213 K (dots).
that found for other thiazole-containing MOFs like NU-1000-BzTz (8.7 wt %).\textsuperscript{23} Zr\textsubscript{6}(OH\textsubscript{4})(TzTz\textsubscript{6})\textsubscript{4} (7.5 wt %, TzTz\textsubscript{2} = [2,2'-bithiazole]-5,5'-dicarboxylate),\textsuperscript{24} or Cu(S-Tz\textsubscript{2})\textsubscript{4} (9.0 wt %, S-Tz\textsubscript{2} = thiazole-5-carboxylate),\textsuperscript{27} but it is half of that measured for NU-1000 (2.8 mmol/g at 298 K)\textsuperscript{15} because of the lower specific surface area. In terms of CO\textsubscript{2} isosteric heat of adsorption at zero coverage (Q\textsubscript{st}), the thiazolium-functionalized MOF is featured by a higher Q\textsubscript{st} value than that found for its parent analogue (25 vs. 1715 kJ/mol, respectively, Figure S14). This value is identical to that found in NU-1000-BzTz (as expected for a similar pore decoration),\textsuperscript{23} and it falls in the range calculated for other perfluorokane-functionalized\textsuperscript{15} or peptide-functionalized\textsuperscript{20} NU-1000 samples studied in the literature (between 24 and 34 kJ/mol). The isosteric heat of adsorption reflects the thermodynamic affinity of the material for CO\textsubscript{2}; the introduction of a polar molecule like a thiazolium salt into the MOF channels is beneficial for the MOF–CO\textsubscript{2} interaction. Screening for good adsorbents of other polluting gases, NU-1000-Phtz has also been tested as a nitrous oxide sponge under the same pressure and temperature conditions used for carbon dioxide. The total N\textsubscript{2}O uptake at p\textsubscript{N\textsubscript{2}O} = 1 bar and T = 298 and 273 K is 7.2 wt % (1.6 mmol/g) and 9.4 wt % (2.1 mmol/g), respectively (Figure S5b). These values are lower than those found in the Ni-based MOF [Ni(bptc)\textsubscript{2}(H\textsubscript{2}O)] (12.4 wt % at 298 K; bptc\textsuperscript{−} = biphenyl-3,3',5,5'-tetracarboxylate)\textsuperscript{65} but higher than those measured in MOF-5 (≈4.0 wt %).\textsuperscript{66} The N\textsubscript{2}O isosteric heat of adsorption at zero coverage equals 27 kJ/mol (Figure S15), and it is slightly higher than that of CO\textsubscript{2}. This value is higher than that found for [Ni(bptc)\textsubscript{2}(H\textsubscript{2}O)] (26.6 kJ/mol)\textsuperscript{65} or for the Zn-based MOFs MFU-4l (17.9 kJ/mol) or Li-MFU-4l (23.6 kJ/mol).\textsuperscript{65} In addition to the presence of a slightly higher thermodynamic affinity of NU-1000-Phtz for N\textsubscript{2}O than for CO\textsubscript{2} (the first ever reported example of this kind, to the best of our knowledge), an unexpected temperature-dependent preferential adsorption has been found. While at T = 298 and 313 K (p = 1 atm) the N\textsubscript{2}O uptake is higher than that of CO\textsubscript{2}, the opposite occurs at temperatures falling out of the 298–313 K range. Table 1 lists the adsorption data for CO\textsubscript{2} and N\textsubscript{2}O for the MOF at various temperatures. This behavior is unprecedented, also given the absence of a comparative study of this kind in the literature. Therefore, NU-1000-Phtz may represent a “smart material” for the discrimination of chemically similar polluting gases, opening new horizons in the field of molecular recognition and gas mixture separation. To shed further light on the title MOF, IAST selectivity (S\textsubscript{IAST}) data for [CO\textsubscript{2}/N\textsubscript{2}], [N\textsubscript{2}O/N\textsubscript{2}], and [N\textsubscript{2}O/CO\textsubscript{2}] binary mixtures at two different temperatures (298 and 323 K) were estimated; the results are summarized in Table 2. S\textsubscript{IAST} for an equimolar mixture reaches its maximum value at T = 298 K (1.1). This value is higher than that measured for

| Table 1. CO\textsubscript{2} and N\textsubscript{2}O Adsorption Data of Experiments and Simulations at p = 1 bar for NU-1000-Phtz |
|---|---|---|---|---|
| Temperature [K] | CO\textsubscript{2} adsorbed [mmol/g] | N\textsubscript{2}O adsorbed [mmol/g] |
| experiments | simulations | experiments | simulations |
| 323 | 0.9 (4.0 wt %) | 0.9 (4.0 wt %) | 0.8 (3.6 wt %) | 0.8 (3.6 wt %) |
| 313 | 1.1 (4.7 wt %) | 1.0 (4.7 wt %) | 1.2 (5.0 wt %) | 1.1 (5.0 wt %) |
| 298 | 1.4 (6.2 wt %) | 1.4 (6.2 wt %) | 1.6 (7.2 wt %) | 1.6 (7.2 wt %) |
| 273 | 2.2 (9.5 wt %) | 2.6 (11.1 wt %) | 2.1 (9.4 wt %) | 2.3 (10.2 wt %) |
| 253 | 3.7 (16.2 wt %) | 4.0 (17.7 wt %) | 3.6 (16.0 wt %) | 3.6 (16.0 wt %) |
| 213 | 13.1 (57.7 wt %) | 10.6 (46.8 wt %) | 9.9 (43.4 wt %) | 10.1 (44.2 wt %) |

NU-1000 (0.8) under the same experimental conditions, proving the beneficial effect of the introduction of the thiazolium pillar on the selectivity for N\textsubscript{2}O at 298 K. According to these results, binary N\textsubscript{2}O/CO\textsubscript{2} equimolar mixtures may be enriched in either component simply through a temperature switch, namely, richer in CO\textsubscript{2} at 298 K or richer in N\textsubscript{2}O at 323 K. As far as S\textsubscript{N\textsubscript{2}O/N\textsubscript{2}} and S\textsubscript{N\textsubscript{2}O/CO\textsubscript{2}} are concerned, the absolute values are much higher than those of S\textsubscript{CO\textsubscript{2}/N\textsubscript{2}} because of the nonpolar nature of nitrogen. The absolute values increase as a function of the temperature; the highest values were recorded at T = 323 K. At this temperature, the amount of N\textsubscript{2} adsorbed is close to zero. Therefore, N\textsubscript{2} separation from both greenhouse gases is more efficient if compared with that achieved at ambient temperature.

| Table 2. IAST Adsorption Selectivity Data of Binary Gas Mixtures for NU-1000-Phtz |
|---|---|---|---|
| Temperature [K] | CO\textsubscript{2}/N\textsubscript{2} [15:85] | N\textsubscript{2}O/N\textsubscript{2} [15:85] | N\textsubscript{2}O/CO\textsubscript{2} [50:50] |
| experiments | simulations | experiments | simulations |
| 298 | 12 | 14 | 1.1 |
| 323 | 37 | 32 | 0.9 |
versus interatomic distance \( [g(r) \text{ versus } r] \) plots (Figures S16 and S17 and Table S3), \( \text{CO}_2 \) interacts with the thiazolium N and S atoms in an “end-on” (terminal) configuration through its oxygen atoms, revealing a partial positive charge delocalized all over the thiazolium ring. On the other hand, \( \text{N}_2\text{O} \) prefers a “side-on” configuration where its three atoms give rise to simultaneous interactions with the thiazolium S atom. This different behavior may be ascribed to the polarity of \( \text{N}_2\text{O} \), coming from its delocalized charge. The RDF probability maxima reveal that at 298(273) K the shortest \( \text{N}_2\text{O} \)−framework distances are found at \( r \sim 3.86(3.90) \text{ Å} \) and \( r \sim 4.06(4.16) \text{ Å} \) between the O/S and N/S atoms (N\( ^{\prime} \)=N\( ^{\prime\prime} \)=O), respectively. In the case of \( \text{CO}_2 \), the shortest contact is between the O/S atoms at \( r \sim 4.06(4.06) \text{ Å} \). The S atom of the thiazolium ring is less sterically hindered than the N\( ^{\prime} \) atom on the same ring, and this is probably at the origin of its strongest interaction with the guest molecules in the pores. Based on the interaction distances, at both temperatures, both gases preferentially interact through their O atoms (in \( \text{N}_2\text{O} \), the negative charge is more likely to be localized on oxygen than on N\( ^{\prime} \) nitrogen, for electronegativity reasons). Molecular dynamics studies on the diffusion of the two gases in \( \text{NU}-1000-\text{PhTz} \) (Figure S18) have revealed that at all the essayed temperatures below ambient the diffusion coefficient (\( D_v \) Table S4) of \( \text{CO}_2 \) is larger than that of \( \text{N}_2\text{O} \). However, at 298 K, the diffusion coefficient of \( \text{N}_2\text{O} \) increases significantly and exceeds that of \( \text{CO}_2 \). Therefore, at this temperature, \( \text{N}_2\text{O} \) preferentially occupies the MOF primary adsorption sites because of its faster diffusion. This is in line with the higher \( \text{N}_2\text{O} \) adsorption capacity, thermodynamic affinity, and selectivity at 298 K observed experimentally, and it is promising for \( \text{NU}-1000-\text{PhTz} \) exploitation in \( \text{CO}_2/\text{N}_2\text{O} \) mixtures separation. Conversely, for \( \text{NU}-1000 \), the \( D_v \) values calculated for \( \text{N}_2\text{O} \) are smaller than those of \( \text{CO}_2 \) at all the investigated temperatures (Figure S19 and Table S4).

### CONCLUSIONS

The SALI methodology has been successfully applied to \( \text{NU}-1000 \) for the preparation of the charged framework \( \text{NU}-1000-\text{PhTz} \) containing a bridging thiazolium dicarboxylic acid that connects adjacent [Zr\( _6 \)] nodes along the crystallographic c-axis. The inserted thiazolium pillar improves the (polar) gas uptake capacity of the pristine MOF, showing excellent performance in the adsorption of both \( \text{CO}_2 \) and \( \text{N}_2\text{O} \) two main greenhouse gases. \( \text{NU}-1000-\text{PhTz} \) is featured by a higher thermodynamic affinity for \( \text{N}_2\text{O} \) than for \( \text{CO}_2 \) (the first case reported so far, to the best of our knowledge) and by an unprecedented temperature-dependent preferential adsorption, storing more
N₂O between 298 and 313 K but more CO₂ at temperatures out of this range. In addition, at T = 298 K, NU-1000-PhTz shows a higher N₂O selectivity and a faster diffusion of this gas in its pores. The functionalized MOF can then discriminate between polluting gases through selective adsorption at different temperatures, possibly enriching a CO₂/N₂O mixture in either component only through a simple temperature switch. Given the utmost importance of reducing the greenhouse gas concentration in the Earth atmosphere in coming years, it is essential to develop new functional materials with enhanced adsorption properties to be exploited in this context. The introduction of ionic linkers in MOFs, followed by ion-exchange reactions may further tune their adsorption properties and allow for a precise regulation of their micro- and mesopore environments. The current ongoing research activity in our laboratories is focused on the synthesis of other thiazole-based MOFs with high surface area to be tested in the adsorption and catalytic transformation of greenhouse gases.

**ASSOCIATED CONTENT**

- Supporting Information
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c21437.

Crystal structure of H₂PhTz and related crystallographic details; ligand quantification in NU-1000-PhTz through ¹H NMR signal integration of a digested sample; Rietveld plot for the refinement of the crystal structure of NU-1000-PhTz; IR and XRF spectra of NU-1000-PhTz; XPS survey scans and Br 3d high-resolution spectra of (H₂PhTz)Br and NU-1000-PhTz; TG-DTG profile of (H₂PhTz)Br; CO₂ and N₂O isosteric heat of adsorption calculations; RDF plots and main interatomic gas–framework distances calculated through GCMD simulations; MDS versus time plots for CO₂ and N₂O in NU-1000-PhTz and NU-1000; self-diffusion coefficients (Dₜ) of the two gases as a function of temperature (PDF)

Crystallographic data of H₂PhTz (CIF)

Crystallographic data of NU-1000-PhTz (CIF)

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