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A combined experimental and theoretical study of gas sorption on nanoporous silver triazolato metal–organic frameworks



Guang Yang^{a,b}, Juan A. Santana^{a,c}, Milton E. Rivera-Ramos^d, Omar García-Ricard^d,
Jose J. Saavedra-Arias^{a,1}, Yasuyuki Ishikawa^a, Arturo J. Hernández-Maldonado^d, Raphael G. Raptis^{a,*}

^a Department of Chemistry and the Institute for Functional Nanomaterials, University of Puerto Rico, P.O. Box 70377, San Juan, PR 00936-8377, USA

^b College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China

^c Space Sciences Laboratory, University of California, Berkeley, CA 94720, USA

^d Department of Chemical Engineering and the Institute for Functional Nanomaterials, University of Puerto Rico-Mayagüez, P.O. Box 9000, Mayagüez, PR 00681-9000, USA

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ABSTRACT

A new silver-triazolate metal–organic framework (MOF), {Ag₃[Ag₅(μ₃-3,5-^tBu₂tz)₆](BF₄)₂]_n (**2**), has been prepared and structurally characterized. The CO₂ sorption properties of this new MOF and previously reported isostructural analog {Ag₃[Ag₅(μ₃-3,5-Ph₂tz)₆](NO₃)₂]_n (**1**), were determined experimentally and probed theoretically by a density functional (DF) method. The structures of **1** and **2** are based on flexible Ag₅tz₆-structural building units (SBUs), which allow the expansion/contraction of the structure, depending on either the steric requirements of the pendant groups – ^tBu, or Ph – of the SBUs, or the pressure of the gaseous sorbate. Both silver-triazolate MOFs sorb CO₂ preferentially to N₂, O₂, CH₄ and H₂. DF calculations show CO₂ to be bound by van der Waals forces to the organic moieties of the porous framework. This work shows that van der Waals interactions of CO₂ and the aromatic and aliphatic hydrocarbons of silver-triazolate MOFs are sufficient to achieve preferential sorption of CO₂.

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1. Introduction

The field of metal–organic frameworks (MOFs) has been expanding, because of the potential utility of MOFs in gas storage and separation [1–5], catalysis [6–9], drug delivery [10], and biomedical imaging [11]. Several reviews on the synthesis, characterization and applications of MOFs are available [12–20].

A large effort has been directed towards the synthesis of materials with ever-increasing pore volume and surface area [21–25], as well as with pore surfaces that interact preferentially with a desired sorbate [26–29]. However, while tight sorbent–sorbate binding on one hand facilitates sorption, it impedes desorption on the other, requiring wider temperature or pressure swings to recycle the sorbent. It follows that fine-tuning of the sorption/desorption properties is required for the successful development of optimum and durable sorbents. Consequently, in-depth understanding of the nature and thermodynamics of sorbent–sorbate interactions is essential for further progress of the field.

* Corresponding author. Address: Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA. Tel.: +1 3053487529.

E-mail address: rraptis@fiu.edu (R.G. Raptis).

¹ Present address: Department of Physics, Universidad Nacional, Heredia 40101, Costa Rica.

Towards that goal, molecular dynamics and Monte Carlo methods have been successfully employed for the simulation of gas sorption on a variety of porous materials [30,14]. Calculations based on density functional theory (DFT) have elucidated the nature of the interaction of small molecules with the surface of porous materials. For instance, in a recent combined experimental and computational study [31], dispersion corrected periodic DF calculations [32] were carried out to investigate the CO₂ interactions with the [Zn₂(3-amino-1,2,4-triazole)₂(oxalate)]_n-MOF. Efforts to develop new force fields that describe accurately the interaction between CO₂ and the sorbent along a complete adsorption isotherm are continuing [33].

The capture and recycling of CO₂ is a contemporary problem, related to global warming by greenhouse gases, but also to the remediation of breathing air in confined environments, such as spacecraft during extended space missions, whose mitigation via the use of MOF-based devices has been proposed [34–36]. The separation of CO₂ from CH₄ and H₂ are also processes of major industrial importance [37–42]. Carbon dioxide sequestration is efficiently achieved by amine scrubbers (chemisorption), whose regeneration, however, is energetically costly [43]. The need for the development of lower cost CO₂ capture technology has led to the proposed application of MOFs to that end [44]. Along these lines, amine-functionalized MOFs have been studied and shown to also have high CO₂ binding energy – approximately 10 kcal/mol for

one of them [45–47]. A γ -cyclodextrin-based MOF binds CO₂ by reversible formation of carbonates with the hydroxy groups of the oligosaccharide frame [48]. Examples of weaker, but still selective CO₂ binding by weak H-bonds to hydroxy groups, or by dispersion forces to exposed metal-ion sites, have been reported [47,49–51]. In a OH-functionalized MOF, the energy of end-on bound CO₂ to a hydroxy group was determined to be 5.4 kcal/mol [38]. While high binding energy is desirable for trace CO₂ removal at low pressure, minimization of that energy is required for a recyclable sorbent system.

As part of our work towards the preparation of readily recyclable CO₂-sorbent MOFs, we present here the results of experimental and computational gas sorption studies on two related nanoporous MOFs based on silver triazolate units with the general formula $\{[\text{Ag}_8(\mu_3\text{-}3,5\text{-R}_2\text{-tz})_6]^{2+}\}_n - \text{tz} = 1,2,4\text{-triazolate anion} - \text{R} = \text{Ph}$ (**1**) and ^tBu (**2**). These two MOFs differ by the dangling R-groups that line the pore surfaces. The synthesis and X-ray structure of **2** are also reported; those of **1** have already been reported [52].

2. Experimental

Reagents were purchased from Sigma Aldrich and used as received. Adsorbate gases used were CO₂ (Ultra High Purity Grade, Praxair), N₂ (Ultra High Purity Grade, Linde), O₂ (Ultra High Purity Grade, Linde), CH₄ (Ultra High Purity Grade, Praxair) and He (High Purity Grade, Linde). Solvents were distilled prior to use. The preparation of 3,5-di-tert-butyl-1,2,4-triazole (3,5-^tBu₂tzH) was carried out by a literature procedure [53]. The thermogravimetric analysis (TGA) was performed with a NETZSCH STA409PC system in air at a heating rate of 10 °C/min. The powder X-ray diffraction pattern of **2** was recorded with a Rigaku D/MAX-3B X-ray diffractometer.

$\{[\text{Ag}_8(\mu_3\text{-}3,5\text{-}^t\text{Bu}_2\text{-tz})_6][\text{BF}_4]_2\}_n$, **2**. An aqueous solution (1 mL) of AgBF₄ (0.1 mmol, 19 mg) was mixed with an acetonitrile solution (1 mL) of 3,5-^tBu₂tzH (0.1 mmol, 18 mg). The resulting solution was allowed to evaporate slowly to afford colorless crystals in 40% yield within 1–2 weeks. Anal. Calcd (%) for C₆₀H₁₀₈N₁₈Ag₈B₂F₈: C, 34.0; H, 5.1; N, 11.9; F, 7.2. Found: C, 34.1; H, 5.1; N, 11.7; F, 7.9%. IR (KBr pellet, cm⁻¹): 2963 s, 1462 m, 1415 w, 1365 w, 1218 m, 1083 s, 486 w.

2.1. X-ray crystallography

Diffraction data were collected with a Siemens SMART 1 K CCD diffractometer using graphite monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation at 298 K using the program SMART-NT and were processed by SAINT-NT [54,55]. An empirical absorption correction was applied by the program SADABS. The space group, *P6₃22*, is not uniquely defined by the systematically absent reflections, therefore, solution of the structure was attempted in the alternative hexagonal space groups, *P6₃/mmm*, *P6₃mm* and *P6₃*. Of those, the first two gave chemically meaningless solutions. A meaningful solution was obtained in *P6₃*, but its refinement was not better than the one in the higher-symmetry *P6₃22*, which was preferred. The structure was solved by direct methods and refined by full-matrix least-squares methods on *F*² [56–58]. All non-hydrogen atoms were refined anisotropically. H-atoms were placed in calculated positions with their thermal parameters riding on those of their C-atoms. The crystallographic disorder of the freely-rotating ^tBu-groups could not be modeled satisfactorily. However, as their presence at the 3- and 5-positions of the tz-ligands is unequivocal, they were included in the refinement using restraints. The BF₄⁻ anions were not located in difference maps, as their electron density was smeared along with that of interstitial solvent molecules. The final structure refinement was performed after the data were treated by the SQUEEZE routine of the PLATON suite of

programs [59] to remove unaccounted for residual electron density due to disordered solvent molecules and anions occupying the void spaces. For **2**: C₆₀H₁₀₈Ag₈B₂F₈N₁₈, *M* = 2118.22, hexagonal, *P6₃22* (No. 182), *a* = *b* = 21.420(3), *c* = 14.320(3) Å, *V* = 5690.0(16) Å³, *Z* = 2, $\rho_{\text{calcd.}}$ = 1.236 g cm⁻³, μ = 1.392 mm⁻¹, 40501 reflections collected, 3801 independent (*R*_{int} = 0.1225), 86 parameters, 36 restraints, *R*₁ = 0.0865 for 2361 observed reflections with *I* > 2 σ (*I*) (0.1194 for all data), *wR*₂ = 0.2341, *S* = 0.992, $\Delta\rho_{\text{max}}$ = 1.002 e Å⁻³.

2.2. Adsorption equilibrium isotherms

Equilibrium adsorption isotherms in the 1 atm pressure range were gathered using a Micromeritics ASAP 2020 static volumetric adsorption system outfitted with molecular drag pumps. Helium was used as a backfill gas after the pre-treatment stage and removed using ultra-high vacuum prior to adsorption tests. All samples (ca. 150 mg each) were loaded into glass holders fitted with isolation valves and then pre-treated in vacuum at 403 K. An evacuation rate of 50 mmHg/s was used and the ultimate vacuum was held at 20 μ mHg/s for 12 h. Once the vacuum set point was achieved, the sample was heated at a 10 K/min rate. The heating phase lasted approximately 3 h. For carbon dioxide, equilibrium tests were performed at temperatures ranging from 298 to 353 K. Tests for N₂, CH₄ and O₂ were performed only at 298 K. During the experiments, the temperature was kept constant by means of a heating blanket. Desorption tests were performed immediately after reaching the 1 atm pressure target.

High-pressure adsorption isotherms were gathered using a Micromeritics ASAP 2050 volumetric instrument capable of reaching a maximum of 10 atm. The procedure for sample activation, including backfill, was identical to the one mentioned above. The adsorption and desorption analyses were performed in the 10 atm range at 273 and 298 K, respectively.

2.3. CO₂ isosteric heat of adsorption (*H*_{ads})

The Clausius–Clapeyron equation (Eq. (1)) and pure CO₂ equilibrium adsorption data at different temperatures and constant surface loading were used to estimate the isosteric heats of adsorption.

$$\left(\frac{d \ln P}{d(1/T)}\right)_{q=\text{const}} = \frac{\Delta H_{\text{ads}}}{R} \quad (1)$$

In this equation *R* is the gas constant, *P* is the equilibrium pressure at a particular coverage *q* and *T* is the absolute temperature.

2.4. DFT calculations

All geometry optimizations were carried out using the DMol³ program of Accelrys Inc [60,61]. During geometry optimization, the experimental geometry of the silver-triazolate MOFs was used and kept fixed, while the gaseous sorbates were allowed full relaxation. Perdew–Burke–Ernzerhof (PBE) exchange and correlation functionals were employed [62,63]. The Kohn–Sham orbitals were expanded in double numerical plus polarization (DNP) basis set. The fractional occupation number technique [60,61] was employed with an energy width of 0.1 eV. Gamma k-point was used for all calculations.

To determine the binding energy of gaseous sorbates in the silver-triazolate MOFs, a semi-empirical dispersion correction was added to the DFT energy [64,32]. Energy calculations were carried out using the QUANTUMESPRESSO package [65] and the geometries optimized with DMol³. The ionic cores were represented by ultrasoft pseudopotentials [66] and the electronic one-particle

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