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Communication

Synthesis and Gas Sorption Properties of a Metal-Azolium Framework (MAF) Material

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A new strut containing an imidazolium tetracarboxylic acid core has been successfully incorporated into a microporous material using paddlewheel-coordinated copper(II) ions as nodes. Sorption studies conducted on this permanently microporous material imply that it can separate carbon dioxide from methane with high selectivity.

Over the past decade, microporous metal−organic framework materials (MOFs) have garnered significant attention for gas storage and separation.[1] The use of organic building blocks provides a unique opportunity to create new, robust materials with tunable pore sizes and desirable properties. MOFs consist of two main units: metal-based building blocks (secondary building units, SBUs, and/or supramolecular building blocks, SBBs)[2,3] and organic struts. The majority of known MOFs employ simple carbon-based spacer elements (struts) that primarily serve to distance the metal nodes appropriately and thus generate microporosity. However, enhancing this organic element with additional attributes (e.g., active catalysis sites, metal ligation)[4] has great potential to expand this field and has seen limited development to date. This approach is complementary to postsynthetic modifications (PSMs), benefits from efficiency and the ability to characterize, and avoids the challenges associated with determining the degree of PSM.[5] The incorporation of charged, aromatic azolium components represents an innovative strategy to generate unusual electrostatic environments within microporous materials a priori. These heterocycles are precursors to N-heterocyclic carbenes, which are excellent ligands for transition metals[6] and unique Lewis base catalysts.[7] Herein, we report the synthesis of a novel imidazolium strut and its incorporation with copper(II) as the organizing element into a three-dimensional array, or metal azolium framework. To the best of our knowledge, this is the first reported example of an azolium salt incorporated into a crystalline coordination polymer.

The new azolium compound *N,N'*-bis(2,6-dimethyl-3,5-carboxylphenyl)imidazolium chloride (<u>IM</u>idazolium <u>T</u>etra<u>A</u>cid, **IMTA**) was synthesized from the symmetric aniline **A** in nine total steps starting from *m*-xylene (Scheme 1).[8] This route allows access to the first multitopic azolium for use in MOFs and/or related materials.

With the organic strut in hand, we surveyed numerous conditions and metal sources. Ultimately, green crystals of $[Cu_2(\textbf{IMTA})(DMSO)_2] \cdot 2H_2O$ (**1**) were synthesized by a solvothermal reaction of $Cu(NO_3) \cdot 2.5H_2O$ (0.2 mmol) and **IMTA** (0.05 mmol) in 3 mL of dimethyl sulfoxide (DMSO) at 80 °C for 12 days. Single-crystal X-ray diffraction shows that **1** is in the *Imma* space group, two Cu ions form a paddle-wheel-type SBU, and two DMSO solvent molecules are coordinated to the axial sites of the Cu SBU (see Figure 1a). Each **IMTA** ligand is linked to four other **IMTA** ligands via the Cu nodes to form hexagonal channels (Figure 1d). The C_2 carbon of the imidazolium is projected into the pore. The cationic imidazolium ring is disordered by a C_2 symmetry operation: this rotational issue obscures the counterion, and we were unable to model it. However, the presence of nitrate and chloride counterions, in varying proportions, was confirmed by multiple elemental analyses.[8]

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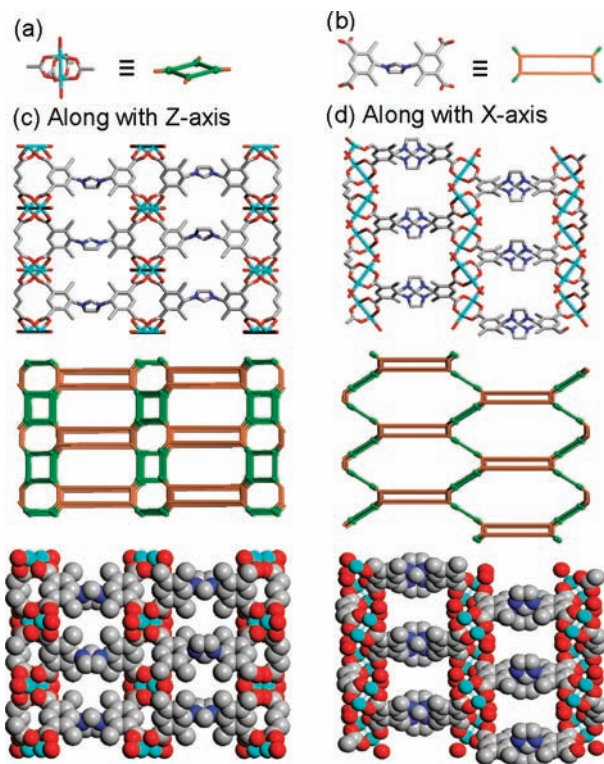
(8) See the Supporting Information for details.

Figure 1. Metal azolium framework Cu$_2$(**IMTA**)(DMSO)$_2$: (a) Cu-(CO$_2$)$_4$ SBU; (b) imidazolium strut and schematic representation; (c and d) channel views along the Z (left three) and X (right three) axes. Carbon is depicted in gray, oxygen in red, nitrogen in blue, sulfur in yellow, and copper in cyan. Hydrogen atoms, guest molecules, and one side of the disordered imidazolium ring are omitted for clarity.

Scheme 1. IMTA Synthesis[a]
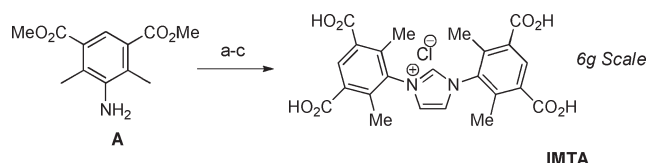
[a] (a) (CHO)$_2$, HCO$_2$H, EtOH, 40 °C, 55%. (b) (CH$_2$O)$_n$, TMSCl, EtOAc, 70 °C, 51%. (c) LiOH·H$_2$O, 3:1 MeOH/H$_2$O, 23 °C, 84%.

Thermogravimetric analysis (TGA) of **1** showed that approximately 5% weight loss occurred below 100 °C[9] and another 15% occurred before 250 °C. The weight loss is attributed primarily to the release of coordinated DMSO molecules. The structure eventually decomposes at temperatures above 300 °C. Powder X-ray diffraction analysis showed that the material treated at 200 °C retains its structural integrity.[8]

The porosity of **1** was examined using CO$_2$ at 273 K. On the basis of TGA, activation was performed at 100 and 200 °C for 24 h to generate materials **1a** and **1b**, respectively (Table 1). These materials have moderate surface areas based on nonlocal density functional theory (NLDFT) analysis. At 77 K, neither **1a** nor **1b** detectably sorbs nitrogen, behavior

(9) A weight decrease below 100 °C is attributed to the loss of two guest water molecules. The proposed structure was refined with contributions from solvate molecules removed from the diffraction data using the bypass procedure in Platon (Spek, 1990). The total potential solvent-accessible void volume was 375.9 Å^3, and the electron count/cell = 178.

Table 1. Summary of CO$_2$ Sorption and IAST CO$_2$/CH$_4$ Selectivity

| | activation conditions | | | | |
	T (°C)	time (h)	SA$_{NLDFT}$ (m^2 g^{-1})[a]	CO$_2$ uptake (mol kg^{-1}) at 1 bar	selectivity (CO$_2$/CH$_4$)
1a	100	24	340	1.2	26[b]−13[d]
1b	200	24	300	0.5	18[c]−9[d]
1c	200	4	520	1.8	38[b]−20[d]

[a] Calculated based on CO$_2$ isotherms at 273 K. [b] Determined at 0.01 bar. [c] Determined at 0.1 bar. [d] Determined at 1.0 bar at 298 K.
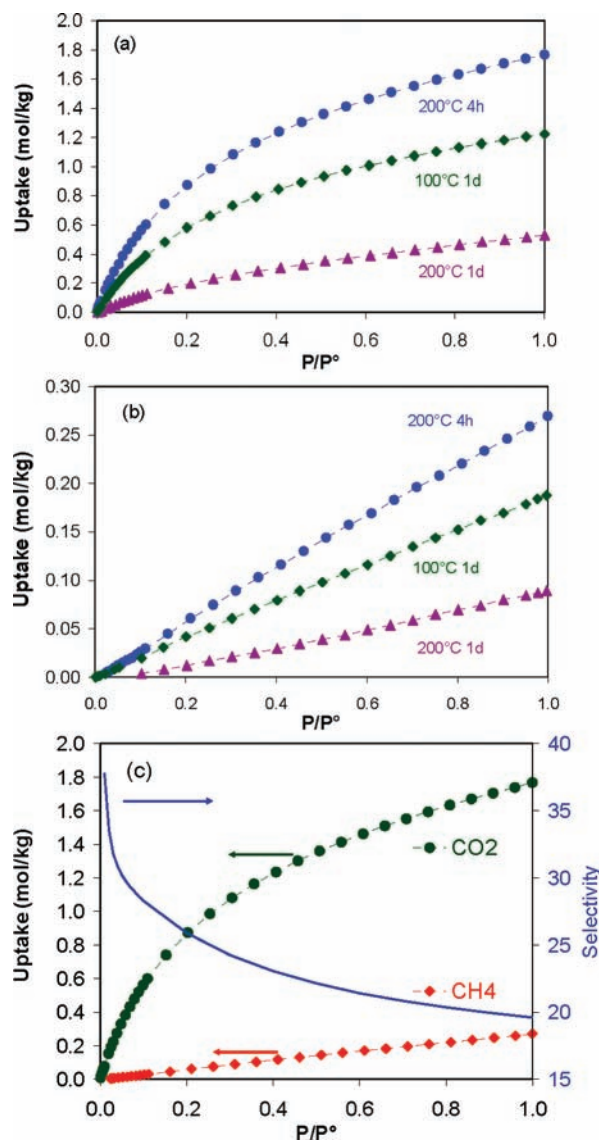

Figure 2. (a) CO$_2$ isotherms at 298 K for various activation conditions. (b) Methane isotherms at 298 K for various activation conditions. (c) IAST selectivity of CO$_2$ over CH$_4$ of **1c** at 298 K.

that has been previously reported with other MOFs.[10] Because **1b** showed a lower porosity than **1a**, a range of activation times at 200 °C was surveyed. Interestingly, 4 h of thermal activation proved to be optimal in terms of maximizing the CO$_2$-accessible surface area (520 m^2 g^{-1}, **1c**). Activation is accompanied by partial loss of the initially

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coordinated DMSO [determined by NMR spectroscopy (500 MHz ^{1}H) after **1c** was dissolved in D_2SO_4/D_2O].[8]

Methane isotherms were also measured for azolium MOFs **1a**–**1c** independently using UHP-grade methane. All three versions of the material feature substantially higher uptake of CO_2 than CH_4 (Figure 2B). This discrimination can be attributed to the non(quadru)polar nature and larger kinetic diameter of methane. The calculated ideal adsorbed solution theory (IAST) selectivities[11] of **1a**–**1c** are listed in the Table 1. The dual-site Langmuir–Freundlich model was applied to experimental isotherms, and IAST calculations were performed under equimolar mixture conditions (CO_2:CH_4 = 50:50).[11]

At low pressure, the CO_2/CH_4 selectivity is extremely high (38), indicating significant favorable interactions between CO_2 and the new material (Figure 2C). The contributing factors for this selectivity likely include the availability of open metal sites and the charged azolium struts and counterions. These two elements generate polar cavities that preferentially sorb CO_2 because of its quadrupole moment. The selectivity of **1a** at 1 bar is 13, which is slightly higher than other reported values for sorption-selective MOFs.[12] Interestingly, the selectivity was increased dramatically to 20 with an optimally activated sample (**1c**), and it is attributed to additional interaction between CO_2 and open metal sites. Recent reports on zeolitic imidazolate frameworks[13] and zeolite 13X showed selectivity values in the 5–10 range.[14] It is worth noting that all aforementioned data were obtained from noncompetitive experiments. Two breakthrough experimental results using a binary or ternary mixture have been reported on MOF-508b[15] and amino-MIL-53[16] with the selectivity in the range between 3 and 6 at 303 K.

In summary, we have successfully incorporated an organic azolium salt as a strut in a microporous MOF material. Among the activated samples, **1c** is the most proficient at selectively adsorbing CO_2 over methane, presumably because of interactions with open metal sites and the unusual ionic environment within the MOF generated from the positively charged aromatic azolium components. The general synthetic approach outlined herein using imidiazolium acids (such as **IMTA**) to create these first-generation materials lays the foundation for tuning of their overall properties, including porosity, ionic conductivity, node accessibility, and electrostatic parameters. Accessing reactive lone pairs, or N-heterocyclic carbenes, from the incorporated azoliums and the applications of this activated material for metal complexation and catalysis are currently under investigation in our laboratories.

Supporting Information Available: X-ray crystallographic data in CIF format and experimental procedures and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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