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A Robust Molecular Porous Material with High CO_2 Uptake and Selectivity

Patrick S. Nugent, Vanessah Lou Rhodus, Tony Pham, Katherine Forrest, Lukasz Wojtas, Brian Space, and Michael J. Zaworotko*

Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE205, Tampa, Florida 33620, United States

Supporting Information

ABSTRACT: We report **MPM-1-TIFSIX**, a molecular porous material (MPM) based upon the neutral metal complex $[Cu_2(adenine)_4(TiF_6)_2]$, that self-assembles through a hydrogen-bonding network. This MPM is amenable to room-temperature synthesis and activation. Gas adsorption measurements and ideal adsorbed solution theory selectivity predictions at 298 K revealed enhanced CO_2 separation performance relative to a previously known variant as well as the highest CO_2 uptake and isosteric heat of adsorption yet reported for an MPM. **MPM-1-TIFSIX** is thermally stable to 568 K and retains porosity and capacity even after immersion in water for 24 h.

Because of their extra-large surface areas and structural tunability, porous coordination polymers (PCPs)[1] and metal−organic frameworks (MOFs)[2] are promising candidates for gas separations,[3] gas storage,[4] heterogeneous catalysis,[5] and sensing.[6] Comparatively, although many molecular inclusion compounds are known,[7] molecular solids that exhibit permanent porosity to the degree observed in PCPs are rare, presumably because molecular building blocks exhibit a tendency to pack more densely than PCPs. Therefore, the design of robust molecular porous materials (MPMs)[8] with fine-tunable components is more challenging than in the case of PCPs. Porosity in MPMs, as defined by reversible gas adsorption, is classified as either intrinsic (inside the molecules) or extrinsic (between the molecules). Intrinsically porous MPMs are exemplified by cucurbit[*n*]urils,[9] *tert*-butylcalix[4]-arene,[10] organic cage compounds,[11] metal−organic squares (MOSs) and cubes (MOCs),[12] metal−organic macrocycles,[13] and metal−organic polyhedra (MOPs).[14] Cucurbit[*n*]urils, organic cage compounds, MOSs, MOCs, and MOPs possess both extrinsic and intrinsic porosity, while triptycene tris-(benzimidazolone) (TTBI),[15] PUNCs,[16] certain dipeptides,[17] SOF-1a,[18] and HOF-1[19] exhibit just extrinsic porosity. TTBI presently exhibits the highest BET surface area among MPMs (2796 m^2/g), but its CO_2 uptake at 273 K and 1 atm is only 81 cm^3/g. While very few MPMs exhibiting surface areas above 1000 m^2/g have been reported,[11a,15,16,20] recent reports suggest that non-covalent forces,[11a,16,21] including hydrogen bonding,[12,15] can be utilized to rationally construct families of porous materials that are fine-tunable (i.e. platforms).

The search for porous materials is driven by the advantages that physisorption might offer over costly and energy-intensive technologies such as amine scrubbing and cryogenic distillation.[3b,c] A viable CO_2 capture material should exhibit high selectivity versus CH_4 and N_2 as well as thermal and water stability. We herein report a new class of MPMs in the context of physisorptive CO_2 capture through the study of an MPM platform that exhibits such features. A number of existing MPMs are known to exhibit selective CO_2 adsorption,[9,11b,c,15,19,22] but their performance does not yet approach that of PCPs.[3c] Specifically, the fact that inorganic anions can enhance CO_2 uptake and selectivity[23] prompted us to study the effect of axial ligand substitution in an extrinsically porous hydrogen-bonding network based upon a discrete dinuclear "paddlewheel" (PW) complex. $[Cu_2(ade)_4Cl_2]Cl_2$ (ade = adenine), designated **MPM-1-Cl**,[24] was thereby modified to afford $[Cu_2(ade)_4(TiF_6)_2]$ (**MPM-1-TIFSIX**), a robust MPM with high CO_2 uptake and selectivity under conditions relevant to carbon capture.

We reasoned that pore functionality could be systematically varied by substituting the Cl^- ligands lining the channels of **MPM-1-Cl**. We chose TiF_6^{2-} ("TIFSIX") for this purpose, as a porous *pcu* net containing TIFSIX exhibited higher CO_2/N_2 selectivity and higher CO_2 uptake at low loading relative to variants containing SiF_6^{2-} (SIFSIX) and SnF_6^{2-} (SNIFSIX).[23b] Accordingly, solvent diffusion of a 1:1 acetonitrile/H_2O solution of ade into an aqueous solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ and $(NH_4)_2TiF_6$ afforded purple, rectangular prismatic single crystals of $[Cu_2(ade)_4(TiF_6)_2]{\cdot}2CH_3CN$ (**MPM-1-TIFSIX**) in 51% yield after 4 days [see the Supporting Information (SI)]. Single-crystal X-ray diffraction (XRD) revealed that **MPM-1-TIFSIX** consists of neutral PWs that crystallize in space group $R\bar{3}m$ with a motif very similar to that of **MPM-1-Cl** (Figure 1 and Table S1 in the SI).

The PW complexes in **MPM-1-TIFSIX** feature four bridging equatorial ade ligands and two monodentate axial TIFSIX ligands, and they self-assemble into an extrinsically porous hydrogen-bonding network. The net is reminiscent of a kagomé lattice,[25] and like that in **MPM-1-Cl**, it contains hourglass-shaped channels (~7.0 and 6.2 Å diameter in **MPM-1-TIFSIX** and **MPM-1-Cl**, respectively) and small trigonal channels that lie parallel to the *c* axis. The larger channels, which are lined with TIFSIX anions, and the small channels, which are occupied by acetonitrile molecules, are wider than those in **MPM-1-Cl**.

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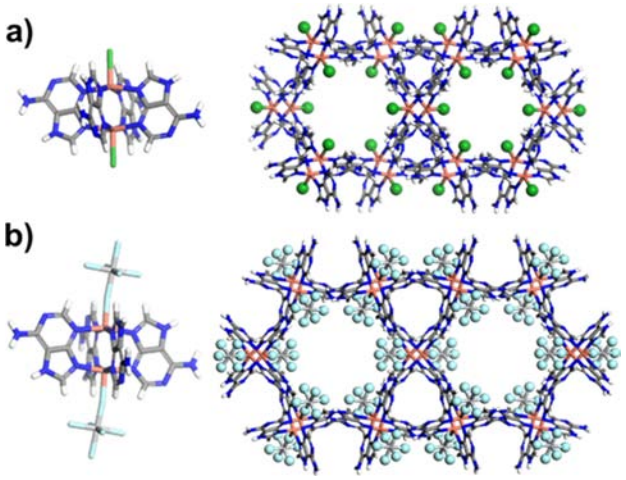

Figure 1. Views of (left) the PW complexes and (right) the networks along the *c* axis in (a) **MPM-1-Cl** and (b) **MPM-1-TIFSIX**. Solvent has been omitted for clarity. Atom colors: Cu, peach; Cl, green; Ti, silver; F, cyan; C, gray; N, blue; H, white.

The hydrogen bonding network in **MPM-1-TIFSIX** is more extensive than that in **MPM-1-Cl**. While each PW in **MPM-1-Cl** forms a total of 12 contacts (eight with its nearest neighbors and four to Cl^- counterions), each PW in **MPM-1-TIFSIX** interacts with its eight nearest neighbors via a total of 24 contacts. While the ade−ade contacts in **MPM-1-TIFSIX** share the same complementary motif as those in **MPM-1-Cl**, differences in the hydrogen bonding in the two networks result from the nature of the axial ligand (Figure 2). In **MPM-1-Cl**, the counterions are directly engaged in the hydrogen-bonding network and link the ade moieties of adjacent PWs. The axial Cl^- ligands form no contacts with other network components. In contrast, the bulkier TIFSIX ligands in **MPM-1-TIFSIX** assume a role in the network analogous to that played by the counterions in **MPM-1-Cl** (Figure 2). The F···HN contacts (2.73, 2.82, and 2.94 Å) in the former are shorter and more numerous than the Cl^-···HN contacts (3.03 Å) in the latter. The hydrogen-bond motif adopted by the TIFSIX ligands causes the PWs to tilt 7.7° (relative to those in **MPM-1-Cl**) towards an orientation that is closer to perpendicular with the *ab* plane. This subtle change in orientation is responsible for the wider channels in **MPM-1-TIFSIX** relative to **MPM-1-Cl**.

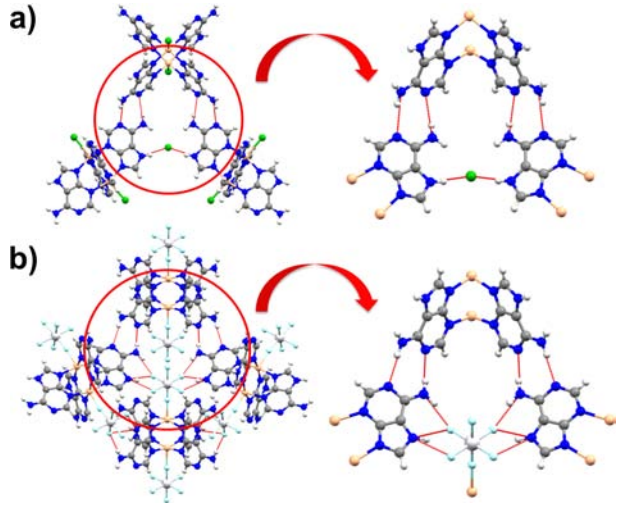

Figure 2. Hydrogen-bonding motifs in (a) **MPM-1-Cl** and (b) **MPM-1-TIFSIX**. Hydrogen bonds are shown as red dashed lines; portions of the enlarged structures at the right have been omitted for clarity.

MPM-1-Cl was synthesized according to the reported procedure[24] to further study its gas sorption behavior and compare it to **MPM-1-TIFSIX**. Powder X-ray diffraction (PXRD) patterns of as-synthesized **MPM-1-TIFSIX** and **MPM-1-Cl** were observed to match those calculated from single-crystal data (Figures S1 and S2 in the SI). We validated that the reported surface area of **MPM-1-Cl** measured by N_2 adsorption at 77 K is much lower than expected (68 m^2/g). However, the CO_2 isotherm measured at 195 K displays reversible type-I character and reveals an experimental (calculated[26]) Langmuir surface area of 637 (786) m^2/g (Figures S3 and S4). The authors of the initial study concluded that strong interactions between N_2 and the channel windows at 77 K hinder diffusion into the material. Restricted N_2 uptake at 77 K but type-I CO_2 uptake at 195 K has been observed previously in materials with pore sizes larger than the kinetic diameter of N_2 (see the SI).[27] Single-gas CO_2, CH_4, and N_2 isotherms were collected for **MPM-1-Cl** at 298 K up to 1 atm (Figure 3). Uptakes of 44.2, 13.8, and 4.7 cm^3/g, respectively, at 1 atm were measured.

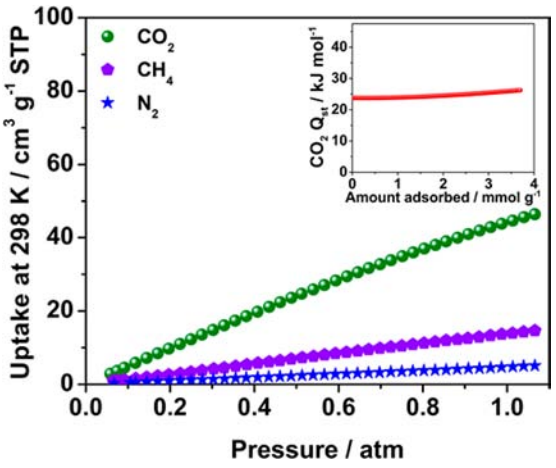

Figure 3. Low-pressure CO_2, CH_4, and N_2 isotherms collected at 298 K and (inset) CO_2 Q_{st} for **MPM-1-Cl**.

Activation of **MPM-1-TIFSIX** at room temperature resulted in reversible type-I adsorption of CO_2 at 195 K and an experimental (calculated) BET surface area of 840 (809) m^2/g. The higher surface area can be attributed to the greater channel width and solvent-accessible volume of **MPM-1-TIFSIX** (49.4 vs 36.5% for **MPM-1-Cl**).[28] Void analysis of the desolvated form of **MPM-1-TIFSIX** using Mercury[29] (probe radius = 1.65 Å) revealed the existence of an accessible passage connecting the large channels that is not present in **MPM-1-Cl**. The analysis also suggested that the small channels in **MPM-1-TIFSIX** are accessible, unlike those in **MPM-1-Cl** (Figures S5−S7). The CO_2 isotherm of **MPM-1-TIFSIX** at 298 K (Figure 4) revealed much steeper adsorption at low partial pressures and 103% greater uptake at 1 atm (89.6 cm^3/g) than observed for **MPM-1-Cl**. Indeed, the CO_2 uptake by **MPM-1-TIFSIX** under ambient conditions is superior to that of most PCPs and is to our knowledge the highest yet exhibited by an MPM. The CH_4

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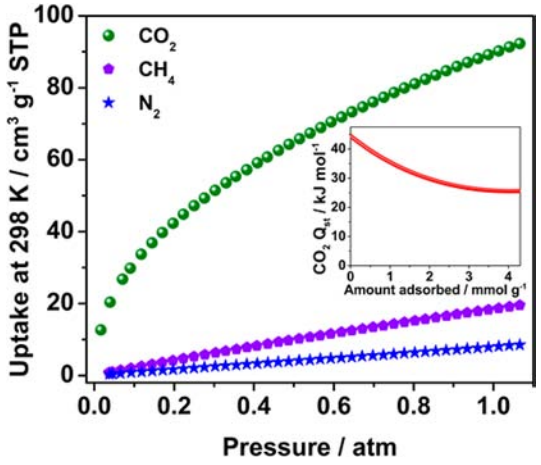

Figure 4. Low-pressure CO_2, CH_4, and N_2 isotherms collected at 298 K and (inset) CO_2 Q_{st} for **MPM-1-TIFSIX**.

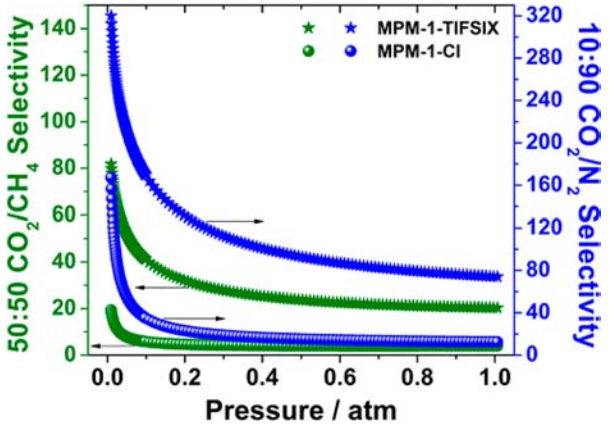

Figure 5. IAST selectivities for 50:50 CO_2/CH_4 (green; left ordinate) and 10:90 CO_2/N_2 (blue; right ordinate) binary mixtures predicted at 298 K for **MPM-1-TIFSIX** (★) and **MPM-1-Cl** (●).

and N_2 uptakes for **MPM-1-TIFSIX** at 1 atm were found to be 18.5 and 8.0 cm^3/g, respectively. The shape of the CO_2 isotherm in **MPM-1-TIFSIX** relative to that of **MPM-1-Cl** suggests that the former exhibits a significantly higher isosteric heat of adsorption (Q_{st}) and selectivity toward CO_2 over CH_4 and N_2. The CO_2 Q_{st} values (Figures 3 and 4), which were calculated by fitting the 273 and 298 K isotherms to the virial equation (Figures S8 and S9), reveal that **MPM-1-TIFSIX** has a far higher affinity toward CO_2 at low loading (44.4 vs 23.8 kJ/mol). To our knowledge, the CO_2 Q_{st} of **MPM-1-TIFSIX** at zero loading is the highest yet observed among MPMs[9,18] and is comparable to that of top-performing PCPs with saturated metal centers (SMCs) such as MOOFOUR-1-Ni,[23c] SIFSIX-3-Zn,[23d] and UTSA-16[30] (Q_{st} = 56, 45, and 35 kJ/mol, respectively). Mg-dobdc, a PCP with unsaturated metal centers (UMCs), exhibits an initial Q_{st} of 47 kJ/mol.[31]

The shapes of the Q_{st} curves further suggest that **MPM-1-TIFSIX** possesses two or more CO_2 binding sites with different affinities whereas **MPM-1-Cl** is much more homogeneous in terms of binding sites. The results of grand canonical Monte Carlo (GCMC) simulations of CO_2 sorption in **MPM-1-TIFSIX** are in good agreement with the experimental data and further suggest the presence of multiple binding sites (Figures S10–S13 and Table S2). The primary binding site involves coordination of CO_2 to two TIFSIX anions in a confined passage connecting the large channels. Secondary binding to the TIFSIX anions lining the large channels also occurs. Charge–quadrupole interactions govern the binding at the first two sites. Lastly, sorption was observed in the small channels. These results are consistent with our assertions that inorganic anions can drive selectivity.[23a,b,d] Because of the confined space at the primary and tertiary sites, size exclusion may also contribute to the selectivity for CO_2 over CH_4 and N_2.

To predict the CO_2 separation performance of **MPM-1-TIFSIX** and **MPM-1-Cl** at 298 K, selectivities for 10:90 CO_2/N_2 and 50:50 CO_2/CH_4 binary mixtures were calculated up to 1 atm from the pure-component isotherms via ideal adsorbed solution theory (IAST) (Table S3).[32] These mixture compositions mimic those found in post-combustion capture and biogas purification, respectively. Strikingly, substitution of TIFSIX in place of Cl^- affords 6-fold and 5-fold enhancements in the CO_2 selectivity at 1 atm (Figure 5) for the CO_2/N_2 and CO_2/CH_4 mixtures, respectively (CO_2/N_2: 74.1 vs 12.5; CO_2/CH_4: 20.3 vs 4.0). The selectivity of **MPM-1-TIFSIX** for CO_2 over CH_4 and N_2 under these conditions is among the highest reported for MPMs and greater than those for the majority of PCPs.[3c] Notably, many MPMs with high selectivity have significantly lower CO_2 uptake than **MPM-1-TIFSIX**.

In addition to selectivity, practical CO_2 separations require materials that possess thermal and water stability (flue gas is composed of ca. 6% water). **MPM-1-TIFSIX** was evaluated for these criteria via variable-temperature PXRD and sorption measurements (Figures S14–S16). PXRD revealed that **MPM-1-TIFSIX** retains its crystal structure at 568 K and after immersion in water at room temperature for 24 h (Figure S1). Sorption isotherms of activated **MPM-1-TIFSIX** after water exposure confirmed that the surface area and CO_2 uptake are minimally affected. By comparison, **MPM-1-Cl** exhibits thermal stability up to 513 K but loses its crystallinity after exposure to water for 24 h.[24]

To conclude, through axial ligand substitution we have diversified an extrinsically porous MPM platform to include a TIFSIX-functionalized variant with SMCs that is sustained by an extensive hydrogen-bonding network. **MPM-1-TIFSIX** can be synthesized in a single step from commercially available starting materials and activated at room temperature. In addition to dramatically surpassing **MPM-1-Cl** with regard to CO_2 separation performance, **MPM-1-TIFSIX** exhibits the highest CO_2 uptake and Q_{st} observed in an MPM and high CO_2/N_2 and CO_2/CH_4 selectivities. **MPM-1-TIFSIX** also exhibits excellent thermal and water stability, which are as important as selectivity for practical applications. Further studies will be conducted on gas mixtures, and the effect of decoration with other inorganic anions (e.g., SiF_6^{2-}, SnF_6^{2-}, and ZrF_6^{2-}) on the selectivity will be addressed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data (CIF); PXRD, gas sorption, and Q_{st} data; void analysis; simulations; IAST details; and structural descriptions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

xtal@usf.edu

Notes

The authors declare no competing financial interest.

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