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High and Selective CO_2 Uptake in a Cobalt Adeninate Metal−Organic Framework Exhibiting Pyrimidine- and Amino-Decorated Pores

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Coal-fired power plants emit flue gas comprising ∼15% CO_2, ∼7% H_2O, and ∼70% N_2.[1] Selective removal of CO_2 from power plant emissions would help stabilize atmospheric CO_2 levels and help render coal a source of cleaner energy. New materials that can selectively capture CO_2 from power plant flue gas emissions in an economical and energy-efficient fashion must be developed. Porous materials relying on physical adsorption of CO_2 are potential candidates for accomplishing this goal because they require less energy for regeneration than materials and solvents relying on chemisorption.[2] Currently, designing and fabricating porous materials that selectively capture CO_2 is an important challenge. Metal−organic frameworks (MOFs) are being intensively investigated to address this challenge because their metrics and chemical functionality can be carefully adjusted for specific applications.[3]

We describe herein our discovery that cobalt adeninate bio-MOFs exhibit exceptional abilities to selectively adsorb CO_2. Recently, we began investigating the preparation, assembly, and physical properties of metal adeninate porous materials.[4] These materials have properties that may enable certain environmental and biomedical applications. Adenine is a particularly effective biomolecular building block[5] because (1) it has many potential coordination modes, allowing for the construction of a topologically diverse family of materials; (2) it is rigid, which helps enable the preparation of permanently porous materials; and (3) it is an ideal building block for constructing materials for CO_2 capture. Indeed, a recent computational study revealed that the interaction energy between CO_2 and adenine is higher than that between CO_2 and other nitrogen-containing MOF linker molecules.[6] Adenine's multiple Lewis basic sites, including an amino group and pyrimidine nitrogens, can interact with CO_2, potentially resulting in materials with high CO_2 adsorption energies. Therefore, adenine-based MOFs would be ideal for selective CO_2 adsorption.

Our current work represents a significant improvement over our initial reports of CO_2 uptake by porous zinc adeninate macrocyclic structures, which selectively adsorbed CO_2 and exhibited rapid CO_2 uptake at low pressures.[4a] We attributed the selectivity to the presence of narrow pore apertures that exclude gases with larger kinetic diameters and the rapid uptake at low pressures to favorable interactions between CO_2 and the pore walls. In this structure, the zinc adeninate macrocycles assemble via hydrogen bonding between the amino group and one pyrimidal nitrogen from each adeninate. These hydrogen-bonding interactions may limit the accessibility of the Lewis basic sites and may therefore decrease the material's affinity for CO_2. We reasoned that exposing these sites within the pores of a MOF should lead to materials with enhanced CO_2 adsorption properties, including high uptake and high selectivity. To more effectively expose the Lewis basic sites, we prepared $Co_2(ad)_2(CO_2CH_3)_2 \cdot 2DMF \cdot 0.5H_2O$ (bio-MOF-11) via a solvothermal reaction between cobalt acetate tetrahydrate and adenine in *N*,*N*-dimethylformamide (DMF). Single-crystal X-ray studies revealed that the structure consists of cobalt−adeninate−acetate "paddle-wheel" clusters (Figure 1A) in which two Co^{2+} are bridged by two adeninates (via the N3 and N9 positions) and two acetates; each cobalt adeninate cluster can be represented as a square secondary building unit (SBU). These SBUs are linked together through apical coordination of the adeninate N7 atoms to Co^{2+} ions on neighboring clusters to generate a three-dimensional (3D) framework structure (Figure 1B) exhibiting the augmented **lvt** network topology (Figure 1C,D), one of the default topologies for connecting square building units with equivalent linkers.[7] This underlying topology results in cavities that are periodically distributed throughout the structure. Each cavity (Figure 1C) is defined by 16 interconnected square building units and can accommodate a 5.8 Å diameter sphere. The aperture to each cavity measures 5.2 Å. The cavities align into channels that run along the *a* and *b* crystallographic directions (Figure 1B).

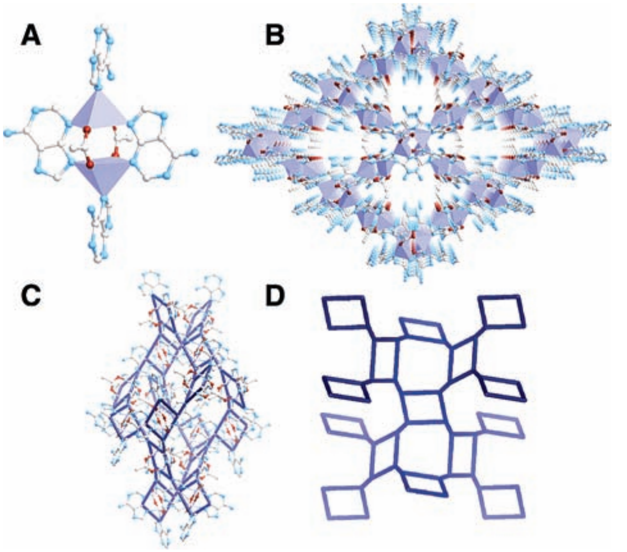

Figure 1. Crystal structure of bio-MOF-11. Co^{2+}−adeninate−acetate clusters (A) are bridged by adeninate to generate an extended 3D porous structure with channels along the *a* and *b* crystallographic directions (B). Each cluster can be represented as a square (dark-blue) building block, and internal cavities within the framework consist of 16 interconnected square clusters (C). The framework adopts the augmented **lvt** topology (D). (Co^{2+}, light-purple; C, gray; O, red; N, light-blue. H atoms have been omitted for clarity.)

Carboxylate cluster building blocks (e.g., paddle-wheel clusters) have been used extensively for constructing structurally rigid and permanently porous MOFs. We hypothesized that MOFs constructed from structurally similar adeninate-based clusters[8] should also be stable and permanently porous. Indeed, bio-MOF-11 remains stable upon heating to 200 °C. We conducted N_2 adsorption experiments at 77 K to evaluate its permanent porosity. The material was activated at 100 °C under reduced pressure after soaking in chloroform for 24 h. The resulting type-I isotherm (Figure 2A)

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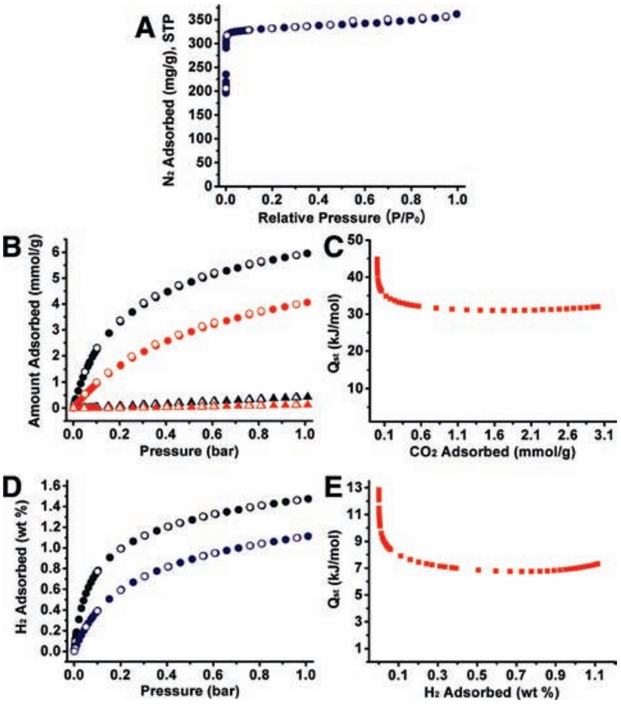

Figure 2. Gas adsorption experiments. (A) Nitrogen adsorption isotherm (77 K). (B) Adsorption isotherms for CO_2 (circles) and N_2 (triangles) at 273 (black) and 298 K (red). (C) Isosteric heat of adsorption for CO_2 at different CO_2 loadings. (D) Hydrogen adsorption isotherms at 77 (black) and 87 K (blue). (E) Isosteric heat of adsorption for H_2 at different H_2 loadings. (In the isotherms, solid and open markers represent adsorption and desorption points, respectively.)

reveals rapid gas adsorption at low pressures and is consistent with permanent microporosity. The estimated Brunauer−Emmett−Teller (BET) surface area is 1040 m^2/g, and the pore volume is 0.45 cm^3/g.

The pores of bio-MOF-11 are densely lined with Lewis basic amino and pyrimidine groups (Figure 1B,C). A total of four amino groups and four pyrimidine groups are directly exposed to each individual cavity. This feature prompted us to examine the material's CO_2 adsorption properties. We first collected the CO_2 isotherm at 273 K. It is completely reversible, exhibits a steep rise at low pressures, and reaches a maximum of 6.0 mmol/g at 1 bar (Figure 2B). Comparatively, the N_2 uptake at 273 K is only 0.43 mmol/g at 1 bar. At 298 K, the maximum CO_2 uptake is 4.1 mmol/g, compared with only 0.13 mmol/g for N_2 (Figure 2B). The initial slopes of the CO_2 and N_2 adsorption isotherms were calculated, and the ratios of these slopes were used to estimate the adsorption selectivity for CO_2 over N_2 (see the Supporting Information).[3d] From these data, the calculated CO_2/N_2 selectivity is 81:1 at 273 K and 75:1 at 298 K. To our knowledge, these selectivity values are the best reported to date for MOF materials.[3d,g,j]

We also calculated the isosteric heat of adsorption (Q_{st}) for CO_2 using adsorption data collected at 298, 303, 308, and 313 K. At the onset of adsorption, Q_{st} is ∼45 kJ/mol, which is similar to values for some other amine-functionalized MOF materials.[3e,k] Q_{st} decreases to 30−35 kJ/mol at higher CO_2 pressures and remains steady at this value throughout the adsorption process. We believe that this high Q_{st} is due to favorable interactions between adsorbed CO_2 molecules and the Lewis basic amine and pyrimidine functionalities decorating the pores.[6,9]

Given the rapid uptake of N_2 at 77 K and CO_2 at 273 K, we decided to study the H_2 adsorption properties to determine whether the relatively small pores of bio-MOF-11 may be intrinsically well-suited for condensing gases at low pressures.[3k,10] The hydrogen isotherms collected at 77 and 87 K were also both steep in the low-pressure regime and completely reversible. At 77 K, the material adsorbs a maximum of ∼1.5 wt % H_2. The maximum Q_{st} for H_2 is ∼13 kJ/mol at low pressure. As the H_2 loading increases to ∼0.7 wt %, Q_{st} decreases to ∼7 kJ/mol, and from 0.7 to 1.1 wt %, Q_{st} increases slightly. The increase in Q_{st} at higher loadings may be due to intersorbate interactions that are promoted in the restricted pore space.[3k,10]

In conclusion, bio-MOF-11 has a high heat of adsorption for CO_2, high CO_2 capacity, and impressive selectivity for CO_2 over N_2. We attribute these favorable CO_2 adsorption properties to the presence of the Lewis basic amino and pyrimidine groups of adenine and the narrow pore dimensions of bio-MOF-11. In terms of several important CO_2 capture and separation performance criteria, this material outperforms other amine-functionalized MOFs[3e,g,k] and imidazole-based frameworks.[3d] Specifically, it exhibits higher CO_2 capacities and higher selectivities for CO_2 over N_2. Collectively, these results point toward the value of utilizing adenine as a building block for constructing MOFs for CO_2 capture applications.

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Supporting Information Available: Experimental procedures, crystallographic data (CIF), and additional supporting data. This material is available free of charge via the Internet at http://pubs.acs.org.

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