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A Robust Sulfonate-Based Metal-Organic Framework with Permanent Porosity for Efficient CO_2 Capture and Conversion

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ABSTRACT: We report a rare example of a sulfonate-based metal-organic framework (MOF) possessing a prototypical primitive-cubic topology, constructed with Jahn-Teller distorted Cu(II) centers and a mixed-linker (organosulfonate and N-donor) system. The inherent high-polar, permanent porosity contributes to the highest reported CO_2 sorption properties to date among organosulfonate-based MOFs, outperforming the benchmark carboxylate MOF counterpart. Importantly, density functional theory calculations confirm that the CO_2-sulfonate interaction plays an important role in CO_2 capture. Indeed, the hydrothermal product demonstrates high robustness over a wide range of pH as well as aqueous boiling conditions, overcoming the moisture sensitivity of conventional Cu_2 paddlewheel-based MOFs. In addition, bulk synthesis of this material has been successfully achieved on the gram-scale (>1 g) in a single batch with high yield. Combining the high CO_2 affinity and robustness nature, this sulfonate porous material is also an efficient, recyclable heterogeneous catalyst for CO_2 fixation to form cyclic carbonates under ambient conditions.

INTRODUCTION

MOFs provide a versatile platform for tuning the chemical functionality of pore surfaces, thus garnering increasing attention for applications in gas storage,[1,2] molecular separation,[3,4] sensing,[5,6] and catalysis.[7,8] Overall, the architecture of the numerous carboxylate-based MOFs is well-defined with reticular chemistry, partly due to their prominent metal-carboxylate secondary building units (SBUs).[9] As a result, the chelation of the carboxyl organic linkers to metal ions gives non-polar porosity that is much more typically observed in MOFs (Figure 1, left). Though some functionalizations may be achieved *via* presynthetic or postsynthetic modification under mild conditions, they usually require sophisticated multiple-step synthesis as well as significant sacrifice in porosity.[10-12]

In contrast to carboxylate-based MOFs, sulfonate-based MOFs have been significantly less investigated and exhibit a lower degree of structural predictability, attributable to the versatile coordination modes of the sulfonate monoanions (RSO_3^-) to the metal.[13] However, permanently porous MOFs constructed with organosulfonates (*i.e.* alkylsulfonates or aromatic sulfonates) as organic linkers may offer a functional platform to highly polar pore surfaces (Figure 1, right), including potential applications in chemical recognition/separation as well as ionic conductivity.[14] Nevertheless, the vast majority of sulfonate frameworks hold a densely packed structure and/or a low-dimensional topology.[15] Among the rather confined examples of 3-D sulfonate-based open frameworks, permanent porosity has rarely been confirmed *via* complete guest-free activation, Brunner-Emmet-Teller (BET) measurements, or gas adsorption; thus, they are not widely recognized within the realm of MOFs.[16,17] In addition, no systematic investigation has been made to study the molecular selectivity of a sulfonate-based prototypical MOF in comparison with its carboxylate counterpart.

Carbon dioxide (CO_2), the anthropogenic-emitted gas, has been recognized as the primary contributor to global warming.[18] The development of CO_2 capture and sequestration (CCS) technologies is imperative to selectively capture CO_2 from existing emission sources.[19] In addition, the well-designed chemical transformation of captured CO_2 into commercially relevant chemicals is of vital importance to utilize CO_2 as a renewable C1 feedstock.[20,21] Owing to the high energy-cost, corrosion and toxicity of conventional amine-based wet-scrubbing systems for CO_2 capture, extensive efforts have been made to discover new solid-state materials for advanced CCS technologies.[22] MOFs are potentially the ideal candidates for the next-generation CO_2 capture and conversion materials due to their exceptionally high surface area, gas sorption capacity and chemical tunability.[23,24] Decorating the pore surfaces with strongly polarizing groups is favorable to enhance CO_2 capture capabilities of MOFs.[1] Meanwhile, employing MOFs as bifunctional materials to catalytically convert the captured CO_2 to high-value chemicals is rather limited at present, especially under very mild reaction conditions.[25-30]

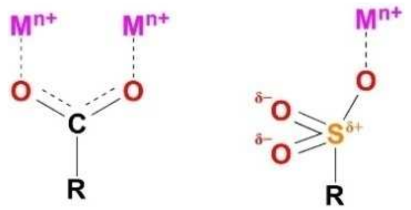


Figure 1. Left: typical binding mode of metal-carboxyl units of carboxylate-based MOFs. Right: binding mode of metal-sulfonate units of the sulfonate-based MOF in this study.

Herein, we employ a mixed-linker strategy to synthesize a rare sulfonate-based 3-D Cu(II)-MOF possessing interconnected square channels. Using Cheetham *et al.*'s proposed nomenclature,[31] the sulfonate MOF possesses an "I^0O^3" connectivity, giving a prototypical primitive-cubic topology with 2-fold interpenetration. Importantly, the permanent porosity of this material can be successfully activated and reveals significantly enhanced CO_2 affinity with respect to its carboxylate-based MOF counterparts. Utilizing dispersion-corrected density functional theory (DFT) calculations and molecular dynamics simulation,[32-34] we further determine the CO_2 adsorption sites and the calculated CO_2 adsorption free energy, which is highly consistent with the experimental results. Moreover, this hydrothermally synthesized material exhibits a high thermal and chemical stability, unlike conventional carboxylate MOFs built with Cu_2 paddlewheel SBUs. Taking advantage of the highly robust nature and strong CO_2 affinity of the material, the embedded Lewis acidic sites achieve efficient and reusable heterogeneous catalysis to convert captured CO_2 into cyclic carbonates under ambient conditions.

RESULTS AND DISCUSSION

Hydrothermal reaction of $Cu(NO_3)_2$, 4,4'-bipyridine (bpy), and disodium 1,2-ethanedisulfonate ($EDSNa_2$) afforded blue cubic crystals of $[Cu(bpy)_2(EDS)]_n$, which we denote as TMOF-1 (TMOF=Tongji-MOF). Employing a flexible sulfonate-based organic linker (instead of rigid terephthalate-type linkers in carboxylic MOFs) is necessary, likely due to the tilted coordination direction of linear organosulfonate linkers towards the metal centers (Figure 1). The high yield and phase purity of TMOF-1 was evidenced by experimental powder X-ray diffraction (PXRD), which matches well with the theoretical pattern simulated from single-crystal data (Figure 2). In addition, refluxing the reaction solution without applied pressure was used to synthesize TMOF-1 with high crystallinity. Importantly, bulk refluxing synthesis of TMOF-1 at the gram-scale (> 1 g) was successfully achieved in a single batch with a comparable yield (see details in experimental section, ESI).

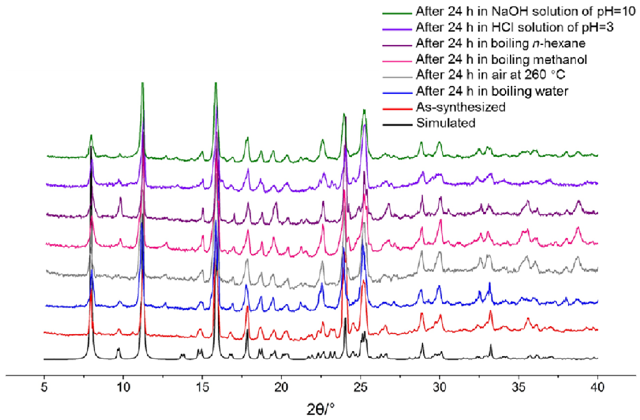


Figure 2. PXRD patterns of TMOF-1.

X-ray crystallography reveals TMOF-1 is a covalently-bonded 3-D framework and crystallized in the monoclinic space group C2. The overall structure consists of doubly interpenetrated nets, where each independent primitive-cubic net can be viewed as cationic two-dimensional (4,4)-connected brick-like layers $[Cu(bpy)]^{2+}$ pillared by EDS linkers (Figure 3). Each single framework is staggered with respect to one another (Figure 4), affording a void space of 21.4% (calculated by PLATON[35], Figure 4). Both of the two crystallographically independent Cu centers residing in TMOF-1 have an octahedral coordination environment. Four ending nitrogens of four separate bpy linkers define a square-plane around the Cu atoms, while two oxygens of two independent EDS ligands bond to Cu in the axial positions to complete the octahedral geometry. To note, only one oxygen of each sulfonate coordinates to the Cu centers, and the axial Cu-O bonds are significantly elongated with atomic distances of 2.309(3)~2.414(3) Å owing to its d^9 Jahn-Teller distortion.

Successful activation of the permanent porosity within TMOF-1 was carried out under vacuum at 105 °C, as evidenced by the agreement of the PXRD patterns of the activated sample and simulated data from X-ray crystallography (Figure S1). TMOF-1 exhibited an overall BET surface area of 256±5 m^2/g with a reversible type I sorption isotherm using Ar at 87 K or N_2 at 77 K, demonstrating its microporous nature (Figures 5a and S2). Since the high-density and strong polarity of the sulfonate groups in TMOF-1 would significantly promote the affinity of CO_2 to have a quadrupole moment, we systematically investigated the affinity of TMOF-1 towards CO_2. Based on low-pressure CO_2 sorption isotherms (Figure 5b), TMOF-1 showed CO_2 uptake of 104.2 cm^3/g (297.4 mg/g) at 200K, 47.1 cm^3/g (98.6 mg/g) at 273 K, 32.4 cm^3/g (62.0 mg/g) at 298 K and 27.7 cm^3/g (51.5 mg/g) at 308 K under 1 bar, respectively. To the best of our knowledge, these numbers are the highest among organosulfonate-based MOFs. Meanwhile, they are not comparable to the highest values in the realm of carboxylate-based MOFs largely due to the relatively limited void space of TMOF-1.[23,24] Nevertheless, the CO_2 uptake of TMOF-1 at 298 K and 1 bar is higher than reported carboxylate MOFs with comparable surface areas (*e.g.* MOF-2[36]) as well as some highly porous benchmark carboxylate MOFs (*e.g.* IRMOF-3,[36] UMCM-1,[37] and MIL-101[38]).

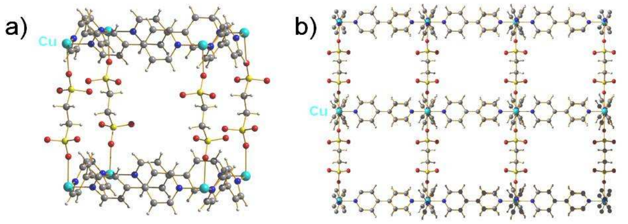


Figure 3. Crystallographic view of a single net of TMOF-1 (hydrogens are omitted for clarity; Cu, cyan; C, gray; S, yellow; O, red; N, blue): a) one single primitive-cubic net; b) a single primitive extended framework viewed along the *a* axis.

The variable-temperature CO_2 adsorption isotherms reveal the zero-coverage isosteric heat of adsorption (Q_{st}) of TMOF-1 to be 30.9 kJ/mol, computed using the Clausius-Clapeyron equation[39] (Figure 5b). Compared to literature values, the Q_{st} of TMOF-1 is higher than most of the unfunctionalized carboxylate-based MOFs without exposed metal sites or amine functionality, confirming the high affinity of TMOF-1 towards CO_2.[23,24] In addition, after soaking TMOF-1 in 1 bar CO_2 for 1 h at room temperature, the material exhibited a characteristic CO_2 absorption band at 2335 cm^{-1} in the infrared spectrum, confirming the strong interaction between CO_2 and TMOF-1 even under ambient conditions (Figure S3).[40] Besides CO_2 sorption, the H_2 sorption isotherms of TMOF-1 exhibits steep increase at low pressure with a Q_{st} of 9.0 kJ/mol, resulting in H_2 uptake capacities of 0.9 wt.% (77 K, 1 bar) and 0.75 wt.% (87 K, 1 bar) (Figure 5d). The high Q_{st} value is likely related to the increased H_2-host interaction, due to the narrow pore size from the 2-fold interpenetration.[2]

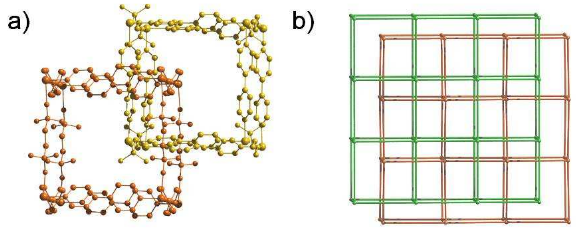


Figure 4. Crystallographic view of the 2-fold interpenetrated TMOF-1: a) a single primitive-cubic net staggered with another cubic net; the nets are presented in yellow and orange; d) representation of the doubly interpenetrated extended frameworks; the networks are presented in green and brown.

In order to examine in detail the interaction between CO_2 and embedded sulfonate moieties in TMOF-1, we employed both control experiments and DFT calculations. First, we synthesized a doubly-interpenetrated carboxylate-based Cu(II) MOF, $[Cu_2(bpy)(bdc)_2]_n$ [MOF-508b(Cu)], which possesses the same N-donor ligand and a prototypical primitive-cubic topology as well.[41] Despite the fact that its BET surface area is slightly higher than that of TMOF-1 (364 m^2/g vs. 256 m^2/g, respectively, Figure S4), its CO_2 uptake value at 298 K and 1 bar is less than 40% compared to TMOF-1 (Figure 5c). More importantly, the zero-coverage Q_{st} of this carboxylate MOF is as low as 19.2 kJ/mol, measured using variable-temperature CO_2 sorption under identical conditions. This value agrees well with the literature value (15~19 kJ/mol) of the isostructural MOF-508b(Zn).[42,43]

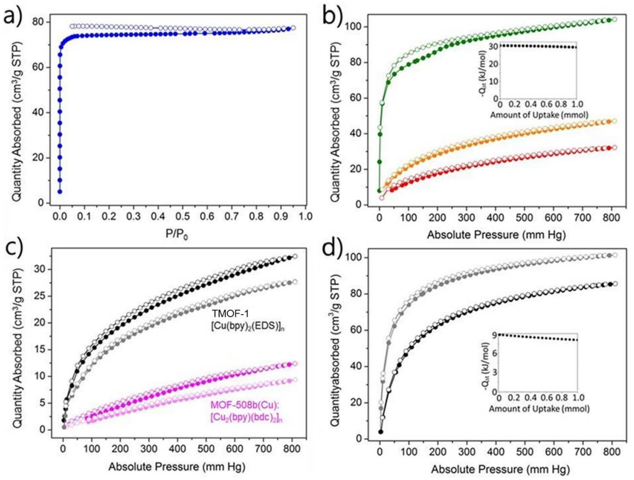


Figure 5. Gas sorption of TMOF-1: a) Ar sorption isotherm at 87K; b) CO_2 sorption isotherms at 200K (green), 273K (yellow), and 298K (red); the inset is the Q_{st} of CO_2 adsorption; c) CO_2 sorption isotherms of TMOF-1 at 298K (black) and 308K (gray), as well as $[Cu_2(bdc)_2(bpy)]_n$ [MOF-508b(Cu)] at 298K (magenta) and 308K (light magenta); d) H_2 adsorption isotherms at 77K (black) and 87K (gray); the inset is the Q_{st} of H_2 adsorption.

In addition to control experiments of CO_2 capture, we performed first-principle calculations based on dispersion-corrected DFT to investigate the CO_2 binding sites residing in TMOF-1 (see ESI for calculation details). By adding CO_2 molecules into the cavity of TMOF-1, we discovered that the adsorbed CO_2 inside TMOF-1 reaches up to 4 molecules per unit cell at 298K and 1 bar CO_2, which is equivalent to a CO_2 uptake of ~78 mg/g. The most energetically stable adsorption site (two such sites per unit cell) is shown in Figure 6, where each CO_2 is surrounded by four sulfonate groups from the two adjacent EDS linkers, confirming the strong binding between CO_2 and organosulfonate functionalities. The calculated free energy of adsorption after the correction of vibrational entropy and the zero-point energy is 29.2 kJ/mol, which agrees well with the experimentally measured Q_{st} (30.9 kJ/mol). Importantly, our first principle molecular dynamics simulation confirms that these captured CO_2 molecules together with TMOF-1 are energetically stable at room temperature (Figure S5). Adding CO_2 above ~39 mg/g capacity, the new additional CO_2 would reside in the spare porosity adjacent to the adsorbed CO_2, which are distal (≥ 5.9 Å) to the sulfonate groups within the TMOF-1 framework. These CO_2 molecules are rather weakly adsorbed, with an adsorption free energy value at -3.3 kJ/mol. The proposed CO_2 diffusion channels were analyzed as well, based on the MD trajectories (Figure S6). According to computational results, the CO_2 molecules can easily diffuse through the 3D-interconnected porosity of the TMOF-1 with a low free energy barrier (only ~0.3 eV).

Overall, the CO_2-sulfonate interaction obviously plays an important role in the CO_2 capture of TMOF-1.

The thermal stability of TMOF-1 was investigated in detail by thermogravimetric ananlysis (TGA) and *ex-situ* PXRD (Figures 2 and S7). A ~10.0% weight loss occurs after heating beyond 100 °C, ascribed to the removal of solvent H_2O molecules in the pores. The anhydrous phase is stable up to *ca.* 300 °C until the decomposition of bpy and EDS. *Ex-situ* PXRD of heating TMOF-1 to 260 °C in air confirms the retention of the as-synthesized 3-D porous topology (Figure 2). The chemical stability of TMOF-1 was examined in polar and non-polar boiling solvents (water, methanol, and *n*-hexane), HCl solution (pH=3), and NaOH solution (pH=10). After incubation in these solutions for 24 h, the high crystallinity of the primitive cubic topology is well retained, as evidenced by PXRD patterns (Figure 2). Besides PXRD, <10 wt. % decrease in mass was observed after the thermal and chemical treatment, which is likely due to the solvent loss after activation (Table S1). In order to further confirm the high water-stable nature of TMOF-1, *in-situ* optical microscopy was employed to monitor the crystallinity throughout the immersion of MOF in acid/base solution (Figure S8). The size and morphology did not change in an observable manner. Importantly, the porosity of the material was largely retained after refluxing in water, evidenced by BET measurements (238 m^2/g) using Ar at 87 K (Figure S9). To note, only a limited number of carboxylate-MOFs with permanent porosity demonstrate excellent stability in boiling water, or in aqueous solutions over a wide-range of pH.[12] Indeed, divalent metal carboxylate MOFs (*e.g.* Cu_2 or Zn_2 paddlewheel) are subject to hydrolysis and usually quite soluble in aqueous solution.[44] It is likely that the typical Jahn-Teller distorted octahedral coordination geometry of Cu(II) in our TMOF-1 was less susceptible to hydrolysis than the conventional 5-coordinate Cu centers in Cu_2-paddlewheel SBUs.

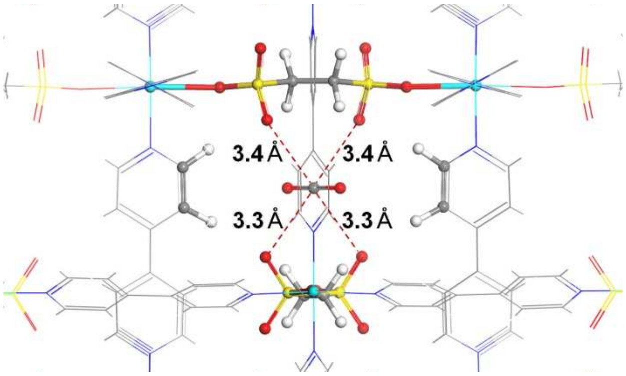
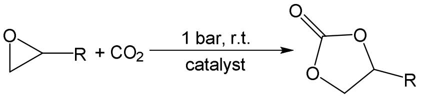
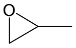
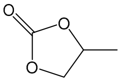
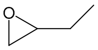
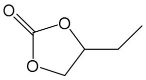
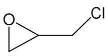
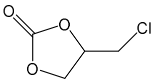
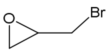
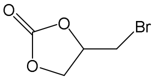
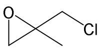
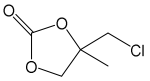
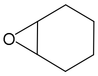
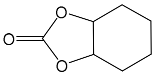


Figure 6. The DFT-optimized most stable CO2 binding configuration in TMOF-1 (Cu, cyan; C, gray; S, yellow; O, red; N, blue).

Given its strong inherent CO_2-affinity and highly robust nature of TMOF-1, we sought to investigate the embedded Cu(II) Lewis acidic sites for CO_2-related heterogeneous catalytic reactions. As a benchmark reaction, cycloaddition of CO_2 and epoxides to form cyclic carbonates is of great interests in chemical industry, due to the wide application of carbonates in pharmaceuticals.[45] High pressure and/or temperature are necessary for this CO_2 fixation by common catalysts, such as metal-salen complexes, metal oxides, and zeolites.[46,47] A few recent studies employed MOFs as promising and efficient catalytic materials to convert captured CO_2 to cyclic carbonates.[25-29] In conjunction with tetra-*n-tert*-butylammonium bromide (TBAB) as a co-catalyst under ambient conditions (*i.e.* room temperature, 1 bar), TMOF-1 exhibited nearly quantitative yield of converting 2-methyloxirane to the corresponding cyclic carbonate (Table 1, entry 1). The high efficiency of this catalytic activity was successfully extended to functionalized (e.g. $–CH_3$, -Cl, or -Br) 2-methyloxirane substrates (Table 1, entries 2-5). By comparison, these catalytic activities are significantly higher than the benchmark Cu(II)-carboxylate MOF, HKUST-1, which showed a moderate yield in the range of 50~60%.[26,30] Meanwhile, a control reaction without any catalyst gave negligible conversion. However, for bulky epoxide substrates such as styrene oxide, TMOF-1 only gave a yield of 39(3)% (Table 1, entry 6). This lower yield is probably due to the steric hindrance on the β-carbon of the substrates, hampering nucleophilic attack from TBAB (see mechanism in Figure S10, ESI).[48] In order to confirm the heterogeneous and reusable nature of the catalysis, TMOF-1 demonstrated excellent recyclability of converting 2-(chloromethyl)oxirane without a significant decrease in yields (86~92%, Figure S11). Between each run, the catalyst was recovered by filtration, rinsed with methanol, dried in air, and reused on subsequent reactions without further treatment. Importantly, the crystallinity of TMOF-1 was maintained after each cycle, as indicated by PXRD (Figure S12). In addition, the filtrate of catalysis reactions contained <0.1 ppm Cu, as evidenced by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). All these results conclude the heterogeneity of the MOF catalyst. Overall, the high efficiency and reusability presented here prove that TMOF-1 can catalytically achieve successful cycloaddition of captured CO_2 to form cyclic carbonates.

Table 1. TMOF-1 Catalyzed Cycloaddition of CO_2 and Epoxides to Form Cyclic Carbonates^{a}



Entry	Substrate	Product	Yield (%)^{b}
1			> 99
2			> 99
3			92(2)
4			95(2)
5			77(3)
6			39(3)

[a]Conditions: 20 mmol epoxide, 1 mol% (based on Cu) TMOF-1, 10 mol% TBAB, CO_2 (1 atm), solvent free, at room temperature.

[b]Yields determined by ^{1}H-NMR, an average value of three runs (error in parentheses).

CONCLUSIONS

In conclusion, a rare example of an organosulfonate-based 3-D MOF possessing a primitive-cubic topology has been realized using a mixed-linker strategy. The resulting material can be easily synthesized at the gram-scale with high yield. Importantly, TMOF-1 exhibits permanent and strongly polar porosity, thus significantly enhancing CO_2 capture capability with respect to its carboxylate MOF counterpart. Indeed, the sulfonate material also overcomes the moisture sensitivity of conventional Cu_2 paddlewheel MOFs. The inherent high-polarity pore surface along with the "inert" feature of the material allow for excellent catalytic efficiency of converting CO_2 to cyclic carbonate. Since the MOF chemistry is far from mature with many potential applications yet to be discovered, the advancement of sulfonate-type porous MOFs will likely play an important role in MOF field with respect to conventional carboxylate MOFs. We are further extending this synthetic strategy to other multitopic organosulfonates, opening up an opportunity for the discovery of a new class of sulfonate-functionalized porous materials.

ASSOCIATED CONTENT

Supporting Information

Experimental details, and additional characterization. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Author Contributions

§These authors contributed equally to this paper.

Notes

The authors declare no competing financial interests.

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SYNOPSIS TOC