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Highly Selective Carbon Dioxide Uptake by [Cu(bpy-*n*)$_2$(SiF$_6$)] (bpy-1 = 4,4′-Bipyridine; bpy-2 = 1,2-Bis(4-pyridyl)ethene)

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Supporting Information

ABSTRACT: A previously known class of porous coordination polymer (PCP) of formula [Cu(bpy-*n*)$_2$(SiF$_6$)] (bpy-1 = 4,4′-bipyridine; bpy-2 = 1,2-bis(4-pyridyl)ethene) has been studied to assess its selectivity toward CO_2, CH_4, N_2, and H_2O. Gas sorption measurements reveal that [Cu(bpy-1)$_2$(SiF$_6$)] exhibits the highest uptake for CO_2 yet seen at 298 K and 1 atm by a PCP that does not contain open metal sites. Significantly, [Cu(bpy-1)$_2$(SiF$_6$)] does not exhibit particularly high uptake under the same conditions for CH_4, N_2, and, H_2O, presumably because of its lack of open metal sites. Consequently, at 298 K and 1 atm [Cu(bpy-1)$_2$(SiF$_6$)] exhibits a relative uptake of CO_2 over CH_4 of *ca.* 10.5:1, the highest value experimentally observed in a compound without open metal sites. [Cu(bpy-2)$_2$(SiF$_6$)] exhibits larger pores and surface area than [Cu(bpy-1)$_2$(SiF$_6$)] but retains a high CO_2/CH_4 relative uptake of *ca.* 8:1.

Metal−Organic Materials (MOMs) are typically comprised of a metal atom or metal cluster (i.e., the "node") that is coordinated to one or more multifunctional organic ligand(s) (i.e., the "linker").[1,2] MOMs combine the following features: unprecedented levels of permanent porosity; crystalline solid forms that afford uniform composition and structure; easy process scale-up and reproducibility; modular compositions that are amenable to crystal engineering strategies that in turn offer control and diversity over both structure and properties. For example, the pore environment in a MOM can be modified to optimize interactions with a target adsorbate[3−5] whereas the geometry and dimensions of the linker and the coordination geometry of the node can impart control over the resulting connectivity and scale of the MOM pores.[6,7] In such a manner, it is possible to regard certain classes of MOMs as platforms that can be optimized for a particular challenge. Selective capture of carbon dioxide[8−10] represents one such challenge that is of topical relevance because there is a pressing need to develop improved processes for purification of methane and society has recognized the need to develop new technologies for carbon capture in the context of greenhouse gases. The perfect MOM for such challenges would offer the following features: high selectivity toward CO_2 vs CH_4, N_2 and H_2O through physisorption; facile synthesis from low cost molecular building blocks; stability to environmental conditions; moderate to high surface area and pore size. In this context there are highly promising materials as exemplified by Mg/DOBDC[11] (DOBDC = 2,5-dihydroxyterephthalate), the Mg analog of MOF-74[12] and CPO-27-Zn.[13] Upon activation, Mg/DOBDC possesses the following features: a BET measured surface area of 1495 m^2/g; open Mg sites that enable an initial heat of adsorption of 47 kJ/mol toward CO_2; an uptake volume of CO_2 that represents 35.2 wt % at 1 atm and 296 K; selectivity vs CH_4 of *ca.* 11.5 at 1 atm and 296 K.[11,14] These features make Mg/DOBDC an attractive material for selective sorption of CO_2. However, the presence of open metal sites can promote chemisorption (i.e., larger energy costs for regenerating the material) and the likelihood of high affinity toward H_2O. In principle, a MOM that does not possess open metal sites and thereby relies upon weaker molecular recognition forces would represent an attractive platform. There are numerous such MOMs that have been screened for selective CO_2 uptake, especially zeolitic imidazolate frameworks (ZIFs).[15−18] However, the best performing ZIF[16] exhibits low selectivity vs CH_4, relatively low surface area and relatively low uptake under ambient conditions. We report herein a MOM platform that does not contain open metal sites, porous *pcu* topology coordination polymers (PCPs) of formula [Cu(bpy-*n*)$_2$(SiF$_6$)] (bpy-1 = 4,4′-bipyridine; bpy-2 = 1,2-bis(4-pyridyl)ethene), and exhibits uptake and selectivity for CO_2 that well surpasses that of ZIFs and even approaches that of Mg/DOBDC.

[Zn(bpy-1)$_2$(SiF$_6$)] was reported in 1995[19] and represents a prototypal "pillared sheet" platform in that the cationic Zn(bipy-1)$_2$ square grid can be contracted by using pyrazine[20] as a linker or expanded with extended bpy ligands,[21] thereby offering an opportunity to control the pore size range from ultramicroporous[20] to mesoporous dimensions, respectively. The Cu analog, [Cu(bpy-1)$_2$(SiF$_6$)], was subsequently shown to be permanently porous (1337 m^2/g) and exhibit relatively high uptake for CH_4 (6.5 mmol/g at 298 K and 36 atm).[22] It occurred to us that [Cu(bpy-*n*)$_2$(SiF$_6$)] represents a platform that is well suited to assess the impact of pore size upon gas

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selectivity and diffusion rate since the SiF_6^{2-} pillars do not facilitate interpenetration unless exceptionally long bpy linkers are used.[23] We therefore prepared [Cu(bpy-1)$_2$(SiF$_6$)] and its expanded analog [Cu(bpy-2)$_2$(SiF$_6$)] in order to study their sorption characteristics for CO_2, CH_4, N_2, and H_2O. Their crystal structures are illustrated in Figure 1 and reveal their isoreticular nature.

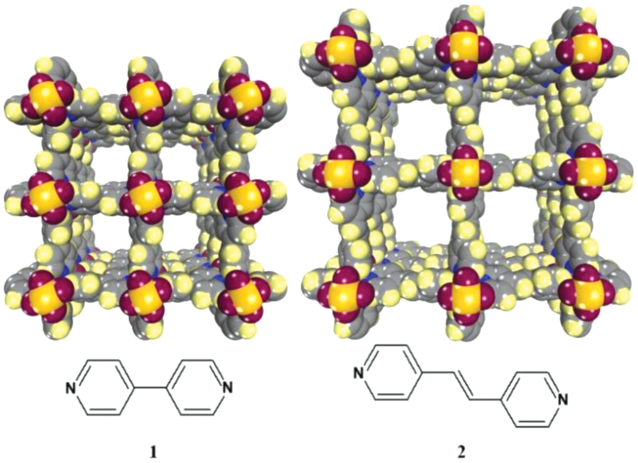

Figure 1. Tetragonal crystal structures of [Cu(bpy-1)$_2$(SiF$_6$)] (left) and [Cu(bpy-2)$_2$(SiF$_6$)] (right) reveal the presence of square channels parallel to the crystallographic *c*-axis. The dimensions of these channels are controlled by the bpy-1 and bpy-2 linkers. The pyridyl moieties are disordered over two positions.

Single crystals of [Cu(bpy-1)$_2$(SiF$_6$)] were prepared by dissolving $CuSiF_6$ in EtOH/H_2O and layering onto a solution of bpy-1 in $CHCl_3$. [Cu(bpy-2)$_2$(SiF$_6$)] was prepared solvothermally by reacting $CuSiF_6$ with bpy-2 in MeOH/H_2O and nitrobenzene at 85 °C for 24 h. The effective window size considering the van der Waals radii of the framework atoms are *ca.* 8 and 10.6 Å, respectively, and both compounds can be activated for gas sorption studies by being subjected to high vacuum at room temperature after MeOH exchange. [Cu(bpy-1)$_2$(SiF$_6$)] was measured to have a saturated N_2 uptake of 425 cm^3/g at 77 K, which corresponds to BET and Langmuir surface areas of 1468 and 1651 m^2/g, respectively. The corresponding values for [Cu(bpy-2)$_2$(SiF$_6$)] were determined to be 740 cm^3/g or 2718 m^2/g and 3118 m^2/g, respectively. Single component gas adsorption isotherms for [Cu(bpy-1)$_2$(SiF$_6$)] toward CO_2, CH_4, N_2, and H_2O were measured at 298 K and are presented in Figures 2 and S8. Notably, a high CO_2 uptake of 23.1 wt % was observed at 1 atm. To put this in perspective, this value is approximately double that seen for Zeolite-13x,[17] it exceeds the values of most MOFs that contain open metal sites, and it even approaches that of Mg/DOBDC at 296 K.[11] Conversely, the uptake for CH_4 is only 0.83 wt % and that of H_2O is ca. 20.5 wt %. The selectivity toward CO_2 over CH_4 exhibited by [Cu(bpy-1)$_2$(SiF$_6$)] is therefore exceptional for a PCP that relies upon physisorption.

An isosteric heat of adsorption (Qst) of *ca.* 27 kJ/mol, Figure S10, at all loadings of CO_2, can be compared to 47 and 63 kJ/mol in compounds with strongly interacting open metal sites such as Mg/DOBDC[11] and Mil-101,[24] respectively. However, other compounds with open metal sites such as MIL-53(Al) and HKUST-1 exhibit values of 20.1 and 30 kJ/mol, respectively.[4,25] A benchmark zeolite such as Zeolite 13X, which has strongly Lewis acidic sites, exhibits a Qst of ca. 49 kJ/mol.[17] Qst values of >40 kJ/mol would be expected to afford high selectivity for CO_2 but if based upon metal binding would typically only exhibit such high values at low loading. IAST calculations[5,26,27] based upon the experimentally measured CO_2 and CH_4 isotherms are presented in Figure 3 and reveal high CO_2/CH_4 selectivities for [Cu(bpy-1)$_2$(SiF$_6$)] and [Cu(bpy-2)$_2$(SiF$_6$)], which remain consistent up to 1 atm. This behavior is as expected for physisorption. The selectivities are close to the ratio of the Henry law constants from the single-component isotherms, as would be expected from the relative linearity of the single component adsorption isotherms.

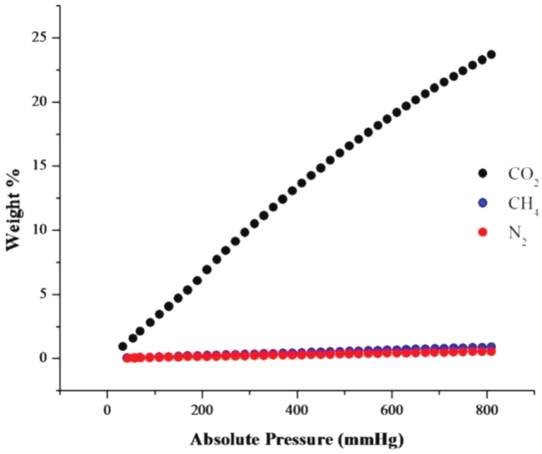

Figure 2. Reversible single component gas adsorption isotherms for [Cu(bpy-1)$_2$(SiF$_6$)] measured at 298 K reveal high uptake for CO_2 but relatively low uptake for CH_4 and N_2.

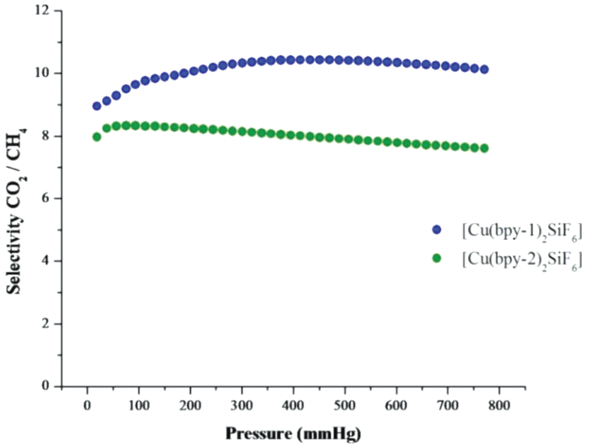

Figure 3. IAST calculated selectivities for adsorption from equimolar gas-phase mixtures based upon the experimentally observed adsorption isotherms of the pure gases for [Cu(bpy-1)$_2$(SiF$_6$)] (blue) and [Cu(bpy-2)$_2$(SiF$_6$)] (green).

CO_2 uptake of [Cu(bpy-2)$_2$(SiF$_6$)] at 1 atm was found to be 12.1 wt % or approximately half that of [Cu(bpy-1)$_2$(SiF$_6$)]. However, CH_4 uptake was only 0.71 wt % meaning that relative uptake remains high at *ca.* 8:1 even with a surface area double that of [Cu(bpy-1)$_2$(SiF$_6$)]. The Qst value for CO_2, *ca.* 21 kJ/mol, is comparable to that of open metal site compounds such as HKUST-1 and MIL-53.

The uptake of H_2O exhibited by [Cu(bpy-1)$_2$(SiF$_6$)], Figure S8, is 20 wt % at $P/P_0 = 1$, relatively low compared to PCPs with open metal sites. For example, HKUST-1 and MIL-101 exhibit corresponding values of 52.0% and 135%, respectively.[28] Furthermore, water uptake can considerably decrease CO_2 uptake: HKUST-1 exposed to water vapor exhibited a 75% decrease in CO_2 uptake at 25 °C.[29] $[Cu(bpy\text{-}2)_2(SiF_6)]$, Figure S8, was also found to exhibit a low H_2O uptake of 19 wt %, suggesting that PCPs with saturated metal centers might exhibit less affinity for H_2O than PCPs with open metal sites.

$[Cu(bpy\text{-}1)_2(SiF_6)]$ and $[Cu(bpy\text{-}2)_2(SiF_6)]$ are examples of low cost, relatively water stable sorbents that exhibit a high uptake of CO_2 combined with a low uptake of CH_4, N_2, and H_2O. That this selectivity is linked to a physisorptive process is likely to be an advantageous feature from a practical perspective since the energy associated with activating and regenerating the sorbent would be lower than that for sorbents that act through chemisorption. In addition, it should be noted that the surface areas for $[Cu(bpy\text{-}1)_2(SiF_6)]$ and $[Cu(bpy\text{-}2)_2(SiF_6)]$ are relatively high compared to other compounds that exhibit good selectivity toward CO_2. Figure 4 presents a plot of CO_2/CH_4 selectivity vs surface area for the title compounds and a range of MOMs. It reveals that most MOMs exhibit selectivities of less than 7.5 and surface areas of less than 1500 m^2/g, therefore suggesting that the title compounds might be highly competitive with MOMs that contain open metal sites, including even Mg/DOBDC. It is tempting to attribute the selective carbon dioxide uptake behavior of $[Cu(bpy\text{-}1)_2(SiF_6)]$ and $[Cu(bpy\text{-}2)_2(SiF_6)]$ to the SiF_6^{2-} moieties, but it is premature to make such an assertion. Nevertheless, the results of this study indicate that MOMs that do not contain open metal sites can exhibit high selectivity and uptake of the type that could prove useful in the context of carbon capture. We shall utilize the platform nature of $[Cu(bpy\text{-}1)_2(SiF_6)]$ and $[Cu(bpy\text{-}2)_2(SiF_6)]$ to further explore this matter through systematic fine-tuning that is designed to address the effect of the SiF_6^{2-} moieties. We shall also address the origin of the selectivity through modeling studies.

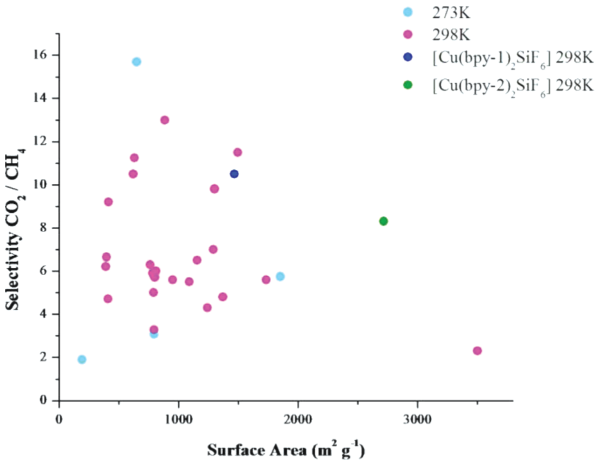

Figure 4. A comparison of CO_2/CH_4 selectivity vs surface area (273 or 298 K, 1 atm) in literature studies vs those obtained herein. The reported points are tabulated and referenced in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, additional gas adsorption isotherms and crystallographic tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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