

# Highly Selective CO<sub>2</sub> Uptake in Uninodal 6-Connected “mmo” Nets Based upon MO<sub>4</sub><sup>2-</sup> (M = Cr, Mo) Pillars

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## Supporting Information

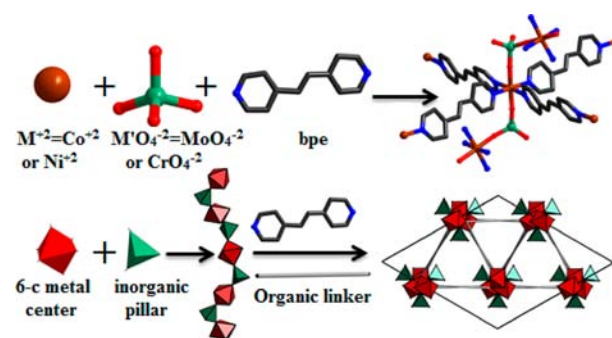
**ABSTRACT:** A novel 4<sup>8</sup>.6<sup>7</sup> topology metal–organic material (MOM) platform of formula [M(bpe)<sub>2</sub>(M'O<sub>4</sub>)] (M = Co or Ni; bpe = 1,2-bis(4-pyridyl)ethene; M' = Mo or Cr) has been synthesized and evaluated in the context of gas sorption. These MOMs have been assigned RCSR code **mmo** and are uninodal 6-connected nets. [Ni(bpe)<sub>2</sub>(MoO<sub>4</sub>)], MOOFOUR-1-Ni, and its chromate analogue, CROFOUR-1-Ni, exhibit high CO<sub>2</sub> affinity and selectivity, especially at low loading. This behavior can be attributed to exceptionally high isosteric heats of adsorption (Q<sub>st</sub>) of CO<sub>2</sub> in MOOFOUR-1-Ni and CROFOUR-1-Ni of ~56 and ~50 kJ/mol, respectively, at zero loading. These results were validated by molecular simulations which indicate that the electrostatics of these inorganic anions affords attractions toward CO<sub>2</sub> that are comparable to those of unsaturated metal centers.

Metal–organic materials (MOMs) are typically comprised from metal ions or metal clusters with three or more points of connection (nodes) and organic ligands or metal clusters that serve as linkers.<sup>1</sup> MOMs have emerged as a class of porous materials with great potential for a wide range of applications, including gas storage,<sup>2</sup> heterogeneous catalysis,<sup>3</sup> drug delivery,<sup>4</sup> magnetism,<sup>5</sup> and conductivity.<sup>6</sup> The drive behind the development of MOMs is their well-defined crystal structure, their extraordinary surface area, and their modular nature, which makes for tunable pore dimensions and surfaces.<sup>7</sup>

In this Communication we report a new variant of a well-established crystal engineering<sup>8</sup> approach for building porous MOMs: pillaring of [M(bpy)<sub>2</sub>] (bpy = 4,4'-pyridine) square grids<sup>9</sup> with inorganic anions.<sup>10</sup> The prototypal nets contain saturated metal centers (SMCs) and exhibit **pcu** topology when anions such as SiF<sub>6</sub><sup>2-</sup> and PF<sub>6</sub><sup>-</sup> serve as linear linkers.<sup>10a,b,11</sup> They represent ideal families or platforms to test the effect of pore size upon gas sorption behavior since the bpy linkers can be expanded (e.g., 1,4-bis(4-pyridyl)benzene)<sup>12</sup> or contracted (e.g., pyrazine)<sup>13</sup> quite readily. Such an approach allows for systematic control of pore size to optimize interactions between the framework and the adsorbent in order to enhance selectivity and/or gas uptake. Other strategies for enhancement of sorbent/sorbate interactions such as unsaturated metal centers (UMCs),<sup>14</sup> basic nitrogen atoms,<sup>15</sup> alkylamine,<sup>16</sup> amide groups,<sup>17</sup> or ion-exchange<sup>18</sup> have been reported. We herein describe a new platform based upon pillaring of [M(bpe)<sub>2</sub>]

square grids by angular MoO<sub>4</sub><sup>2-</sup> or CrO<sub>4</sub><sup>2-</sup> pillars (Scheme 1). Such pillars are underexplored in MOMs. Indeed, there are just

**Scheme 1. Self-Assembly of Octahedral Metal Centers (Red), M'O<sub>4</sub><sup>2-</sup> Moieties (Green), and bpe Ligands Affords Chiral Helices of Metal Centers and M'O<sub>4</sub><sup>2-</sup> Moieties Cross-Linked by bpe Linkers, Thereby Affording a 6-c mmo Net**

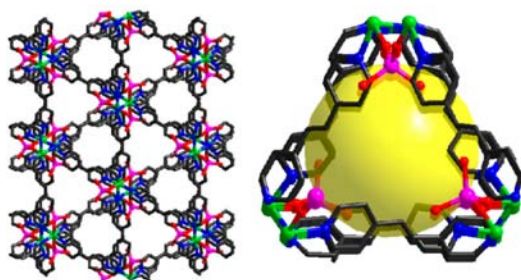


three reports concerning MoO<sub>4</sub><sup>2-</sup> acting as a linker,<sup>19</sup> whereas there are no examples reported for CrO<sub>4</sub><sup>2-</sup>. [M(bpe)<sub>2</sub>(M'O<sub>4</sub>)] (M = Co, Ni; M' = Mo, Cr) have been synthesized, structurally characterized, and evaluated in terms of their sorption behavior with respect to three industrially important gases: CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>.

[M(bpe)<sub>2</sub>(M'O<sub>4</sub>)] (M = Co, Ni; M' = Mo, Cr) were synthesized at room temperature (see Supporting Information) by dissolving CoCl<sub>2</sub> (or NiCl<sub>2</sub>) and Na<sub>2</sub>MoO<sub>4</sub> (or K<sub>2</sub>CrO<sub>7</sub>) in water and layering the resulting solution under bpe in water/acetonitrile. Single crystals of [Co(bpe)<sub>2</sub>MoO<sub>4</sub>] (MOOFOUR-1-Co), [Ni(bpe)<sub>2</sub>MoO<sub>4</sub>] (MOOFOUR-1-Ni), [Co(bpe)<sub>2</sub>CrO<sub>4</sub>] (CROFOUR-1-Co), and [Ni(bpe)<sub>2</sub>CrO<sub>4</sub>] (CROFOUR-1-Ni) were thereby afforded. Crystal structures were determined by single-crystal X-ray diffraction (Supporting Information), which revealed that all four compounds crystallize in the chiral space group R32 with one formula unit per unit cell. The six-coordinated metal centers serve as 6-connected (6-c) nodes, and only two of the four oxygen atoms of each M'O<sub>4</sub> linker are coordinated; the remaining oxygen atoms are oriented toward the interior of one-dimensional channels along [001] (Figure 1). To our knowledge, these nets

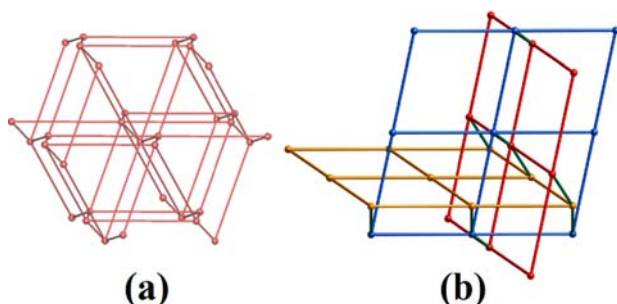
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**Figure 1.** Single-crystal X-ray structure of MOOFOUR-1-Ni viewed along [001], H atoms omitted for clarity (left). View of the cavity of MOOFOUR-1-Ni (right).

represent the first examples of 6-c 4<sup>8</sup>.6<sup>7</sup> topology nets,<sup>20</sup> and the symbol **mno** has been assigned by RCSR<sup>21</sup> (Figure 2). The

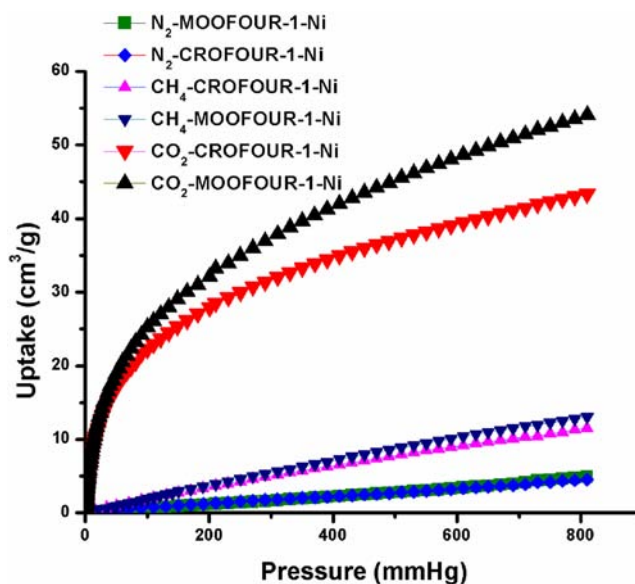


**Figure 2.** (a) Topological representation of the **mno** nets reported herein. (b) Three self-catenated square grids (red, blue, and yellow) are connected with  $M'O_4^{2-}$  pillars (green).

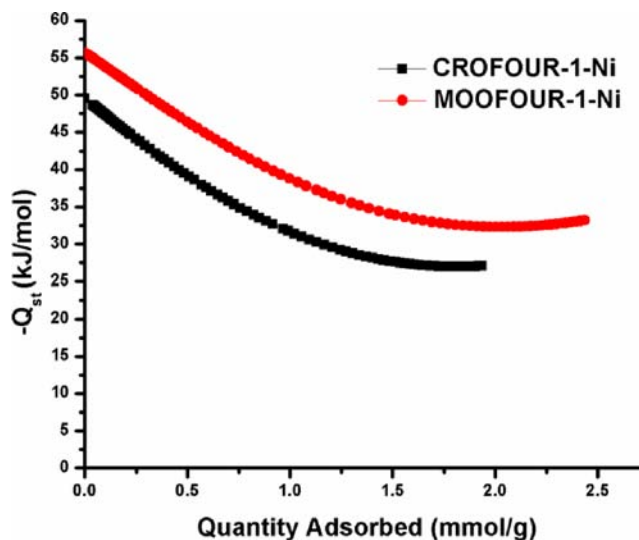
tetrahedral  $M'O_4$  pillars play a key role in directing the **mno** topology as they pillar the square grids in angular fashion ( $112^\circ$ ), resulting in self-catenation<sup>1d,22</sup> of square grid nets and a helix of alternating 6-c SMCs and  $M'O_4$  pillars along [001] (Scheme 1). This platform represents a new heterometallic class of MOMs that complements those reported recently through an approach based upon heterometallic clusters.<sup>23</sup>

The affinity of anions such as  $SiF_6^{2-}$  and  $PF_6^-$  toward  $CO_2$ <sup>24,25</sup> prompted us to evaluate the gas sorption properties of MOOFOUR-1-Ni and CROFOUR-1-Ni. Permanent porosity was confirmed via  $CO_2$  adsorption measurements at 195 K, and Langmuir surface areas of 456 and 505  $m^2/g$  were determined for MOOFOUR-1-Ni and CROFOUR-1-Ni, respectively (Supporting Information).  $CO_2$ ,  $CH_4$ , and  $N_2$  adsorption isotherms were measured at 298 K and reveal high affinity toward  $CO_2$ , as exemplified by the steep  $CO_2$  uptakes in the low-pressure regions compared to  $CH_4$  and  $N_2$  (Figure 3). The  $CO_2$  uptake of MOOFOUR-1-Ni at 1 atm is 55  $cm^3/g$ , whereas that of CROFOUR-1-Ni is 43  $cm^3/g$ . The  $CH_4$  and  $N_2$  uptakes for MOOFOUR-1-Ni and CROFOUR-1-Ni are 11.5 and 4.5  $cm^3/g$ , and 13 and 4  $cm^3/g$ , respectively. MOOFOUR-1-Ni therefore outperforms CROFOUR-1-Ni despite its higher density, which, given that this is an “apples-to-apple” comparison, suggests that  $MoO_4^{2-}$  exhibits a stronger binding affinity for  $CO_2$  than  $CrO_4^{2-}$ .

In order to rationalize these observations, the isosteric heat of adsorption ( $Q_{st}$ ) of  $CO_2$  for both structures was calculated using adsorption data at 273, 283, and 298 K according to the virial equation (see Supporting Information). Figure 4 reveals that the  $Q_{st}$  of MOOFOUR-1-Ni is at least 5  $kJ/mol$  greater than that of CROFOUR-1-Ni across all loadings. The  $Q_{st}$  values



**Figure 3.** Reversible single-component gas adsorption isotherms for MOOFOUR-1-Ni and CROFOUR-1-Ni measured at 298 K.



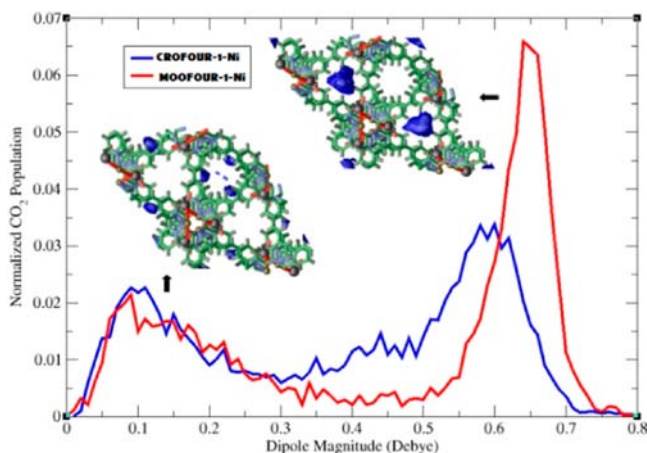
**Figure 4.**  $CO_2$  isosteric heats of adsorption ( $Q_{st}$ ) of CROFOUR-1-Ni and MOOFOUR-1-Ni.

of MOOFOUR-1-Ni and CROFOUR-1-Ni are  $\sim 56$  and  $\sim 50$   $kJ/mol$ , respectively, at zero loading, although they decrease to  $\sim 33$  and  $\sim 27$   $kJ/mol$ , respectively, at 1 atm. To put this in perspective, both compounds exhibit higher  $Q_{st}$  values at low loading than MOMs with UMCs such as HKUST-1,<sup>26</sup> MIL-53 (Al),<sup>27</sup> Mg-MOF-74,<sup>28</sup> Co-MOF-74,<sup>28</sup> and Ni-MOF-74,<sup>28</sup> which exhibit values of 30, 35, 47, 37, and 41  $kJ/mol$ , respectively. They also surpass  $NaY^{29}$  (36  $kJ/mol$ ), zeolite 13X<sup>30</sup> (40  $kJ/mol$ ), and a number of MOFs with amine-group ligands (35–45  $kJ/mol$ ).<sup>31,32</sup> A value of 45  $kJ/mol$  has been reported for a MOM in which phosphonate monoester linkers afford confined space.<sup>33</sup>

$Q_{st}$  values of  $>40$   $kJ/mol$  would be expected to afford high selectivity for  $CO_2$  vs  $CH_4$  and  $N_2$ .  $CO_2/CH_4$  molar selectivity for a 50:50 mixture was calculated by IAST to be 182 and 170 for MOOFOUR-1-Ni and CROFOUR-1-Ni, respectively, at zero coverage. The corresponding values at 1 atm were found to be 40 and 25. The  $CO_2/N_2$  selectivity for a 10:90 mixture,

which represents a typical composition for flue gas from power plants, was 1820 and 1240 for MOOFOUR-1-Ni and CROFOUR-1-Ni, respectively, at zero loading. These values decrease to 86 and 195 at 1 atm (Supporting Information). Whereas there are MOMs that exhibit a higher uptake capacity for CO<sub>2</sub>, we are unaware of any that exhibit such high selectivity at low loading. We also calculated the CO<sub>2</sub>/N<sub>2</sub> gravimetric selectivity in the context of post-combustion CO<sub>2</sub> capture by determining wt% at 0.15 and 0.75 bar for CO<sub>2</sub> and N<sub>2</sub>, respectively, at ambient temperature.<sup>2c</sup> The wt% of CO<sub>2</sub> at 0.15 bar in MOOFOUR-1-Ni and CROFOUR-1-Ni was 5.2% and 4.6%, respectively, whereas for N<sub>2</sub> at 0.75 bar values were found to be 0.39% and 0.37%, respectively. Therefore, the selectivity of CO<sub>2</sub> over N<sub>2</sub> in MOOFOUR-1-Ni and CROFOUR-1-Ni under these conditions was found to be 67 and 62. These values exceed those of most MOMs that contain UMCs, including Mg-MOF-74(44 at 303 k)<sup>34</sup> and amine-grafted MOMs.<sup>16a</sup>

The high affinity and selectivity toward CO<sub>2</sub> exhibited by MOOFOUR-1-Ni and CROFOUR-1-Ni was addressed through molecular simulations involving explicit polarization for CO<sub>2</sub> adsorption in CROFOUR-1-Ni and MOOFOUR-1-Ni to identify the most favorable sorption sites. Similar assessments have been performed for H<sub>2</sub> adsorption in MOMs.<sup>35,36</sup> Examination of the distribution of induced dipoles for CO<sub>2</sub> molecules in CROFOUR-1-Ni and MOOFOUR-1-Ni revealed two distinct regions of occupancy inside the MOMs. Figure 5



**Figure 5.** Normalized CO<sub>2</sub> dipole distribution in CROFOUR-1-Ni (blue) and MOOFOUR-1-Ni (red) at 298 K and 0.10 atm produced from simulation. The three-dimensional histograms showing the primary and secondary sites of CO<sub>2</sub> sorption (blue) are presented. Atom colors: green, C; white, H; red, O; black, Cr or Mo.

presents a plot of the CO<sub>2</sub> dipole magnitudes against the normalized CO<sub>2</sub> population in both compounds. In MOOFOUR-1-Ni, the peak from 0.60 to 0.70 D corresponds to the primary sorption site that is located within the region where three pairs of terminal oxygen atoms extend from their respective metal ions. This is the energetically favorable site to which the CO<sub>2</sub> molecules bind at initial loading. The primary sorption site for CROFOUR-1-Ni is similar, although the magnitudes of the dipoles are slightly lower, ranging from 0.55 to 0.65 D.

The simulations therefore indicate that MOOFOUR-1-Ni induces higher dipoles on the CO<sub>2</sub> molecules upon adsorption, presumably due to the higher polarizability of Mo<sup>VI</sup> cations. In

addition, a larger peak is seen for MOOFOUR-1-Ni relative to CROFOUR-1-Ni, indicating higher occupancy of CO<sub>2</sub> molecules onto this primary sorption site. For both compounds, a peak from 0.05 to 0.20 D is also observed, corresponding to a secondary sorption site located within the channel next to the primary sorption site. Specifically, CO<sub>2</sub> molecules bind to the region where two different terminal oxygen atoms from their respective ions form an apex within the channel. The geometries of the adsorbed carbon dioxide molecules (sites I and II) with respect to the MOOFOUR-1-Ni host structure are shown in Supporting Information.

We addressed the stability of MOOFOUR-1-Ni and CROFOUR-1-Ni by confirming that as-prepared samples retain crystallinity even when immersed in water for months, boiling water for one day, or 0.1 N NaOH for a week (Supporting Information). Samples also retain their porosity after activation and being exposed to the atmosphere.

In conclusion, we have synthesized a new class of porous MOM platforms based upon SMCs and MoO<sub>4</sub><sup>2-</sup> or CrO<sub>4</sub><sup>2-</sup> as inorganic anion pillars. They exhibit a novel 6-c uninodal topology, **mmo**, which facilitates evaluation of MoO<sub>4</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup> in terms of their effect upon gas sorption. MOOFOUR-1-Ni and CROFOUR-1-Ni were found to exhibit exceptional Q<sub>st</sub> and highly selective adsorption for CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub>, and we ascribe this behavior to strong quadrupole–quadrupole interactions between CO<sub>2</sub> and MoO<sub>4</sub><sup>2-</sup> (MOOFOUR-1-Ni) and CrO<sub>4</sub><sup>2-</sup> (CROFOUR-1-Ni) binding sites. These inexpensive, facile to synthesize, and robust CO<sub>2</sub> adsorbents outperform many other MOMs, even these with UMCs or amine-functionalized MOMs. Future work will focus upon systematic evaluation of the effect of pore size control on the adsorption behavior of MoO<sub>4</sub><sup>2-</sup>- and CrO<sub>4</sub><sup>2-</sup>-based **mmo** topology MOMs. We will also address the use of other inorganic anions as linkers/pillars in order to evaluate their effect upon gas adsorption.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

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

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<sup>§</sup>M.H.M. and S.K.E. contributed equally.

### Notes

The authors declare no competing financial interest.

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