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Systematic and Dramatic Tuning on Gas Sorption Performance in Heterometallic Metal–Organic Frameworks

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Supporting Information

ABSTRACT: Despite their having much greater potential for compositional and structural diversity, heterometallic metal–organic frameworks (MOFs) reported so far have lagged far behind their homometallic counterparts in terms of CO_2 uptake performance. Now the power of heterometallic MOFs is in full display, as shown by a series of new materials (denoted CPM-200s) with superior CO_2 uptake capacity (up to 207.6 cm^3/g at 273 K and 1 bar), close to the all-time record set by MOF-74-Mg. The isosteric heat of adsorption can also be tuned from −16.4 kJ/mol for CPM-200-Sc/Mg to −79.6 kJ/mol for CPM-200-V/Mg. The latter value is the highest reported for MOFs with Lewis acid sites. Some members of the CPM-200s family consist of combinations of metal ions (e.g., Mg/Ga, Mg/Fe, Mg/V, Mg/Sc) that have never been shown to coexist in any known crystalline porous materials. Such previously unseen combinations become reality through a cooperative crystallization process, which leads to the most intimate form of integration between even highly dissimilar metals, such as Mg^{2+} and V^{3+}. The synergistic effects of heterometals bestow CPM-200s with the highest CO_2 uptake capacity among known heterometallic MOFs and place them in striking distance of the all-time CO_2 uptake record.

Metal–organic framework (MOF) materials[1,2] are predominantly based on transition metals, and there are comparatively much fewer MOFs based on main-group elements. Despite such great disparity statistically favoring transition-metal MOFs, it is the magnesium form of MOF-74 (MOF-74-Mg) that exhibits the highest CO_2 uptake capacity (228 cm^3/g at 273 K, 180 cm^3/g at 298 K and 1 atm),[3] outshining its transition metal analogues such as MOF-74-Co and MOF-74-Ni and highlighting the unique significance of main-group metals in the design of high-performance gas sorption materials.

Advances with Mg-MOFs, in terms of gas sorption performance, stalled following the original discovery of MOF-74-Mg in 2008,[3a] as further exploration has yielded no new Mg-MOFs with CO_2 uptake capacity anywhere near that of MOF-74-Mg, casting doubts over the important role of main-group elements (Mg in particular) in MOF design. Given literature data illustrating respective advantages and disadvantages of different metals, we envisage a new family of high-performance materials that might be developed by some form of integration between different metals. This concept of heterometallic MOFs is by no means new, and the challenge is how to deal with the infinite possibilities, and more so the perceived impossibilities, of combining metals to create high-performance materials. Prior to this work, there were few, if any, high-performance CO_2 capture materials based on heterometallic MOFs.

We are particularly interested in the integration of chemically dissimilar metals, as such combinations are more likely to lead to much greater variations in properties. Heterometallic MOFs containing similar metals (e.g., many combinations of 3d metals, any combination of 4f metals) are not uncommon. In addition, a number of heterometallic MOFs containing dissimilar metals (e.g., In and Co) have also been reported.[4] In general, dissimilar metals play distinct structural roles, as determined by their differing coordination properties such as radii, coordination geometry, and preference for donor atoms according to chemical hardness or softness. In most cases, dissimilar heterometals are separated by organic ligands, making them behave structurally in much the same way as in homometallic MOFs.[5]

Synergy between heterometals would most likely occur through the most intimate form of integration. In this work, we focus on a special family of heterometallic MOFs that are more difficult to prepare because they consist of dissimilar metal ions (e.g., Mg^{2+} and V^{3+}, or Ni^{2+} and In^{3+}) occupying crystallographically equivalent sites and exhibiting indistinguishable structural roles. Such an intimate form of integration between dissimilar metals allows both fine and dramatic tuning of their properties across a large range and all within the same framework type, which provides an unprecedented opportunity to probe the role of each metal type in the performance of new materials. For example, in this work, thanks to the diverse metal combinations in the same MOF framework, we demonstrate for the first time the observation of a strong correlation between isosteric heat for CO_2 and the charge-to-radius ratio (z/r) of metal ions in MOFs.

It is not easy to integrate dissimilar metals in the same structural units. In fact, prior to this work, some metal combinations (such as Ga/Mg, Fe/Mg, V/Mg, and Sc/Mg reported here) have never been observed in any crystalline porous material. In fact, a grand challenge in materials design is to bring together chemical elements previously unknown to coexist. This is particularly true for crystalline materials prepared from low-temperature processes such as solution-based crystal growth, in which there is a great tendency for macroscopic phase separation. Some metal combinations reported are so unusual and unprecedented that we, ourselves, considered them highly unlikely prior to this study.

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The synergistic effect of heterometals extends beyond structural, physical, and chemical properties in crystals, and it turned out that there is an unusual synergistic effect at the very beginning when two metals are brought together. In fact, the synergy during crystallization of CPM-200 is so essential that corresponding homometallic MOFs could not be made under the same conditions in the absence of any one of two metal sources.

We have systematically explored various metal combinations by focusing on the role of main-group elements. In addition, to study the effects of two main-group elements on Mg in Mg−Ga and Mg−In MOFs, Mg from the s-block and In from the p-block are used as the main-group elements for integration with transition metals, resulting in six more combinations (Mg with Sc, V, and Fe; In with Mn, Co, and Ni). Our method is quite general and is certainly capable of overcoming chemical dissimilarity.

Here, eight combinations between trivalent metals (M^{3+} = In^{3+}, Ga^{3+}, Fe^{3+}, V^{3+}, Sc^{3+}) and divalent metals (M^{2+} = Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) were achieved for trimeric $[M^{II}_2M^{III}(\mu_3\text{-OH})(CO_2)_6]$ clusters (Figure 1), leading to a series of MOFs (denoted here as

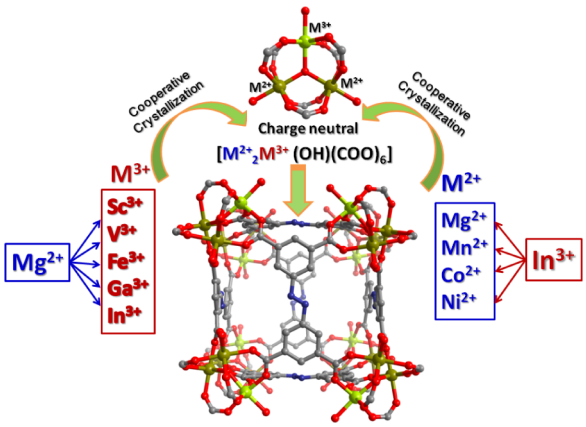

Figure 1. M^{2+} and M^{3+} combinations for CPM-200s in this work.

CPM-200-In/Mg, -In/Ni, -In/Co, -In/Mn, -Ga/Mg, -Fe/Mg, -V/Mg, and -Sc/Mg, where CPM = crystalline porous materials). Impressively, the CO_2 uptakes of CPM-200-Fe/Mg and CPM-200-In/Mg at 273 K and 1 bar reach 207.6 $cm^3\ g^{-1}$ (9.27 mmol/g) and 190.8 $cm^3\ g^{-1}$ (8.52 mmol/g), which surpass the values of all reported MOFs based on $[M_3(\mu_3\text{-O/OH})(CO_2)_6]$ and are also the highest among heterometallic MOFs. CPM-200-Fe/Mg is among the top four highest CO_2 uptake MOFs under the same conditions. For MOFs made with ligands with −4 (or less negative), CPM-200-Fe/Mg is only behind MOF-74-Mg.

A systematic search for a suitable cooperative crystallization condition is crucially important for the development of CPM-200s. For chemically dissimilar metals such as Mg^{2+} and V^{3+}, the rates of hydrolysis and condensation (olation for M-OH-M formation or oxolation for M-O-M formation) of each metal ion can differ greatly, negating any chance of cocrystallization. To achieve the matching kinetics for chemically dissimilar metal ions, we focused on the types of metal precursors, as well as types of and ratios between solvents and cosolvents. In this work, we first chose In^{3+} and Mg^{2+} to search for conditions capable of inducing cocrystallization of heterometals, because of our prior experience with In-MOFs[6] and Mg-MOFs[7] and because some metals such as V^{3+} and Ga^{3+} are known to be difficult to crystallize into MOFs. Numerous experiments led to the finding that the combination of $InCl_3$ and $Mg(OAc)_2$ in DMA/H_2O (mass ratio = 5/1) is optimal for the formation of pure CPM-200-In/Mg single crystals (see Supporting Information). A different DMA/water ratio gives a mixture of unknown yellow powder and cubic crystals, while $In(NO_3)_3$ or $Mg(NO_3)_2$ also gives yellow powder. Despite the essential role of $InCl_3$ for making CPM-200-In/Mg, $InCl_3$ itself fails to give the homometallic analogue, CPM-200-In. The use of only $Mg(OAc)_2$ was equally fruitless. Extension of the In^{3+}/Mg^{2+} cooperative crystallization method allows other members of the CPM-200s family to be made. It is worth emphasizing that the crystallization of homonuclear MOFs with only one metal source (Ga^{3+}, Fe^{3+}, V^{3+}, and Sc^{3+}, or Mn^{2+}, Co^{2+}, and Ni^{2+}) under the same reaction conditions was unsuccessful. All these demonstrate the importance of the cooperative crystallization.

Crystal structures of CPM-200-In/Mg, -In/Ni, -In/Co, -In/Mn, -Ga/Mg, and -V/Mg were determined by single-crystal X-ray diffraction (Tables S1−S3). The phase purity of all bulk samples was confirmed by powder X-ray diffraction (PXRD) (Figure S3). Due to the large difference in X-ray scattering factors, the M^{2+}-to-M^{3+} ratio (2:1) could be determined by site occupancy refinement and further supported by EDS analysis (Figures S5 and S6). CPM-200s exhibit the soc-type framework topology (Figure S1), originally reported for an In-MOF with a cationic framework.[8] Heterometallic CPM-200s have a neutral framework due to the mixed M^{2+}/M^{3+}. Formation of the charge-neutral framework by taking advantage of the heterometallic cooperative crystallization process is quite general and can be applied to other trimer-based homonuclear MOFs as well.

To probe the effect of metal types on gas sorption properties, all as-synthesized CPM-200 samples were activated by immersion in CH_3OH for 3 days, followed by evacuation at 80 °C for 12 h. The high framework stability was evident, as shown by the TGA results (Figure S4) and PXRD patterns (Figure S3). The N_2 sorption isotherms of activated CPM-200s at 77 K all exhibit typical type I behavior (Figures 2 and S7−S17). Their Langmuir and BET surface areas vary from 1216 to 2024 and 877 to 1459 cm^3/g, respectively. In comparison, CPM-200-In with the cationic framework has Langmuir and BET surface areas of 1244 and 888 cm^3/g, respectively.

At 273 K and 1 bar, the CO_2 uptakes by CPM-200s, in $cm^3\ g^{-1}$ (mmol/g), are 207.6 (9.27) for the Fe/Mg form, 190.8 (8.52) for In/Mg, 155.4 (6.94) for V/Mg, 136.9 (6.11) for In/Co, 136.2 (6.08) for Ga/Mg, 126.5 (5.65) for In/Mn, 122.4 (5.46) for Sc/Mg, and 100.4 (4.48) for In/Ni (Figures S7−S17 and Table S4). All these CO_2 uptake values are impressive (Table S5). Even considering all MOFs, only Mg-MOF-74 (10.2 mmol/g),[2b] Cu-TDPAT (10.1 mmol/g),[9] and Cu-TPBTM (9.7 mmol/g)[10] have higher CO_2 uptake performance than CPM-200-Fe/Mg under the same conditions.

At 298 K and 1 bar, the CO_2 uptakes by CPM-200s, in $cm^3\ g^{-1}$, are 127.3 (Fe/Mg), 113.7 (In/Mg), 80.4 (V/Mg), 79.2 (Ga/Mg), 77.6 (In/Co), 72.7 (In/Mn), 61.5 (In/Ni), and 61.4 (Sc/Mg) (Figures S7−S17 and Table S4). At these conditions, the CO_2 uptake value of CPM-200-Fe/Mg is comparable to those of CPM-33b (126.4),[11] PCN-88 (123.2),[12] and SIFSIX-2-Cu-i (121.2)[13] and much higher than those of some well-known MOFs, including HKUST-1 (108.9),[14] en-Mg_2(dobpdc) (102.4),[15] MAF-66 (98.8),[16] and bio-MOF-11 (91.8).[17]

For comparison, the CO_2 uptake of homometallic CPM-200-In was also studied. It absorbs 109.6 cm^3/g (4.9 mmol/g) at 273 K and 61.7 cm^3/g (2.8 mmol/g) at 298 K and 1 bar. Clearly, introduction of M^{2+} (Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) dramatically tunes the CO_2 uptake performance. In particular, it was observed that there is an increase in CO_2 uptake for CPM-200 with increasing

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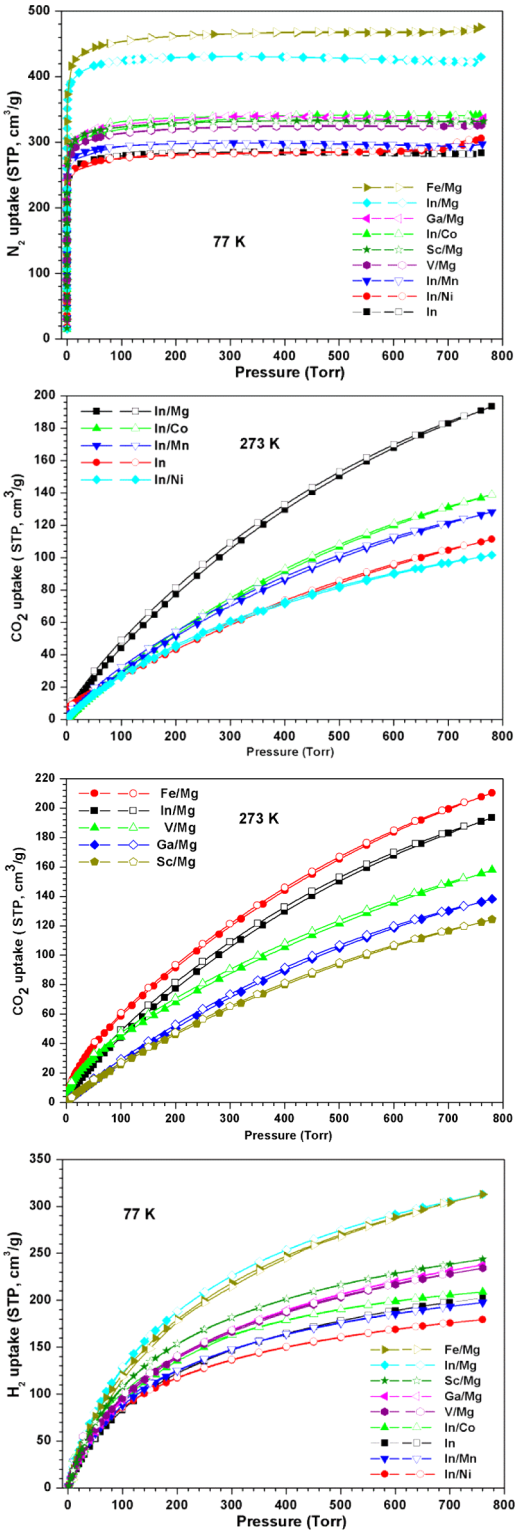

Figure 2. N_2, CO_2, and H_2 sorption study on CPM-200s.

Mg/In ratios (Figure S12), likely due to the increasing concentration of open Mg^{2+} sites. Changes in the framework charge and concentration of charge-balancing anions should also influence the gas uptake due to variations in electrostatic interactions and pore volume.

When In^{3+} was fixed, the CO_2 uptakes of CPM-200-In/M^{II} followed the order Mg > Co > Mn > Ni (Figure 2), similar to that of MOF-74 with different metals.[2a] When Mg^{2+} was fixed, CO_2 uptakes of CPM-200-M^{III}/Mg followed the order Fe > In > V > Ga > Sc (Figure 2). In addition to the influence of molecular mass, the CO_2 adsorption performance may be attributed to the interactions between CO_2 and open metal sites.

To further understand CO_2 adsorption properties of CPM-200s, the isosteric heat of adsorption (Q_{st}) for CO_2 was determined by fitting adsorption data collected at 273 and 298 K to the virial model (Figures S18–S20). At zero loading, indicative of the interaction of CO_2 with open metal sites, Q_{st}^0 (in kJ/mol) was determined to be −28.5 (In/Ni), −25.0 (In/Co), −27.3 (In/Mn), −29.3 (In/Mg), −19.7 (Ga/Mg), −34.3 (Fe/Mg), −79.6 (V/Mg), and −16.4 (Sc/Mg) (Figure 3).

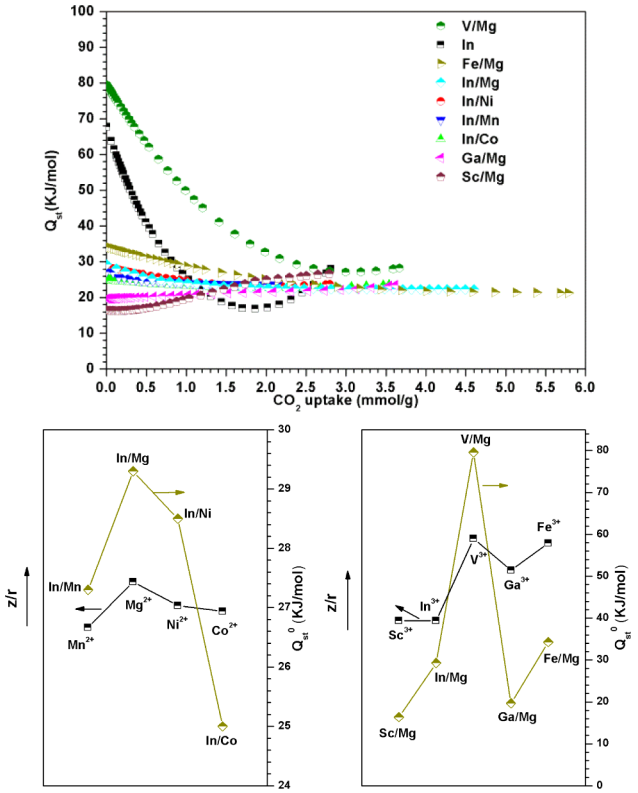

Figure 3. Top: Isosteric heat for CO_2 for CPM-200s. Bottom: Correlation between isosteric heat at zero loading of CO_2 (Q_{st}^0) and charge-to-radius ratio (z/r) of metal ions for CPM-200s.

Notably, the isosteric heat for CPM-200-V/Mg (−79.6 kJ/mol) is higher than those of all reported MOFs containing open metal sites, and only lower than those of Cu-BTTri-mmen (−96 kJ/mol)[18] and Cu-BTTri-en (−90 kJ/mol)[19] with amines entrapped as Lewis base sites. This extremely high isosteric heat value is likely due to the additional contribution from vanadium ions, which may have significant π back-bonding. Based on such π back-bonding induced high interaction energies, hypothetical V-MOF-74 has been predicted to be the best MOF for N_2/CH_4 separation.[20] Here, the V^{3+}/Mg^{2+} cooperative crystallization strategy may open up a new route for the development of V-MOFs. It is worth noting that CPM-200-In also exhibits a high Q_{st}^0 for CO_2 (−67.8 kJ/mol), likely due to the charged framework.

The Q_{st}^0 sequence matches well with the order of initial CO_2 uptake values at very low pressure (<5 Torr) (Figure S21), which indicates the contribution of open metal sites. To further understand the roles of metal ions, we examined their z/r,

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which is an important indication of electrostatic contribution to the bond energy and is related to the role of open metal sites on gas sorption properties. So far, no systematic correlation between z/r and Q_{st}^0 has been observed for MOFs. Here, with the availability of a series of heterometallic MOFs, for the first time, we are able to clearly observe a strong correlation between z/r and the isosteric heat for CO_2 (Figure 3).

The sorption properties of three fuel molecules (i.e., H_2, C_2H_2, and CH_4) were also studied. At 77 K and 1 bar, CPM-200-Fe/Mg and -In/Mg both adsorb 2.8 wt% H_2 (Figure 2), while values for other CPM-200s range from 1.6 to 2.2 wt% H_2 (Table S4). At 1 bar, the uptake capacity of CPM-200-Fe/Mg for C_2H_2 and CH_4 reaches 217.2 and 39.5 cm^3/g, respectively, at 273 K and 160.8 and 23.5 cm^3/g at 298 K. Other CPM-200s also show superior sorption performance for C_2H_2 at 273 K (Table S4).

CPM-200s show negligible N_2 uptake performance at 273 K (Figure S22). To predict CO_2−N_2 binary mixture selectivity, an ideal adsorbed solution theory calculation based on a dual-site Langmuir−Freundlich simulation was employed, based on single-component CO_2 and N_2 adsorption isotherms. Figure S22 shows the adsorption selectivity of five members of CPM-200s for CO_2 (50%) and N_2 (50%) at 273 K. The selectivity values vary from 406 (V/Mg), 201 (Fe/Mg), 48 (In/Mg), 33 (In/Co), to 24 (Ga/Mg), which are higher than those of many other MOFs.[1g,21] Since the order matches well with the Q_{st}^0 sequence, such tunable CO_2 selectivity over N_2 could be attributed to the different interactions between gas molecules and open metal sites.

In summary, a family of heterometallic MOFs (CPM-200 series) with systematic and unprecedented combinations of trivalent (In^{3+}, Ga^{3+}, Fe^{3+}, V^{3+}, Sc^{3+}) and divalent metals (Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) has been achieved. Even metal ions difficult in MOF synthesis (e.g., Ga^{3+}, V^{3+}) succumb to this cooperative crystallization strategy and become MOF-friendly. Significantly, CPM-200-Fe/Mg can adsorb CO_2, 9.27 mmol/g at 273 K and 1 bar, which outperforms all trimer-based as well as all heterometallic MOFs. It is among the top four highest CO_2 uptake MOFs under the same conditions. The isosteric heat of adsorption for CO_2 binding in CPM-200-V/Mg, −79.6 kJ/mol, is the highest reported for MOFs with Lewis acid sites. Finally, with various combinations of metal ions in the same MOF platform, a strong correlation between charge-to-radius ratio of metal cations and isosteric heat for CO_2 has been established for the first time in MOFs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13491.

Experimental details, Figures S1−S22, and Tables S1−S5 (PDF)

X-ray crystallographic data for six CPM-200s (CCDC 1444374−1444379) (CIF)

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Notes

The authors declare no competing financial interest.

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