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Metal–Organic Frameworks |Hot Paper|

Ligand and Metal Effects on the Stability and Adsorption Properties of an Isoreticular Series of MOFs Based on T-Shaped Ligands and Paddle-Wheel Secondary Building Units

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Abstract: The synthesis of stable porous materials with appropriate pore size and shape for desired applications remains challenging. In this work a combined experimental/ computational approach has been undertaken to tune the stability under various conditions and the adsorption behavior of a series of MOFs by subtle control of both the nature of the metal center (Co^{2+} , Cu^{2+} , and Zn^{2+}) and the pore surface by the functionalization of the organic linkers with amido and *N*-oxide groups. In this context, six isoreticular MOFs based on T-shaped ligands and paddle-wheel units

with $ScD_{0.33}$ topology have been synthesized. Their stabilities have been systematically investigated along with their ability to adsorb a wide range of gases (N₂, CO₂, CH₄, CO, H₂, light hydrocarbons (C₁–C₄)) and vapors (alcohols and water). This study has revealed that the MOF frameworks based on Cu²⁺ are more stable than their Co²⁺ and Zn²⁺ analogues, and that the *N*-oxide ligand endows the MOFs with a higher affinity for CO₂ leading to excellent selectivity for this gas over other species.

Introduction

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are the most recent emerging class of porous materials with an unprecedented richness in terms of structure and chemical composition,^[1] which makes them good candidates for applications in the areas of, for example, gas adsorption and separation,^[2] catalysis,^[3] and sensors.^[4,5] More than 20000 different MOFs have been discovered so far, and their properties with respect to diverse applications intensively explored.^[6–11] In comparison with metal oxides, porous carbons,

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zeolites, silica, and heteropolyanion salts,^[12] MOFs usually show limited thermal, mechanical, and chemical stability, which hampers their use in industrial applications.^[13,14] This drawback has motivated numerous investigations aimed at the development of novel, robust MOFs under harsh conditions. One strategy is to use high-valence metals focusing on 3p (e.g., Al^{3+} , Ga^{3+} , and In^{3+}) or transition-metal cations (e.g., Fe^{3+} , Cr^{3+} , Sc^{3+} , Zr^+ , and Ti^{4+}), but not lanthanides, actinides or POM MOFs (POM = poly(oxometallate)).^[15] However, such stable MOFs based on high-valence metals are often poorly crystallized, presumably due to the kinetic inertness of the metal–ligand bonds.^[16-23]

Another approach is to combine multi-topic carboxylate ligands with divalent transitional-metal clusters of Zn^{2+} , Ni^{2+} , Co^{2+} , or $Cu^{2+[24-26]}$ to form well-crystallized MOFs that can be produced in high yields. Therefore, there is great interest in discovering novel divalent-based MOFs and to characterize their thermal/chemical stability as well as their adsorption properties.^[13,27]

In this work we aimed to investigate the stability and gas adsorption properties of two series of isoreticular MOFs based on divalent metal ions (Co^{2+} , Cu^{2+} , and Zn^{2+}) and two comparable T-shaped^[28-32] bipolar ligands.^[33] The two ligands each have two carboxylic coordination donors but differ in their third coordination donor; one is pyridine and the other is pyridine *N*-oxide (Scheme 1). Different combinations of the metal ions and ligands would produce six isoreticular MOFs, thereby facilitating a comparative evaluation of the impact of the metal and ligand on the stability and adsorption/separation

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Scheme 1. (a) Molecular structure of the H₂INIA ligand showing coordinating sites and functional groups, (b,c) the two primary types of cavities viewed along the *b* axis, (d) molecular structure of the H₂INOIA ligand showing coordinating sites and functional groups, (e) isoreticular framework in LIFM-10(M) and LIFM-11(M) showing the 1D channel along the *c* axis, and (f) representation of the pore surface. All hydrogen atoms have been omitted for clarity.

properties of the MOFs. As shown in Scheme 1, the first T-shaped ligand, 4-pyridylaminocarbonyl (H₂INIA), contains two carboxylate groups and a pyridine function as coordinating sites as well as an amido group that can potentially act as the site of interaction for guest molecules. Further functionalization of H₂INIA by nitrogen oxidation led to the second ligand, 1-oxidopyridin-1-ium-4ylaminocarbonyl (H₂INOIA), that is, the introduction of a charge-separated group as the open donor site (ODS) for modification of the metal–ligand interaction and the pore features. As previously reported, the solvothermal reaction of Cu²⁺ with H₂INIA and H₂INOIA affords two isoreticular Cu-MOFs, LIFM-10(Cu) and LIFM-11(Cu).^[34] By using Co²⁺ and Zn²⁺ in this reaction, we have developed to two series of isoreticular MOFs, namely LIFM-10(M) and LIFM-11(M) (M=Co, Cu, and Zn).

Results and Discussion

Crystal structure

The six MOFs were structurally characterized by single-crystal X-ray diffraction analyses (Tables 1 and S1 in the Supporting Information), which confirmed that all the solids show a isoreticular framework and porosity. It is well established that the assembly of T-shaped ligands with paddle-wheel secondary building units (SBUs) by a ligand-to-axial approach can lead to the formation of 3D MOFs of *rtl* or ScD_{0.33} topology based on the pillaring of the 2D edge transitive nets sql and kgm, respectively.^[34,35] If the M₂(O₂CR)₄ clusters are viewed as 6-connecting nodes and the T-shaped ligands serve as 3-connecting nodes, the six MOFs can be described by the same (3,6)-connected framework of ScD_{0.33} topology consisting of three different metal centers (Co^{2+} , Cu^{2+} , and Zn^{2+}) and two different ligands with similar coordination behavior but slightly different coordination donors (Scheme 1). All six MOFs exhibit considerable void space, possessing 1D hourglass-shaped channels aligned alternately in parallel along the *c* axis (Scheme 1b,c). Calculations performed by using PLATON^[36] with a N₂ probe molecule with a kinetic diameter of 3.6 Å indicated that the contact surface area is 49.1% for LIFM-10(Co), 44.4% for LIFM-10(Cu), 47.3% for LIFM-10(Zn), 45.1% for LIFM-11(Co), 46.8% for LIFM-11(Cu), and 43.7% for LIFM-11(Zn).

As shown in Figure 1, the two LIFM-10(M) and LIFM-11(M) MOF series contain similar $M_2(COO)_4$ clusters as SBUs, however, the H_2INIA and H_2INOIA ligands are linked to these SBUs in a distinct manner at the axial positions. The coordination geometries of the metals in the paddle-wheel SBUs can be regarded as square pyramidal with the metal centers slightly offset from the equatorial plane. Although the pyridine group is nearly perpendicular (a slope of ca. 11°, the angle is defined as the angle between a line through the metal center to the

| Table 1. Crystallographic data for LIFM-10(Co, Cu, Zn) and LIFM-(Co, Cu, Zn). | | | | | | | |
|---|--|---------------------|---------------------|---------------------|---------------------|---------------------|--|
| | LIFM-10(Co) | LIFM-10(Cu) | LIFM-10(Zn) | LIFM-11(Co) | LIFM-11(Cu) | LIFM-11(Zn) | |
| formula | C ₁₄ H ₈ CoN ₂ O ₅ | $C_{14}H_8CuN_2O_5$ | $C_{14}H_8N_2O_5Zn$ | $C_{14}H_8CoN_2O_6$ | $C_{14}H_8CuN_2O_6$ | $C_{14}H_8N_2O_6Zn$ | |
| <i>M</i> _r | 343.15 | 347.76 | 349.59 | 359.15 | 363.76 | 365.59 | |
| <i>T</i> [K] | 150.15 | 150(2) | 293(2) | 150(2) | 173(2) | 173(2) | |
| crystal system | trigonal | trigonal | trigonal | trigonal | trigonal | trigonal | |
| space group | R3m | R3m | R3m | R3m | R3m | R3m | |
| a [Å] | 19.4724(6) | 18.9171(15) | 19.3411(4) | 18.7069(8) | 18.5692(10) | 18.7376(4) | |
| b [Å] | 19.4724(6) | 18.9171(15) | 19.3411(4) | 18.7069(8) | 18.5692(10) | 18.7376(4) | |
| c [Å] | 37.7540(11) | 37.995(5) | 37.8517(8) | 41.0149(19) | 40.907(4) | 40.9892(12) | |
| α [°] | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | |
| β [°] | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | |
| γ[°] | 120.00 | 120.00 | 120.00 | 120.00 | 120.00 | 120.00 | |
| V [Å ³] | 12397.5(8) | 11775(2) | 12262.5(6) | 12430.1(9) | 12215.6(17) | 12463.2(6) | |
| Ζ | 18 | 18 | 18 | 18 | 18 | 9 | |
| $ ho_{ m calcd} [m g cm^{-3}]$ | 0.827 | 0.883 | 0.850 | 0.861 | 0.890 | 0.877 | |
| $\mu [mm^{-1}]$ | 5.013 | 1.315 | 1.383 | 5.044 | 0.822 | 1.404 | |
| R _{int} | 0.0524 | 0.0584 | 0.0310 | 0.0703 | 0.0818 | 0.0301 | |
| <i>R</i> ₁ | 0.1118 | 0.0834 | 0.0654 | 0.0951 | 0.0686 | 0.0950 | |
| wR ₂ | 0.3095 | 0.2595 | 0.1999 | 0.2868 | 0.2251 | 0.2925 | |
| $R_1 [l > = 2\sigma(l)]$ | 0.1284 | 0.906 | 0.0720 | 0.1386 | 0.0941 | 0.1055 | |
| wR ₂ [all data] | 0.3234 | 0.2713 | 0.2099 | 0.3207 | 0.2454 | 0.3124 | |
| goodness-of-fit on F ² | 1.303 | 1.101 | 1.470 | 1.057 | 1.097 | 1.361 | |

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Figure 1. Representations of the paddle-wheel SBU units in (a–c) the LIFM-10(M) and (d–f) the LIFM-11(M) MOF series showing metal coordination environments and the bent configuration of the *N*-oxide ligand offering an open donor site (ODS). For clarity, only one coordinative N/O atom in the axial position is shown.

equatorial plane and the M–N or M–O bond for LIFM-10 and LIFM-11, respectively) at the top of the paddle-wheel clusters in the LIFM-10(M) series, the *N*-oxide groups in the LIFM-11(M) series are bent to allow the electron pairs of the oxygen atoms to point towards the center of the pore, thus serving as potential "open donor sites" (ODSs).^[34] The presence of ODSs slightly reduces the effective pore size (see Figure S1 in the Supporting Information), but is concurrently expected to enhance the affinity of the MOFs for the guests. Moreover, these ODSs can be easily attacked by other emulative coordination atoms from the enthetic guest molecules. This might lead to MOFs with poor stability (see below).

Stability

The stability of the six MOFs under various conditions, such as activation at high temperature or under vacuum to remove guests from the pores, immersion in water, and exposure to air, has been evaluated through comprehensive measurements (Figure 2and Figures S2–S8 in the Supporting Information). The thermal stability of the MOFs was evaluated by thermal gravimetric analysis (TGA) and variable-temperature powder X-ray diffraction (VT-PXRD). Their stability towards water was assessed by comparison of the PXRD patterns collected before and after treatment of the MOFs in aqueous solution and in humid air. Finally, the stability of the MOF frameworks was examined by means of PXRD analysis after removal of solvent/guests from the MOFs at elevated temperature or under high vacuum.^[37]

The thermal stability of MOFs can be evaluated by determining the temperatures that induce either chemical decomposition or collapse of the frameworks. The former process is related to bond breaking and the corresponding temperature can be estimated by TGA measurements, whereas the latter is related to the crystallinity of the solids, which can be characterized by VT-PXRD. As seen in Figure S2 in the Supporting Information, the TGA curves of the as-prepared crystals show con-

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Figure 2. Stability of the LIFM-10(M) and LIFM-11(M) MOFs under diverse conditions evaluated by PXRD analyses.

siderable weight loss below 150°C, which indicates that all the MOFs contain large numbers of solvent molecules in their pores. After desolvation, TGA of the dried samples indicated that the chemical decomposition of the cobalt- and zinc-based MOFs mainly occurs in the temperature range of 350-500°C, that is, significantly higher than that of the copper-based MOFs (250–350 $^{\circ}\text{C}).$ The desolvated MOFs can re-absorb water molecules when immersed in water or exposed to humid air (see Figure S3). In contrast, the VT-PXRD patterns of the six MOFs reveal another trend with regard the collapse of their frameworks (Figure 2and Figure S4); the PXRD patterns evidence that the copper-based MOFs are thermally more stable than the cobalt- and zinc-based analogues. Specifically, LIFM-11(Zn) retains its crystallinity up to 90°C, and LIFM-11(Co) up to 120 °C, LIFM-10(Zn) and LIFM-10(Co) show better stability, up to 200 and 250°C, respectively, and the frameworks of LIFM-10(Cu) and LIFM-11(Cu) collapsed at 260 and 300 $^\circ\text{C},$ respectively. These results suggest that the zinc- and cobaltbased MOFs lose their porosity after removal of the solvents, and that the stability of the frameworks can be enhanced by the H₂INIA ligand compared with the H₂INOIA ligand. Nevertheless, LIFM-11(Cu) maintains its crystallinity to a slightly higher temperature than LIFM-10(Cu) (300 vs 260 °C). These observations reveal that the thermal stability of a MOF may be different with regard to chemical decomposition and framework collapse. Furthermore, the permanent porosity of a MOF may not solely be dominated by the robustness of the material compared with solvent/guest evacuation, but also by the affinity of the pore wall for guest molecules.

The enhancement of the chemical stability of MOFs involves reinforcing the resistance of these solids towards water in aqueous solution or humid air. In aqueous solution, it is sup-

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posed that hydrolysis leads to the protonation of the organic linkers and that the metal centers are simultaneously attacked by hydroxide ions, both processes contributing to the destruction of the MOF frameworks.^[14] Here, the water stability of the LIFM-10(M) and LIFM-11(M) series was tested by monitoring their PXRD patterns before and after immersing the activated samples in water or exposing them to air at room temperature for a certain period of time. As can be seen in Figure 2 and Figure S5 in the Supporting Information, LIFM-10(Co, Zn) and LIFM-11(Co, Zn) lost their original crystallinity in water in a few minutes, with LIFM-10(Co) converting into an unknown structural phase. For comparison, the frameworks of both LIFM-10(Cu) and LIFM-11(Cu) remain almost unaltered in water with only some minor structural changes over a long period. The poor water stability of the cobalt- and zinc-based MOFs can be attributed to the unfavorable square-pyramidal coordination geometries of Co^{2+} (d⁷ configuration) and Zn^{2+} (d¹⁰ configuration) with a low ligand-field stabilization energy (LFSE). In contrast, Cu²⁺ (d⁹ configuration) is known to prefer the squarepyramidal coordination geometry and exhibits an efficient Jahn-Teller effect to resist ligand substitution processes by water.^[14]

The stability of the copper-based MOFs towards water was confirmed under conditions of humidity. The cobalt- and zincbased MOFs gradually lose their crystallinity in air over several hours or days, whereas LIFM-10(Cu) and LIFM-11(Cu) show excellent stability in air at diverse temperatures for at least several months (Figure 2and Figure S6 in the Supporting Information). As far as the ligand effect is concerned, the LIFM-10(M) series show higher stability towards water than the LIFM-11(M) analogues, probably owing to the presence of ODSs in the LIFM-11(M) MOFs, with the lone electron pairs of the oxygen donor more easily able to interact with water molecules leading to the destruction of the MOF framework.

In our study of the stability of the MOFs we mainly considered the robustness of the evacuated MOFs under conditions of high vacuum or heating, the ability of the framework to exist when exposing the empty framework to air, as well as the ability of the collapsed framework to recover. As shown in Figure S7 in the Supporting Information, the monitoring of the desolvation process by PXRD analysis revealed that LIFM-11(Co) and LIFM-11(Zn) collapse over a short period of time under a high vacuum of 10^{-3} mbar, whereas the other four MOFs maintain their structural integrity much longer under the same conditions. However, when the six desolvated MOFs were exposed to air, all the MOFs lost their crystallinity in a time ranging from a few minutes to 24 h (see Figure S8). Experiments performed with a view to regenerating the framework structure of the samples in *N*,*N*-diethylformamide (DEF) or N,N-dimethylformamide (DMF) solution revealed that LIFM-10(Cu) and LIFM-11(Cu) can recover their frameworks after 48 and 20 h, respectively. LIFM-10(Zn) was able to partially recover its framework, whereas LIFM-11(Zn) and the cobalt-based MOFs totally lost their crystallinity and it could not be recovered (see Figure S8).

From the above stability tests we may conclude that, although the cobalt- and zinc-based MOFs have good thermal stability towards chemical decomposition, they generally show poor framework stability towards water and solvent/guest evacuation. The copper-based MOFs display better chemical and framework stability, however, the dried framework still suffers instability towards moisture. However, recovery of the crystallinity is possible, which suggests that the framework partially collapses without a total loss of the long-range order. With regard the ligand effect, nitrogen coordination in INIA is helpful to maintain the framework stability of the cobalt- and zincbased MOFs in comparison with N-oxide coordination in INOIA, for example, making activation of LIFM-10(Co) and LIFM-10(Zn) possible under vacuum. However, no significant impact on the stability of the copper-based MOFs is observed, which facilitates comparison of the ligand effect on the gas adsorption/separation behavior of the two stable Cu-MOFs LIFM-10(Cu) and LIFM-11(Cu).

Experimental gas/vapor adsorption isotherms, enthalpies, and selectivity

Based on a careful evaluation of the stability of all the solids, only LIFM-10(Co, Cu, Zn) and LIFM-11(Cu) have been found to be of interest for further gas adsorption study owing to the successful activation of the porosity of these MOFs upon removal of the guest solvent molecules. As expected, the N₂ sorption measurements at 77 K showed that LIFM-11(Co, Zn) are characterized by very low gas uptakes, which confirms that they lose porosity during the activation procedure (Figure 3). In contrast, LIFM-10(Co, Cu, Zn) and LIFM-11(Cu) exhibit significant gas sorption capacities, showing type-I adsorption isotherms characteristic of a microporous solid (Figure 4). Hence, we will discuss the adsorption properties of LIFM-10(Co, Cu, Zn) and LIFM-11(Cu), and focus further on the comparison between the two stable LIFM-10(Cu) and LIFM-11(Cu) solids. The difference in the inclination angles of *N*-oxide–M in LIFM-11(M) in comparison with those of pyridine-N-M in LIFM-10(M) (Figure 1) indicates that these two series of isoreticular MOFs are expected to present slightly different pore geometries. Although both structures have very similar pore size and adsorption capacity (Tables 2and 3), the accessibility of gases to the pores should be slightly hampered in the case of LIFM-11(Cu)



Figure 3. N_2 sorption isotherms of LIFM-11(Co) and LIFM-11(Zn) at 77 K. Solid symbols: adsorption; open symbols: desorption.

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| Table 2. Pore features and gas-adsorption data for all the investigated MOFs. | | | | | | | | | | | | |
|---|--------|-------|--------|--------|-------|--------|-------|--------|--------|--------|-------|--------|
| | LIFM-1 | 0(Co) | LIFM- | 10(Cu) | LIFM- | 10(Zn) | LIFM- | 11(Co) | LIFM- | 11(Cu) | LIFM- | 11(Zn) |
| | Exptl | Calcd | Exptl | Calcd | Exptl | Calcd | Exptl | Calcd | Exptl | Calcd | Exptl | Calcd |
| Accessible surface area [%] | | 49.1 | | 44.4 | | 47.3 | | 45.1 | | 46.8 | | 43.7 |
| BET area [m ² g ⁻¹] | 1577.9 | 1589 | 1550.2 | 1690 | 905.9 | 2165 | 24.8 | 1880 | 1175.6 | 1580 | 70.4 | 1600 |
| | | | | | | | | | | | | |
| Pore volume [mLg ⁻¹] | 0.79 | 0.60 | 0.64 | 0.72 | 0.47 | 0.71 | 0.05 | 0.67 | 0.68 | 0.73 | 0.08 | 0.65 |

| Table 3. Gas adsorption data for LIFM-10(Cu) and LIFM-11(Cu). | | | | | | | | |
|---|-------|---------|-------|--------|--|--|--|--|
| Gas (Temperature) Gas uptake [mLg ⁻¹] | | | | | | | | |
| | LIFM- | -10(Cu) | LIFM- | 11(Cu) | | | | |
| | Exptl | Calcd | Exptl | Calcd | | | | |
| N ₂ (77 K) | 440.1 | 417.9 | 449.8 | 391.2 | | | | |
| CO ₂ (298 K) | 65.9 | 175.0 | 78.0 | 114.2 | | | | |
| CH ₄ (298 K) | 20.7 | 35.4 | 19.1 | 32.4 | | | | |
| CO (298 K) | 9.6 | 15.5 | 8.7 | 15.3 | | | | |
| N ₂ (298 K) | 6.7 | 10.7 | 4.3 | 10.4 | | | | |



Figure 4. N_2 sorption isotherms of LIFM-10(Co), LIFM-10(Cu), LIFM-10(Zn), and LIFM-11(Cu) at 77 K. Solid symbols: adsorption; open symbols: desorption.

due to the presence of ODSs, which reduce the effective pore size (see Figure S1 in the Supporting Information) thereby leading to a lower adsorption capacity compared with LIFM-10(Cu) (Table 2). The sharp reduction of the experimental BET area of LIFM-10(Zn) is associated with a partial collapse of the MOF framework during the activation of the sample. Comparison of the N₂-accessible surface areas, pore volumes, and pore sizes reveals that the experimental results for LIFM-10(Co), LIFM-10(Cu), and LIFM-11(Cu) match well the simulated values, whereas those of LIFM-10(Zn), LIFM-11(Co), and LIFM-11(Zn) deviate from the simulations due to poor framework stability. As listed in Table 2, the simulations indicate that LIFM-10(Cu) and LIFM-11(Cu) have similar N₂-accessible surface areas (calculated by the standard geometrical approach) and pore volumes (by the thermodynamic approach). LIFM-10(Zn) shows an abnormally low experimental BET surface area compared with the simulated value, most probably due to the partial disorder of the structure after activation. For comparison with the experimental data for LIFM-10(Cu) and LIFM-11(Cu), the amount of gases adsorbed at 1 bar were calculated (Table 3), the calculations providing overestimates in comparison with the experimental data, except for N_2 adsorption at 77 K.

The adsorption isotherms collected for CO₂, CH₄, CO, and N₂ at 298 K indicate that the adsorption uptake at low pressure (below 1 bar) shows the usual sequence of CO₂ > CH₄ > CO > N₂ for the four selected MOFs (see Figures S9–S12 in the Supporting Information). LIFM-11(Cu) shows the highest CO₂ adsorption uptake with a value of 78 mL g⁻¹ (Figure 5). This high CO₂ uptake can probably be attributed to the preferential adsorption of this guest molecule by the ODSs.



Figure 5. CO_2 sorption isotherms of LIFM-10(Co), LIFM-10(Cu), LIFM-10(Zn), and LIFM-11(Cu) at 298 K. Solid symbols: adsorption; open symbols: desorption.

High-pressure adsorption isotherms were measured for H₂ and CH₄ in LIFM-10(Cu), and for CO₂ and CH₄ in LIFM-11(Cu) (Figure 6) to evaluate the saturation capacities of these solids. LIFM-10(Cu) shows a high uptake of H₂ with an adsorbed amount of 469.9 mLg⁻¹ (4.15 wt%) at 60 bar and 77 K. Interestingly, this value is comparable to the data previously reported for a series of MOFs with much larger BET areas, that is, 6.1 wt % for MIL-101(Cr)^{[38,39]} (BET area = 4200 m²g⁻¹) and 8.3 wt% for MOF-210 (BET area = $6200 \text{ m}^2\text{g}^{-1}$).^[40] The adsorption capacity for CH_4 at 35 bar and 298 K is 131.6 mLg⁻¹ for LIFM-10(Cu) (5.87 mol kg⁻¹), but is reduced to 70.78 mLg⁻¹ $(3.15 \text{ mol kg}^{-1})$ for LIFM-11(Cu). The uptake capacity for CO₂ of LIFM-11(Cu) is 141.24 Lg^{-1} (6.30 mol kg⁻¹), higher than that of MIL-102(Cr) $(3.1 \text{ mol kg}^{-1})^{[41]}$ and MOF-2 $(3.2 \text{ mol kg}^{-1})^{[42]}$ and comparable to the value of HKUST-1 (7.3 mol kg⁻¹) and Zn-MOF-74 (7.1 molkg⁻¹), but lower than the highest value observed for IRMOF-1 (11.1 molkg⁻¹) at 298 K and 35 bar.^[43]







Figure 6. High-pressure adsorption isotherms of (a) H_2 at 77 K and CH_4 at 298 K for LIFM-10(Cu) and (b) CO_2 and CH_4 at 298 K for LIFM-11(Cu). Solid symbols: adsorption.

Figure 7. Adsorption isotherms of (a) light hydrocarbons and (b) MeOH, EtOH, and *n*-propanol in LIFM-10(Cu) at 298 K.

Based on these experimental single-component adsorption isotherms, Henry's law of selectivity for CO₂ versus N₂, CO, and CH₄ was calculated by the virial-based method.^[44] As seen from the data presented in Table 4and Tables S2–S5 in the Supporting Information, LIFM-11(Cu) is the most selective adsorbent among the four MOFs, with relatively good separation selectivity of CO₂/CH₄ (17.4) and CO₂/N₂ (64.4) at low pressure, and showing higher selectivity than MOF-5,^[45] ZIF-78,^[46] en-Cu-BTTri^[47] and some other widely used porous materials in industry (e.g., BPL AC)^[48] under similar conditions (Table 4), and only slightly lower selectivity than a few MOFs with open metal sites, chemisorbed groups, or small pores.^[49–60]

The adsorption capacities of light hydrocarbons (CH₄, C₂H₆, C₃H₈, and *n*-C₄H₁₀) were also investigated at 298 K for LIFM-10(Cu) as a typical example (Figure 7a). The results reveal that the hydrocarbon uptake at low pressure increases as the

carbon chain extends, which indicates a clear increase in affinity of the adsorbate with longer chains, as has already been reported for both MOFs and zeolites.^[61-65] The adsorption of methanol, ethanol, and n-propanol was also studied for LIFM-10(Cu) at 298 K (Figure 7b). The sorption capacity for methanol (307 mLg^{-1}) is much higher than those for ethanol and *n*-propanol. Thus, an inverse increase in adsorption with carbon chain length is observed in comparison with light hydrocarbons. This is mainly caused by the increase in the dipole moment from npropanol to methanol (1.56 to 1.70 D).[66] As illustrated in Figure S13 in the Supporting Information, LIFM-10(Cu) and LIFM-11(Cu) show similar water adsorption capacities of 231.8 and 235.6 mLg⁻¹, respectively. However, the process of adsorption shown by these two MOFs is different. LIFM-10(Cu) shows a sharp adsorption step at relative pressure $P/P_0 = 0.2$ with the desorption occurring at a pressure lower than that of the ad-

| Table 4. Separation selectivity shown by LIFM-10(Co, Cu, Zn) and LIFM-11(Cu). | | | | | | | | | | |
|---|---|---------------------|------------|----------------------------------|-----------------------|------------|----------------------------------|--|---------------------------------|--|
| | Virial selectivity (298 K) | | | | IAST ^[a,b] | | | Co-adsorption selectivity (calcd at 298 K) ^[a] | | |
| | CO ₂ /CH ₄ | CO ₂ /CO | CO_2/N_2 | CO ₂ /CH ₄ | CO ₂ /CO | CO_2/N_2 | CO ₂ /CH ₄ | CO ₂ /CO | CO ₂ /N ₂ | |
| LIFM-10(Co) | 3.6 | 7.9 | 13.0 | NA | NA | NA | NA | NA | NA | |
| LIFM-10(Cu) | 5.0 | 5.8 | 18.3 | 4.7-4.3 | 6.2-10.0 | 16.3–14.5 | 7.5–7.9 | 19.5-24.0 | 30.6-29.2 | |
| LIFM-10(Zn) | 5.5 | 10.9 | 18.0 | NA | NA | NA | NA | NA | NA | |
| LIFM-11(Cu) | 17.4 | 5.2 | 64.4 | 17.2–9.4 | 6.4–22.8 | 81.9–68.9 | 20.7-5.7 | 73.1–17.9 | 96.4–30.7 | |
| [a] CO ₂ /CH ₄ =5 | [a] CO ₂ /CH ₄ =50:50; CO ₂ /CO=50:50; CO ₂ /N ₂ =15:85, 0–1 bar. [b] See ref. [25]. | | | | | | | | | |

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sorption such that a large hysteresis loop is observed. In contrast, the water uptake of LIFM-11(Cu) exhibits a pseudo-type-I adsorption isotherm, that is, it shows relatively fast adsorption at low pressure followed by gradual uptake to saturation.^[13,27] This different behavior is expected to be associated with different hydrophilicities and hydrophobicities of the two solids.

The isosteric heats (Q_{st}) for CO₂ were calculated from the adsorption data of CO₂ measured at 273, 298, and 303 K by the virial-fitting method (see Figure S14 in the Supporting Information). At zero coverage, the Q_{st} for CO₂ in LIFM-11(Cu) reaches 53.3 kJ mol⁻¹, which is substantially higher than the values obtained for LIFM-10(Co), LIFM-10(Cu), and LIFM-10(Zn) of 28.1, 28.7, and 31.9 kJ mol⁻¹, respectively, but nearly 40 kJ mol⁻¹ lower than those determined for CuBTTri and mmen-CuBTTri with the alkylamine functionalities interacting strongly with CO₂.^[53,68]

Comparison of grand-canonical Monte Carlo simulations with experimental results

Grand-canonical Monte Carlo (GCMC) simulations were carried out to gain a deeper insight into the microscopic adsorption mechanism of small gas molecules in the water-stable LIFM-10(Cu) and LIFM-11(Cu). In complement to this, mixed-gas adsorption measurements were also performed at 298 K.

The simulated adsorption isotherms for N_2 , CH_4 , and CO are shown in Figures S15–S17 in the Supporting Information. Both LIFM-10(Cu) and LIFM-11(Cu) show similar simulated adsorption isotherms and enthalpies (Table 5), which indicates the absence of strong interactions between these gases and the MOF frameworks.

| Table 5. Calculat 11(Cu) for differe | ed adsorption enthalpies nt gases at 298 K. | of LIFM-10(Cu) and LIFM- |
|--|--|--------------------------------------|
| | | $Q_{\rm sc}$ [kJ mol ⁻¹] |
| | LIFM-10(Cu) | LIFM-11(Cu) |
| CO ₂ | 27.1 | 37.9 |
| CH ₄ | 18.4 | 19.2 |
| CO | 16.2 | 17.7 |
| N ₂ | 14.3 | 14.7 |

In contrast, the simulations of the single-component adsorption isotherms for CO₂ in LIFM-10(Cu) and LIFM-11(Cu) reveal different adsorption behavior. As seen in Table 5and Figures S17 and S18 in the Supporting Information, the adsorption enthalpies (Q_{st}) determined for CO₂ are much higher than the values obtained for CH₄, CO, and N₂, which suggests strong interactions between the oxygen atom of the amido and *N*-oxide groups with CO₂. Figure S18a shows the variation of the calculated Q_{st} values for CO₂ as a function of loading. At very low pressure, the calculated value of Q_{st} for LIFM-11(Cu) is higher than that for LIFM-10(Cu) (37.9 vs. 27.1 kJ mol⁻¹), which indicates that LIFM-11(Cu) has a higher affinity for CO₂ in the initial stages of adsorption. The amount of CO₂ adsorbed is thus higher in LIFM-11(Cu) for a pressure below 0.1 bar (see

Figure S17a). This predicted trend is in very good agreement with the experimental data for LIFM-10(Cu) and LIFM-11(Cu) (see Figure S18b). A significant decrease in adsorption enthalpy is observed for uptakes lower than 50 mL(STP) q^{-1} . This is gualitatively in agreement with the experimental results. As a result, LIFM-10(Cu) adsorbs more CO₂ than LIFM-11(Cu) at intermediate pressures. For pressures higher than 0.1 bar (uptake higher than 50 mL(STP) g^{-1}), LIFM-10(Cu) shows a higher calculated Q_{st} than LIFM-11(Cu), which indicates that LIFM-10(Cu) has a greater affinity towards CO_2 . The inversion of Q_{st} is consistent with the simulated isotherms (see Figure S17). At high pressures both MOFs have approximately the same calculated saturation capacity (ca. $300 \text{ mL}(\text{STP}) \text{ g}^{-1}$), which is consistent with their similar pore volumes. The predicted amount of CO₂ adsorbed at 1 bar is higher than the experimental value (Table 3), which should attribut to the loss of porosity rather than to the slight collapse of the frameworks after activation at high temperature or under vacuum.

To explain the adsorption behavior shown by the two copper-based MOFs, analysis of the preferential arrangements of the guest molecules was carried out. Figure 8 reports the radial distribution functions (RDF) between the carbon atoms of CO_2 and the oxygen atoms at low loading of the *N*-oxide group in LIFM-11(Cu) and of the carbonyl group of the linker



Figure 8. (a) RDF between the carbon atom of CO_2 and the oxygen atom of the *N*-oxide group in LIFM-11(Cu) and (b) RDF between the carbon atom of CO_2 and the oxygen atom of the carbonyl group of the linker in LIFM-10(Cu) and LIFM-(Cu) calculated at low pressure.



in both MOFs. According to Figure 8a, the *N*-oxide group present in LIFM-11(Cu) is an extra adsorption site for CO₂. These adsorption sites are responsible for the relatively high adsorption enthalpy at low concentration.^[67,68] In the initial stages of adsorption, CO₂ is adsorbed by the oxygen atom of the *N*-oxide group, however, this site is saturated at low CO₂ concentration, which accounts for the rapid drop in the adsorption enthalpy. In complement to this, Figure 8b shows that CO₂ interacts mainly with the oxygen atom of the carbonyl group in LIFM-10(Cu). Such interactions also exist for LIFM-11(Cu), but to a lesser extent. This site has relatively low energetics, which is consistent with the lower calculated adsorption enthalpy compared with LIFM-11(Cu).

The co-adsorption of three binary mixtures, CO_2/N_2 (50:50), CO_2/CH_4 (50:50), and CO_2/CO (50:50), with the same molar compositions as used in the experiments, was calculated for LIFM-10(Cu) and LIFM-11(Cu) (see Figures S19–S24 in the Supporting Information). LIFM-11(Cu) shows a better selectivity than LIFM-10(Cu) at low pressure, consistent with the virial and IAST^[25] predictions (Table 4). Analysis of the co-adsorption mechanism shows that CO_2 is preferentially adsorbed around the oxygen atom of the *N*-oxide group, similarly to the single-component adsorption, whereas the other gas molecules, CH_4 , N_2 , and CO, only very weakly interact with the pore wall (see the corresponding RDFs and snapshots in Figures S25 and S26). Pore size distribution analysis revealed that both of the structures have very similar pore size and adsorption capacity (see Figure S27).

Conclusion

Six isoreticular MOFs of ScD_{0.33} topology containing hourglassshaped channels and two types of cavities have been constructed from bivalent metal ions of Co^{2+} , Cu^{2+} , and Zn^{2+} and two comparable T-shaped ligands with different donor configurations. The metal and ligand effects on the stability and adsorption properties of these isoreticular MOFs have been comprehensively evaluated. This study has revealed that appropriate selection of the metal center and fine-tuning of the coordination termini can help to optimize the stability of the MOF towards heat and water to achieve promising adsorption/ separation properties for a wide range of gases (N₂, CO₂, CH₄, CO, H_2 , and light hydrocarbons (C_1 – C_4)) and vapors (alcohols and water). In general, the copper-based MOFs are more stable than the cobalt- and zinc-based MOFs in terms of the M₂(COO)₄ paddle-wheel SBUs utilized. A combined experimental/computational approach has been used to examine and understand the adsorption behavior of the MOFs and the resulting microscopic mechanisms in water-stable MOFs. This has revealed that the ingenious decoration of the ligands with Noxide and amido groups assists in increasing the adsorbateadsorbent interactions, the functionalization by N-oxide significantly enhancing the adsorption enthalpy as well as the CO₂/ CH_4 , CO_2/CO , and CO_2/N_2 selectivity at room temperature. These results suggest that the incorporation of N-oxide into MOFs may be a promising strategy for generating high CO₂ selectivity, especially for natural gas purification.

Experimental Section

Materials and physical measurements: All chemicals were obtained from commercial sources and utilized directly without further purification. Solid-state IR spectra were recorded by using a Nicolet/Nexus-670 FT-IR spectrometer in the range of 4000–400 cm⁻¹ using KBr pellets. Elemental analysis was performed by using a PerkinElmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 AD-VANCE diffractometer at 40 kV and 40 mA with a copper target tube and a graphite monochromator. TGA was performed on a NETZSCH TG209 system in under 1 atm nitrogen at a heating rate of 10° Cmin⁻¹. Gas adsorption isotherms were obtained by a volumetric method using a quantachrome autosorb-iQ2-MP gas adsorption analyzer.

Synthesis of ligands and complexes

Synthesis of LIFM-10(Co): A mixture of $Co(NO_3)_2$ ·6H₂O (0.05 mmol) and 4-pyridylaminocarbonyl (H₂INIA, 0.05 mmol) was dissolved in DEF (3 mL) and heated in a 15 mL Teflon-lined stainless-steel vessel at 120 °C for 7200 min and then cooled to 30 °C at a rate of 10 °C/ 100 min. The green powder formed was collected by filtration and washed with DEF several times to give a yield of 71.3%. IR (KBr): $\tilde{\nu} =$ 3424 (s), 2937 (m), 1653 (s), 1559 (s), 1408 (s), 1373 (s), 1284 (m), 1213 (w), 1110 (m), 1067 (m), 869 (w), 777 (w), 722 (w), 549 cm^{-1} elemental analysis calcd (%) (w); for Co(C₁₄H₈N₂O₅)·2.5(C₅NOH₁₁)·(H₂O) (formula mass, 614.04): C 51.83, H 6.15, N 10.26; found: C 51.30, H 6.56, N 10.53.

Synthesis of LIFM-10(Cu): A mixture of Cu(NO₃)₂·3H₂O (0.2 mmol) and H₂INIA (0.1 mmol) was dissolved in DMF (8 mL) and heated at 60 °C for 5 min to provide blue floccules. Then 2 drops of HNO₃ were added to give a clear green solvent. The solvent was transferred a 15 mL Teflon-lined stainless-steel vessel and heated at 80 °C for 60 h, then cooled to 30 °C at a rate of 10 °C/100 min. The green powder formed was collected by filtration and washed with DMF several times to give a yield of 80.4%. IR (KBr): \tilde{v} = 3436 (s), 1673 (m), 1617 (s),1585 (m), 1564 (s), 1416 (m), 1383 (s), 1286 (s), 779 (w), 722 cm⁻¹ (w); elemental analysis calcd (%) for Cu(C₁₄H₈N₂O₅)·2.5(C₃H₇NO)·2(H₂O) (formula mass, 566.53): C 45.58, H 5.25, N 11.13; found: C 45.33, H 5.37, N 11.18.

Synthesis of LIFM-10(Zn): A mixture of Zn(NO₃)₂·6H₂O (0.05 mmol) and H₂INIA (0.05 mmol) was dissolved in DEF (3 mL) and heated in a 15 mL Teflon-lined stainless-steel vessel at 120 °C for 7200 min, then cooled to 30 °C at a rate of 10 °C/100 min. The green powder formed was collected by filtration and washed with DEF several times to give a yield of 68.4%. IR (KBr): $\tilde{v} = 1650$ (s), 1560 (s), 1366 (s), 1287 (m), 1215 (w), 1116 (w), 1030 (w), 852 (w), 779 (m), 725 (m), 644 (w), 602 (w), 464 cm⁻¹ (w); elemental analysis calcd (%) for Zn(C₁₄H₈N₂O₅)·1.5(C₅NOH₁₁)·3(H₂O) (formula mass, 555.40): C 46.49, H 5.53, N 8.82; found: C 46.15, H 5.42, N 10.11.

Synthesis of LIFM-11(Co): A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mmol) and H₂INOIA (1-oxidopyridin-1-ium-4ylaminocarbonyl, 0.1 mmol) was dissolved in DMF (3 mL), triethylamine (6 µL) was added to provide a violet turbid solution, and the mixture was heated in a 15 mL Teflon-lined stainless-steel vessel at 80 °C for 4000 min, then cooled to 30 °C at a rate of 10 °C/100 min. The green powder formed was collected by filtration and washed with DMF several times to give a yield of 78.9%. IR (KBr): $\tilde{v} = 3408$ (s), 1656 (s), 1623 (s), 1563 (s), 1492 (w), 1428 (m), 1374 (s), 1288 (w), 1228 (w), 1182 (m), 1108 (m), 782 (w), 716 (w), 617 (w), 460 cm⁻¹ (w); elemental analysis calcd (%) for $Co(C_{14}H_8N_2O_6)\cdot(C_3H_7NO)\cdot5(H_2O)$ (formula mass, 522.33): C 39.09, H 4.82, N 8.04; found: C 38.73, H 4.98, N 10.01. **Synthesis of LIFM-11(Cu)**: A mixture of $Cu(NO_3)_2\cdot3H_2O$ (0.2 mmol) and H₂INOIA (0.1 mmol) was dissolved in DMF (8 mL) and heated

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in a 15 mL Teflon-lined stainless-steel vessel at 80 °C for 60 h, then cooled to 30 °C at a rate of 10 °C/100 min. The green powder formed was collected by filtration and washed with DMF several times to give a yield of 78.3%. IR (KBr): $\tilde{\nu}$ = 3436 (m), 1713 (m), 1672 (m), 1636 (m), 1585 (m), 1563 (m), 1489 (w), 1434 (m), 1374 (s), 1292 (w), 1228 (m), 1095 (w), 865 (w), 774 (w), 729 (w), 589 (w), 487 cm⁻¹ (w); elemental analysis calcd (%) for Cu(C₁₄H₈N₂O₆)·2(C₃H₇NO)·3(H₂O) (formula mass, 564.00): C 42.59, H 5.00, N 9.93; found: C 42.04, H 5.16, N 11.38.

Synthesis of LIFM-11(Zn): A mixture of Zn(NO₃)₂·6H₂O (0.1 mmol) and H₂INOIA (0.1 mmol) was dissolved in DMF (8 mL) and heated in a 15 mL Teflon-lined stainless-steel vessel at 80 $^\circ\text{C}$ for 4000 min, then cooled to 30 °C at a rate of 10 °C/100 min. The green powder formed was collected by filtration and washed with DMF several times to give a yield of 60.5 %. IR (KBr): $\tilde{\nu} = 3416$ (m), 1656 (s), 1562 (s), 1489 (w), 1431 (m), 1373 (m), 1289 (w), 1233 (w), 1181 (w), 1106 (m), 863 (w), 780 (w), 723 (w), 663 (w), 617 (w), 589 (w), 464 cm⁻¹ elemental calcd (%) for (w); analysis Zn(C₁₄H₈N₂O₆)·1.5(C₅NOH₁₁)·3(H₂O) (formula mass, 571.40): C 41.98, H 4.67, N 9.26; found: C 42.90, H 5.03, N 10.59.

Crystal structure determination: Single crystals of LIFM-10(Co, Zn) and LIFM-11(Co, Zn) were carefully picked and coated in paratone oil, attached to a glass silk inserted in a stainless-steel stick, and then quickly transferred to the Agilent Gemini S Ultra CCD diffractometer equipped with the Enhance X-ray Source of copper radiation ($\lambda = 1.54178$ Å) using the $\omega - \phi$ scan technique. Structural solution and refinement against F^2 were carried out by using the SHELXL programs^[69] for LIFM-10(Co, Zn) and LIFM-11(Co, Zn) as well as for LIFM-10(Cu) and LIFM-11(Cu) published previously. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process by using the riding model with isotropic thermal parameters: $U_{iso}(H) = 1.2U_{eq}(CH)$. For all structures, the contribution of the heavily disordered solvent molecules was treated by the Squeeze procedure implemented in PLATON.^[70,71] The pyridine ring and amido group within the frameworks displayed orientational disorder, therefore, they were located and refined with restraints (DFIX, FLAT, ISOR, and SIMU) to obtain satisfactory displacement parameters. Crystal and refinement parameters are presented in Table S1 in the Supporting Information. The space groups of the crystal structures for LIFM-10(Cu) and LIFM-11(Cu) were corrected from R-3 to R-3m after re-solving.

CCDC 1487326 (LIFM-10(Co)), 1487327 (LIFM-10(Zn)), 1487328 (LIFM-11(Co)), 1487329 (LIFM-11(Zn)), 1012810 (LIFM-11(Cu)), and 1012811 (LIFM-11(Zn)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Gas adsorption measurements: Gas adsorption measurements were performed by using ultra-high pure N₂, CO, CO₂, and CH₄ gases. The as-synthesized sample (ca. 100–200 mg) was placed in a sample tube and dried for 20 h at 150 °C for the LIFM-10(M) series and at 120 °C for the LIFM-11(M) series to remove remnant solvent molecules prior to measurement. N₂ (99.99%), CO₂ (99.999%), CH₄ (99.999%), and CO (99.99%) were used for all adsorption isotherm measurements. The temperatures were controlled by using a liquid nitrogen bath (77 K) or a water bath (273, 298, and 303 K).

Simulation of adsorption, selectivity, and enthalpies: The Lennard Jones (LJ) parameters for each atom of an MOF were taken from the DREIDING force field^[72,73] for the organic linker and from the UFF^[74] force field for the inorganic node. The partial charges were obtained through DFT calculations using the PBE GGA functional combined with the double numerical basis set containing DNP polarization functions on all atoms (see Table S6 in the Sup-

porting Information). Grand-canonical Monte Carlo (GCMC) simulations were performed at 298 K to probe the adsorption of the single components H₂, CO₂, CH₄, CO, and N₂ and their binary mixtures of CO₂/N₂, CO₂/CH₄, and CO₂/CO (same molar compositions as used in the experiments) using the Complex Adsorption and Diffusion Simulation Suite (CADSS) code.^[75] N₂ and CO₂ were described by charged models^[76] and EP M2^[77] respectively, CH₄ by the united atom model,^[78] and CO by the model derived by Straub and Karplus.^[79] The cross-term parameters for the host–guest interactions were calculated by using the Lorentz–Berthelot combination rules.

The simulation box comprised of four $(2 \times 2 \times 1)$ unit cells of each LIFM-10(Cu) and LIFM-11(Cu) structure. Short-range dispersion forces described by LJ potentials were truncated at a cut-off radius of 14 Å whereas the long-range electrostatic interactions were handled by using the Ewald summation technique. The fugacities of each adsorbed species under given thermodynamic conditions were computed with the Peng–Robinson equation of state (EoS).^[80] For each state point, 2×10^7 Monte Carlo steps were used for both equilibration and production runs. The adsorption enthalpy (ΔH) at low coverage (Δh) for each single gas was calculated by using the revised Widom particle insertion test method.^[81]

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Keywords: adsorption · carbon dioxide capture · ligand effects · light hydrocarbons · metal–organic frameworks · water stability

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