Non-Interpenetrated Metal–Organic Frameworks Based on Copper(II) Paddlewheel and Oligoparaxylene-Isophthalate Linkers: Synthesis, Structure, and Gas Adsorption

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Abstract: Two metal–organic framework materials, MFM-130 and MFM-131 (MFM = Manchester Framework Material), have been synthesized using two oligoparaxylene (OPX) tetracarboxylate linkers containing four and five aromatic rings, respectively. Both fof-type non-interpenetrated networks contain Kagomé lattice layers comprising \([\text{Cu}_2(\text{COO})_4]\) paddlewheel units and isophthalates, which are pillared by the OPX linkers. Desolvated MFM-130, MFM-130a, shows permanent porosity (BET surface area of 2173 m²/g, pore volume of 1.0 cm³/g), high H₂ storage capacity at 77 K (5.3 wt% at 20 bar and 2.2 wt% at 1 bar), and a higher CH₄ adsorption uptake (163 cm³(STP)/cm³ (35 bar and 298 K)) compared with its structural analogue, NOTT-103. MFM-130a also shows impressive selective adsorption of C₂H₂, C₂H₄, and C₂H₆ over CH₄ at room temperature, indicating its potential for separation of C₂ hydrocarbons from CH₄. The single-crystal structure of MFM-131 confirms that the methyl substituents of the paraxylene units block the windows in the Kagomé lattice layer of the framework, effectively inhibiting network interpenetration in MFM-131. This situation is to be contrasted with that of the doubly interpenetrated oligophenylene analogue, NOTT-104. Calculation of the mechanical properties of these two MOFs confirms and explains the instability of MFM-131 upon desolvation in contrast to the behavior of MFM-130. The incorporation of paraxylene units, therefore, provides an efficient method for preventing network interpenetration as well as accessing new functional materials with modified and selective sorption properties for gas substrates.

INTRODUCTION

Nanoporous metal–organic frameworks (MOFs) constructed from metal cations or clusters bridged by polyfunctional organic linkers are an important class of hybrid materials which show great promise for gas storage and separation applications. An advantage of porous MOFs is that their design, structure, and properties can be varied by modification of the organic linkers, which can have different lengths, topologies, and geometries and can incorporate functional groups to enhance preferential binding of guest substrates via optimized pore shapes/diameters for molecular separation. We have developed a series of framework materials employing linear tetracarboxylate linkers and \([\text{Cu}_2(\text{COO})_4]\) paddlewheel units to generate fof-type networks. The assembly of isophthalate (benzene-3,5-dicarboxylate) units within tetracarboxylate linkers with \([\text{Cu}_2(\text{COO})_4]\) paddlewheels generates two-dimensional Kagomé lattices, which are pillared by the aromatic backbones of these linkers. Two types of cage structures are formed within this assembly: Cage A, an ellipsoid-shaped cage formed by six linkers and two triangular \(\{([\text{Cu}_2]\text{isophthalate})_3\}\) windows at the two ends, with a larger hexagonal \(\{([\text{Cu}_2]\text{isophthalate})_6\}\) core structure, and Cage B, a more cylindrical cage formed also by six linkers and two triangular \(\{([\text{Cu}_2]\text{isophthalate})_3\}\) windows. These materials show high porosity and high H₂ and CH₄ storage capacity, with the porosity, storage capacity, and binding energies with H₂ and CH₄ being tuned by modification of the organic linkers.

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Elongation of the linear tetracarboxylate units can increase the porosity of the resultant structures, but network interpenetration in these fof-systems can occur when the linker is lengthened beyond a certain point. Thus, development of highly porous and non-interpenetrated structures in these systems remains a challenge. There are several strategies for building non-interpenetrated networks with large organic linkers: (i) building networks with intrinsically non-interpenetrating topologies, such as ρht and fln; (ii) optimizing the synthesis of MOF materials using different solvents, conditions, and template effects to target preferred non-interpenetrating networks; and (iii) introducing bulky functional groups in the organic units to create steric hindrance.

Oligoparaxylenes (OPXs) have been developed as efficient building blocks for the construction of MOFs with Zn(II)/Mg(II) nodes. The methyl substituents present in OPXs increase dramatically the solubility of longer oligomers compared to oligophenylene analogues, which become increasingly less soluble with increasing length over just a few aromatic rings. OPX linkers can thus serve as stable, extended, and, most importantly, soluble organic building units or struts. A series of non-interpenetrating MOF-74 analogues have been successfully constructed from 4-carboxylate OPX tectons to give a series of isoreticular Mg(II) frameworks with pore apertures ranging from 1.4 to 9.8 nm. We reasoned that the synthesis of non-interpenetrating fof-type network structures might be achieved using OPX units serving as linear aromatic backbones to connect two isophthalate units to form extended, yet soluble, tetracarboxylate linkers. We envisaged that frameworks with optimized pore size, geometry, and functionality could be accessed by employing such OPX-derived linkers rather than using the more problematic, insoluble oligophenylene units. It is worth noting that methyl substituents present in the OPX struts can not only create hydrophobic pockets, which can aid gas adsorption and separation, but can also impart a degree of steric bulk within pores.

We report herein the synthesis of two new OPX-based linkers, the tetracarboxylates H_4L^{IV}V and H_4L^{V}V (Figure 1), incorporating isophthalate moieties, and their coordination to [Cu_2(COO)_4] paddlewheel nodes to form the non-interpenetrated fof-type frameworks MFM-130 and MFM-131. MFM-131 is the first example of a fof-type MOF with ultra-long organic struts that does not show network interpenetration. The adsorption of H_2, CH_4, CO_2, and small hydrocarbons in the desolvated form of MFM-130, MFM-130a, has been investigated, and the selective adsorption of CO_2 over N_2 and C_2 hydrocarbons (acetylene, ethylene, and ethane) over CH_4 in this material is discussed. Desolvation of MFM-131, however, leads to collapse of this material and loss of porosity. Calculation of the mechanical properties of these two MOFs in the elastic regime was, therefore, performed to confirm and explain their distinct properties upon desolvation.

**EXPERIMENTAL SECTION**

**Materials and Instrumentation.** All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. 4,4′-Diiodo-2,2′,5,5′-tetracarboxylate-tetramethyl-1,1′-biphenyl was synthesized as previously reported. Thin-layer chromatography (TLC) was performed on Merck TLC plates (F254 indicator), and column chromatography carried out on Merck silica gel 60 (Merck grade 9385, 0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a BrukerAvance III 500 MHz NMR spectrometer at working frequencies of 499.842 (1H) and 125.579 (13C) MHz. The signal corresponding to the residual non-deuterated solvent (CDCl_3, δ_C = 7.26 ppm and δ_H = 77.16 ppm; DMSO-d_6, δ_C = 2.50 ppm and δ_H = 39.52 ppm; PhMe-d_8, δ_C = 20.43 ppm) was used as a reference. Solutions of 1 and 4 in PhMe-d_8 were preheated at 90°C for 30 min before acquiring their ^1H and ^13C NMR spectra at 25°C. High-resolution mass spectra (HRMS) were measured on an Agilent 6210 time-of-flight (ToF) LC-MS using an ESI source coupled with Agilent 1100 HPLC stack via direct infusion (0.6 μL/min). Fourier-transform infrared (FTIR) spectra were performed on a Nicolet iS5 spectrometer using the attenuated total reflectance (ATR) mode. Elemental analyses were carried out on a CE-440 elemental analyzer, and thermogravimetric analyses (TGA) were performed using a TA SDT-600 thermogravimetric analyzer under a flow of N_2 (20 mL/min) with a heating rate of 5°C/min. Powder X-ray diffraction (PXRD) measurements were carried out at room temperature on a PANalytical X’Pert PRO diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV, 40 mA with a scan speed of 0.02°/s and a step size of 0.005° in 2θ (Figures S2 and S3).

**Gas Sorption Measurements.** H_2, CO_2, and N_2 isotherms were collected using an IGA gravimetric adsorption apparatus (Hiden) in a clean ultra-high-vacuum system with a diaphragm and turbo pumping system. Approximately 120 mg of solvent-exchanged sample was loaded into the sample basket within the adsorption instrument and then degassed under dynamic vacuum at 110°C for 12 h to obtain the fully desolvated sample. In H_2 adsorption experiments, ultra-pure grade H_2 (99.9995%, BOC Gases) was purified further using calcium aluminosilicate and activated carbon adsorbents to remove trace amounts of water and other impurities before introduction into the IGA system. Volumetric CH_4 sorption measurements were performed over the pressure range 0–70 bar using an automatically controlled Sievert’s apparatus (PCT-Pro 2000 from Hy-Energy LLC). Low-pressure (<1 bar) adsorption measurements for C_2 hydrocarbons were performed using an Autosorb 1-MP instrument (Quantachrome Instruments). Ultra-high-purity grade C_2H_6, C_2H_4, and C_2H_2 were used for adsorption measurements.

The temperature-dependent adsorption data were analyzed using the virial equation:

\[
\ln(n/p) = A_0 + A_1 n + A_2 n^2 + \ldots
\]

where \( p \) is pressure, \( n \) is the amount adsorbed, and \( A_0, A_1, \text{etc.} \) are virial coefficients. The Henry’s law constant (\( K_H \)) is equal to \( A_0 \), and the selectivity can be derived from the ratio of the constants \( K_i \) for different gases.

**Synthesis of H_4L^{IV}V and H_4L^{V}V.** A mixture of 5-(4,4,5,5-tetracarboxylate-1,3,2-dioxaborolan-2-yl)benzene-1,3,5,5′-tetracarboxylate Tetramethyl Ester (I). A mixture of 5-(4,4,5,5-tetracarboxylate-1,3,2-dioxaborolan-2-yl)benzene-1,3,5,5′-tetracarboxylate Tetramethyl Ester (II).
and H2O (5 mL) was heated at reflux for 18 h under Ar before H2O2 (50 mL) was added. The reaction mixture was extracted twice with CH2Cl2, and the combined organic extracts were washed with brine and dried over MgSO4. After filtration, the solvent was removed by evaporation and the residue purified by column chromatography over silica gel using hexane/CH2Cl2 (1:1 to 0.1) as eluent to afford the pure product (759 mg, 54%) as a white solid and as a 1:1 mixture of two diastereoisomers, a pair of enantiomers (R and S) and one meso isomer (RR or SS), undergoing fast isomerization at room temperature.1H NMR (500 MHz, CDCl3, ppm): δ 8.86 (t, J = 1.7 Hz, 1H), 7.16 (t, J = 1.7 Hz, 2H), 6.95 (s, 1H), 7.05 (s, 1H), 3.96 (s, 6H), 2.54 (s, 3H), 2.22 (s, 3H), 1.87 (s, 12H). C, 50.46; H, 5.88; N, 7.45. Found 699.2959. 

Synthesis of H4LV. 2,2′,5′,5′-Tetramethyl-1,1′,1″,1‴-quaterphenyl-3,3′,3″,3‴-tetracarboxylic Acid (H4LV). A mixture of 2 (1.12 g, 1.88 mmol), aqueous NaOH (0.5 M, 30 mL), and THF (30 mL) was heated at 50 °C for 2 h. THF was then removed by evaporation and concentrated HCl added to the aqueous residue (pH ∼1) to the azeo point. The precipitate thus formed was collected by filtration, washed with H2O, and dried in air to afford the product (759 mg, 97%) as a white solid and as a mixture of two enantiomers (R and S), undergoing fast racemization at room temperature. 1H NMR (500 MHz, CDCl3, ppm): δ 8.12 (m, two overlapped triplets, J = 1.5 Hz, 2H), 7.26 (m, two overlapped triplets, J = 1.6 Hz, 2H), 7.10 (m, two almost resolved singlets, 2H), 7.03 (m, two almost resolved singlets, 2H), 8.42 (m, two partially overlapped triplets, J = 1.5 Hz, 2H). The THF was removed by evaporation and concentrated HCl added to the aqueous residue to pH ∼1. The precipitate thus formed was collected by filtration, washed with H2O, and dried in air to afford the pure product (705 mg, 98%) as a white solid and as a 1:1 mixture of two diastereoisomers, a pair of enantiomers (RR and SS) and one meso isomer (RS), undergoing fast isomerization at room temperature. 1H NMR (500 MHz, DMF-d6, ppm): δ 8.10 (m, two broadened singlets, 2H), 7.88–7.08 (m, 16H). C: 54.03; H: 6.15; N: 7.31. Found 659.2416. 

Synthesis of [CuLIV]2+ ([CuLIV]2+)2DMF-3H2O (MFM-130). H4LV (50 mg, 0.093 mmol) and Cu(NO3)2·2H2O (1.07 g, 0.072 mmol) were dissolved in a mixture of DMF (70 mL) and H2O (0.5 mL), and the solution was placed in a tube (15 mL). Upon addition of 6 M HCl (15 µL), the tube was capped and heated at 90 °C for 16 h, and a large amount of microcrystalline product precipitated. The blue crystals were collected by filtration, washed with warm DMF, and dried in air. Yield: 58.6 mg (80% based on H4LV). Selected FTIR (cm−1): 3404 (br, w), 2927 (w), 1657 (vs), 1625 (m), 1573 (m), 1494 (m), 1445 (m), 1417 (m), 1367 (vs), 1308 (m), 1304 (w), 1284 (w), 1254 (m), 1187 (w), 1149 (w), 1094 (s), 1062 (m), 923 (w), 888 (w), 778 (m), 727 (s), 701 (w), 686 (w), 660 (s), 632 (w). Anal. Calc (%) for Cu2LIV·2Cu(NO3)2·H2O·6DMF: C, 44.67; H, 2.07; N, 9.91. Found: C, 44.73; H, 2.03; N, 9.93. 

Synthesis of [CuLIV]2+ ([CuLIV]2+)3DMF-4H2O (MFM-131). H4LV (50 mg, 0.078 mmol) and Cu(NO3)2·2H2O (1.17 g, 0.062 mmol) were dissolved in a mixture of DMF (70 mL) and H2O (1.0 mL) in a tube (15 mL). Upon addition of 6 M HCl (20 µL), the tube was capped and heated in an oil bath at 85 °C for 48 h to afford blue crystals. The reaction mixture was allowed to cool to room temperature, and the crystals were washed with warm DMF and dried in air. Yield: 60.9 mg, 85% based on H4LV. FTIR (cm−1): 3399 (br, w), 2924 (m), 1656 (w), 1626 (m), 1499 (m), 1435 (w), 1417 (w), 1367 (vs), 1303 (w), 1254 (m), 1186 (w), 1094 (s), 1062 (m), 955 (s), 887 (m), 777 (w), 736 (m), 724 (s), 700 (w). Anal. Calc (%) for Cu2LIV·3Cu(NO3)2·H2O·6DMF: C, 42.28; H, 6.62; N, 7.08. Found: C, 42.28; H, 6.62; N, 7.45.
X-ray Crystallographic Analyses. Single-crystal diffraction data for MFM-130 were collected at 150(2) K on a Bruker SMART APEX CCD area detector using graphite-monochromated Mo Kα radiation. Data for MFM-131 were collected using synchrotron radiation at Beamline I19 at Diamond Light Source. The details for data collection are included as part of the Crystallographic Information File (CIF) in the Supporting Information. The structures were solved by the direct method and refined by full-matrix least-squares methods on F² using SHELXL-2013. Hydrogen atoms on the ligands were placed geometrically and refined using a riding model; the hydrogen atoms of the coordinated water molecules could not be located but are included in the formula. DFIX, SADI, and PART instructions were included in the formula. DFIX, SADI, and PART instructions were used to deal with the disorder of the paraxylene moieties in the structures. The SQUEEZE option of PLATON was used to model the contribution of disordered guest molecules to the reflection intensities.

## RESULTS AND DISCUSSION

Single-Crystal X-ray Structures. The tetracarboxylate ligands H₄LIV and H₄LV (Figure 1) were synthesized by a series of Suzuki cross-coupling reactions (Scheme 1), followed by hydrolysis of the resultant tetraesters. The synthetic procedures and characterization of the target compounds and all their precursors are provided in full detail in the Experimental Section. On the basis of the lengths of these two linear struts (approximately 19 Å for H₄LIV and 23 Å for H₄LV), it was anticipated that nanosized porous structures can be assembled.

Solvolothermal reactions of H₄LIV and H₄LV with Cu(NO₃)₂·2.5H₂O in a mixture of DMF and H₂O at 80 °C for 16 h afforded blue highly crystalline solids of [Cu₂(LIV)₄(H₂O)₂]·6DMF·3H₂O (MFM-130) and [Cu₂(LV)₄(H₂O)₂]·7DMF·4H₂O (MFM-131), respectively. The formulae of these two compounds were confirmed by elemental analysis, single-crystal X-ray structure determinations, and TGA (Figure S1). The phase purity of the two bulk crystalline solids was confirmed by PXRD and Le Bail analyses (Figures S2–S4). Single-crystal X-ray structure analysis revealed that both MFM-130 and MFM-131 crystallize in the trigonal space group R3. Both rhombohedral lattices in MFM-130 and MFM-131 have similar a-axes due to the same type of Kagomé lattice formed by the two-connected isophthalate units with four-connected [Cu₂(COO)₄] paddlewheels. In MFM-130 (Figure 2), because of the steric hindrance caused by methyl substituents, the two-connected paraxylene units in (LIV)₄⁺ are almost perpendicular to each other. The methyl group of the paraxylene unit adjacent to the isophthalate ring forces these two rings to be noncoplanar with a torsion angle of approximately 51°. Thus, the geometrical conformation of the central pair of paraxylene units lock the two terminal isophthalate moieties within the same plane, making the linker (LIV)⁺ a planar four-connected node when bound to [Cu₂(COO)₄] paddlewheels. MFM-130 has an fof-type network topology constructed by the packing of two types of cages (A and B), and is isostructural with the analogous NOTT-102 constructed from tetracarboxylate linkers containing phenylene instead of paraxylene units. With the methyl groups projecting into the pores, both Cage A and Cage B in MFM-130 have reduced accessible voids compared to those of the non-functionalized analogue NOTT-102. Cage A has a slim ellipsoid shape with a length of 33 Å, a narrow diameter of 7 Å at the two ends and a larger diameter of 18 Å in the center, while Cage B has a thicker cylindrical shape with diameter of 13 Å and length of 16 Å (Figure 2).

MFM-131 has the same fof topology as MFM-130 with the Kagomé nets pillared by three consecutive paraxylene units from (LV)₄⁺ (Figure 3). Significantly, MFM-131 is non-interpenetrating despite the extra-long strut (LV)⁺ used, and this is a rare example of a fof framework with large internal voids (63%). Cage A in MFM-131 is significantly elongated to 42 Å in length compared to MFM-130 (33 Å) due to the presence of an additional paraxylene unit in the tetracarboxylate strut. With a dense population of methyl groups on the walls of the cage, the diameters of the two ends of the ellipsoid are narrowed to 5 Å compared to the oligophenylene analogue NOTT-104. Cage B in MFM-131 is an elongated nanosized cylinder of 13 Å × 20 Å (13 Å × 16 Å for MFM-130). The structural analogue NOTT-104 constructed from a linear tetracarboxylate linker incorporates the same length of strut used in MFM-131, but without the methyl groups. In this case, two identical fof-type lattices interpenetrate to form a doubly interpenetrated network in NOTT-104 (Figure 3c). The [Cu(isophthalate)]ₙ Kagomé lattice in NOTT-104 has two types of windows: a smaller triangular window ([Cu₃(isophthalate)]ₙ) of 6 Å in diameter and a larger hexagonal window ([Cu₄(isophthalate)]ₙ) with an opening of 18 Å. Therefore, the narrow end of the ellipsoidal cage from one framework can cross through the wider central opening of a second network, thus allowing network interpenetration in NOTT-104. The π–π interaction between the phenylene units from two

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Scheme 1. Synthesis of H₄LIV and H₄LV

(a)
different networks further facilitates and stabilizes the network interpenetration. In MFM-131, the opening of the hexagonal window in the Kagomé lattice is significantly smaller because of the presence of six paraxylene units around the window and \( \pi - \pi \) interactions between the paraxylene units are inhibited, thus successfully preventing interpenetration of the two fof lattices.

Stabilities of MFM-130 and MFM-131 and Mechanical Property Calculations. The activation of as-synthesized MFM-130 and MFM-131 was investigated for subsequent gas adsorption studies. Both materials were exchanged with acetone for 24 h before being dried under vacuum at 110 °C to afford the desolvated samples MFM-130a and MFM-131a, respectively. MFM-130a maintained crystallinity after thermal treatment under vacuum as confirmed by the PXRD analysis (Figure S2). However, after the desolvation process (using both thermal treatment and supercritical CO\(_2\) drying) MFM-131 showed almost complete loss of crystallinity, indicating an inherent instability upon desolvation. In order to understand and rationalize the reasons behind the distinct behaviors of MFM-130 and MFM-131 upon desolvation, we calculated the mechanical properties of both structures in the elastic regime (see Supporting Information). The second-order elastic stiffness tensors are shown in Figures S7 and S8, and a summary of their average and directional elastic properties is presented in Table 1. It can be observed that both structures have relatively similar mechanical features (due to their isostructural nature), including a marked anisotropy with stiffer directions (as defined by high Young’s modulus) along or near the \( c \) axis which is, on average, the principal axis of the organic linkers. Surprisingly, both structures display remarkable negative linear compressibility along the \( c \) axis (–9.9 TPa\(^{-1}\) for MFM-130 and –67.6 TPa\(^{-1}\) for MFM-131), which we attribute to a hinging mechanism in the fof topology. This suggests that testing of MFM-130, MFM-131, and other MOFs
of fof topology under pressure may generate unusual dynamic effects.

The main difference in the mechanical properties of MFM-130 and MFM-131 turns out to be the value of their lowest elastic modulus: the shear modulus (Figure 4). While MFM-131 shows lower average Young’s and shear moduli than MFM-130, MFM-131 shows an especially low directional shear modulus of 0.48 GPa compared to 1.73 GPa for MFM-130. This difference is linked to the lower density and higher porosity of MFM-131 and not to any change in mechanism since both minimal shear moduli correspond to the same direction. The very low shear modulus of MFM-131 is, to our knowledge, the lowest ever calculated for a non-flexible MOF. It explains the low resistance of MFM-131 to solvent evacuation, during which shear forces develop inside the crystal and which can, if they exceed the shear modulus in a specific direction, lead to mechanical instability and trigger a structural transition or collapse. This behavior is similar to the instability shown by some experimentally synthesized ZIF structures upon removal of solvents and guest molecules, suggesting that a gentler method of desolvation needs to be developed for the highly porous MFM-131 to remain structurally intact upon activation. However, with its densely functionalized methyl groups and large pore structure, MFM-131 may find other applications such as sensing and catalysis where desolvation is not required for the process. The above calculation represents a unique example of how computational simulation of the mechanical properties of MOFs, in this case, a fof-type system consisting of layered Kagomé lattices pillared by OPX units of different lengths, can help rationalize and explain the experimental results. This also improves our understanding of the mechanochemical properties of MOFs, especially those with large pore structures comprising large organic units.

**Porosity of MFM-130a.** The total accessible volume in MFM-130a after removal of guest solvates and coordinated water molecules is 60% as determined by the PLATON/VOID routine, and the desolvated framework has a calculated density of 0.642 g/cm³, which is more dense than NOTT-102a (0.587 g/cm³) reflecting the presence of methyl functionalities in the former. The N₂ isotherm for MFM-130a at 77 K shows typical Type I characteristics, indicative of the microporous nature of MFM-130a (Figure 5). The BET surface area is 2173

Table 1. Summary of the Mechanical Properties of the Structural Models of MFM-130 and MFM-131 in the Elastic Regime

<table>
<thead>
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<th>MFM-130</th>
<th>MFM-131</th>
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<tr>
<td>bulk modulus (Hill average) (GPa)</td>
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<td>Young’s modulus (Hill average) (GPa)</td>
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<tr>
<td>maximal shear modulus (GPa)</td>
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<tr>
<td>largest negative linear compressibility (TPa⁻¹)</td>
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<td>−67.6</td>
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<tr>
<td>largest positive linear compressibility (TPa⁻¹)</td>
<td>96.7</td>
<td>136.9</td>
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Figure 4. Directional shear modulus of MFM-130 and MFM-131 in the (xy), (xz), and (yz) planes. Minimal and maximal values of shear modulus for each direction are plotted in green and blue, respectively.
m²/g and total pore volume is 1.0 cm³/g derived from the N₂ isotherm. Due to the multiple methyl substituents occupying additional space, MFM-130a shows both a lower BET surface area and total pore volume than the isostructural frameworks NOTT-102, NOTT-110, and NOTT-111 containing biphenyl, phenanthrene, and hydrophenanthrene subunits, respectively, in the backbones of the tetracarboxylate linkers. The pore diameters in MFM-130a based on the nonlocal density functional theory (NLDFT) model are narrowly distributed between 11 and 15 Å.

**H₂, CH₄, and CO₂ Sorption Properties of MFM-130a.**

Cu(II)-based MOFs have been intensively investigated for their H₂ storage properties because of their high surface area and the availability of open Cu(II) sites for providing strong H₂ binding sites. Gravimetric H₂ sorption isotherms for MFM-130a were collected at 77 and 88 K up to 20 bar (Figure 6). MFM-130a has a lower surface area compared to non-functionalized NOTT-102 leading to a lower H₂ adsorption capacity of 5.3 wt% at 20 bar and 77 K (6.07 wt% for NOTT-102), consistent with the physical sorption nature of these materials. MFM-130a can adsorb 2.2 wt% of H₂ at 77 K and 1 bar, higher than most other MOFs without open metal sites. The isosteric heat of adsorption for H₂ in MFM-130a was calculated to be 6.6 kJ/mol at zero coverage using the virial method, higher than those for NOTT-102a, NOTT-110a, and NOTT-111a, confirming that the methyl groups in MFM-130a can increase the overlapping potential for H₂ molecules.

CH₄ storage has been widely studied due to the importance of natural gas as a promising alternative to petroleum-based fuels for mobile applications. The CH₄ adsorption isotherms for MFM-130a have been measured at 298 and 273 K up to 20 bar using the same gravimetric method as for the H₂ measurements (Figure S6). MFM-130a can adsorb a total of 6.9 mmol/g (154 cm³ (STP)/g) of CH₄ at 298 K and 20 bar, which is moderate compared to other Cu(II)-based MOF materials with high CH₄ capacities (Table 2). At 273 K, the total CH₄ adsorption capacity reaches 9.0 mmol/g (203 cm³ (STP)/g) at 20 bar. High-pressure CH₄ adsorption data up to 65 bar at 298 K were also collected using a volumetric method and the results match well with the gravimetric measurements in the range of 0–20 bar (Figure 7). The excess CH₄ uptake increases with pressure and then reaches a maximum value of 222 cm³ (STP)/g (equivalent to 143 cm³ (STP)/cm³) at 47 bar. The total CH₄ uptake, calculated using the crystal and skeletal densities of the material, reaches a value of 274 cm³ (STP)/g at 65 bar, corresponding to volumetric uptake of 176 cm³ (STP)/cm³. At 35 bar and 298 K, although MFM-130a shows lower gravimetric CH₄ uptake (excess: 219 cm³ (STP)/g; total: 254 cm³ (STP)/g) than highly porous MOFs such as NOTT-119 and NU-111, it exhibits higher volumetric CH₄ capacity (excess: 141 cm³ (STP)/cm³; total: 163 cm³ (STP)/cm³, Table 2). The deliverable CH₄ capacity is also an important factor when considering a material for practical onboard CH₄ storage applications. The deliverable amount of CH₄ in MFM-130a, defined as the difference in uptake between 65 and 5 bar, is 131 cm³/cm³. To gain further insight into the nature of framework–CH₄ interactions, the isosteric heats of adsorption (Qₑ) were calculated from isotherms collected at different temperatures. The Qₑ for CH₄ is 16.0 kJ/mol at zero surface coverage and, importantly, remains almost constant with increased loading. At loadings higher than 5.0 mmol/g, Qₑ starts to increase slowly due to the CH₄–CH₄ interactions, which may play an important role at high loadings.

The CO₂ and N₂ adsorption isotherms for MFM-130a were also measured in the pressure range of 0–1 bar at 298 and 273 K (Figure 8). The CO₂ adsorption capacities for MFM-130a at

**Figure 5.** N₂ isotherm for MFM-130a at 77 K. The inset shows the pore size distribution, indicating that the pore diameters are distributed between 11 and 15 Å according to the NLDFT model.

**Figure 6.** H₂ isotherms for MFM-130a at 77 and 87 K (a) up to 20 bar and (b) up to 1 bar. (c) Isosteric heat of H₂ adsorption as a function of loading for MFM-130a. "Ads" and "Des" represent adsorption and desorption, respectively.
1 bar are 109 cm$^3$/g (21.3 wt%) and 59 cm$^3$/g (11.6 wt%) at 273 and 298 K, respectively. Although these values are lower than those for other highly porous Cu(II)-based MOF materials such as NOTT-122$^{6f}$ (39.7 wt% at 273 K; 20.4 wt% at 298 K) and NOTT-125$^{25}$ (40.0 wt% at 273 K; 18.2 wt% at 298 K), which is attributed to the smaller pore size and the absence of CO$_2$-favorable organic functionalities in MFM-130a, they are higher than for most other frameworks without open metal sites such as ZIFs under the same conditions.$^{26}$ The heats of adsorption for CO$_2$ were calculated based on the isotherms at different temperatures by using the virial method. MFM-130a shows a high heat of CO$_2$ adsorption of 26 kJ/mol at zero surface coverage, reflecting a strong framework–CO$_2$ interaction due to the synergistic effects from the narrowed pores caused by the presence of methyl groups and open Cu(II) sites. Compared to the CO$_2$ adsorption, MFM-130a shows limited N$_2$ and CH$_4$ uptakes at 1 bar and room temperature. The CO$_2$/N$_2$ adsorption selectivity values for MFM-130a are 29.2:1 at 298 K and 38.2:1 at 273 K, as determined by evaluating the ratios of Henry’s law constants from single-component isotherms. The CO$_2$/N$_2$ selectivity for MFM-130a is significantly higher than those for NOTT-122a (14.3:1) and NOTT-125a (16:1) at 298 K. This increase in the selective adsorption of CO$_2$ is because the methyl groups from the paraxylene units in MFM-130a reduce the accessible pore

![Figure 7](image1.png)

**Figure 7.** (a) CH$_4$ sorption in MFM-130a in the pressure range of 0–70 bar. (b) Variation of heat of adsorption for CH$_4$ in MFM-130a as a function of loading.

![Figure 8](image2.png)

**Figure 8.** CO$_2$, CH$_4$, and N$_2$ adsorption isotherms for MFM-130a at 298 and 273 K up to 1 bar.
volume, thus creating enhanced overlapping potential for CO₂ molecules, but at the same time, lowering the adsorption of N₂. Also, MFM-130a shows respectable CO₂/CH₄ selectivities of 9.4 at 273 K and 7.1 at 298 K.

**Hydrocarbon Adsorption and Selectivities in MFM-130a.** Light hydrocarbons (C₁–C₂) are important raw chemicals for various industrial applications, and the separation of the pure components from mixtures involves energy-intensive cryogenic distillation processes. In particular, separation of C₂ hydrocarbons from CH₄ is an important industrial process for purification of CH₄ and adsorptive separation has been shown to be an efficient and energy-economic approach to these separation tasks. Several MOFs have been realized for their potential excellent selectivities of C₂ hydrocarbons over CH₄ due to the fine control of pore size/shape and the presence of strong C₂ hydrocarbon binding sites in the MOF structures. Although MOFs with pore sizes comparable to the kinetic diameters (3.3–4.4 Å) of C₂ hydrocarbons show enhanced C₂/C₁ selectivities, they typically suffer from low separation capacities. Therefore, the ideal MOFs for such separations should be ones showing optimized pore sizes and moderately high porosity, and at the same time, high affinities to C₂ hydrocarbons. Accordingly, pure-component C₂H₂, C₂H₄ and C₂H₆ isotherms for MFM-130a were collected at ambient temperatures (Figure 9). MFM-130a shows moderately high C₂H₂ uptakes of 144 cm³ (STP)/g at 273 K and 85.9 cm³/g at 298 K and 1 bar. The C₂H₄ capacities of MFM-130a are comparable to those of other MOFs with open metal sites showing high C₂H₂ uptakes under the same conditions (Table 3). MFM-130a also adsorbs high amounts of C₂H₄ (115.2 cm³/g at 273 K; 78.7 cm³/g at 298 K) and C₂H₆ (124.6 cm³/g at 273 K; 77.1 cm³/g at 298 K) at 1 bar. Compared to C₂H₂, C₂H₄ and C₂H₆, MFM-130a shows considerably low CH₄ uptake (18.6 cm³/g at 273 K; 10.6 cm³/g at 298 K) at 1 bar, indicating its potential for efficient separation of C₂ hydrocarbons from CH₄.

Virial analyses on the temperature-dependent hydrocarbons adsorption isotherms were performed to evaluate the binding interactions of C₂ hydrocarbons with the framework of MFM-130a and the separation selectivities (Table S2). The isosteric heats of adsorption at zero coverage, calculated based on the virial parameters, are 33.1, 34.0, and 25.0 kJ/mol for C₂H₂, C₂H₄ and C₂H₆, respectively (i.e., 16 kJ/mol for CH₄). It is worth noting that the C₂H₂ adsorption enthalpy for MFM-130a at low loading is higher than those for other Cu(II)-based MOFs such as MOF-505 (25.4 kJ/mol) and Cu₃(BTC)₂ (30.4 kJ/mol), indicating that the open Cu(II) sites, coupled with the optimized pore diameter induced by the functionalization of methyl groups in MFM-130a, play an important role in enhancing the binding energy between C₂ hydrocarbons and the framework. The selectivities for C₂ hydrocarbons/CH₄, derived using Henry’s law constants for individual hydrocarbons, on the equation $S_i = K_i / K_i(CH_4)$, MFM-130a reveals moderate selectivities for C₂H₂ vs CH₄ of 14.4 at 273 K and 10.1 at 298 K. This is consistent with the fact that the interactions of saturated C₂H₄ with the framework is solely based on van der Waals interactions and the selective adsorption of C₂H₆ over CH₄ is mainly based on the size effect of the adsorbates. Importantly, MFM-130a shows high selectivities for C₂H₂/C₂H₄ over CH₄ of 66.5/60.0 at 273 K and 34.7/30.3 at 298 K, respectively. Thus, MFM-130a represents a rare example of a framework material showing simultaneously high C₂ hydrocarbons adsorption capacities and high C₂ hydrocarbons/CH₄ selectivities at ambient temperature.

![Figure 9](image-url)  
*Figure 9. Adsorption isotherms for hydrocarbons in MFM-130a at (a) 298 and (b) 273 K in the pressure range of 0–1 bar.*

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**CONCLUSIONS**

In summary, we have successfully synthesized in a novel and efficient manner two linear tetracarboxylate linkers containing paraxylenol units and the respective [Cu₂(COO)₄]₁-based fof-type networks MFM-130 and MFM-131. Both these frameworks are non-interpenetrating, despite the extra-long organic linkers used, and comprise Kagomé lattice layers pillared by the oligoparaxylenol backbones. In these structures, the paraxylenol moieties adjacent to the isothphalate units significantly reduce the accessible openings of windows in the Kagomé lattice layers, thus effectively preventing interpenetration by two networks. This study provides a novel and efficient way for generating non-interpenetrating structures by using paraxylenol units as building blocks for organic struts. The mechanical properties calculated for these two MOFs revealed that MFM-131 shows lower average Young’s and shear moduli than MFM-130, explaining its instability upon desolvation. This approach gives further understanding of the mechanochemical properties in MOFs, especially those with large pore structures containing large organic units. The desolvated framework MFM-130a, densely decorated with methyl groups, shows moderately high porosity with BET surface area of 2173 m²/g and pore volume of 1.0 cm³/g, with high H₂ uptake capacities at both low and high pressures (2.2 wt% at 1 bar; 5.3 wt% at 20 bar), albeit at low temperature (77 K). The observed increased isosteric heat of adsorption for H₂ in MFM-130a compared to those of its structural analogues NOTT-102a, NOTT-110a,
Table 3. Adsorption of C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ in Various MOFs at 298 K and 1 bar

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume$^a$ (cm$^3$/g)</th>
<th>D$_r$ (g/cm$^3$)</th>
<th>C$_2$H$_2$ uptake (cm$^3$ (STP)/g)</th>
<th>Q$_{ads}$ for C$_2$H$_2$ (kJ/mol)</th>
<th>C$_2$H$_4$ uptake (cm$^3$ (STP)/g)</th>
<th>C$_2$H$_6$ uptake (cm$^3$ (STP)/g)</th>
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</thead>
<tbody>
<tr>
<td>MFM-130a</td>
<td>2173</td>
<td>1.0</td>
<td>0.642</td>
<td>85.9</td>
<td>33.1</td>
<td>78.7</td>
<td>77.1</td>
</tr>
<tr>
<td>Cu$_2$(pzdc)$_2$(pyz)$^{30}$</td>
<td>571</td>
<td></td>
<td>1.745</td>
<td>42</td>
<td>42.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HKUST-1$^{31a}$</td>
<td>1401</td>
<td>0.76</td>
<td>0.879</td>
<td>201</td>
<td>30.4</td>
<td>165.9$^d$</td>
<td>137.7$^d$</td>
</tr>
<tr>
<td>MOF-505$^{31a}$</td>
<td>1139</td>
<td>0.68</td>
<td>0.927</td>
<td>148</td>
<td>25.4</td>
<td>113.4$^d$</td>
<td>123.4$^d$</td>
</tr>
<tr>
<td>NOTT-102$^{1b}$</td>
<td>3342</td>
<td>1.28</td>
<td>0.587</td>
<td>146</td>
<td>128.2</td>
<td>125.9</td>
<td></td>
</tr>
<tr>
<td>ZIF-8$^{31a}$</td>
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<td>0.924</td>
<td>25</td>
<td>13.3</td>
<td>26.7</td>
<td>44.2$^b$</td>
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<tr>
<td>ZnMOF-74$^{31b}$</td>
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<td>1.231</td>
<td>122</td>
<td>24.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The pore volume values were calculated from N$_2$ isotherms at 77 K.
$^b$Crystal density calculated from the single-crystal structure for the activated sample.
$^c$pyzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine.
$^d$These data were taken from ref 31b.
$^{31a}$Measured at 301 K.$^{31b}$

and NOTT-111a clearly indicates that the methyl functionality can enhance the H$_2$—framework interactions. MFM-130a also shows high volumetric CH$_4$ adsorption (total 163 cm$^3$ (STP)/cm$^3$ at 35 bar) and deliverable (131 cm$^3$/cm$^3$ from 65 to 5 bar) capacities at room temperature. Furthermore, the high CO$_2$ vs N$_2$, C$_2$H$_2$ vs CH$_4$, and C$_2$H$_4$ vs CH$_4$ selectivities revealed by MFM-130a suggest it to be a promising material for potential carbon capture and natural gas purification applications.

**REFERENCES**


