Lawrence Berkeley National Laboratory
Recent Work

Title
Guest-Controlled Incommensurate Modulation in a Meta-Rigid Metal-Organic Framework Material.

Permalink
https://escholarship.org/uc/item/0qr4w35w

Journal
Journal of the American Chemical Society, 142(45)

ISSN
0002-7863

Authors
Li, Jiangnan
Zhou, Zhengyang
Han, Xue
et al.

Publication Date
2020-11-01

DOI
10.1021/jacs.0c08794

Peer reviewed
Guest-Controlled Incommensurate Modulation in a Meta-Rigid Metal–Organic Framework Material

Jiangnan Li,* Zhengyang Zhou,* Xue Han, Xinran Zhang, Yong Yan, Weiyao Li, Gemma L. Smith, Yongqiang Cheng, Laura J. M’Cormick M’Pherson, Simon J. Teat, Mark D. Frogley, Svemir Rudić, Anibal J. Ramirez-Cuesta, Alexander J. Blake, Junliang Sun,* Martin Schröder,* and Sihai Yang*

ABSTRACT: Structural transitions of host systems in response to guest binding dominate many chemical processes. We report an unprecedented type of structural flexibility within a meta-rigid material, MFM-520, which exhibits a reversible periodic-to-aperiodic structural transition resulting from a drastic distortion of a [ZnO4N] node controlled by the specific host–guest interactions. The aperiodic crystal structure of MFM-520 has no three-dimensional (3D) lattice periodicity but shows translational symmetry in higher-dimensional (3 + 2)D space. We have directly visualized the aperiodic state which is induced by incommensurate modulation of the periodic framework of MFM-520·H2O upon dehydration to give MFM-520. Filling MFM-520 with CO2 and SO2 reveals that, while CO2 has a minimal structural influence, SO2 can further modulate the structure incommensurately. MFM-520 shows exceptional selectivity for SO2 under flue-gas desulfurization conditions, and the facile release of captured SO2 from MFM-520 enabled the conversion to valuable sulfonamide products. MFM-520 can thus be used as a highly efficient capture and delivery system for SO2.

INTRODUCTION

Metal–organic framework (MOF) materials are synthetic porous materials constructed from bridging metal centers and organic ligands.1 MOFs can be either rigid2 or flexible3 depending upon the metal–ligand coordination combination, framework topology, and organic functionality. Rigid MOFs retain a well-defined framework structure and pore interior against external variables (e.g., temperature, pressure, and guest inclusion), making them useful for the separation and purification of substrates.2,4 In contrast, flexible MOFs can undergo reversible breathing transitions between typically two well-defined periodic crystal structures. One form is often described as narrow-pored and the other form is described as large-pored, and these two forms therefore show different porosities and properties.5–10

Figure 1 illustrates various structural responses to guest binding within a MOF lattice. Breathing and metastable MOFs show two prevailing types of phase transitions, namely, periodic-to-periodic and periodic-to-amorphous. Beyond that, there is also an intriguing class of mesoporous MOFs, allowing the formation of adsorbate superlattices based upon long-range collective adsorbate–adsorbate interactions.11 The periodic-to-aperiodic transition observed here for MFM-520 represents a new type of framework flexibility in crystalline porous solids. Superspace group theory12 has been used to describe the commensurate structure of crystalline zeolite SSZ-5713 in higher-dimensional space, and this has been applied to interpret the incommensurate modulated structures described here.

EXPERIMENTAL SECTION

Synthesis of MFM-520. All reagents were used as received from commercial suppliers without purification. The synthesis of H4L (4,4′-bipyridine-2,6,2′,6′-tetracarboxylic acid) and [{Zn2(L)·4H2O}]∞
Figure 1. Representation of structural transitions in various types of MOFs upon guest inclusion and removal. MOFs and guest molecules are shown by solid lines and shaded spheres, respectively. (a) Rigid MOF showing full retention of the framework structure on gas adsorption and desorption. (b) Flexible MOF showing reversible framework breathing between a narrow-pore phase and a large-pore phase. (c) Metastable MOF showing irreversible framework amorphization. (d) Mesoporous MOF showing the formation of superlattices of adsorbates. (e) Meta-rigid MOF, MFM-520, showing reversible incommensurate modulation of the framework structure on going from (top to bottom) MFM-520 to MFM-520-H2O (CO2 represented by blue spheres) to MFM-520-SO2 (SO2 represented by green spheres) (bottom).

(MFM-520-H2O) was carried out using previously reported methods.

**In Situ Synchrotron Single-Crystal X-ray Diffraction and Structural Characterization.** In situ synchrotron X-ray single-crystal diffraction data were collected on beamline 11.3.1 of the Advanced Light Source using monochromated radiation [\( \lambda = 0.7749(1) \) Å]. After data collection for as-synthesized sample MFM-520-H2O, the same single crystal (0.10 × 0.05 × 0.05 mm³) was placed in a capillary gas handling cell and evacuated in situ under dynamic vacuum and a stream of N2 at 340 K centered on the capillary for 4 h. The single-crystal diffraction data of dehydrated MFM-520 were collected at 290 K. Upon loading of CO2 into MFM-520 at 1.0 bar and 290 K, three diffraction data sets were collected at 180 K to examine the possible dynamic behavior of the structural relaxation (i.e., adsorbate–adsorbent equilibrium and change in the modulation vector). The single crystal was then reactivated under dynamic vacuum (10⁻¹⁰ bar) for 1 day and heating to remove all adsorbed gases. The in situ single-crystal diffraction data for SO2-loaded MFM-520 were collected using the same method as for the CO2-loaded sample.

The influence of temperature on the periodic-to-aperiodic phase transition was monitored by collecting in situ single-crystal diffraction data for dehydrated MFM-520 at 180–350 K on a Rigaku Oxford XtaLAB diffractometer using Mo-Kα radiation. No change in the modulation vectors of MFM-520 was observed between 180 and 350 K (Table S2), confirming the negligible impact of temperature on the modulation vector of MFM-520.

To examine the reversibility of the periodic-to-aperiodic phase transition observed in MFM-520, a single crystal of rehydrated MFM-520-H2O, formed by the treatment of dehydrated MFM-520 with water, was studied by single-crystal diffraction at 180 K. This experiment confirms the absence of satellite reflections of the rehydrated sample (Figure S6).

In the (3 + 2)D incommensurately modulated structure, each parameter of modulation can be expanded as a Fourier series using
\[
p_{m}^{i}(x_{i}, x_{j}) = \sum_{n,m} \left[ p_{nm}^{i} \sin(2\pi nx_{i} + 2\pi nx_{j}) + p_{nm}^{i} \cos(2\pi nx_{i} + 2\pi nx_{j}) \right]
\]
where \( x_{i} = q_{i} r_{i} + t_{i}, x_{j} = q_{j} r_{j} + u_{j}, \) and \( t_{i} \) and \( u_{j} \) are initial phases in the range of 0 to 1. The real structural parameters can be expressed as
\[
p_{m}^{i}(x_{i}, x_{j}) = p_{m}^{i}(x_{i}, x_{j}) + p_{m}^{i}
\]

The average structure parameters \( p_{m}^{i} \) were determined by direct methods and least-squares refinements, and the modulations were refined globally using free variables. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed using a riding model. Given the complexity of the structure, soft constraints on the bond length/angle to both host and guest were applied in the final stage of refinement. All refinements of the crystal structures were performed on the JANA2006 software platform.

**Gas Adsorption Isotherms.** Gravimetric sorption isotherms for N₂, CO₂, SO₂, CH₄, CO, and O₂ were recorded at various temperatures on a Hiden Isochema IGA-003 system under high vacuum (10⁻¹⁰ bar) produced by a turbo pumping system. Temperatures were maintained using a programmed water bath. Ultra-pure research grade gases (99.999%) were purchased from BOC or Air Liquide. In a typical gas adsorption experiment, 50 mg of acetone-exchanged MFM-520 was loaded into the IGA system and activated at 393 K under dynamic high vacuum (10⁻¹⁰ bar) for 1 day.
to give fully desolvated MFM-520. BET surface areas and porosity data were obtained from N$_2$ isotherm data at 77 K.

Gas Separation by Breakthrough Experiments. In the breakthrough experiments, the flow rate of the entering gas mixture was maintained at 50 mL min$^{-1}$, and the gas concentration, C, of SO$_2$, CO$_2$, and N$_2$ at the outlet was determined by mass spectrometry and compared with the corresponding inlet concentration C$_0$, where C/C$_0$ = 1 indicates complete breakthrough. Breakthrough separation of SO$_2$/CO$_2$ was conducted using a mixture containing SO$_2$ (2500 ppm) and 15% CO$_2$ (v/v) diluted in He through a fixed bed packed with MFM-520 at 298 and 318 K and 1 bar at a flow rate of 50 mL min$^{-1}$.

Figure 2. Column I: views of in situ synchrotron X-ray diffraction images of the hk0 plane. Column II: views of the corresponding crystal structures of MFM-520 as a function of guest inclusion/removal. 8 × 8 × 2 means the unit cell of the modulated structure is 8 times that of the average structure along the $a$ and $b$ axes and 2 times along the $c$ axis; 7 × 7 × 2 means the unit cell of the modulated structure is 7 times that of the average structure along the $a$ and $b$ axes and 2 times along the $c$ axis. Column III: details of the structure shown in the red box in column II. Column IV: molecular details of host–guest interactions. The MOF framework, zinc, oxygen, carbon, and sulfur are shown in blue, green, red, gray, and yellow, respectively. Bond distances are shown in Å. (a) MFM-520·H$_2$O, (b) MFM-520, (c) MFM-520·CO$_2$, and (d) MFM-520·SO$_2$. A comparison of all in situ synchrotron X-ray diffraction images of the hk0.5 and hk1 planes is shown in Figure S5. The reflection conditions of MFM-520·H$_2$O are $l = 2 \times$ integer and $h = 2 \times$ integer. According to superspace group theory,$^{17}$ there is a supercentered setting with $a_s = a$, $b_s = b$, $c_s = 2c$, $Q_4 = \alpha(a_s^* + b_s^*)$, and $Q_5 = \alpha(-a_s^* + b_s^*) + 0.5c^*$, and $Q_6 = \alpha(-a_s^* + b_s^*) + 0.5c^*$. Because the tables of (3 + 2)D superspace groups$^{19}$ provide only reflection conditions with supercentered settings, we transformed the basic setting to supercentered settings to determine the reflection conditions. With the supercentered setting, the hk0, hk0.5, and hk1 planes are transformed to HK0, HK1, and HK2, respectively (Figure S5). The reflection conditions of MFM-520, MFM-520·CO$_2$, and MFM-520·SO$_2$ are HKLMN: $L + M + N = 2 \times$ integer, HK0MN: $M = 2 \times$ integer, HHLM0: $L = 2 \times$ integer, HHL0N: $N = 2 \times$ integer, H0LMM: 2H + L + 2M = 4 \times$ integer, and 0KLMM: 2K + L + 2M = 4 \times$ integer, corresponding to (3 + 2)D superspace group 136.2.69.10, adopting the symbol P4$_2$/mnm($\alpha$, $\alpha$, 1/2) 00qs($-\alpha$, $\alpha$, 1/2)0sq0 with basic settings.
The final results have been converted to dimensionless plots as shown in Figure 4.

Inelastic Neutron Scattering (INS) Experiments. INS spectra were recorded on the TOSCA spectrometer at the ISIS Facility at the STFC Rutherford Appleton Laboratory. TOSCA is an indirect geometry instrument that provides a wide spectral range (10–2000 cm\(^{-1}\)) with resolution optimized in the 200–2000 cm\(^{-1}\) range. In this region, TOSCA has a resolution of 1.25% of the energy transfer. The instrument is composed of 130 \(^{3}\)He detectors in forward and backscattering geometries located 17 m downstream from a 300 K Gd poisoned water moderator. A temperature of 10 ± 0.2 K was maintained during data collection by two \(^{3}\)He closed-cycle refrigerators with 30 mbar \(^{3}\)He as an exchange gas. Each Zn(II) center binds to the N(pyridyl)-donor of L4 with an equivalent to 1.18 mmol of SO\(_2\) for 1 h to reach adsorption equilibrium. Morpholin-4-amine (128.0 mg, 1.25 mmol) and SO\(_2\)@MFM-520 (357 mg, 0.25 mmol) in CH\(_3\)CN (1 mL) was added dropwise to the above mixture was stirred for 1 h. 4-Methoxy-aryldiazonium tetrafluoroborate (55.0 mg, 0.25 mmol) in CH\(_3\)CN (1 mL) was added dropwise to the above suspension, and the mixture was stirred at room temperature for 1 h. The mixture was filtered, and the filtrate was evaporated. NMR spectroscopy and preparative thin layer chromatography (TLC) were used to quantify the conversion of 4-methoxy-aryldiazonium tetrafluoroborate and the yield of the sulfonamide. Benzenaldehyde was used as an internal standard.

**RESULTS AND DISCUSSION**

MFM-520-H\(_2\)O, \([\text{Zn}_2(\text{L})_2\text{H}_4\text{O} (\text{H}_4\text{L}= 4,4\text{-bipyridyl}-3,3',5,5'\text{-tetracarboxylic acid})],\) adopts a 3D open-framework structure comprising square-based pyramidal five-coordinate Zn(II) centers bridged by the tetracarboxylate linker. Each Zn(II) center binds to the N(pyridyl)-donor of L\(^{\text{c}}\) along the c axis, and four bridging carboxylates propagate the structure along the diagonals of the ab plane, thus defining an unusual and rigid sqp topology. MFM-520-H\(_2\)O exhibits bow-tie-shaped pores with dimensions of 6.6 × 4.0 Å\(^2\) which...
are filled with guest water molecules which assemble into 1D helical chains along the [110] direction. These chains are stabilized by strong intermolecular hydrogen bonds \([Ow···Ow = 2.934(11), 2.887(11) \text{ Å}]\) (Figure S2). The water molecules are also hydrogen bonded to the framework oxygen center of the ligand \([Ow···O2 = 3.064(9) \text{ Å}]\) (Figure 2a-IV), inducing the overall structure to crystallize in tetragonal space group \(P4_2212\) \([a = b = 7.0211(6), c = 19.9558(15) \text{ Å}]\). These complementary host–guest and guest–guest hydrogen bonds stabilize the periodic structure of MFM-520·H₂O and restrict its freedom for structural relaxation.

On heating MFM-520·H₂O at 340 K under dynamic vacuum, additional satellite reflections appear at positions defined by modulation vectors \(0.1240(3)(a^* + b^*) + 0.5c^*\) and \(0.1240(3)(-a^* + b^*) + 0.5c^*\) on the plane diffraction patterns (Figure 2b-I), indicating that an intriguing structural transition has occurred. The loss of guest water molecules removes the stabilizing network of hydrogen bonding and thus creates voids and freedom for the \([\text{ZnO}_4\text{N}]\) polyhedra to relax. Bond distances \(\text{Zn}—\text{N}1, \text{Zn}—\text{O}1,\) and \(\text{Zn}—\text{O}2\) in MFM-520·H₂O \([2.002(6), 2.214(6),\) and \(1.959(5) \text{ Å}, \text{respectively}]\) change with the loss of water and lie in ranges of \(2.07—2.12,\) \(2.25—2.58,\) and \(1.79—2.11 \text{ Å}, \text{respectively}, \text{for dehydrated MFM-520.}\) This is accompanied by the modulation of the electron density at the \(\text{Zn}(II)\) center with the formal oxidation state ranging from 1.70(10) to 1.93(10) in MFM-520 as determined by bond valence sum (BVS) calculations for the different \(\text{Zn}(II)\) centers (Figure 3a). In contrast, those in MFM-520·H₂O have the same charge of 1.974(14). The resulting structure of dehydrated MFM-520 is aperiodic in 3D space but periodic in \((3 + 2)\)D space, and the two modulated vectors \((q1\) and \(q2\)) are projections of the additional two dimensions along the three directions of 3D reciprocal space. Importantly, all satellite reflections of dehydrated MFM-520 disappear on rehydration to MFM-520·H₂O, demonstrating the reversibility of this periodic-to-aperiodic phase transition.

Figure 4. Gas adsorption, selectivity, stability, thermodynamic, spectroscopy, and dynamic separation data. (a) Adsorption isotherms for SO₂, CO₂, CH₄, CO, O₂, and N₂ in MFM-520 at 298 K (solid symbols, adsorption; open symbols, desorption). (b) Comparison of the SO₂ adsorption capacity of MFM-520 over 75 cycles at 298 K. (c) Variation of isosteric heats of adsorption \((\Delta Q_s)\) and adsorption entropy \((\Delta S)\) for SO₂ and CO₂ uptake in MFM-520. (d) Comparison of experimental FTIR spectra for bare and CO₂- and SO₂-loaded MFM-520. (e) Comparison of DFT-calculated FTIR spectra for bare and CO₂- and SO₂-loaded MFM-520. (f) Comparison of the difference plots for experimental and DFT-calculated INS spectra of D₂O, CO₂-, and SO₂-loaded MFM-520 (black, experiment; red, calculation). The discrepancies, particularly for the lattice modes at low energy (<200 cm⁻¹), are due to the limitation that DFT simulations can be conducted only on average unit cells, which does not take the incommensurate modulation into consideration. (g) Dimensionless breakthrough plots for SO₂/N₂ mixtures under dry (solid lines) and humid (dashed lines) conditions. Dry conditions: 2500 ppm SO₂, 99.75% N₂, total flow rate 50 mL min⁻¹. Wet conditions: 1.5% H₂O, 2500 ppm SO₂, 98.25% N₂, total flow rate 50 mL min⁻¹. (h) Dimensionless breakthrough plots for SO₂/CO₂ mixtures at 298 K (15% CO₂, 2500 ppm SO₂, 84.75% He, total flow rate 50 mL min⁻¹). (i) Dimensionless breakthrough plots for cyclic SO₂ adsorption under both dry and humid conditions. Dry conditions: 2500 ppm SO₂, 99.75% He, total flow rate 50 mL min⁻¹. Wet conditions: 1.5% H₂O, 2500 ppm SO₂, 98.25% He, total flow rate 50 mL min⁻¹. For experiments under humid conditions, the bed was first exposed to a flow of 1.5% H₂O in He until the breakthrough of water.
transition (Figure S6). No change was observed in the modulation vectors for dehydrated MFM-520 between 180 and 350 K (Table S2). Interestingly, for the periodic-toaperiodic phase transitions in inorganic materials, metal alloys, and organic compounds, which are induced by changes in temperature and electric and magnetic fields, the periodic-toaperiodic transition observed in MFM-520 is controlled by hostguest interactions, representing the first example of such a phenomenon for an inorganicorganic hybrid material or porous solid.

Dehydrated MFM-520 displays a BET surface area of 313 m² g⁻¹ and a pore volume of 0.146 cm³ g⁻¹, and single-component adsorption isotherms for SO₂, CO₂, CH₄, CO, O₂, and N₂ in MFM-520 have been recorded at 273-318 K up to 1.0 bar (Figure 4a, Figures S9-S12). The excess adsorption uptake of SO₂ at 298 K and 1.0 bar is 3.38 mmol g⁻¹, which is higher than those of CO₂, CH₄, CO₂, O₂, and N₂ (0.77, 0.71, 0.36, 0.19, and 0.18 mmol g⁻¹, respectively). More significantly, at low pressure (e.g., 0.01 bar, 298 K), where all other gases show negligible uptakes (0.09 mmol g⁻¹ for CO₂, 0.01 mmol g⁻¹ for CH₄, CO₂, O₂, and N₂), MFM-520 displays a notably higher isothermal uptake of SO₂ (1.66 mmol g⁻¹), accompanied by fast adsorption kinetics typically within minutes (Figures S13 and S14). The static SO₂ uptake of MFM-520 is comparable to those of the best-behaving sorbents but is lower than the dynamic SO₂ uptake of SIFSIX-2-Cu-i, which possesses very narrow pores (Table S3). Often, there is a trade-off between high adsorption at low pressure and difficulties in the complete regeneration of narrow-pored MOFs. Facile regeneration of the SO₂-saturated MFM-520 can be readily achieved solely via a pressure swing, and no loss of SO₂ adsorption capacity or crystallinity of MFM-520 was observed after 75 cycles of SO₂ adsorptiondesorption (Figure 4b).

Further analysis of the adsorption thermodynamics of MFM-520 reveals that the isosteric heat of adsorption (Qₑ) for CO₂ is 32-48 kJ mol⁻¹ and the entropy of adsorption (ΔS) decreases steadily with increasing surface coverage, consistent with the expected ordering of adsorbed CO₂ molecules in MFM-520. In comparison, Qₑ for SO₂ adsorption reaches ~120 kJ mol⁻¹ at low surface coverage and decreases gradually to 60 kJ mol⁻¹ with increasing loading of SO₂. The calculated value of Qₑ is consistent with the calorimetric measurements of 43 and 96 kJ mol⁻¹ for CO₂ and SO₂ adsorption, respectively (Figures S15 and S16). The higher value of Qₑ for SO₂ uptake is consistent with the expected stronger interaction between the framework and SO₂ compared with CO₂. However, the ΔS for SO₂ adsorption increases steadily from an initial ~260 to ~135 J K⁻¹ mol⁻¹ with increasing loading of SO₂. This observation is opposite to the prevailing understanding of gas adsorption in porous materials, where ordering of the gas molecules results in a decrease in ΔS on gas loading and implies increasing disorder of the system on SO₂ loading in MFM-520.

We sought to understand the origin of this intriguing pattern in ΔS and have determined the hostguest structures of CO₂ and SO₂-loaded MFM-520 by in situ synchrotron X-ray single-crystal diffraction (Table S1). On loading CO₂ into MFM-520 at 270 K and 1.0 bar, adsorbed CO₂ molecules are clearly observed in the pores, corresponding to a crystallographic uptake of 2.18 mmol g⁻¹, in excellent agreement with the isotherm uptake (2.14 mmol g⁻¹). All guest CO₂ molecules in MFM-520-CO₂ were found to be incommensurate (Figure 2c).

Thus, instead of showing a constant distance between adjacent CO₂ molecules, the intermolecular distances range from 6.6 to 7.4 Å (Figure S3), indicating no apparent interaction between adjacent CO₂ molecules. The distances between CO₂ and phenyl rings (C1···pyridyl ring) and between CO₂ and aromaticCH groups (O3···H1C2C2) are longer than 3.0 Å (Figure 2c-IV), suggesting only very weak supramolecular interactions between the host framework and CO₂. Therefore, MFM-520 experiences no change in structure upon CO₂ adsorption, and both the oxidation state of Zn(II) centers (ranging from 1.73(9) to 2.07(9)) and the geometry of [ZnO₄N] nodes in MFM-520-CO₂ [Zn≡N1, Zn≡O1, and Zn≡O2 bond distances ranging between approximately 2.00 and 2.07, 2.20 and 2.50, and 1.72 and 2.25 Å, respectively] are similar to those of bare MFM-520 (Figure 3b, Figures S7 and S8). Thus, the two modulation vectors (0.1243(3)(a* + b*) + 0.5c* and 0.1243(3)(−a* + b*) + 0.5c*) in MFM-520 remain upon adsorption of CO₂.

Upon loading of SO₂ into MFM-520 at 270 K and 1.0 bar, a crystallographic uptake of SO₂ of 3.16 mmol g⁻¹ is observed, in excellent agreement with the isotherm uptake (3.38 mmol g⁻¹). Since the occupancy of adsorbed SO₂ molecules is 0.359(13) in the refined structural model of MFM-520-SO₂, half of the closely contacted SO₂ molecules (ca. 1.7 to 1.9 Å) were removed, and the remaining SO₂ molecules have an intermolecular distance of ca. 3.5 Å (Figure S4), which is shorter than that in MFM-520-CO₂, suggesting stronger guestguest interactions between adsorbed SO₂ molecules.

On the other hand, strong MOF−SO₂ binding is indicated by the short distances between SO₂ and aromaticCH groups (O3···H1C2C2: ca. 2.33 to 2.75 Å) and between SO₂ and [ZnO₄N] polyhedra (S1···O2: ca. 2.78 to 3.34 Å) (Figure 2d-IV, Figures S7 and S8). As a result, the structure of MFM-520 is heavily affected by adsorbed SO₂ molecules. The ranges of bond distances Zn≡N1, Zn≡O1, and Zn≡O2 in MFM-520 are varied from 1.97 to 2.14, 1.92 to 2.73, and 1.75 to 2.19 Å, respectively, much wider than those observed in MFM-520 and MFM-520-CO₂. The oxidation state of the Zn(II) centers also shows a greater range between 1.79(9) and 2.29(9) (Figure 3c) compared with that in MFM-520 and MFM-520-CO₂. In MFM-520-SO₂, the modulation vectors become 0.1407(6)(a* + b*) + 0.5c* and 0.1407(6)(−a* + b*) + 0.5c*, demonstrating a unique incommensurately ordered dynamic equilibrium for SO₂ adsorption. Interestingly, before reaching this equilibrium state, we also identified a transient structure of MFM-520-SO₂ with a corresponding crystallographic SO₂ uptake of 0.352 mmol g⁻¹ that has intermediate modulation vectors of 0.1331(4)(a* + b*) + 0.5c* and 0.1331(4)(−a* + b*) + 0.5c* (Table S1). The change in the incommensurate modulation of MFM-520 induced by the uptake of SO₂ is a dynamic process as a function of diffusion and the settling of SO₂ molecules within the pores of the MOF. This result rationalizes the unusual increase in ΔS on SO₂ loading and confirms that it emanates from a subtle increase in the structural flexibility of meta-rigid MFM-520 upon SO₂ adsorption.

Overall, the incommensurate modulated structure reported here will stimulate a reassessment of a wider range of hostguest systems with unusual adsorption behaviors and encourage the search for new structural flexibility in other MOFs and porous solids that otherwise may be regarded as entirely rigid.
The binding dynamics and effects on the structural relaxation of MFM-520 have been analyzed further using in situ synchrotron infrared microspectroscopy, inelastic neutron scattering (INS), and DFT modeling (Figure 4d–f and Figures S19–S30). Dehydrated MFM-520 has a number of characteristic peaks at 3104, 1080, 1689, 1571, and 1390 cm$^{-1}$ (denoted as I, II, III, IV, and V), which are assigned based upon DFT modeling to the stretching (I) and bending (II) modes of the aromatic C–H groups on the pyridyl ring and the symmetric stretching (III) and asymmetric stretching (IV) modes of C–O and the bending (V) mode of C–H groups, respectively. On dosing CO$_2$ (0–1 bar), peak I shows a blue shift ($\Delta = 9$ cm$^{-1}$) to 3113 cm$^{-1}$, indicating a stiffening of the framework as a result of the binding of CO$_2$ molecules to −CH groups. No notable changes occur in peaks II–V on CO$_2$ loading, consistent with the very weak MOF–CO$_2$ interactions. Upon loading SO$_2$, a larger blue shift of 12 cm$^{-1}$ is observed for peak I, accompanied by near-depletion of this band on increasing SO$_2$ loading, demonstrating a stronger −CH···SO$_2$ supramolecular interaction. Furthermore, distinct red shifts of peaks III and IV (C–O, carboxyl) to 1682 and 1566 cm$^{-1}$ ($\Delta = 6$ and 5 cm$^{-1}$, respectively) and peak V (C–H, pyridyl ring) to 1385 cm$^{-1}$ ($\Delta = 5$ cm$^{-1}$) are observed, entirely consistent with the presence of structural distortion as observed in crystallographic studies and DFT-calculated IR spectra (Figure 4e). Difference INS spectra recorded (Figure 4f) between bare and CO$_2$-, SO$_2$-, and D$_2$O-loaded MFM-520 reveal shifts of peaks associated with deformation and twisting modes of the pyridyl rings at low frequencies (200–300 cm$^{-1}$) as well as C–H bending modes at higher frequencies (900–1300 cm$^{-1}$), as confirmed by DFT modeling. SO$_2$ and D$_2$O both display notably stronger interactions with MFM-520 than CO$_2$, again consistent with the crystallographic studies.

Unlike conventional once-through FGD (flue gas desulfurization) methods where SO$_2$ permanently binds to sorbent materials to form solid inorganic waste, the SO$_2$ captured by MFM-520 can thus be used to drive organic reactions e.g., immobilization and then release of SO$_2$ using a stable MOF as an SO$_2$ delivery system for subsequent reactivity.

CONCLUSIONS

The metal–organic framework material MFM-520 exhibits a reversible periodic-to-apерiodic structural transition. The apерiodic crystal structure of MFM-520 has no three-dimensional (3D) lattice periodicity but shows translational symmetry in higher-dimensional (3 + 2)D space. Filling of MFM-520 with CO$_2$ and SO$_2$ reveals that while CO$_2$ has a minimal structural influence, SO$_2$ can further modulate the structure incommensurately. In addition, MFM-520 shows high selectivity for SO$_2$ under flue gas desulfurization conditions, and the facile release of captured SO$_2$ from MFM-520 can be used as an SO$_2$ delivery system for subsequent reactivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08794.

Additional experimental details, diffraction data, views of crystal structures, INS and IR spectroscopy, adsorption isotherms, and IAST selectivity (PDF)

Crystal data for MFM-520-H$_2$O (CIF)

Crystal data for MFM-520 (CIF)

Crystal data for MFM-520-CO$_2$ (CIF)

Crystal data for MFM-520-SO$_2$ intermediate (CIF)

Crystal data for MFM-520-SO$_2$ (CIF)

AUTHOR INFORMATION

Corresponding Authors

Junliang Sun − BNLMS, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China; orcid.org/0000-0003-4074-0962; Email: junliang.sun@pku.edu.cn

Martin Schröder − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.; orcid.org/0000-0001-6992-0700; Email: M.Schroder@manchester.ac.uk

Sihai Yang − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.; orcid.org/0000-0002-1111-9272; Email: Sihai.Yang@manchester.ac.uk

Authors

Jiangnan Li − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Zhengyang Zhou − BNLMS, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China

Xue Han − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Xinran Zhang − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Yong Yan − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Weiya Li − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Gemma L. Smith − Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Yongqiang Cheng − Neutron Scattering Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/0000-0002-3263-4812
Laura J. M’Cormick M’Pherson — Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
Simon J. Teat — Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
Mark D. Fogley — Diamond Light Source, Harwell Science Campus, Oxfordshire OX11 0DE, U.K.
Svein Rudić — ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, U.K.
Anibal J. Ramirez-Cuesta — Neutron Scattering Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/0000-0003-1231-0668
Alexander J. Blake — School of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c08794

Author Contributions
*J.L. and Z.Z. contributed equally.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
We thank the EPSRC (EP/1011870), the Royal Society and University of Manchester, the National Basic Research Program (nos. 2013CB933402 and 2016YFA0301004), and the National Natural Science Foundation of China (nos. 21527803, 21471009, 21621061, and 21871009) for funding. This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Programme (grant agreement no. 742401, NANOCHM). We are grateful to the Diamond Light Source and the STFC/ISIS Facility for access to beamlines B2 and TOSCA, respectively. This research used the resources of beamlines 11.3.1 and 12.2.1 at the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. The computing resources were made available through the VirtuES and ICE-MAN projects, funded by the Laboratory Directed Research and Development Program and the Compute and Data Environment for Science (CADES) at ORNL. J.L., X.Z., and Z.Z. thank the China Scholarship Council (CSC) for funding.

REFERENCES
(1) Kalmutzki, J. M.; Hanikel, N.; Yaghi, M. O. Secondary building units as the turning point in the development of the reticular chemistry of MOFs. Sci. Adv. 2018, 4, eaat9180.
(2) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. Hydrocarbon separation in a metal-organic framework with open iron(II) coordination sites. Science 2012, 335, 1606.
(3) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible metal-organic frameworks. J. Am. Chem. Soc. 2014, 43, 6062–6066.
(4) Han, X.; Godfrey, H. G. W.; Briggs, L.; Davies, A. J.; Cheng, Y.; Daemen, L. L.; Sheleva, A. M.; Tuna, F.; McNees, E. J. L.; Sun, J.; Drathen, C.; George, M. W.; Ramirez-Cuesta, A. J.; Thomas, K. M.; Yang, S.; Schröder, M. Reversible adsorption of nitrogen dioxide within a robust porous metal-organic framework. Nat. Mater. 2018, 17, 691–696.
(5) Krause, S.; Bon, V.; Senkovska, I.; Stoeck, U.; Wallacher, D.; Többens, D. M.; Zander, S.; Pillai, R. S.; Maurin, G.; Coudert, F.-X.; Kaskel, S. A pressure-amplifying framework material with negative gas adsorption transitions. Nature 2016, 532, 348–352.
(6) Katsoulidis, A. P.; Antypov, D.; Whitehead, G. F. S.; Carrington, E. J.; Adams, D. J.; Berry, N. G.; Darling, G. R.; Dyer, M. S.; Rosseinsky, M. J. Chemical control of structure and guest uptake by a conformationally mobile porous material. Nature 2019, 565, 213–217.
(7) Gu, C.; Hosono, N.; Zheng, J.-J.; Sato, Y.; Kusaka, S.; Sakaki, S.; Kitagawa, S. Design and control of gas diffusion process in a nanoporous soft crystal. Science 2019, 363, 387–391.
(8) Goodwin, A. L.; Calleja, M.; Conterio, M. J.; Dove, M. T.; Evans, J. S. O.; Keen, D. A.; Peters, L.; Tucker, M. G. Colossal positive and negative thermal expansion in the framework material Ag$_2$(Cu(CN)$_3$)$_2$. Science 2008, 319, 794–797.
(9) Serre, C.; Millange, F.; Thouvenot, C.; Nougès, M.; Marsolier, G.; Louër, D.; Férey, G. Very large breathing effect in the first nanoporous chromium(III)-based solids: MIL-53 or Cr(III)(OH)$_2$·(O$_2$C-C$_6$H$_4$-CO$_2$)$n$$_2$·H$_2$O. J. Am. Chem. Soc. 2002, 124, 13519–13526.
(10) Deria, P.; Gómez-Gualdrón, D. A.; Bury, W.; Scharif, H. T.; Wang, T. C.; Thallapally, P. K.; Sarjeant, A. A.; Smr, R. Q.; Hupp, J. T.; Prabh, O. K. Ultraporous, water stable, and breathing zirconium-based metal-organic frameworks with twow topology. J. Am. Chem. Soc. 2015, 137, 13183–13190.
(11) Sung Cho, H.; Deng, H.; Miyasaka, K.; Dong, Z.; Cho, M.; Neimark, A. V.; Ku Kang, J.; Yagi, O. M.; Terasaki, O. Extra adsorption and adsorbate superlattice formation in metal-organic frameworks. Nature 2015, 527, 503–507.
(12) Jansen, T.; Chapuis, G.; Boissieu, M. Aperiodic Crystals: From Modulated Phases to Quasicrystals: Structure and Properties; Oxford University Press: Oxford, 2018.
(13) Baerlocher, C.; Weber, T.; McCusker, L.; Palatinus, L.; Zones, I. S. Unraveling the perplexing structure of the zeolite SSZ-57. Science 2011, 333, 1134–1137.
(14) Lin, X.; Blake, A. J.; Wilson, C.; Sun, X. Z.; Champsness, N. R.; George, M. W.; Hubberstey, P.; Mokaya, R.; Schröder, M. A porous framework polymer based on a zinc(II) 4,4′-bipyridine-2, 2′, 6′-tetracarboxylato: synthesis, structure, and “zeolite-like” behaviors. J. Am. Chem. Soc. 2006, 128, 10745–10753.
(15) Petricek, V.; Dusek, M.; Palatinus, L. Crystallographic computing system JANA2006: general features. Z. Kristallogr. - Cryst. Mater. 2014, 229, 345–352.
(16) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. First principles methods using CASTEP. Z. Kristallogr. - Cryst. Mater. 2005, 220, 567–571.
(17) Cheng, Y. Q.; Daemen, L. L.; Kolesnikov, A. I.; Ramirez-Cuesta, A. J. Simulation of inelastic neutron scattering spectra using OCLIMAX. J. Chem. Theory Comput. 2019, 15, 1974–1982.
(18) Boyer, L. L.; Kaxiras, E.; Feldman, J. L.; Broughton, J. Q.; Mehl, M. J. New low-energy crystal structure for silicon. Phys. Rev. Lett. 1991, 67, 715.
(19) Stokes, H. T.; Hatch, D. M.; Campbell, B. J. ISO(3+d)D, ISOTROPY Software Suite, iso.byu.edu.
(20) Brese, N. E.; O’Keeffe, M. Bond-valence parameters for solids. Acta Crystallogr., Sect. B: Struct. Sci. 1991, 47, 192–197.
(21) Ovsyannikov, S. V.; Bykov, M.; Bykovka, E.; Kozlenko, D. P.; Tsirlin, A. A.; Karkin, A. E.; Shchennikov, V. V.; Kichanov, S. E.; Gou, H.; Abakumov, A. M.; Egoavil, R.; Verbeeck, J.; McCammon, C.; Dyadkin, V.; Chernyshov, D.; van Smaalen, S.; Dubrovinsky, L. S. Charge-ordering transition in iron oxide Fe$_4$O$_5$ involving competing IR ＄d$-$d$ and ＄d$-$p$ hybridizations. Nat. Chem. 2016, 8, 501–508.
(22) Prokel, K.; Hartwig, S.; Gukasov, A.; Miyoshi, J. A.; Huang, Y. K.; Niehaus, O.; Pöttgen, R. Coexistence of different magnetic moments in CeRuSn probe by polarized neutrons. Phys. Rev. B: Condens. Matter Mater. Phys. 2015, 91, 014424.
(23) Sun, Z.; Li, J.; Ji, C.; Sun, J.; Hong, M.; Luo, J. Unusual long-range ordering incommensurate structural modulations in an organic molecular ferroelectric. J. Am. Chem. Soc. 2017, 139, 15900–15906.
(24) He, H.; Tan, X. Electric-field-induced transformation of incommensurate modulations in antiferroelectric Pb0.99Nb0.02(Zr1-xSnx)1-yTiyO3. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 72, 024102.

(25) Cui, X.; Yang, Q.; Yang, L.; Krishna, R.; Zhang, Z.; Bao, Z.; Wu, H.; Ren, Q.; Zhou, W.; Chen, B.; Xing, H. Ultrahigh and selective SO2 uptake in inorganic anion-pillared hybrid porous materials. Adv. Mater. 2017, 29, 1606929.

(26) Yang, S.; Liu, L.; Sun, J.; Thomas, K. M.; Davies, A. J.; George, M. W.; Blake, A. J.; Hill, A. H.; Fitch, A. N.; Tang, C. C.; Schröder, M. Irreversible network transformation in a dynamic porous host catalyzed by sulfur dioxide. J. Am. Chem. Soc. 2013, 135, 4954–4957.

(27) Yang, S.; Sun, J.; Ramirez-Cuesta, A. J.; Callear, S. K.; David, W. I. F.; Anderson, D. P.; Newby, R.; Blake, A. J.; Parker, J. E.; Tang, C. C.; Schröder, M. Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host. Nat. Chem. 2012, 4, 887–894.

(28) Bell, J. G.; Morris, S. A.; Aidoudi, F.; McCormick, L. J.; Morris, R. E.; Thomas, K. M. Physisorption-induced structural change directing carbon monoxide chemisorption and nitric oxide coordination on hemilabile porous metal organic framework NaNi3(OH)-(SIP)2(H2O)3H2O (SIP = 5-sulfoisophthalate). J. Mater. Chem. A 2017, S, 23577–23591.

(29) Dubbeldam, D.; Calero, S.; Maesen, T. L. M.; Smit, B. Incommensurate diffusion in confined systems. Phys. Rev. Lett. 2003, 90, 245901.

(30) Banerjee, D.; Wang, H.; Gong, Q.; Plonka, A. M.; Jagiello, J.; Wu, H.; Woerner, W. R.; Emge, T. J.; Olson, D. H.; Parise, J. B.; Li, J. Direct structural evidence of commensurate-to-incommensurate transition of hydrocarbon adsorption in a microporous metal organic framework. Chem. Sci. 2016, 7, 759–765.

(31) Han, X.; Yang, S.; Schröder, M. Porous metal-organic frameworks as emerging sorbents for clean air. Nat. Rev. Chem. 2019, 3, 108–118.

(32) Wu, W.; Han, B.; Gao, H.; Liu, Z.; Jiang, T.; Huang, J. Desulfurization of flue gas: SO2 absorption by an ionic liquid. Angew. Chem., Int. Ed. 2004, 43, 2415–2417.

(33) Zheng, D.; An, Y.; Li, Z.; Wu, J. Metal-free aminosulfonylation of aryldiazonium tetrafluoroborates with DABCO-(SO2)2 and hydrazines. Angew. Chem., Int. Ed. 2014, 53, 2451–2454.