Metal–organic frameworks with dynamic interlocked components

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The dynamics of mechanically interlocked molecules such as rotaxanes and catenanes have been studied in solution as examples of rudimentary molecular switches and machines, but in this medium, the molecules are randomly dispersed and their motion incoherent. As a strategy for achieving a higher level of molecular organization, we have constructed a metal–organic framework material using a [2]rotaxane as the organic linker and binuclear Cu(II) units as the nodes. Activation of the as-synthesized material creates a void space inside the rigid framework that allows the soft macrocyclic ring of the [2]rotaxane to rotate rapidly, unimpeded by neighbouring molecular components. Variable-temperature ^{13}C and ^{2}H solid-state NMR experiments are used to characterize the nature and rate of the dynamic processes occurring inside this unique material. These results provide a blueprint for the future creation of solid-state molecular switches and molecular machines based on mechanically interlocked molecules.

A variety of artificial molecular switches and machines have been reported that are based on the relative motion of the constituent components of mechanically interlocked molecules (MIMs)[1–5]. However, these and other elaborate systems only operate in solution or in a condensed phase where the molecular devices are randomly dispersed and their motion is incoherent[6,7]. If these tiny devices could be organized in a predictable and orderly manner, the creation of ultradense molecular-based memory or indeed controlling the electronic properties of materials at the molecular level would be very much closer to realization[8,9].

One way to achieve a higher level of molecular organization and coherency would be to precisely place the soft, dynamic molecular components that undergo motion (for example, rotation or translation) into the pores of metal–organic framework (MOF) materials[10–14]. In this way, the soft MIM would be clearly separated from the hard, structural skeleton of the MOF that holds it in place[15,16]. To date, there have been reports on the use of MIMs (almost exclusively using pseudorotaxane precursors) as linkers in coordination polymers to create interesting 1-, 2- and 3-periodic crystalline lattices[17–25], but none of these materials has been shown to exhibit any type of dynamic motion related to the MIM components. As both MIM chemistry and MOF design are mature fields of research, it seems reasonable to suggest that, although challenging, this merger of ideas could be accomplished.

To demonstrate that such a dynamic MIM in MOF material could be created and the internal motion of the interlocked component characterized, a [2]rotaxane ligand containing a single macrocyclic ring was targeted. Although rotation of the wheel component of a simple [2]rotaxane is not a molecular switch or a sophisticated molecular machine, the preparation of such a prototype material and demonstration of its internal dynamics in the solid state provides a working design and methodological blueprint for the inclusion of more complex MIM systems into MOFs.

Based on our previous experiences investigating the structures and properties of metal–organic rotaxane frameworks (MORFs), five design criteria were taken into account in this work. (1) Metal nodes and linkers that result in a neutral, 3-periodic, non-interpenetrated framework were used to eliminate counterions in the lattice, maximize stability and allow for the porosity essential to create

internal space such that the MIM is able to undergo uninhibited motion. (2) A permanently interlocked ligand was used to ensure retention of the mechanical link during the vigorous reaction conditions required to prepare the MOF. (3) A MIM template was chosen in which the initial (non-covalent) templating interactions were easily removed so as to maximize the freedom of motion of the wheel components. (4) The MIM axle was designed to be compact and rigid to minimize framework flexibility and skeletal vibrations. (5) The system was designed to make use of a characterization tool capable of unambiguously characterizing the dynamics of the MIM components in the solid state. (These points should not be seen as a set of rigid guidelines or a recipe for success, but simply a roadmap to accompany this particular discovery.)

Here, we report the preparation of a MOF designated **UWDM-1** (University of Windsor Dynamic Material) containing a [2]rotaxane as a linker, as well as experimental observation by solid-state NMR (SSNMR) of the interlocked wheel undergoing dynamic motion inside this unique solid-state material. The structural design components used to create such a material are outlined in Fig. 1. The key element is a crossbar, which provides clear separation of the carboxylate struts that form the skeletal core of the MOF from the axle and wheel of the [2]rotaxane that is the source of the dynamics. This design allows for generation of what Garcia-Garibay has previously identified as the free volume necessary for observation of dynamic motion in a crystalline molecular machine[26–28].

Results and discussion

A compact and rigid MIM linker was designed with two 3,5-benzene-dicarboxylic acid groups as the linking struts, a benzyl-aniline recognition site as the crossbar and a [24]crown-6 macrocycle as the wheel (Fig. 2a). Importantly, this struts/axle combination should result in a MOF skeleton with no freely rotating bonds, providing a situation in which only the macrocyclic wheel is free to undergo large-amplitude structural changes, thus greatly simplifying any study of the dynamics of the system.

The axle was prepared by condensation of diethyl-5-amino-isophthalate with diethyl-5-formyl-isophthalate to give the corresponding imine, followed by reduction with NaBH$_4$ to yield the

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Free volume
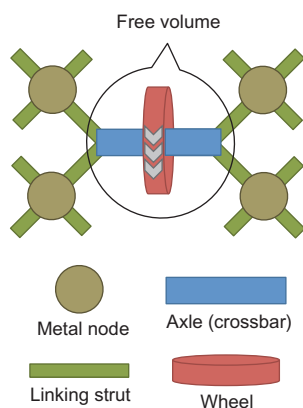
Metal node

Axle (crossbar)

Linking strut

Wheel

Figure 1 | MOF materials are commonly constructed from a combination of rigid linking struts (green) and metal nodes (brown). In a new design, the components of a MIM—that is, the axle (blue) and wheel (red) of a [2]rotaxane—are inserted as part of a crossbar between the struts. This provides the wheel component of the MIM with the free volume required to undergo unencumbered motion inside the pores of the MOF.

neutral benzyl-aniline **1**. Subsequent protonation of **1** with HBF_4 produced the charged benzyl-anilinium axle **2**[BF_4], which acts as a good recognition site[29] for a ring-closing metathesis (RCM) reaction[30,31] using Grubbs's I catalyst. The RCM methodology allowed clipping of a 24-membered crown ether around the axle, producing [2]rotaxane **3**[BF_4] (E and Z isomers) in very good yield, after which hydrogenation of the residual double bond yielded tetraester **4**[BF_4]. Finally, treatment of **4**[BF_4] with base to both hydrolyse the four esters groups and deprotonate the anilinium site gave neutral, tetra-carboxylate MIM linker **6** in excellent yield (see Supplementary Fig. S1 for details). It should be noted that facile deprotonation of the anilinium [2]rotaxane by NEt_3 or NaOH is a key design element, because traditional secondary ammonium-based [2]rotaxanes are notoriously difficult to neutralize[32].

A representation of the single-crystal X-ray structure of the neutral tetraethyl ester MIM precursor **5** is shown in Fig. 2b; the

axle and wheel components are clearly interpenetrated with only a single hydrogen bond between the aniline N–H group on the axle and an oxygen atom of the crown ether wheel (d(N–H···O) = 3.09 Å, $\angle$(NHO) = 177°) remaining from the interactions used to template [2]rotaxane formation. The structure of **5** can be considered a model for the structure of MIM **6** inside the MOF, as it is neutral and contains exactly the same structural features.

The Cu(II)-based MOF designated **UWDM-1** was prepared by combining $Cu(NO_3)_2 \cdot 3H_2O$ and the tetracarboxylate MIM linker **6** in a 3:2:2 mixture of dimethylformamide (DMF)/EtOH/H_2O with two drops of HNO_3 and heating in a temperature-controlled oven at 65 °C for 48 h followed by slow cooling to room temperature at a rate of 0.1 °C min^{-1}. Green crystalline material could be repeatedly produced in this manner with isolated yields of >75%. Single-crystal X-ray analysis of the as-synthesized material determined the formula of **UWDM-1** to be $[Cu_2(MIM)(H_2O)_2]\cdot 3H_2O$. **UWDM-1** is a porous MOF that adopts a rare β-phase of NbO topology[33] in which water occupies a small void space (11%) in the lattice. The recognition site comprising the $-NHCH_2-$ link of the axle and a complete [24]crown-6 macrocycle is disordered end-to-end with 50:50 site occupancy due to the random and irreversible nature of the metal–ligand bond formation during crystallization. Figure 3a,b shows representations of the repeating unit in ball-and-stick and space-filling models, respectively. Figure 3c,d shows how these repeating units assemble into a larger polyhedron, and Fig. 3e,f illustrates how these polyhedra are linked to create narrow channels along the c-axis of the crystal that contain molecules of water (not shown).

Initially, the wheel is locked in place by virtue of hydrogen bonding from an ether oxygen atom on the macrocycle to a copper-bound H_2O molecule. Removal of the water molecules from both the channel and the copper centres by heating to 150 °C under vacuum (activation) provides a void space in which the MIM can undergo motion unimpeded by neighbouring molecular components. The structural integrity of the rigid MOF skeleton is completely unaffected by repeated ON/OFF cycles comprising starting (activation) and stopping (deactivation) of the ring dynamics. Figure 4 presents powder X-ray diffraction (PXRD) data for the simulated, as-synthesized and activated
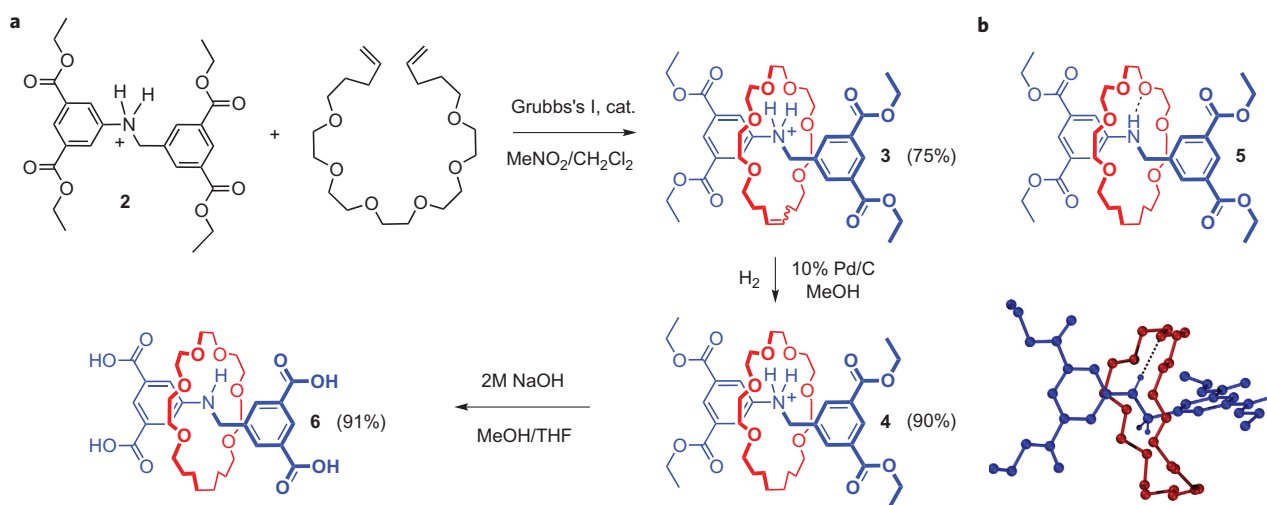

Figure 2 | Synthesis and X-ray structural characterization of a mechanically interlocked MOF linker. a, Major steps in the synthesis of a neutral MOF linker comprising a benzyl-aniline axle and a [24]crown-6 ether wheel (see Supplementary Fig. S1 and pages S5–S18 for full synthetic and spectral details). MIM linker **6** comprises a neutral benzyl-aniline axle with four carboxylic acid groups for coordination to metal ions and a [24]crown-6 ether macrocycle wheel. **b**, Single-crystal X-ray diffraction was used to verify the structure of **5**, which is the tetra-ester precursor to **6**. Neutral [2]rotaxane **5** contains all the same structural features as the actual MIM linker **6**. A ball-and-stick representation of the single-crystal X-ray structure of **5** shows the single hydrogen bond between axle and wheel (only hydrogen atoms of the central benzyl-aniline unit are shown for clarity).
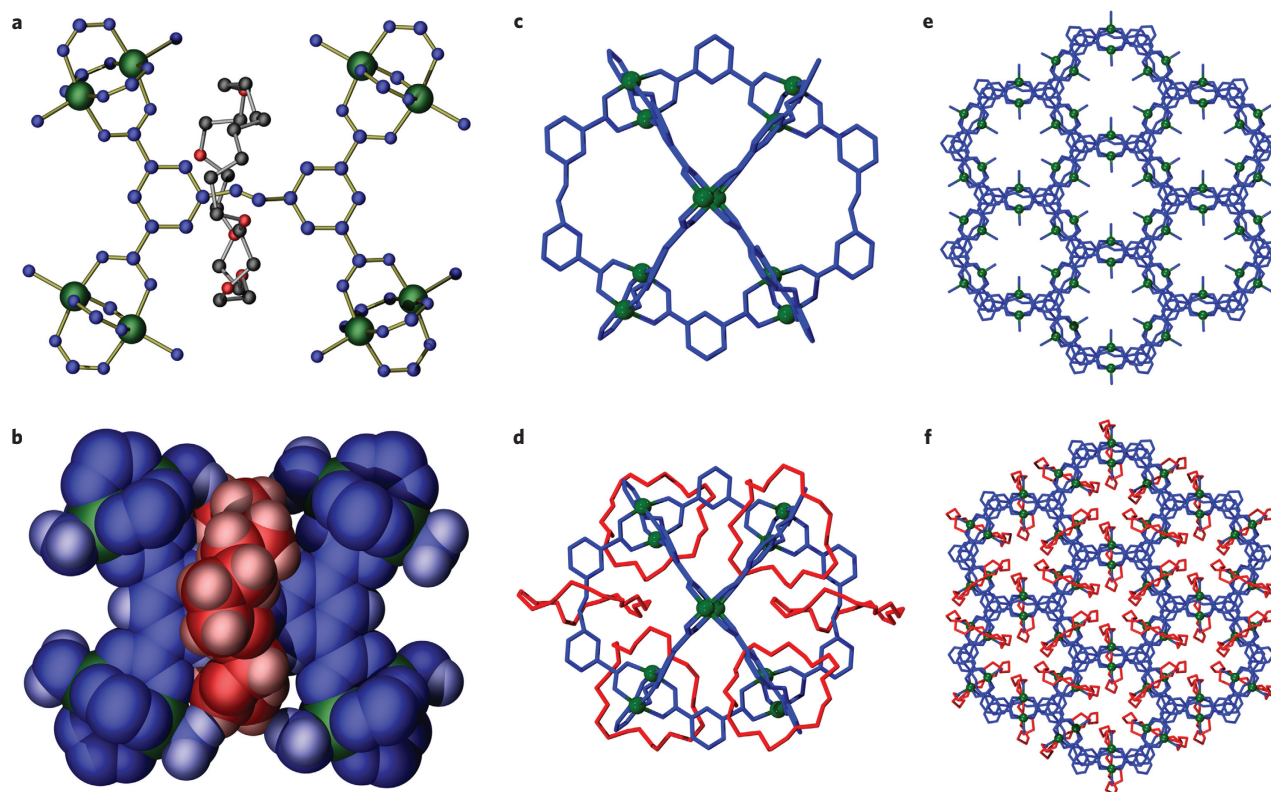
Figure 3 | Structure of UWDM-1 determined by single-crystal X-ray diffraction. a, Ball-and-stick representation of a single unit of the MIM coordinated to four Cu(II) paddlewheel clusters (hydrogen atoms are omitted for clarity). **b**, As in **a**, but as a space-filling model. **c**, Polyhedron comprising six paddlewheel units with macrocyclic rings omitted. **d**, As in **c**, but with macrocyclic rings shown. **e**, Linked polyhedra, with macrocyclic rings omitted, viewed down the c-axis, showing the channels that contain H_2O. **f**, As in **e**, but with macrocyclic rings shown.

versions of the material, as well as pictures of samples before and after activation. The overall stability of **UWDM-1** was verified by variable-temperature PXRD, which showed no variation between 25 and 225 °C (Supplementary Fig. S24).
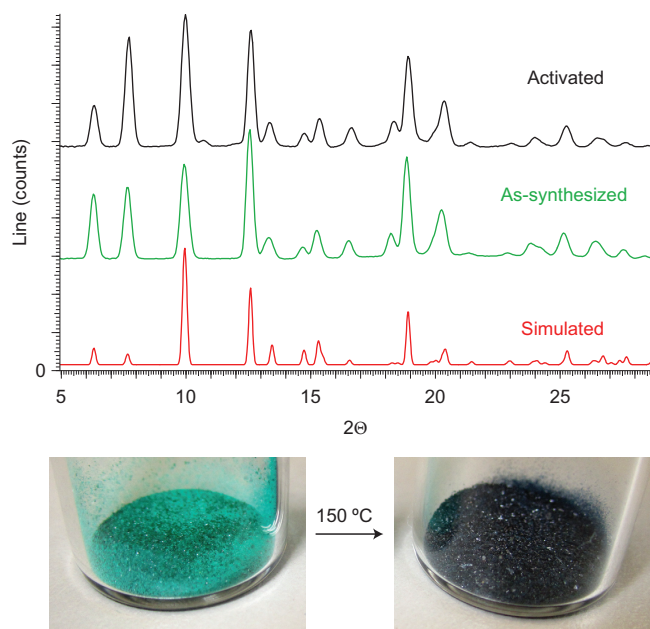

Figure 4 | PXRD traces for UWDM-1. Red, simulated from single crystal data; green, as-synthesized material; black, activated material prepared by heating as-synthesized material to 150 °C under high vacuum for 12 h.

^{13}C and ^{2}H SSNMR spectra of activated **UWDM-1** (and d_2-**UWDM-1**) were acquired over a large temperature range to investigate the dynamics of the macrocyclic component in the MOF. SSNMR spectroscopy is particularly useful as it allows for a targeted study of the individual molecular components of the material. The variable-temperature ^{1}H–^{13}C cross-polarization/magic-angle spinning (CP/MAS) spectra of the crown ether carbons in activated **UWDM-1** display a dramatic increase in resolution as the temperature is raised from 292 K to 477 K (Fig. 5a). The spectra increasingly resemble the solution ^{13}C NMR spectrum of the tetraethyl ester rotaxane, suggesting that the crown ether is free to undergo rapid motion at high temperature.

To determine the nature of the motion, the MIM was labelled with two chemically equivalent deuterium atoms using deuterium gas for hydrogenation of the double bond (E and Z isomers), yielding d_2-**UWDM-1**. Variable-temperature ^{2}H SSNMR spectra of activated d_2-**UWDM-1** are shown together with spectral simulations in Fig. 5b,c. Analysis of the ^{2}H powder patterns using models developed for simpler molecular systems[34,35] provides strong evidence of the four motional regimes depicted schematically in Fig. 5d. Spectra acquired at 160 and 203 K indicate that there is no rotation of the macrocycle or any other sort of motion that averages the ^{2}H quadrupolar interaction on the NMR timescale. Starting at 251 K, the ring begins to undergo conformational changes that result in reorientations of the ^{2}H-labelled CH_2 groups; that is, the pseudo-axial and pseudo-equatorial C–H positions are interconverted. At 324 K, the local CH_2 reorientation is accompanied by a second mode of motion that can be assigned to a rocking, or partial rotation, of the ring. At 373 K and above, the spectra unambiguously indicate that the ring is undergoing full rotations with a jump rate greater than 10 MHz, in combination
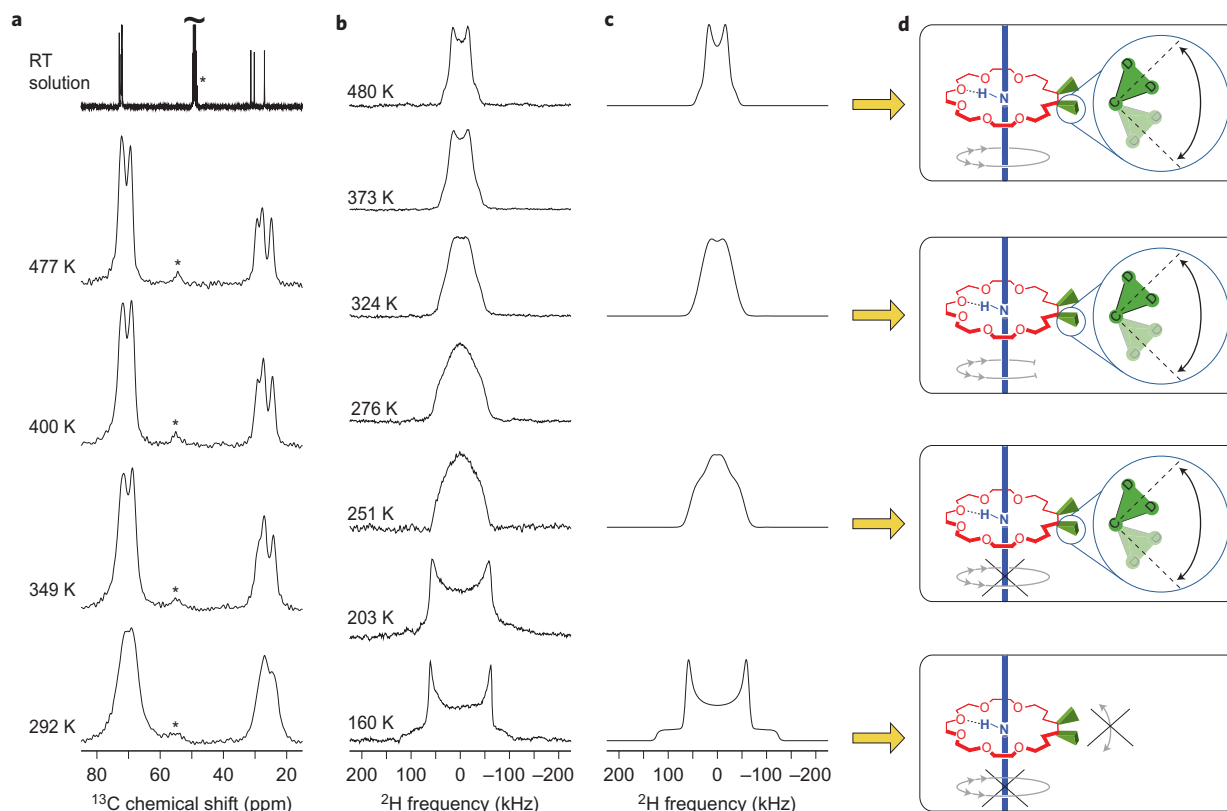
Figure 5 | Solid-state ^{13}C and ^{2}H NMR (SSNMR) were used to identify and determine the nature of the dynamic motions occurring inside activated samples of UWDM-1 at various temperatures. a, ^{13}C SSNMR spectra of **UWDM-1** showing resonances for the [24]crown-6 macrocycle (* identifies the ^{13}C resonance for the benzylic carbon atom of the axle). **b**, Experimental ^{2}H SSNMR spectra of activated **d_2-UWDM-1** as a function of temperature. **c**, Simulated ^{2}H SSNMR spectra of activated **d_2-UWDM-1. d**, Schematic representations of the dynamic motion of the [24]crown-6 macrocycle inside the MOF.

with the conformational changes (which reorient the CH_2 groups with respect to the ring). This translates to a lower limit for the activation energy associated with a rotational step of $\sim$50 kJ mol^{-1} (see Supplementary page S30 for details). The ^{2}H SSNMR spectra therefore clearly identify the two-component nature of **UWDM-1**, in which a dense array of soft [24]crown-6 macrocycles are able to rapidly rotate and sample multiple conformations while mechanically linked to the rigid three-dimensional framework of the MOF.

To further demonstrate the utility of our design and synthetic methodology, an analogous MIM linker was constructed with a slightly smaller macrocycle, [22]crown-6. Preliminary PXRD and variable-temperature ^{2}H SSNMR data indicate that the MOF material is isomorphous with **UWDM-1**, but the conformational freedom of the smaller macrocyclic ring is restricted and this material does not exhibit the same motion observed for **UWDM-1** (Supplementary Fig. S35). It may be that a series of MOFs with different macrocycles, each with a set of uniquely characteristic motions, can be constructed using the same metal–organic framework; research into this is ongoing.

Conclusions

We have prepared **UWDM-1**, a robust MOF material with a mechanically interlocked molecule as part of its internal skeletal structure, and have shown by SSNMR that the macrocyclic ring component of the MIM can undergo independent motion about the rigid MOF to which it is interlocked. The preparation of such a unique material and demonstration of its internal dynamics in the solid state provides a roadmap for the inclusion of more complex MIM systems into MOFs. Indeed, the small size of the MIM unit ($\sim$1 nm^3) and the regularity of the MOF framework in

UWDM-1 allows for an incredibly high density of these dynamic components in the material ($\sim$1 × 10^{21} cm^{-3}). The ability to arrange mobile and functional molecular components in a highly dense and predictable array is a crucial step towards the generation of solid-state devices with multiple functions and properties.

Methods

Preparation of tetra-carboxylate MIM linker 6. The axle was prepared by condensing diethyl-5-amino-isophthalate with diethyl-5-formyl-isophthalate in chloroform in the presence of excess $MgSO_4$, followed by reduction of the imine in a 3:1 mixture of tetrahydrofuran (THF)/EtOH with 1.1 equiv. of $NaBH_4$ to give **1** (90%) and then protonation with HBF_4 in diethyl ether to produce **2** (93%). The [24]crown-6 macrocycle was clipped around the axle to give **3** (75%) using the precursor pentaethyleneglycol-dipent-4-enyl ether and Grubbs I catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$ in 10:1 CH_2Cl_2:MeNO$_2$. The residual double bond was then reduced using H_2(g) and Pd/C 10 wt% in MeOH to give **4** (90%), the axle deprotonated with NEt_3 producing **5** (94%) and the ester groups hydrolysed to the acids with 2 M NaOH in a 2:1 mixture of MeOH/THF to yield the tetracarboxylate MIM linker **6** (91%). M_p > 250 °C (dec.). ^{1}H NMR (500 MHz, CD_3OD): $\delta = 8.63$ (s, 2H, Ar–H), 8.51 (s, 1H, Ar–H), 7.84 (s, 1H, Ar–H), 7.77 (s, 2H, Ar–H), 4.79 (s, 2H, Ar–CH_2), 3.6–3.2 (m, 24H, OCH_2CH_2OCH_2CH_2), 1.38–1.27 (m, 8H, O$CH_2CH_2CH_2CH_2$), 1.22 (m, 4H, O$CH_2CH_2CH_2CH_2$), ^{13}C NMR (125 MHz, CD_3OD): $\delta = 170.4$, 169.5, 151.7, 143.3, 137.1, 132.3, 132.1, 130.4, 120.3, 119.2, 72.9, 72.3, 72.2, 72.1, 71.9, 48.2, 31.3, 30.2, 27.0. HR-MS (ESI-TOF): calcd for $[M + H]^+$ $[C_{35}H_{50}NO_{14}]^+$ $m/z = 708.3226$; found $m/z = 708.3233$.

Preparation of UWDM-1. Neutral MIM linker **6** and $Cu(NO_3)_2$·3H_2O were dissolved in a solution of DMF/EtOH/H_2O (3:3:2 v/v/v), to which two drops of HNO_3 were added. The solution was then injected through a syringe filter into a 20 ml borosilicate scintillation vial. The vial was heated at a constant rate of 1 °C min^{-1} to 65 °C, kept at that temperature for 48 h, and cooled to room temperature at a constant heating rate of 0.1 °C min^{-1}. A green crystalline product was collected and washed with acetone several times to yield pure **UWDM-1** (78%).

Single-crystal X-ray diffraction. Reflection data were collected on a Bruker APEX diffractometer using MoKα radiation and a charge-coupled device detector. Crystals

of the neutral tetraethyl ester MIM precursor **5** were of good quality. The unit cell contained two molecules of the neutral [2]rotaxane ($C_{43}H_{65}NO_{14}$). The structure was solved in the triclinic space group P–1 with $Z = 2$. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed in idealized positions and refined using a riding model. Crystals of **UWDM-1** were of good quality and size but only weakly diffracting. The difference between **UWDM-1** and other porous MOFs is that most MOFs are filled with large amounts of highly disordered solvent, which results in poor diffraction. Although there are 27 molecules of water in the unit cell of **UWDM-1**, this is a minor problem[36]. It is the nine highly disordered [24]crown-6 macrocycles that are largely responsible for the poor diffraction. The structure was solved in the hexagonal space group R–3 with $Z = 9$ for a formula of $[Cu_2(MIM)(H_2O)_2]\cdot 3H_2O$. The asymmetric unit contains half of a MIM axle, one Cu(II) ion with a coordinated water molecule, and one macrocycle with half occupancy. The non-hydrogen atoms of the framework were easily located and well behaved, but various standard restraints were necessary to achieve a chemically sensible model for the macrocyclic ring.

Detailed descriptions of the synthesis and characterization for all compounds as well as all SSNMR and X-ray diffraction data and modelling can be found in the Supplementary Information. Crystal structure data for tetraester **5** and **UWDM-1** can be accessed from the Cambridge Crystallographic Data Centre (CCDC; www.ccdc.cam.ac.uk) and have been allocated accession numbers CCDC 847320 and 847321.

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Author contributions

S.J.L. supervised the project. S.J.L. and V.N.V. designed the experiments. V.N.V. performed the synthetic experiments with assistance from K.Z. V.N.V. collected and analysed the PXRD, thermal gravimetric analysis (TGA) and single-crystal X-ray diffraction (SCXRD) data with assistance from S.J.L. K.J.H. collected and analysed the SSNMR data. R.W.S. supervised all SSNMR data collection, analysis and interpretation. S.J.L. wrote the manuscript with significant input from V.N.V., K.J.H., K.Z. and R.W.S.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to R.W.S. and S.J.L.