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A mesoporous metal–organic framework based on a shape-persistent macrocycle†

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A mesoporous Zn-based metal–organic framework (MOF) was prepared from a shape-persistent phenylene ethynylene macrocycle functionalized with three –COOH groups. The rigid ligand has a ∼9 Å wide central cavity which serves as a predesigned pore. The macrocycles [π···π] stack into pairs, with their carboxylate groups connected *via* three $Zn_3O_{14}C_6H_2$ clusters. The resulting MOF has a void volume of 86%.

Metal–organic frameworks (MOFs) are ordered porous materials assembled from inorganic metal cluster nodes and organic linkers that connect those nodes into infinite frameworks.[1] Because of their high permanent porosities, easily modified surface characteristics, and thermal stability, MOFs are promising materials for uses in gas storage and separation, fuel processing, environmental remediation, sensing, and catalysis.[1] High porosity MOFs are especially important in gas storage applications, and have been pursued for decades.[2] Mesoporous[3] (pore size 2–50 nm) MOFs are considerably more difficult to obtain than the microporous (pore size <2 nm) ones. As the size of the organic linker increases, interpenetration and catenation become significant—and often unavoidable—obstacles in the design of MOFs with mesopores; the process of self-assembly avoids the entropically unfavorable formation of large regions of empty space by generating multiple copies of the MOF, which interlock with each other and are thus rendered inseparable.[4] So far, the majority of mesoporous MOFs have been directly synthesized from extended ligands[2,5] or stepwise through post-synthetic modification.[6]

Here, we present a mesoporous MOF based on a shape-persistent *m*-phenylene ethynylene[7] macrocyclic ligand **1** (Fig. 1A). To date, three classes of macrocyclic linkers have been used in the synthesis of MOFs: (a) catenanes and (pseudo)rotaxanes,[8] (b) azamacrocycles,[9] and (c) cyclodextrins.[10] However, most of these macrocycles were not shape-persistent and hence likely flexed into a conformation that did not leave a significant void. Shape-persistent macrocycles have a regular repeating unit with much fewer degrees of conformational freedom compared to flexible macrocycles. The development of MOFs based on shape-persistent macrocycles is still an under-explored area, which could yield new materials with increased surface areas and pore sizes—as the macrocycle could be used to "pre-program" a pore within a MOF. Analogs of **1** also have unusual host–guest chemistry: we have recently shown that an ester derivative of ligand **1** (Fig. 1A) encapsulates fluoroarenes within its cavity.[11] Thus, incorporation of shape-persistent macrocyclic ligands into MOFs could also provide new routes to highly specific encapsulation of guest molecules.

We have synthesized a novel macrocycle triacid ligand **1** (Fig. 1A)[11] based on the well-studied family of *m*-phenylene ethynylene macrocycles established by Moore.[12] Compound **1** has a transannular distance of 8.6177(7) Å (defined as the distances between the internal hydrogen atoms positioned furthest away from each other across the macrocycle),[12a] suggesting that its cavity can serve as a predesigned pore.

A mixture of **1** and $Zn(NO_3)_2\cdot6H_2O$ in *N*,*N*-dimethylacetamide (DMA) was heated at 100 °C for 1 d and yellowish cubic single crystals were isolated. The obtained material was designated as Zn-based MacroCyclic Metal Organic Framework (**Zn-MCMOF**), to emphasize the shape-persistent macrocyclic nature of the ligand used. The **Zn-MCMOF** has a cubic unit cell ($a = b = c = 33.261(4)$ Å). A large amount of massively disordered included solvent necessitated the use of synchrotron X-ray radiation (and subtraction of disordered solvent electron density using the SQUEEZE routine)[13] to obtain data of sufficiently high quality to permit full refinement of the single crystal structure of the **Zn-MCMOF**. The refined structure allows the formulation of the **Zn-MCMOF** as $[Zn_3(\mathbf{1}\text{-}3H^+)_2(H_2O)_2]$. The macrocyclic linkers [π···π] stack with each other and two molecules form a complex building block with six carboxylate groups (Fig. 1C). Each such complex coordinates to three secondary building units (SBUs), each of which is built from

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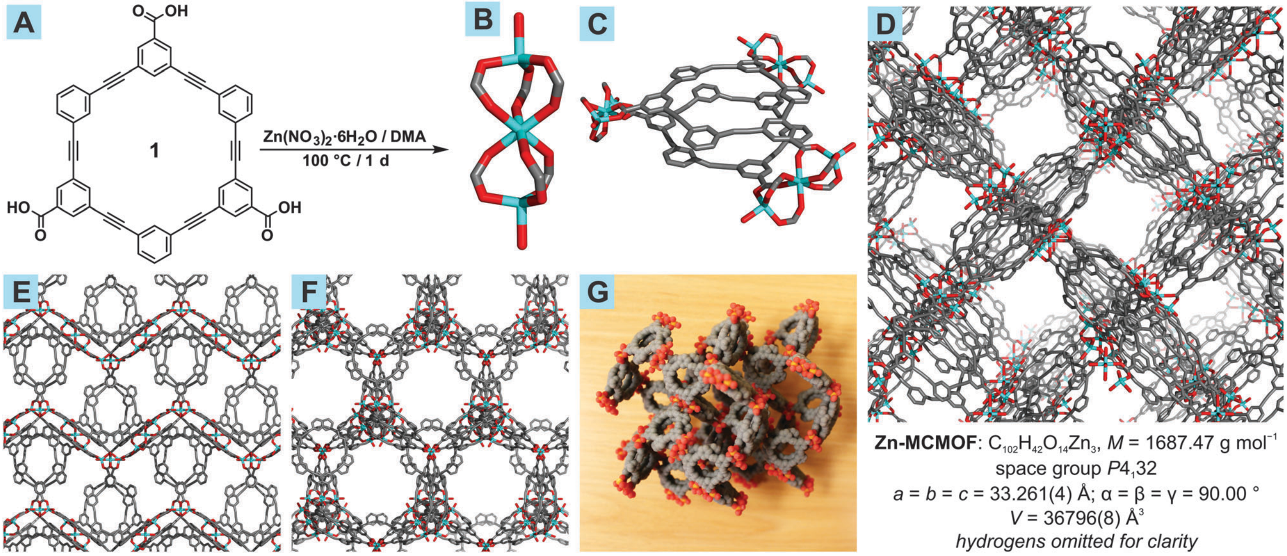

Fig. 1 Upon deprotonation, shape-persistent macrocyclic ligand **1** (A) coordinates to Zn, to form a $Zn_3O_{14}C_6H_2$ cluster (B)—the basic SBUs of the porous **Zn-MCMOF** (D). Within the material, macrocycle **1** forms a [π···π] stacked dimer (C), held together by three of the $Zn_3O_{14}C_6H_2$ clusters. (E) Structure viewed perpendicular to the edge of a 2 × 2 × 2 cubic cell. (F) One-dimensional mesoporous channels viewed along the space diagonal of the 2 × 2 × 2 cubic cell. (G) Three-dimensional printed model of a **Zn-MCMOF**. Element colors: C, gray; Zn, cyan; and O, red. Hydrogen atoms and disordered solvent molecules omitted for clarity.

three Zn atoms and six carboxylate groups from six discrete molecules of **1** (3 pairs of complexes). The central Zn atom in the SBU is octahedrally coordinated to six oxygen atoms from six discrete carboxylates, and the other two Zn atoms are tetrahedrally coordinated by one H_2O molecule and three oxygen atoms from three discrete carboxylates—resulting in an overall $Zn_3O_{14}C_6H_2$ cluster (Fig. 1B). The two offset-stacked macrocycles are not entirely parallel, and are presented in a twisted asymmetric hexagonal geometry due to their flexible acetylene backbones. The distance between the two stacked macrocycles is 3.64 Å (measured as the distance between their centroids of voids, which were defined by the six carbon atoms of **1** closest to the center of the void), matching a typical [π···π] stacking separation.[14] The macrocyclic complex leads to a mesoporous framework with infinite 3D channels. From the view along the *c*-axis (Fig. 1D), perpendicular to the edge (Fig. 1E), and along the space diagonal line (Fig. 1F) of the 2 × 2 × 2 cell of the **Zn-MCMOF**, channels with different geometries are apparent; they are connected to each other to form 3D channels. The 1D apertures shown in Fig. 1D and F are approx. 20 Å wide. The visualization of this complex structure is challenging, and we found a color 3D-printed model (Fig. 1G)[15] indispensable in analyzing the structure of the **Zn-MCMOF**.

Thermogravimetric analysis (TGA) of the **Zn-MCMOF** was performed under N_2 with a 2 °C min^{-1} heating rate, and it suggested that the framework begins to decompose at around 325 °C (Fig. S3, ESI†). The crystal density of 0.30 g cm^{-3} and the void volume of 86% have been calculated using PLATON software.[13] Nitrogen adsorption–desorption (77 K) measurements were performed to experimentally assess the porosity of the **Zn-MCMOF**: the obtained isotherms (Fig. 2) are intermediate between type I (which indicates microporosity) and type IV, characteristic of a hysteresis loop owing to the capillary condensation of adsorbate in the mesopores.[16] Nitrogen adsorption in the powder of ligand **1** alone is negligible (12 cm^3 g^{-1} at P/P_o = 0.9, Fig. S4, ESI†), suggesting that the porosity of the **Zn-MCMOF** is truly brought about by the unique arrangement of molecules of **1** within the framework.

For the **Zn-MCMOF**, the experimentally obtained Brunauer–Emmett–Teller (BET) surface area of 518 m^2 g^{-1} and pore volume of 0.48 cm^3 g^{-1} are much lower than what would be expected based on the crystal structure (4203 m^2 g^{-1}),[17] suggesting the collapse of cavities upon activation.[18] The micropore surface area is 324 m^2 g^{-1} and the mesopore-to-micropore pore-volume ratio is 1.17 (see ESI† for details). The NLDFT pore size distribution shows a range of micropore diameters from 8.8 to 11.9 Å (Fig. S10, ESI†), which is close to the sizes of pores within macrocyclic ligand **1**.

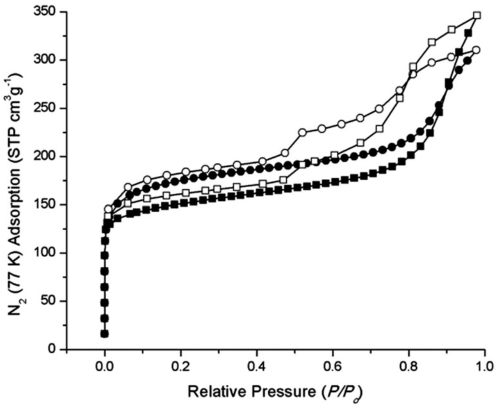

Fig. 2 Adsorption (filled symbols) and desorption (empty symbols) isotherms for N_2 (77 K) sorption within the **Zn-MCMOF**. As-synthesized (●) and resolvated (■) samples (*vide infra*) are plotted separately.

Using powder X-ray diffraction (PXRD) patterns, we concluded that even gently activated material (supercritical CO_2 drying over 3 d) loses its crystallinity during activation (Fig. S12, ESI,† the third PXRD pattern from the top). However, after soaking the activated material back in DMA, its crystallinity was restored (Fig. S12, ESI,† the bottom PXRD pattern). Moreover, the N_2 adsorption–desorption behavior of the resolvated (and then re-activated) sample is similar to that of the as-synthesized sample (Fig. 2): the two isotherms are virtually identical at $P/P_o < 0.01$ and slightly different afterward.

In summary, a novel shape-persistent macrocyclic ligand was synthesized and used in the synthesis of a **Zn-MCMOF** with large void volume of 86%. Its rigid backbone and propensity for $[\pi\cdots\pi]$ stacking gave rise to a macrocyclic building complex, possibly playing a role in preventing interpenetration. The mesopores of the **Zn-MCMOF** collapse upon solvent removal but appear to be reconstituted after resolvation. In future derivatives of the **Zn-MCMOF**, site-specific substitution with functional groups could be accomplished on both the interior and exterior of macrocycles. All these properties make shape-persistent macrocycles attractive—and now viable—building blocks for the synthesis of MOFs. The synthesis of other MCMOFs will be further explored in our lab.

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18 Another less likely possibility is the presence of massively disordered non-volatile guests (*e.g.* unreacted **1**) in the pores of the **Zn-MCMOF**.