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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 were 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** (Figure 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 underexplored 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** (Figure 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 novel macrocycle triacid ligand **1** (Figure 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 $Zn(NO_3)_2\cdot 6H_2O$ 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 **Zn**-based **M**acro**C**yclic **M**etal **O**rganic **F**ramework (**Zn-MCMOF**), to emphasize the shape-persistent macrocyclic nature of the ligand used. **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 **Zn-MCMOF**. The refined structure allows the formulation of **Zn-MCMOF** as $[Zn_3(\mathbf{1}-3H^+)_2(H_2O)_2]$. The macrocyclic linkers [π···π] stack with each other and two molecules form a complex building block with six carboxylate groups (Figure 1C). Each such complex coordinates to three secondary building units (SBUs), each of which is built from 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

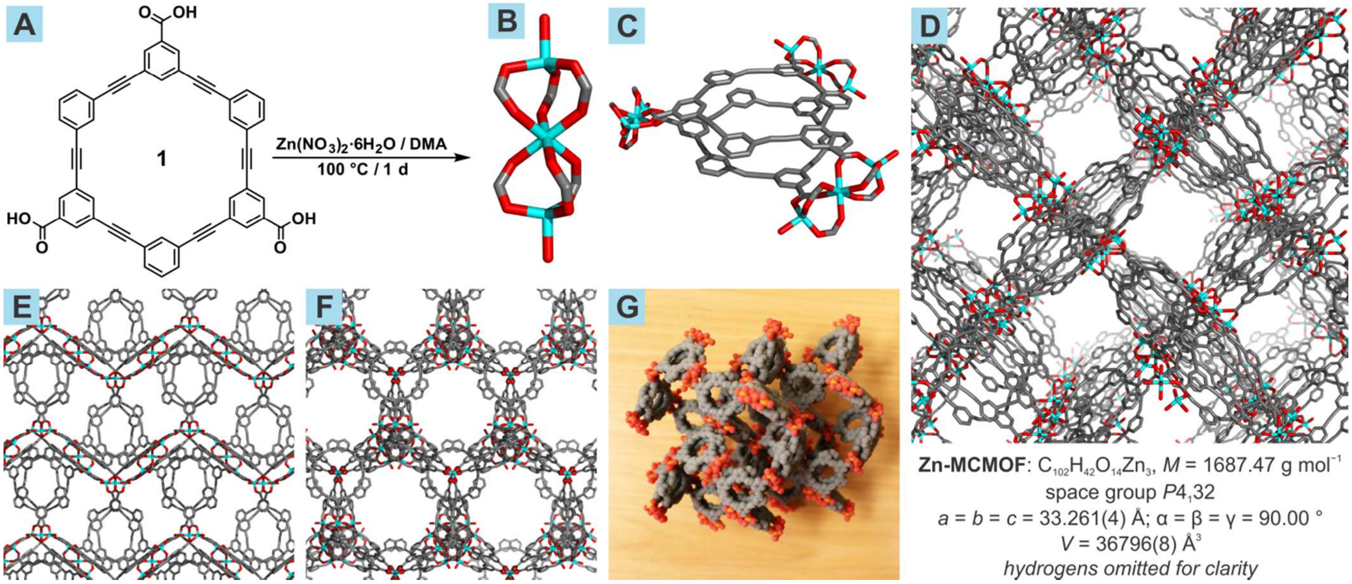

Figure 1. Upon deprotonation, shape-persistent macrocyclic ligand **1** (**A**) coordinates to Zn, to form a $Zn_3O_{14}C_6H_2$ cluster (**B**)—the basic SBU of porous **Zn-MCMOF** (**D**). Within the material, macrocycle **1** forms a [π•••π] stacked dimer (**C**), held together by three of the $Zn_3O_{14}C_6H_2$ clusters. **E:** Structure viewed perpendicular to the edge of 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 **Zn-MCMOF**. Element colors: C, gray; Zn, cyan; O, red. Hydrogen atoms and disordered solvent molecules omitted for clarity.

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 (Figure 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 (Figure 1D), perpendicular to the edge (Figure 1E), and along the space diagonal line (Figure 1F) of the 2×2×2 cell of **Zn-MCMOF**, channels with different geometries are apparent; they are connected to each other to form 3D channels. The 1D apertures shown in Figure 1D and 1F are approx. 20 Å wide. The visualization of this complex structure is challenging, and we found its color 3D-printed model (Figure 1G)[15] indispensable in analyzing the structure of **Zn-MCMOF**.

Thermogravimetric analysis (TGA) of **Zn-MCMOF** was performed under N_2 with 2 °C/min heating rate, and suggested that the framework begins to decompose around 325 °C (Figure S3). The crystal density of 0.30 g cm^{-3} and void volume of 86% have been calculated by PLATON software.[13] Nitrogen adsorption-desorption (77 K) measurements were performed to experimentally assess the porosity of **Zn-MCMOF**: the obtained isotherms (Figure 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, Figure S4), suggesting that the porosity of **Zn-MCMOF** is truly brought about by the unique arrangement of molecules of **1** within the framework.

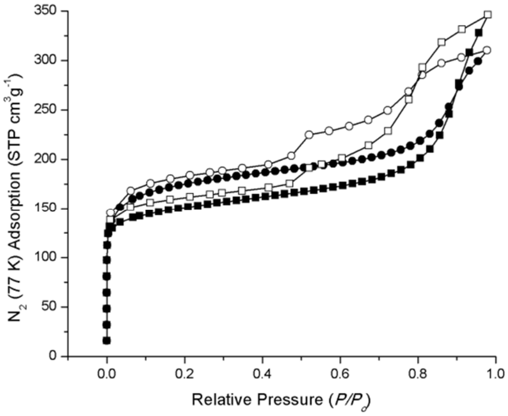

Figure 2. Adsorption (filled symbols) and desorption (empty symbols) isotherms for N_2 (77 K) sorption within **Zn-MCMOF.** As-synthesized (●) and resolvated (■) samples (vide infra) are plotted separately.

For **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 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 (Figure S10), which is close to the sizes of pores within macrocyclic ligand **1**. 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 (Figure S12, third PXRD pattern from the top). However, after soaking the activated material back into DMA, its crystallinity was restored (Figure S12, 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 (Figure 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 **Zn-MCMOF** with large void volume of 86%. Its rigid backbone and propensity for [π···π] stacking gave rise to macrocyclic building complex, possibly playing a role in preventing interpenetration. The mesopores of **Zn-MCMOF** collapse upon solvent removal but appear to be reconstituted after resolvation. In future derivatives of **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. Synthesis of other MCMOFs will be further explored in our lab.

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Notes and references

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Electronic Supplementary Information (ESI) available: [synthetic details and characterization data for **1** and **Zn-MCMOF**]. CCDC 1030073. See DOI: 10.1039/c000000x/

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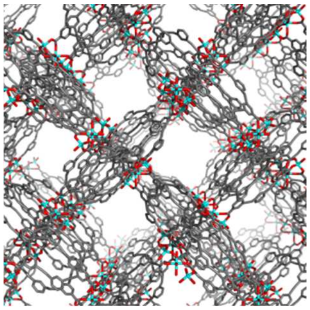
18 Another less likely possibility is the presence of massively disordered non-volatile guests (e.g. unreacted **1**) in the pores of **Zn-MCMOF**.

Table of Contents Text and Graphics



A mesoporous metal-organic framework (**Zn-MCMOF**) with 86% void volume was synthesized from Zn atoms and a shape-persistent macrocyclic ligand. In this unique framework, the macrocyclic ligand is used to "pre-program" porosity of the overall network. Upon activation, pores of **Zn-MCMOF** collapse, but are then regenerated through resolvation of crystals.