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**Metal–Organic Frameworks**

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# Crystalline Capsules: Metal–Organic Frameworks Locked by Size-Matching Ligand Bolts**

*Hao Wang, Jian Xu, Da-Shuai Zhang, Qiang Chen, Rong-Mei Wen, Ze Chang, and Xian-He Bu**

**Abstract:** *Metal–organic frameworks (MOFs) are shown to be good examples of a new class of crystalline porous materials for guest encapsulation. Since the encapsulation/release of guest molecules in MOF hosts is a reversible process in nature, how to prevent the leaching of guests from the open pores with minimal and nondestructive modifications of the structure is a critical issue. To address this issue, we herein propose a novel strategy of encapsulating guests by introducing size-matching organic ligands as bolts to lock the pores of the MOFs through deliberately anchoring onto the open metal sites in the pores. Our proposed strategy provides a mechanical way to prevent the leaching of guests and thereby has less dependence on the specific chemical environment of the hosts, thus making it applicable for a wide variety of existing MOFs once the size-matching ligands are employed.*

Metal-organic frameworks (MOFs) have proved to be a promising and versatile class of crystalline porous materials.[1–4] With highly regular and tunable pore structures, this type of materials exhibits excellent feasibility in diverse applications, such as gas storage and separation,[5] catalysis,[6] sensing and recognition,[7] and drug delivery.[8] Recently, the direct utilization of MOFs as guest-encapsulating matrices to entrap a wide range of functional molecules has received growing attention, because of the fact that the encapsulated guest molecules in MOF hosts usually play a vital role in achieving the above-mentioned intriguing functions.[9] The introduction of guests usually engenders new features and/or significantly improves the intrinsic properties of the host materials by host–guest interaction.[10]

MOF materials offer two unique advantages as a promising class of guest-encapsulating matrices.[11] Firstly, in principle, MOFs can be constructed from a broad variety of inorganic nodes and organic linkers that exhibit remarkable compositional diversity and structural tunability.[12] Encapsulating the target guest molecules can be easily achieved by tailoring the frameworks or regulating the pore structures.[13] In addition, a variety of post-synthetic modifications can further improve the diversity in terms of structures and functions.[14] Secondly, the unambiguous crystal structures of MOFs make it possible for high-quality computational modeling of static and dynamic host–guest interactions.[15] To some extent, this will facilitate the architectural design of suitable MOF-based guest-encapsulating matrices for specific needs.[16]

Prior to modulating the guest-encapsulation properties of MOFs, a critical issue needs to be addressed: how to prevent the leaching of encapsulated molecules from the open pores, since the encapsulation/release of guests in such porous hosts is a reversible process in nature.[17] Indeed, this problem can be addressed in many different ways; however, most of them depend on a highly specific chemical environment or a rather complicated structural modulation has to be carried out.[18] Herein we propose a novel strategy for encapsulating guest molecules in porous MOF materials, that is, to "lock" the pores of the MOFs by anchoring preselected size-matching organic ligands onto the open metal sites (OMSs) in the pores.[19] These auxiliary ligands serve as the "bolts" and can effectively prevent the leaching of guests in a mechanical way. Thus, this approach has less dependence on the specific chemical environment of the hosts and thereby can be carried out with no need to consider complex chemical interactions, such as hydrogen-bond, π–π stacking, cation–anion interaction, etc.[20] It could be anticipated that, with our proposed strategy, most existing MOFs containing OMSs could be, in principle, tailored as suitable guest-encapsulating matrices once size-matching auxiliary ligands are identified. It is worth noting that Calzaferri et al. proposed a similar stopcock (or stopper) strategy, which was successfully applied to zeolite L crystals and other interesting systems.[21] Therein, the stopcock molecules plugged the channel entrances to prevent guests from leaving the hosts and other small molecules from entering, or to offer some intriguing functions (e.g. energy transfer and information exchange). Thus, our strategy can be seen as an extension of the well-established stopcock principle to prepare novel MOF materials with rich chemistry, in which the unique OMSs are adopted as anchor sites to direct the targeted linkage of ligand bolts.

For proof-of-concept, we herein report a new three-dimensional (3D) Na-Zn-MOF, $[Na_4Zn_2(fda)_4(H_2O)_2]\cdot(H_2O)$ (**1**), which was synthesized by the solvothermal reaction of $Zn(NO_3)_2\cdot6H_2O$, 2,5-furandicarboxylic acid ($H_2fda$), and NaOH in a binary solvent of *N*,*N*′-dimethylacetamide (DMAC) and water. Upon activation, each of the $Na^+$ ions coordinated with two water molecules in **1** can be transformed to provide two OMSs that are the necessary anchor sites on which the size-matching auxiliary ligands can graft. The organic ligand 2,4,6-tris(4-pyridyl)pyridine (pytpy), which has

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[*] Dr. H. Wang, J. Xu, D.-S. Zhang, Q. Chen, R.-M. Wen, Z. Chang, Prof. X.-H. Bu
Department of Chemistry, TKL of Metal- and Molecule-Based Material Chemistry, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University
Tianjin 300071 (China)
E-mail: buxh@nankai.edu.cn

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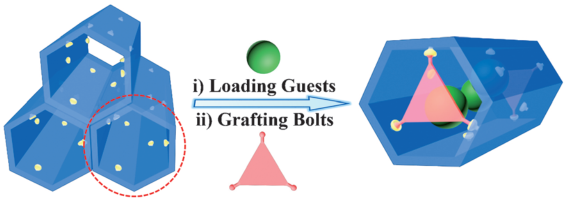
a matching size to the pore size of **1**, was selected and can be conveniently grafted onto the prepared OMSs of **1** by a milling process. Guest encapsulation can then be implemented through a straightforward two-step "loading-locking" process (Scheme 1). Finally, a series of experimental results corroborate the bolt role of the grafted ligands and suggest **1** to be a good candidate as a crystalline capsule, as it can effectively encapsulate guest molecules of suitable size, such as azobenzene and indole molecules, and rapidly release them under pH stimulus.



***Scheme 1.*** Schematic representation of the proposed two-step "loading-locking" guest-encapsulation process.

Complex **1** possesses a 3D open framework (Figure 1 a) and crystallizes in the rhombohedral space group $R\bar{3}C$,[22] with an asymmetric unit consisting of one-half crystallographically independent $Zn^{2+}$ ion and two one-half $Na^{+}$ ions (denoted as Na1 and Na2, respectively). In this unit, each $Zn^{2+}$ ion is four-coordinated by four carboxylate oxygen atoms in a tetrahedral geometry, while each $Na^{+}$ ion is surrounded by six oxygen atoms (six carboxylate oxygen atoms for Na1; two carboxylate oxygen atoms, two furan oxygen atoms, and two water oxygen atoms for Na2; see Figure S4 in the Supporting Information). The distinct coordination modes of the Na1 and Na2 ions lead to their different roles in the construction of **1**: Na1 ions participate in the formation of the helical Zn-O-Na-O rod-shaped secondary building units (SBUs; Figure 1 a) that are further bridged by $fda^{2-}$ to produce a 3D framework with 1D hexagonal channels; Na2 ions act as charge-compensating cations and each of them provides two potential OMSs that are initially occupied by two water molecules (Figure 1 b). The topology analysis shows that the whole framework of **1**, without considering the $Na^{+}$ ions, can be simplified to a typical *NbO* topology represented by the Schläfli symbol of $(6^{4}.8^{2})$ (see Figure S7 in the Supporting Information).

Thermogravimetric analysis (TGA) shows that all of the coordinated water molecules in **1** were removed below 160 °C and the framework is stable even at approximately 280 °C (see Figure S5 in the Supporting Information). According to our proposed strategy, an activation process was then carried out to generate the necessary OMSs by immersing the as-synthesized sample of **1** in methanol for three days and subsequently degassing at 160 °C for 24 h. The powder X-ray diffraction (PXRD) pattern reveals that **1** retained its crystallinity during this activation process (see Figure S6 in the Supporting Information). Furthermore, the single-crystal X-ray diffraction data of **1** suggests that the potential OMSs on the Na2 ions that correspond to the water oxygen atoms in **1** point preferentially toward the centers of the channels, with the distance between two neighboring OMSs at the same height being about 9.7 Å (considering van der Waals radii; see Figure 1 b). Coincidentally, we found that the arrangement of OMSs along the channels precisely matches the dimension and configuration of a neutral pytpy ligand (see Figure S8 in the Supporting Information).[23] This matching thus provides the possibility of introducing pytpy to lock the channels of **1** by anchoring them to the prepared OMSs.

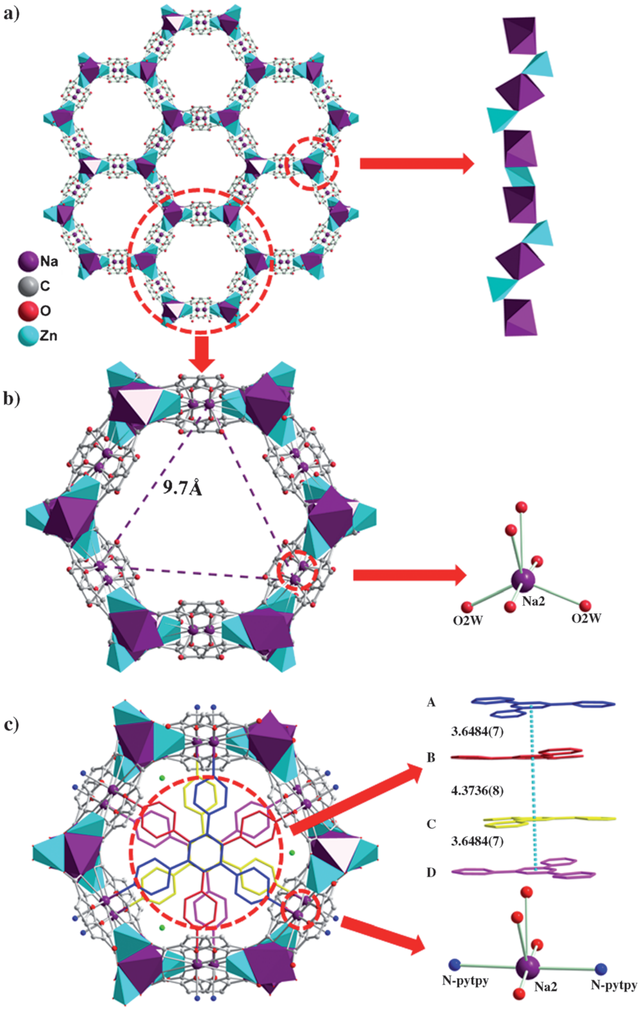


***Figure 1.*** a) View of the 3D framework of **1** consisting of helical Zn-O-Na-O rod-shaped SBUs. b) View of the 1D hexagonal channel in **1** as well as the coordination environment of the Na2 ion. c) Similar 1D hexagonal channel in **2** but locked by a composition of four pytpy ligands stacking in parallel that are anchored to the OMSs on Na2 ions (free water atoms: green).

Subsequently, we verified this possibility through a straightforward test by implementing a one-pot solvothermal synthesis similar to that of **1** but with the pytpy ligands added at the beginning of the reaction. The single-crystal X-ray diffraction analysis suggests the molecular formula of the resulting complex to be $[Na_4Zn_2(pytpy)_{4/3}(fda)_4]\cdot(H_2O)_2$ (**2**).[24] Complex **2** possesses a similar 3D framework structure as that of **1**, with the same helical Zn-O-Na-O rod-shaped SBUs and also involving two different types of $Na^{+}$ ions. Nevertheless, in contrast to **1**, the 1D channels of **2** are occupied by the pytpy ligands as well as the encapsulated water molecules, in which the OMSs on the Na2 ions coordinate to the nitrogen atoms from pytpy rather than the water oxygen atoms (Figure 1c). Based on this connection mode, a series of repetitive units are grafted along the channels of **2** and each of them is composed of four pytpy ligands stacking in parallel but at different orientations (the angles between A and B, A and C, A and D are 60°, 10.7°, 70.2°, respectively; Figure 1c). Such a parallel arrangement results in two different face-to-face $\pi$-$\pi$ interactions between the ligand cores at distances of 3.6484(7) and 4.3736(8) Å.

The single-crystal X-ray diffraction analysis also reveals that the encapsulated water molecules in **2** are located only between the stacking ligands B and C along the channel. Interestingly, the TGA result of **2** indicates that these guest water molecules can be retained in the channels up to about 310°C until the framework collapses (see Figure S9 in the Supporting Information). This observation is quite rare for MOF materials, in which the free and coordinated water molecules can be removed below 120°C and 200°C, respectively.[25] Considering the high similarity between the structures of **1** and **2**, we suggest that the near-absolute preservation of water molecules in **2** at high temperatures could be exclusively attributed to the introduction of the size-matching pytpy ligands. The thermal stability tests corroborate that these auxiliary ligands serve as the bolts and can effectively lock the pores of the MOFs and prevent the leaching of guest molecules.

To further confirm the feasibility of our proposed strategy, we carried out a two-step "loading-locking" guest encapsulation process with respect to azobenzene (other characteristic guest molecules were also studied, see Table S1 in the Supporting Information). The detailed manipulation sequence occurs as follows (see the Supporting Information for details). Firstly, the azobenzene molecules were permeated into the channels of fully activated **1** at 95°C, followed by the removal of excess azobenzene molecules external to the host crystal under reduced pressure at 120°C.[26] This is the "loading" process and we will denote the so-obtained composite as **1**⊃azobenzene, for clarity. The elemental analysis result of **1**⊃azobenzene agrees well with the release experiment data collected when the sample was soaked in ethanol. Both results reveal that the guest uptake was about 2.0 azobenzene molecules per unit cell of **1** (see Figure S3 in the Supporting Information). In addition, the PXRD pattern of the sample, measured after complete release of azobenzene, is nearly identical to the simulated result of **1** (see Figure S10 in the Supporting Information), thus suggesting that **1** could retain its crystallinity during the encapsulation and release process. This is also a clear indication of facile reversible encapsulation and release of guests by conventional MOF hosts.

Secondly, after the loading process finished, the pytpy ligands were mixed with the sample of **1**⊃azobenzene in an agate mortar and milled. During this "locking" process, the introduced auxiliary ligands were gradually grafted onto the prepared OMSs. The longer the milling process, the more ligand bolts could be successfully anchored. It is worth mentioning that **1** could retain its structure during the locking treatment, as evidenced by the PXRD patterns (see Figure S11 in the Supporting Information). The treated sample was then soaked in ethanol and centrifuged several times to eliminate the excess azobenzene molecules again, until there were no more guests released into the ethanol solution (monitored by UV spectroscopy).

Whether or not the azobenzene molecules were effectively encapsulated can be easily established by observing the color change of the sample of **1**⊃azobenzene. The initially white color of **1** was changed to dark yellow with the loading of azobenzene guests and reverted back to the original white color at the end of release experiment provided that the pytpy ligand bolts were absent (Figure 2), thus indicating a complete release of azobenzene molecules. Nevertheless, in the case when the pytpy ligands were introduced as bolts after the loading process, the sample retained a pale yellow color during the release process, thus suggesting that a considerable amount of azobenzene guests were preserved in the channels locked by pytpy. In the latter case, the slight difference in the color of **1**⊃azobenzene before and after release treatment (dark yellow versus pale yellow), in relation to the amount of azobenzene guests encapsulated in the channels, implies that the locking treatment at the time did not cover all the pores of **1**, which might be ascribed to insufficient milling time (ca. 30 min).

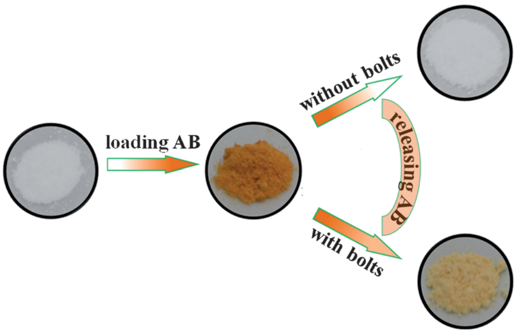


***Figure 2.*** Color changes of the sample of **1**⊃azobenzene with and without ligand bolts during the encapsulation and release process. AB = azobenzene.

Further tests also reveal that the guest half-lives of the pore-locked **1**⊃azobenzene in ethanol can be more than 3 months,[10a] while that of **1**⊃azobenzene with open pores was only about 2.5 min (see Figure S3 in the Supporting Information). This is further strong evidence of the bolt role of the pytpy ligands under the proposed strategy, which suggests that the encapsulated guests can be maintained in such host crystals for a much longer time because of the protection by the ligand bolts. We also performed a contrast experiment to check the grafting mode of these ligand bolts, which are presumed to be anchored on the OMSs of **1**. We did not carry out the activation process before the locking treatment, so that all of the Na2 ions in **1**⊃azobenzene were still coordinated to water molecules and could no longer offer the OMSs as necessary anchor sites. In that case, the color change of **1**⊃azobenzene reveals that the azobenzene guests were completely lost during the release treatment even if the pytpy ligands were added after the loading process. Furthermore, the relevant elemental analysis results indicate that only a negligible content of nitrogen existed in the sample after the release experiment, which implies the absence of both azobenzene guests and pytpy ligands. Thus, these results strongly support our supposition that the introduced ligand bolts are anchored onto the OMSs.

To explore the potential application of **1** as a crystalline capsule, we also examined the release performance of the encapsulated azobenzene guests under external stimulus, for example, the pH response of the pore-locked **1**⊃azobenzene composite. In this test, when the sample was soaked in ethanol, the solution was initially colorless, which implies that the azobenzene molecules were well-encapsulated and no azobenzene guests leached under this normal condition. Impressively, the addition of concentrated HCl resulted in the color of the solution immediately changing to yellow, which indicates that the encapsulated guests were released again under the acidic conditions (Figure 3). The framework of **1** also decomposed after this treatment, just like the disintegration of a capsule in gastric juice for drug release. This result suggests that this MOF-based guest-encapsulating matrix constructed on the basis of our proposed strategy could be employed as a crystalline capsule, in which the encapsulated target molecules can also be conveniently released by tuning the pH value of the solution.

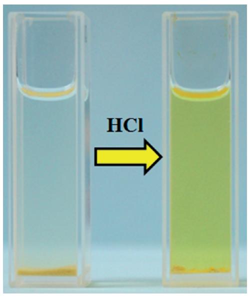


***Figure 3.*** Release of azobenzene guests from the host under acidic conditions.

In summary, we present a novel strategy for effectively encapsulating guest molecules in porous MOF materials, whereby size-matching auxiliary ligands are deliberately anchored onto the OMSs to lock the pores of the MOFs. For proof-of-concept, a new 3D Na-Zn-MOF featuring 1D channels with potential OMSs was obtained, along with the size-matching pytpy ligands selected to serve as the ligand bolts. The experimental results corroborate that the pytpy ligands anchored on OMSs can mechanically prevent the leaching of guests encapsulated by a two-step "loading-locking" process. Moreover, the encapsulated guests could also be easily released again from the MOF host under pH stimulus. Therefore, this study may shed new insights into the design and construction of novel MOF-based guest-encapsulating matrices, which can also be regarded as a new choice for crystalline capsules.

**Keywords:** crystalline capsules · host–guest systems · ligand design · metal–organic frameworks · open metal sites

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[22] Crystal data for **1** ($C_{24}H_{13}Zn_2Na_4O_{23}$): $M_r = 892.04$, trigonal, space group $R\bar{3}C$, $a = b = 29.007(10)$ Å, $c = 16.175(6)$ Å, $Z = 9$, $\rho = 1.131\ \mathrm{g\,cm^{-3}}$. Of 39329 total reflections collected, $R_1 = 0.0859$, $wR_2 = 0.1946$, and GOF = 1.257. CCDC 991281 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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