

# Cooperative Template-Directed Assembly of Mesoporous Metal–Organic Frameworks

Lin-Bing Sun, Jian-Rong Li, Jinhee Park, and Hong-Cai Zhou\*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012, United States

**S** Supporting Information

**ABSTRACT:** Despite great efforts, the development of a reliable way to assemble mesoporous metal–organic frameworks (mesoMOFs) remains a challenge. In this work, we have designed a cooperative template system, comprising a surfactant (cetyltrimethylammonium bromide) and a chelating agent (citric acid), for the generation of a mesoMOF containing a hierarchical system of mesopores interconnected with micropores. The surfactant molecules form micelles and the chelating agent bridges the MOF and the micelles, making self-assembly and crystal growth proceed under the direction of the cooperative template. However, when the surfactant or the chelating agent was applied individually, no mesoMOF was obtained.

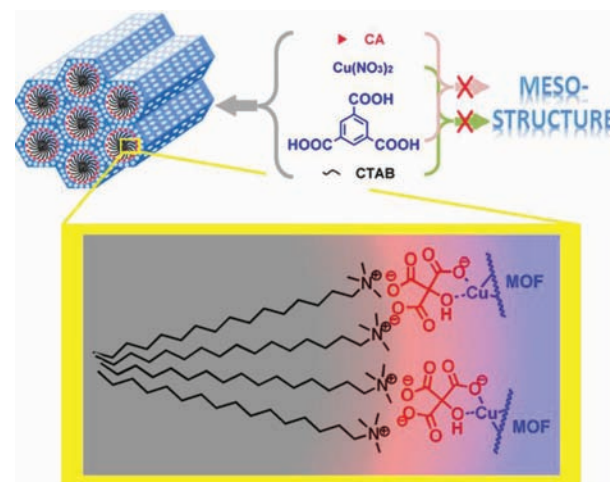
Metal–organic frameworks (MOFs) are assembled from organic linkers and metal ion or cluster nodes. The structure of a MOF can be tailored by the judicious choice of metal-based building blocks and organic linkers with almost endless geometrical and chemical variations.<sup>1</sup> Due to their diverse structure, adjustable functionality, and large surface areas, MOFs are of great interest for potential applications such as gas storage and separation, catalysis, and drug delivery.<sup>2</sup> However, most MOFs are microporous (pore size < 2 nm).<sup>3</sup> Albeit suitable for gas storage, the small pore size slows down diffusion and denies the access of large molecules to the active sites inside a MOF, which limits their applications involving bulky molecules.<sup>4</sup> One method to increase the pore size is to expand the linker, but framework instability and interpenetration are almost unavoidable in a MOF with an extended ligand.<sup>5</sup>

Although the surfactant-templating method has been widely utilized to prepare various mesoporous silicas and metal oxides,<sup>6</sup> the application of such supramolecular templates in the preparation of mesoporous MOFs (mesoMOFs) is sporadic at best. In the presence of surfactants, so far only two mesoMOFs have been synthesized, in ionic liquid/CO<sub>2</sub> and ethanol/H<sub>2</sub>O systems, respectively.<sup>7</sup> A generalized co-assembly mechanism was proposed in which soluble inorganic precursors combine with surfactant molecules to form intermediates, which become building blocks for the final mesostructured hybrid.<sup>6b,8</sup> The key for this co-assembly is the interaction between precursors and template molecules. For the assembly of a mesoMOF, therefore, the existence of such an interaction of considerable strength is essential, which should lead to the growth of a MOF directed by the template and subsequently to

the formation of mesostructured intermediates. Otherwise, macroscopic phase segregation owing to the weak interaction may take place, and the MOF will crystallize by itself despite the template. To the best of our knowledge, a rational adjustment of the interaction between MOF precursors and surfactant molecules has not been reported until now, despite the significance of such an interaction for mesoMOF synthesis.

Herein, we present a novel cooperative template system to direct the synthesis of mesoMOFs. A chelating agent was employed to establish an interaction between metal ions and surfactant molecules (Scheme 1) through Coulombic attraction

**Scheme 1. Cooperative Template-Directed Synthesis of MesoMOFs via Self-Assembly of Metal Ions and Organic Ligands**



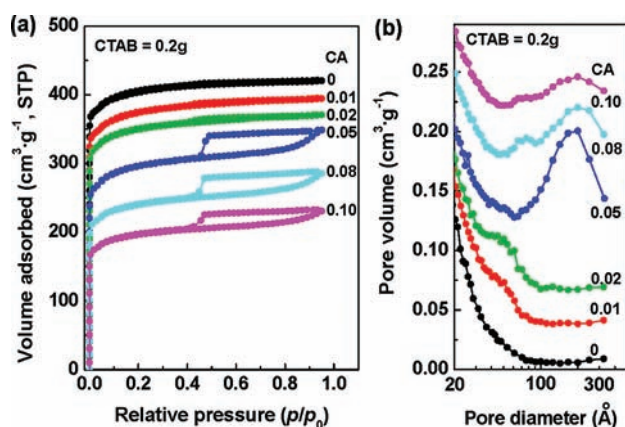
and coordination. The surfactant played a structure-directing role by using the chelating agent as a co-template, while no mesopores were formed in the presence of either the surfactant or the chelating agent individually. By utilizing the cooperative template, mesoMOFs have been successfully assembled, and the amount of mesopores is tunable by varying the ratio of surfactant to chelating agent. The obtained materials possess well-defined mesostructure, and more importantly, the mesopore walls consist of crystalline microporous frameworks. A three-dimensional hierarchical pore system has therefore been fabricated, in which mesopores are interconnected with

Received: October 14, 2011

Published: December 13, 2011

micropores. These materials thus combine the merits of both micropores and mesopores. We shall incorporate other surfactants into MOF synthesis utilizing such a cooperative template strategy, which should become a general pathway toward novel crystalline frameworks with hierarchical pore systems.

The mesoMOFs were synthesized in solvothermal reaction conditions. Copper nitrate hemipentahydrate and benzene-1,3,5-tricarboxylic acid ( $H_3BTC$ ) were used to synthesize crystalline frameworks. An anionic surfactant, cetyltrimethylammonium bromide (CTAB), and a hydroxy polyacid, citric acid (CA), were selected as structure-directing agent and chelating agent, respectively, to form the cooperative template system. The resultant mesoMOFs were denoted as mesoMOF-( $SmCn$ ), where  $m$  and  $n$  represent the amount of CTAB and CA in grams, respectively. In the absence of the cooperative template, the reaction of  $Cu(NO_3)_2$  and  $H_3BTC$  yielded microporous MOFs,  $Cu_3(BTC)_2$  (HKUST-1) with a pore diameter of 0.86 nm. The introduction of CTAB alone to the synthetic system did not result in mesopores (Figure 1), despite

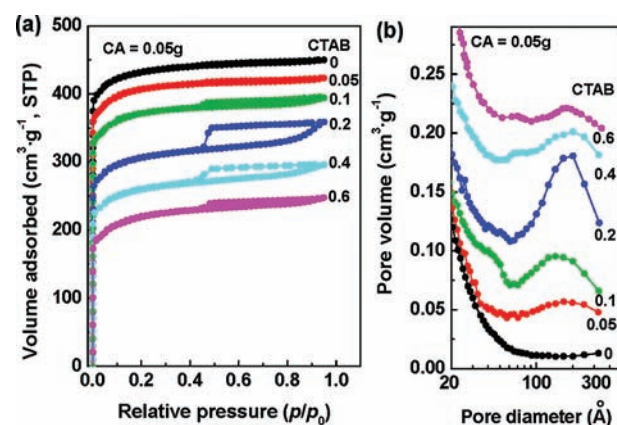


**Figure 1.** (a)  $N_2$  adsorption–desorption isotherms and (b) pore size distributions of mesoMOFs synthesized in the presence of different amounts of CA. For clarity, isotherms with 0.01–0.10 g of CA are offset by  $-30$ ,  $-30$ ,  $-100$ ,  $-80$ , and  $-70$   $cm^3 \cdot g^{-1}$ , respectively, while pore size distributions with 0.01–0.10 g of CA are offset by 0.015, 0.030, 0.046, 0.100, and 0.145  $cm^3 \cdot g^{-1}$ , respectively.

the fact that CTAB has been widely used as a template for mesoporous oxides synthesis.<sup>6a,b,9</sup> This means that CTAB alone cannot act as a structure-directing agent due to its weak interaction with MOF precursors. Interestingly, in the presence of both CTAB and only small amount of CA (0.01 g), some mesopores have been produced, as evidenced by hysteresis in the isotherm and the pore size distribution. Moreover, with the increased dose of CA, the amount of mesopores increases, followed by a slight decrease. For a representative sample, mesoMOF(S0.2C0.05), with a CTAB/CA molar ratio of 2.3 (Table S1), the isotherm is between type I, characteristic of microporous materials, and type IV, characteristic of mesoporous materials. These results, in combination with the pronounced hysteresis in the  $N_2$  isotherm, give evidence of a porous structure constructed from both mesopores and micropores.<sup>10</sup> The BET surface area reaches  $1162$   $m^2 \cdot g^{-1}$  with a pore volume of  $0.694$   $cm^3 \cdot g^{-1}$ . In addition to the mesopores with a diameter of 19.6 nm, the sample contains micropores with a diameter of 0.86 nm, which is in line with the micropore diameter (0.86 nm) estimated from crystallographic

data of  $Cu_3(BTC)_2$ .<sup>11</sup> These results demonstrate that, by using a cooperative template, mesoporous MOFs with hierarchical structure have been successfully fabricated, in which mesopore walls consist of microporous frameworks.

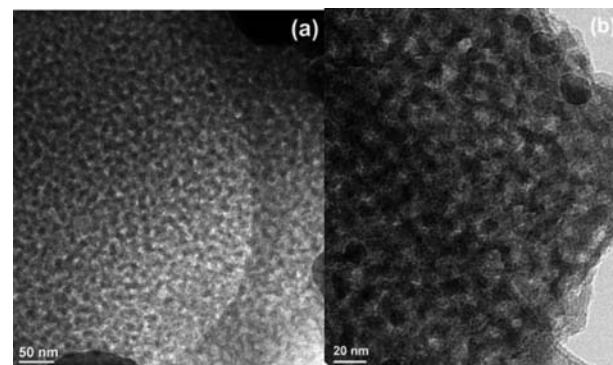
It was noticeable that without CTAB, the presence of 0.05 g of CA did not result in the formation of any mesopores, either (Figure 2). Nevertheless, the hysteresis loops in  $N_2$  adsorption–



**Figure 2.** (a)  $N_2$  adsorption–desorption isotherms and (b) pore size distributions of mesoMOFs synthesized in the presence of different amounts of CTAB. For clarity, isotherms with 0.05–0.6 g of CTAB are offset by  $-30$ ,  $-40$ ,  $-90$ ,  $-110$ , and  $-200$   $cm^3 \cdot g^{-1}$ , respectively, while pore size distributions with 0.05–0.6 g of CTAB are offset by 0.015, 0.03, 0.045, 0.100, and 0.135  $cm^3 \cdot g^{-1}$ , respectively.

desorption isotherms became observable when CTAB and CA coexist. The amount of mesopores reached the highest at the CTAB/CA molar ratio of 2.3. Further increase of the amount of CTAB made the hysteresis loop shrink noticeably. These results, in combination with those from the variation of CA amount, demonstrate that the optimum ratio of surfactant to chelating agent is around 2.3.

Transmission electron microscopy is an important technique to characterize the mesostructure. Because MOFs are generally quite sensitive to the electron beam, it is difficult to obtain high-quality images. However, well-defined mesoporous structure can still be observed from the images displayed in Figure 3.



**Figure 3.** TEM images of the sample mesoMOF(S0.2C0.05) at two different levels of magnification.

This corroborates well with the  $N_2$  adsorption studies and confirms the mesoporosity of the samples.

For the samples synthesized with high CTAB/CA ratios (including low CA amount or high CTAB amount in Figures S1



and S2, respectively), their X-ray diffraction patterns are in good agreement with that reported for  $\text{Cu}_2(\text{BTC})_3$ .<sup>11a,12</sup> Nonetheless, an excess amount of CA favors the generation of a new crystalline phase with a typical diffraction line at  $2\theta = 10.1^\circ$ . The incorporation of excessive CA into frameworks should be responsible for the new phase (see Supporting Information for details). Infrared spectra presented in Figures S3 and S4 agree well with XRD results. Typical IR bands ascribed to  $\text{Cu}_2(\text{BTC})_3$  are observable on the samples with high CTAB/CA ratios,<sup>13</sup> while new bands emerge with decreasing CTAB/CA ratios. That means, from the viewpoint of acquiring pure  $\text{Cu}_2(\text{BTC})_3$  phase, the quantity of CA should be well controlled.

For all samples with pure  $\text{Cu}_2(\text{BTC})_3$  phase despite the number of mesopores, thermogravimetric analysis showed similar weight alteration during thermal treatment, that is, a weight loss centered at about  $100^\circ\text{C}$  originated from water desorption, accompanied by a weight loss located at about  $310^\circ\text{C}$  due to framework degradation (Figures S5 and S6). These results reflect that the introduction of mesopores does not undermine the stability of the materials. It can also be seen from TGA curves that the crystal phase related to CA is not as stable as  $\text{Cu}_2(\text{BTC})_3$ , which undergoes decomposition at a relatively low temperature of  $230^\circ\text{C}$ .

In comparison with their siliceous analogues, the interaction between MOF precursors and surfactants is much weaker. The use of CTAB as a single template did not direct the construction of mesoporous structure, although the formation of micelles from CTAB molecules has already been clarified.<sup>9,14</sup> Also, the presence of CA itself did not lead to the generation of mesopores, because CA, as small molecules, cannot form micelles.<sup>15</sup> However, when CTAB and CA were employed together, a cooperative template system was generated, and it exhibited excellent structure-directing effect. This is because CA interacts with metal and surfactant simultaneously, and a chemical interaction between MOF precursors and micelles is built. This interaction leads to the positioning of the building blocks of MOFs. The cooperative template thus played a directing role, making nucleation and crystal growth proceed in the continuous solvent phase between micelles. A mesostructured intermediate with the pores occupied by micelles has thus been fabricated. After the removal of templates, porous materials with hierarchical pores have been produced, in which mesopore walls consist of microporous frameworks.

It should be stated that the ratio of surfactant to chelating agent has a significant effect on mesostructure fabrication. On one hand, if the amount of CA is too low, only a weak interaction can be established between MOF precursors and surfactants, or only part of the precursors can interact with surfactants. In this case, microporous MOFs will be produced due to the lack of structure directing in the process of crystal growth. On the other hand, too much CA does not help, either, taking into account that only CA molecules cooperating with surfactants are effective. In addition, the excessive amount of CA favors the formation of another phase. On the basis of the aforementioned results, we propose that the optimal CTAB/CA molar ratio should be around 2. That means one CA molecule bridges the interaction of two CTAB molecules with one copper cation, as illustrated in Scheme 1. In the present study, more than 10 different CTAB/CA ratios were employed for the preparation of mesoporous MOFs. The sample mesoMOF-(S0.2C0.05), with a CTAB/CA ratio of 2.3, exhibits the optimum mesostructure. These experimental results, therefore, support the proposed mechanism of a cooperative template.

In summary, we have developed a new strategy for the synthesis of mesostructured MOFs by taking advantage of a cooperative templating effect. The chelating agent can well establish the interaction between framework building blocks and surfactants. The crystal growth is thus directed by micelles on a nano scale. MesoMOFs containing a hierarchical pore structure with a three-dimensional intersection network are successfully prepared, in which mesopore walls are constructed from a microporous framework. These crystalline materials with advantages of both micropores and mesopores may be promising candidates for bulky molecule capture, heterogeneous catalysis, and controlled drug release because of merits such as improved mass transfer.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, discussion on CA-related phase, structural parameters, powder XRD, IR, and TGA of mesoMOFs, as well as powder XRD, IR, and  $\text{N}_2$  adsorption results of samples related to CA, and complete ref 2g. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

zhou@chem.tamu.edu

## ■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE DE-SC0001015 and DE-AR0000073), the National Science Foundation (NSF CBET-0930079), and the Welch Foundation (A-1725).

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