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Growing Crystalline Zinc-1,3,5-benzenetricarboxylate Metal−Organic Frameworks in Different Surfactants

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S *Supporting Information*

ABSTRACT: Six new zinc-1,3,5-benzenetricarboxylate-based metal−organic frameworks (MOFs) have been successfully synthesized using three different surfactants (PEG 400, octanoic acid, and hexadecyltributylphosphonium bromide) as reaction media. These surfactants with different characteristics, such as being neutral, acidic, and cationic, have been demonstrated to show strong effects on directing the crystals' growth and resulted in different secondary building units (SBUs) including an unusual SBU unit $[Zn_4(\mu_4\text{-}O)(CO_2)_7]$. Our results clearly indicated that the surfactant−thermal method could offer exciting opportunities for preparing novel MOFs or other inorganic crystalline materials with diverse structures and interesting properties.

A surfactant−thermal method has emerged as a new synthetic route to prepare novel crystalline materials such as chalcogenides and zeolites, in which surfactants were used as either solvents (reaction media) or templates.[1] Because of their low or no vapor pressure, surfactants have been widely employed as reaction media to fabricate different nanocrystals at much higher temperatures.[2] Moreover, surfactants have been already demonstrated as powerful agents to control the size and shape of nanomaterials (both inorganic and organic) due to the strong interaction between surfactants and crystal surfaces during the formation of nanocrystals.[3] Thus, logically, surfactants should also possess the power to control the growth of bulky crystals if surfactants were used as reaction media. In addition, compared with traditional solvents used in hydro/solvo−thermal methods, surfactants possess tunable characteristics and multifunctional properties such as being cationic, anionic, neutral, zwitterionic, acidic, and basic, which are expected to provide diverse reaction conditions.[4] Meanwhile, compared with ionic liquids (ILs)[5] and ureas,[6] surfactants have much more commercially available sources and lower prices, making them more attractive as reaction media to grow new crystalline materials.

Because metal−organic frameworks (MOFs) have been demonstrated to show diverse structures and different connecting modes in various reaction conditions such as metal sources, temperature, and solvents, and have shown potential applications in many fields such as gas storage and separation,[7] catalysis,[8] nonlinear optics,[9] and sensors,[10] we believe that the Janus characteristics of surfactants could also make them perfect media for growing diverse MOFs because the structure of surfactants contains both hydrophilic and hydrophobic groups that may efficiently increase the solubility of metal ions and organic ligands and may have strong interaction with metals ions and organic ligands.[11] Although surfactants have been demonstrated to control the formation of mesoMOFs,[12] using surfactants as reaction media to grow bulky MOF crystals is still unexplored. Recently, our group has successfully explored the surfactant−thermal synthesis of crystalline MOFs.[13] Various novel MOFs with two-dimensional (2-D) or three-dimensional (3-D) structures have been obtained in polyethylene glycol (PEG) surfactants.[13] Yet, the influence of different surfactants on the structures of MOFs has not been well investigated. To the best of our knowledge, it is first time for us to report the surfactant−thermal synthesis of crystalline MOFs under different surfactant−thermal conditions.

Because the coordination chemistry between zinc ions and 1,3,5-benzenetricarboxylate (BTC) ligands has been numerously investigated under various conditions and diverse MOF structures have been reported,[14] we believe that the Zn-BTC system should be a promising platform to study the influence of different surfactants as reaction media. Herein, we report the synthesis and characterization of six new zinc-1,3,5-benzenetricarboxylate (Zn-BTC) MOFs prepared in different surfactants (neutral, acidic, and cationic, Figure 1) as reaction media.

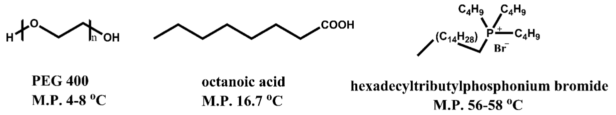

Figure 1. Three different surfactants used in synthesizing crystalline Zn-BTC MOFs and their melting points (M.P.).

The reactions of zinc acetate, H_3BTC, and triethylamine (TEA) in PEG 400 produced compound **NTU-Z8** with the formula of $(HTEA)_4[(Zn_4O)_2Zn(BTC)_6]$. Single-crystal XRD analysis shows that **NTU-Z8** crystallizes in the orthorhombic space group *Fdd*2. In **NTU-Z8**, there are two different secondary building units (SBUs) (Figure 2a). The combination of four Zn^{2+} atoms, seven carboxylate groups and one μ_4-O gives the tetrameric $[Zn_4(\mu_4\text{-}O)(CO_2)_7]$ SBU, which is an

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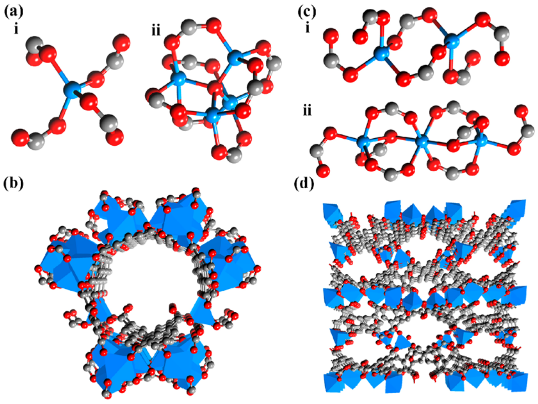

Figure 2. (a) SBUs in MOF **NTU-Z8**: (i) $[Zn(COO)_4]$ and (ii) $[Zn_4(\mu_4\text{-}O)(CO_2)_7]$. (b) 1-D channel of **NTU-Z8** viewed along the *c*-axis. (c) SBUs in MOF **NTU-Z9**: (i) $[Zn_2(COO)_6]$ and (ii) $[Zn_3(\mu_3\text{-}O)(COO)_6]$. (d) 3-D framework of **NTU-Z9** viewed down the *c*-axis. HTEA guests and H atoms were removed for clarity. C, O, and Zn atoms are shown in gray, red, and green−blue.

unusual SBU and different from the well-known trimetric $[Zn_4O(CO_2)_6]$ SBU in **MOF-5** and new $[Zn_4O(CO_2)_8]$ SBU in **CPM-7**.[15] In this new tetrameric SBU, two Zn^{2+} ions display tetrahedral coordination with three oxygen atoms from different carboxylate groups and one μ_4-O, while other two Zn^{2+} ions are five-connected with four oxygen atoms from different carboxylate groups and one μ_4-O. **NTU-Z8** has another mononuclear $[Zn(COO)_4]$ SBU, which is formed by one Zn^{2+} and four oxygen atoms from four different carboxylate groups with monodentate coordination mode. The ratio between $[Zn_4O(CO_2)_7]$ SBU and$[Zn(COO)_4]$ SBU in **NTU-Z8** is 2:1. The SBUs are further connected together through BTC ligands to construct 3-D frameworks with intercrossed channel dimensions of about 10.1 × 8.2 Å along the *c*-axis and [101] direction (Figure 2b). Protonated $HTEA^+$ molecules fill the space in the channels as the charge balance cations.

When PEG 400 was changed to an acidic surfactant, octanoic acid, a new Zn-BTC framework was obtained as colorless block crystals (**NTU-Z9**, $(HTEA)_4[Zn_5(BTC)_2(HBTC)_4]$). **NTU-Z9** crystallizes in the monoclinic space group *P*2(1)/*c*, and there are two different SBUs in **NTU-Z9** (Figure 2c): $[Zn_2(COO)_6]$ and $[Zn_3(COO)_8]$. SBU $[Zn_2(COO)_6]$ was formed by connecting two tetrahedrally coordinated Zn^{2+} atoms with six carboxylate groups (Figure 2c(i)), while SBU $[Zn_3(COO)_8]$ was generated by linking three octahedrally coordinated Zn^{2+} atoms with eight carboxylate groups. (Figure c(ii)). There are two crystallographically independent ligands in **NTU-Z9**. One BTC ligand is connected to two $[Zn_3(COO)_8]$ SBUs and one $[Zn_2(COO)_6]$ SBU via all its carboxylate groups, while another type of ligand only used two carboxylate groups to link with one $[Zn_3(COO)_8]$ SBU and one $[Zn_2(COO)_6]$ SBU and left one carboxylate group uncoordinated (Figure S2, Supporting Information, SI). The connections between the organic ligands and two SBUs lead to the formation of 3-D frameworks, where 1-D rhombic channels with the dimensions of about 8.1 Å × 6.8 Å along the *c*-axis are observed (Figure 2d). The experimental powder XRD patterns for compounds **NTU-Z8** and **NTU-Z9** match very well with the simulated ones (generated on the basis of single-crystal structure analysis), which confirmed the phase purity of the bulk materials (Figure S11, SI).The reactions of zinc acetate, H_3BTC, and pyridine (Py) in PEG 400 produced 3-D compound **NTU-Z10** with the formula of $[(Zn_3(\mu_3\text{-}O))_2Zn_3(BTC)_6(H_3O)_3]$. Single-crystal XRD analysis shows that **NTU-Z10** crystallizes in the cubic space group *I*23.[14a] There are two types of SBUs: trimeric $[Zn_3(\mu_3\text{-}O)(COO)_6]$ SBU and dimeric paddle-wheel $[Zn_2(COO)_4]$ SBU (Figure S3a). The paddle-wheel SBU is an isostructure of the SBU in the famous **HKUST-1** with two water molecules occupied two coordination sites along the axial direction.[16] In the trimeric $[Zn_3(\mu_3\text{-}O)(COO)_6]$ SBU, all the Zn^{2+} atoms are tetrahedrally connected with one μ_3-O and three oxygen atoms from different carboxylate groups. Six dimeric SBUs and eight trimeric SBUs are connected via a BTC ligand to form a dodecahedral cavity with a diameter about 7.1 Å (Figure S5, SI). Then each dodecahedral cavity is surrounded by irregular hexahedral cavities and extend to a 3-D framework (Figure 3a).

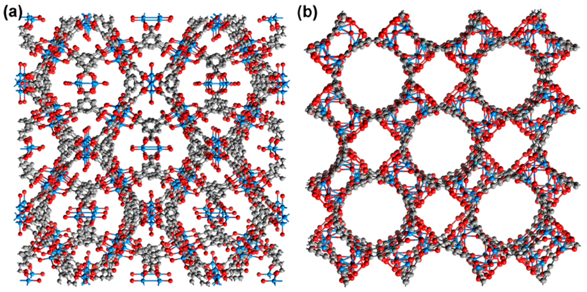

Figure 3. (a) 3-D framework structure of **NTU-Z10** viewed along the *c*-axis. (b) 3-D framework structure of **NTU-Z11** viewed along the *c*-axis. H atoms were removed for clarity. C, O, N, and Zn atoms are shown in gray, red, blue and green−blue.

When zinc acetate was replaced by zinc nitrate as the starting material, rod crystals with the formula of $[(Zn_3(\mu_3\text{-}O)(BTC)_2H_2O]$ (**NTU-Z11**) were obtained. Single-crystal analysis revealed that **NTU-Z11** is composed of the trimetric $[Zn_3(\mu_3\text{-}O)(COO)_6]$ SBU and BTC ligand. Note that the trimetric $[Zn_3(\mu_3\text{-}O)(COO)_6]$ SBU in **NTU-Z11** is different with the trimetric SBU in **NTU-Z10** (Figure S3b, SI). The trimetric SBU in **NTU-Z11** is constituted from one octahedrally coordinated Zn^{2+} with four oxygen atoms from different carboxylate groups, μ_3-O and one water molecule, and two other Zn^{2+} ions with trigonal dipyramidal coordination, which are coordinated with three oxygen atoms from different carboxylate groups, μ_3-O, and one water molecule. Linking trimetric SBU with BTC ligand results in an infinite 3-D (3,6)-connected framework with 1-D channel of about 11.5 Å × 11.5 Å dimension along the *c*-axis (Figure 3b). **NTU-Z11** is the isostructure of **MOF-38,** in which HTEA filled the channels, and the synthesis cannot be repeated as mentioned in the literature.[17] Instead, **NTU-Z11** can be repeatedly synthesized with high yield, and the channels are empty, not like the previous report with organic solvents.

Employing octanoic acid as the reaction media, compound **NTU-Z12** (composition) was synthesized through the reactions of zinc acetate, H_3BTC, and Py. The asymmetric unit of **NTU-Z12** contains one Zn atom, one HBTC ligand, one H_2BTC, and one Py molecule. The Zn atom is tetrahedrally coordinated to three oxygen atoms from different carboxylate groups and a nitrogen atom from Py (Figure S7a, SI). The connection between Zn atoms and organic ligands form a 1-D chain structure along the *b*-axis (Figure S8, SI). Interestingly, when cationic surfactant hexadecyltributyl-phosphonium bromide was chosen as the reaction media, compound **NTU-Z13** (composition) was obtained. The asymmetric unit contains one Zn atom, one HBTC ligand, and two Py molecules. Tetrahedrally connected Zn^{2+} ions are linked together via a HBTC ligand to generate 1-D chains along the *a*-axis (Figure S9, SI). All the experimental powder XRD patterns for compounds **NTU-Z10**, **NTU-Z11**, **NTU-12**, and **NTU-Z13** match very well with the simulated ones, which confirmed the phase purity of the bulk materials (Figure S12, SI).

In conclusion, three different surfactants (PEG 400, octanoic acid, and hexadecyltributylphosphonium bromide) with neutral, acidic, and cationic characteristics, respectively, have been employed as reaction media to control the structures of crystalline MOFs. Six new Zn-BTC-based metal−organic frameworks (MOFs) were successfully fabricated by a surfactant−thermal method. Our results indicated that different surfactants can be used as reaction media for the synthesis of crystalline MOFs with interesting structures. We believe that the surfactant−thermal method should be a promising strategy to prepare various bulky crystal materials with diverse structures and interesting properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, summary of crystal and structure refinement data, crystal structures of MOFs, powder-XRD pattern, TGA curves, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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