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# Tuning metal–carboxylate coordination in crystalline metal–organic frameworks through surfactant media



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## ABSTRACT

Although it has been widely demonstrated that surfactants can efficiently control the size, shape and surface properties of micro/nanocrystals of metal–organic frameworks (MOFs) due to the strong interactions between surfactants and crystal facets of MOFs, the use of surfactants as reaction media to grow MOF single crystals is unprecedented. In addition, compared with ionic liquids, surfactants are much cheaper and can have multifunctional properties such as acidic, basic, neutral, cationic, anionic, or even block. These factors strongly motivate us to develop a new synthetic strategy: growing crystalline MOFs in surfactants. In this report, eight new two-dimensional (2D) or three-dimensional (3D) MOFs have been successfully synthesized in an industrially-abundant and environmentally-friendly surfactant: polyethylene glycol-200 (PEG-200). Eight different coordination modes of carboxylates, ranging from monodentate  $\eta^1$  mode to tetra-donor coordination  $\mu_3\text{-}\eta^1:\eta^2:\eta^1$  mode, have been founded in our research. The magnetic properties of Co-based MOFs were investigated and MOF NTU-Z6b showed a phase transition with a Curie temperature ( $T_c$ ) at 5 K. Our strategy of growing crystalline MOFs in surfactant could offer exciting opportunities for preparing novel MOFs with diverse structures and interesting properties.

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## 1. Introduction

Metal–organic frameworks (MOFs) have attracted huge attentions due to their promising applications in gas storage [1–4], separation [5–8], catalysis [9–11], sensors [12–17] and biology [18–20]. Various synthetic methods such as hydrothermal, solvothermal, ionothermal, and urea-thermal methods have been explored to synthesize MOFs with complex structures and fascinating properties [21–24]. However, previous methods have significant limitations associated with the use of solvents. The reaction temperature has to be kept low as most of solution processes (e.g. hydrothermal, solvothermal, and urea-thermal methods) involve the use of low-boiling-point solvents. Additionally, organic solvents are a health and environmental concern. Although green solvents such as ionic liquids have been used in the synthesis of

MOFs [25–30], they have had limited scope for large-scale fabrication because of their high cost.

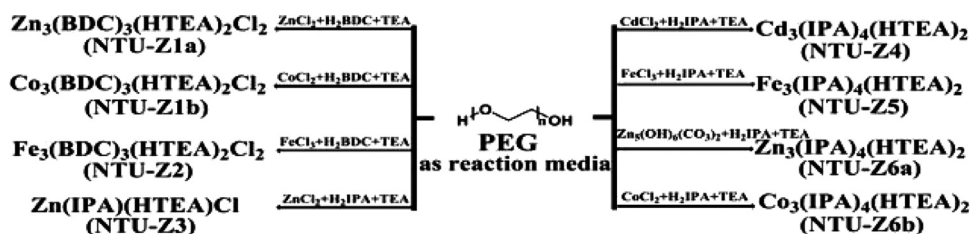
As surfactants have been widely demonstrated to efficiently control the sizes, shapes, and surface properties of nanocrystals, and the pore sizes and phases of porous frameworks [31–37], we reason that the surfactants can be used to control the growth of crystalline materials. Notably, compared with ionic liquids, the surfactants not only have high chemical and thermal stability and low vapor pressure, but also display multifunctional properties such as acidic, basic, neutral, anionic, cationic, etc. Furthermore, a large collection of surfactants are generally low cost and readily accessible. Although our group recently reported that crystalline chalcogenides can be grown under surfactant-thermal condition [38,39], the use of surfactants as reaction media to control the growth of MOF crystals is still rare [40]. Here we report a general method for controlling the growth of crystalline MOFs in surfactant media. We discover that the surfactant enables tuning of metal–carboxylate coordination, resulting in the formation of a wide range of previously inaccessible MOFs.

The selection of surfactants in this research is based on their melting point, charge, and ability to coordinate with metals. As a

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Scheme 1. Synthesis of eight new crystalline MOFs in surfactant PEG-200.

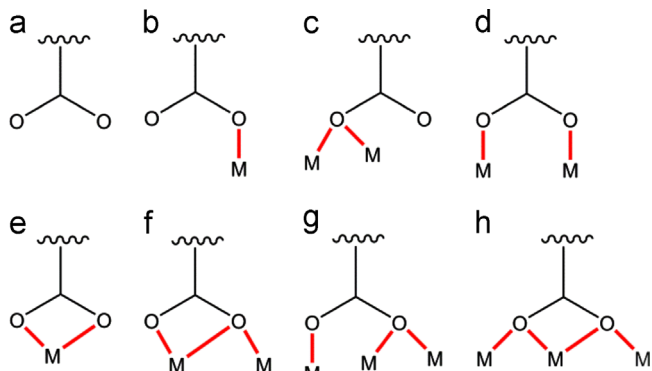


Fig. 1. Eight different coordination modes of carboxylate groups found in MOFs NTU-Z1-Z6: (a)  $\eta^0$ , (b)  $\eta^1$  mode, (c)  $\mu_2$ - $\eta^2$  mode, (d)  $\mu_2$ - $\eta^1$ : $\eta^1$  mode, (e) chelating  $\eta^2$  mode, (f)  $\mu_2$ - $\eta^2$ : $\eta^1$  mode, (g)  $\mu_3$ - $\eta^1$ : $\eta^2$  mode, and (h)  $\mu_3$ - $\eta^1$ : $\eta^2$ : $\eta^1$  mode.

proof-of-concept experiment, polyethylene glycol (PEG) was chosen as the reaction medium because (i) PEG has been widely used in materials science for shape-controlled growth of nanoparticles and in medicinal chemistry; (ii) PEG is a biodegradable polymer with low toxicity; (iii) PEG has various melting points with the change of the weight; and (iv) PEG has many oxygen atoms suitable for bonding with metal atoms [20,41–46].

In a typical experiment, we examined surfactant (PEG-200) as the solvent and 1,4-benzenedicarboxylate acid ( $H_2BDC$ ) or isophthalic acid ( $H_2IPA$ ) as the ligand to construct MOFs. Eight new 2D or 3D crystal structures were prepared under similar reaction conditions (Scheme 1). Interestingly, eight different coordination modes of carboxylate groups, ranging from no binding with metal, to monodentate  $\eta^1$  mode, and to tetra-donor coordination  $\mu_3$ - $\eta^1$ : $\eta^2$ : $\eta^1$  mode, have been found in our studies (Fig. 1). It is noteworthy that no crystals were obtained for all the reaction systems when PEG-200 was removed or replaced by an organic solvent such as ethylene glycol, methanol and *N,N*-dimethylformamide.

## 2. Experimental section

### 2.1. Materials and general methods

All chemicals were purchased from Alfa Aesar, TCI chemical and Aldrich and used without further purification. Polyethylene glycol 200 (PEG 200) were purchased from Alfa Aesar. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized  $CuK\alpha$  radiation. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR SpectrumGX spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min up to 800 °C under  $N_2$  atmosphere. The DC magnetic susceptibility measurements were made on an MPMS magnetometer at temperatures between 2.0 and 300 K.

### 2.2. Synthesis

#### 2.2.1. Synthesis of $(HTEA)_2[Zn_3(BDC)_3Cl_2]$ (NTU-Z1a)

A mixture of  $ZnCl_2$  (3 mmol, 0.41 g),  $H_2BDC$  (3 mmol, 0.35 g), triethylamine (TEA) (1 mL), and 4 mL PEG-200 was put into a 30 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 days. Then, the mixture was naturally cooled to room temperature and washed with methanol to give colorless crystals of NTU-Z1a. Yield: 52% (based on  $H_2BDC$ ). CCDC number: 921229.

#### 2.2.2. Synthesis of $(HTEA)_2[Co_3(BDC)_3Cl_2]$ (NTU-Z1b)

A mixture of  $CoCl_2 \cdot 6H_2O$  (1 mmol, 0.24 g),  $H_2BDC$  (3 mmol, 0.35 g), TEA (1 mL), and 4 mL PEG-200 was put into a 30 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 days. Then, the mixture was naturally cooled to room temperature and washed with methanol to give purple crystals of NTU-Z1b. Yield: 46% (based on  $CoCl_2 \cdot 6H_2O$ ). CCDC number: 921230.

#### 2.2.3. Synthesis of $(HTEA)_2[Fe_3(BDC)_3Cl_2]$ (NTU-Z2)

A mixture of  $FeCl_3 \cdot 6H_2O$  (2 mmol, 0.54 g),  $H_2BDC$  (4 mmol, 0.46 g), TEA (1 mL), and 4 mL PEG-200 was put into a 30 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 days. Then, the mixture was naturally cooled to room temperature and washed with methanol to give yellow crystals of NTU-Z2. Yield: 31% (based on  $FeCl_3$ ). CCDC number: 921231.

#### 2.2.4. Synthesis of $(HTEA)[Zn(IPA)Cl]$ (NTU-Z3)

A mixture of  $ZnCl_2$  (4 mmol, 0.54 g),  $H_2IPA$  (4 mmol, 0.46 g), TEA (1 mL), and 4 mL PEG-200 was put into a 30 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 days. Then, the mixture was naturally cooled to room temperature and washed with methanol to give colorless crystals of NTU-Z3. Yield: 61%. CCDC number: 921232.

#### 2.2.5. Synthesis of $(HTEA)_2[Cd_3(IPA)_4]$ (NTU-Z4)

A mixture of  $CdCl_2$  (3 mmol, 0.55 g),  $H_2IPA$  (5 mmol, 0.58 g), TEA (2 mL), and 5 mL PEG-200 was put into a 30 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 days. Then, the mixture was naturally cooled to room temperature and washed with methanol to give colorless crystals of NTU-Z4. Yield: 55% (based on  $CdCl_2$ ). CCDC number: 921233.

#### 2.2.6. Synthesis of $(HTEA)_2[Fe_3(IPA)_4]$ (NTU-Z5)

A mixture of  $FeCl_3 \cdot 6H_2O$  (2 mmol, 0.54 g),  $H_2IPA$  (4 mmol, 0.46 g), TEA (1 mL), and 4 mL PEG-200 was put into a 30 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 days. Then, the mixture was naturally cooled to room temperature and washed with methanol to give orange crystals of NTU-Z5. Yield: 34% (based on  $FeCl_3 \cdot 6H_2O$ ). CCDC number: 921234.

#### 2.2.7. Synthesis of $(HTEA)_2[Zn_3(IPA)_4]$ (NTU-Z6a)

A mixture of  $Zn_5(OH)_6(CO_3)_2$  (1 mmol, 0.55 g),  $H_2IPA$  (4 mmol, 0.46 g), TEA (1 mL), and 4 mL PEG-200 was put into a 30 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for

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