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## COMMUNICATION

## A new surfactant-introduced strategy for separating pure single-phase of metal-organic frameworks

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By introducing different surfactants into reaction system, two previous mixed-phase Ni(II)-MOFs constructed from an undeveloped pyridyl-tetracarboxylate and Ni(II) salts were successfully isolated to two pure products. Compound **1** exhibits a 3D H-bonded network with (3,8)-connected  $\{4.5^2\}_2\{4^2.5^6.6^{14}.7^2.8^4\}$  topology, while **2** features a 3D 2-fold interpenetrating framework with a self-penetrating (3,4,4)-connected  $\{6^2.10^3.12\}\{6^3\}_2\{6^4.8.10\}_2$  topological net.

Developing new strategies to prepare pure single-phase of crystalline MOFs is of importance in both fundamental sciences and technological applications.<sup>1-3</sup> Currently, in the domain of MOFs, the puzzling is the fact that mixed phases, such as bulk, powder and sediment which is composed of different elements, of crystalline compounds are often observed in the synthesis process. In fact, the preparation of MOFs can be conducted in various conditions such as solid-state reaction, solution process, hydro(solvo)thermal or ionothermal or other environments.<sup>4-7</sup> Generally speaking, the formation of MOFs phase is strongly dependent on several internal and/or external factors, such as metal ions, the templating agents, the metal-ligand ratio, the pH values, the counter ions and the number of coordination sites provided by organic ligands. Previous research mainly focused on the design, synthesis, characterization, and application of bulk MOFs materials, however, the effective separation and purification of MOFs from their mixtures is rarely reported. This urgent situation motivated us to develop a novel convenient strategy for separating pure single-phase of MOFs materials, especially in one-pot reaction system, and to understand the self-assembly mechanisms.

It has been widely demonstrated that surfactants, as powerful agents, not only can tailor the sizes, shapes, and surface properties of nanocrystals, but also can control the pore sizes and phases of mesoporous frameworks, due to the strong interaction between surfactants and crystal faces during the formation of such materials.<sup>8</sup> Inspired by these advantages of surfactants, we have firstly developed surfactant-thermal method to grow crystalline chalcogenide materials.<sup>9</sup> Furthermore, various novel MOFs with diverse dimensional structures have successfully been obtained through using different surfactants as reaction media by our groups.<sup>10</sup> Thus, logically, these results convinced us that the mixed-phase crystals of MOFs could be separable if proper surfactants have

been employed as reaction media to control the crystal growth. In this context, we firstly demonstrated that mixed-phase crystals of Ni(II)-MOFs system could be separated through employing two different surfactants.

The two-phase mixtures of  $[\text{Ni}_2(\text{H}_2\text{L}_2)(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$  (**1**) (yellow-green block crystals) and  $\text{Ni}_2\text{L}(\text{bpy})_{1.5}$  (**2**) (bright-green cluster crystals) were simultaneously obtained under one-pot reaction by heating a mixture of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_4\text{L}$ , bpy and  $\text{H}_2\text{O}$  at 160 °C. Although single crystals of **1** and **2** for X-ray single crystal diffraction could be manually separated under the optical microscope, it is an extremely tedious work to use microscope to get enough amount of pure phases of **1** and **2** for property studies. Further efforts have been input to try to obtain pure phases of **1** and **2** through controlling the reaction temperature, metal-ligand molar ratio and different solvents, however, none of them could give us satisfied results until surfactants were introduced into the reaction system. As expected, each surfactant could only favor one-phase crystal growth and the other phase growth was inhibited. Namely, the usage of two different surfactants can completely separate two previous two mixed phases: adding poly(ethylene glycol)-400 (PEG-400) or sodium *n*-octanoate ( $\text{NaC}_8$ ) into the above-mentioned reaction system can successfully result in pure single-phase of **1** or **2** eventually (Chart 1).

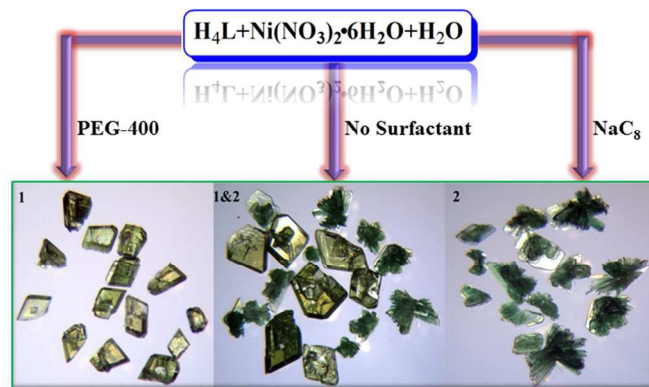
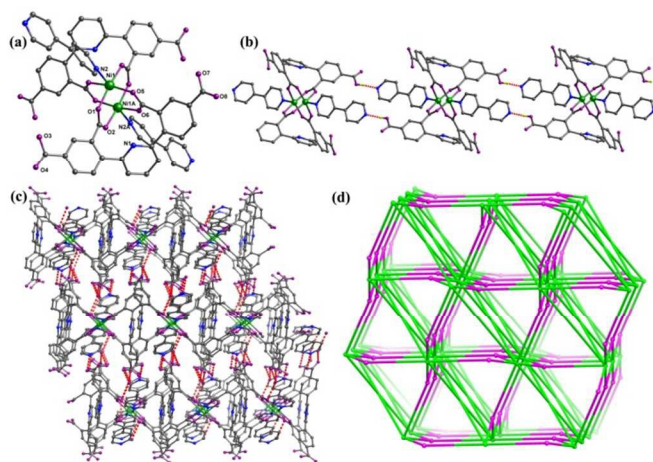


Chart 1 Schematic representation of the surfactant-induced phase separation of MOFs from two mixed phases.

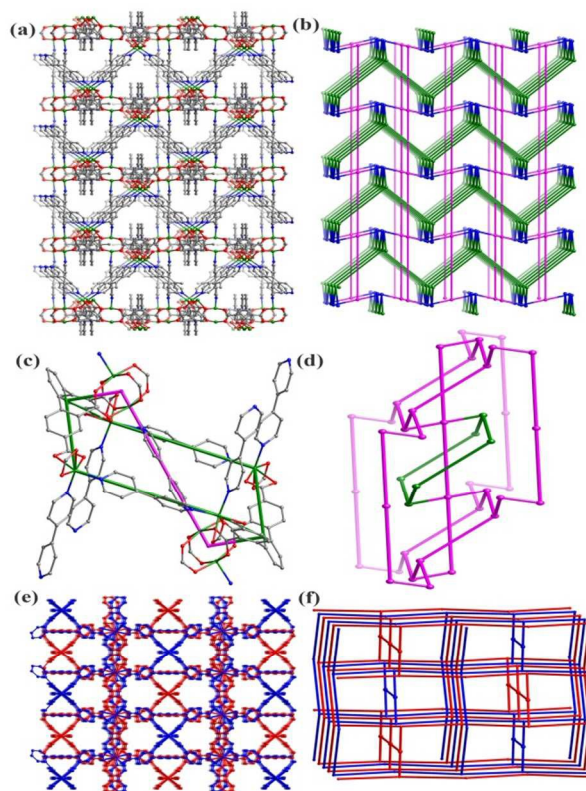
Single-crystal X-ray analysis (ESI†) reveals that compound **1** crystallizes in the monoclinic space group  $P2_1/n$  and exhibits a paddlewheel dinuclear  $[\text{Ni}_2(\text{R-COO})_4]$  unit terminally appended by two *bpy* ligands. The asymmetric unit contains one independent Ni(II) atom, one bi-deprotonated  $\text{H}_2\text{L}^{2-}$  anion, one *bpy* ligand, and one aqua ligand. Ni1 adopts a distorted tetragonal pyramidal geometry with a five-coordinated mode linking to four O atoms from four carboxylate groups in two  $\text{H}_2\text{L}^{2-}$  anions and one N atom from *bpy* ligand, (Fig. 1a). Each  $\text{H}_2\text{L}^{2-}$  ligand connects two Ni(II) atoms through two carboxylate groups, and adopts a  $\mu_2\text{-}\eta^1\text{:}\eta^1$  coordination mode (Fig. S1, ESI†), resulting in a centrosymmetric binuclear  $[\text{Ni}_2(\text{R-COO})_4]$  unit. Interestingly, each binuclear unit is strongly linked to others through  $\text{O-H}\cdots\text{N}$  hydrogen bonds ( $\text{O3-H3A}\cdots\text{N3}\#1 = 2.618 \text{ \AA}$ ;  $\#1: -x+1, -y, -z$ ; Table S3, ESI†) among *bpy* units and nondeprotonated carboxylic acid groups, resulting in a 1D ribbon-like chain (Fig. 1b). These 1D chains are further connected together through  $\text{O-H}\cdots\text{O}$  hydrogen-bonding interactions between water molecules and carboxylate groups to form a 3D supramolecular network. Notably, each  $[\text{Ni}_2(\text{R-COO})_4]$  unit and water molecule serve as 8-connected and 3-connected H-bond nodes respectively (Fig. S2, ESI†). Thus, considering the hydrogen-bonding interactions, **1** features a (3,8)-connected 3D H-bonded network with the point symbol of  $\{4.5^2\}_2\{4^2.5^6.6^{14}.7^2.8^4\}$  (Fig. 1c, 1d).



**Fig. 1** (a) The coordination environment of Ni(II) atoms of **1** with hydrogen atoms omitted for clarity (A: -x, 1-y, -z); (b) The view of 1D ribbon-like chains linked through  $\text{O-H}\cdots\text{N}$  hydrogen-bonding interactions; (c) The view of 3D supramolecular network built by extensive hydrogen-bonding interactions; (d) The topological view of the (3,8)-connected net with  $\{4.5^2\}_2\{4^2.5^6.6^{14}.7^2.8^4\}$  topology.

Compound **2** crystallizes in the orthorhombic space group  $\text{Cmca}$  and features a 3D 2-fold interpenetrating framework with self-penetrating (3,4,4)-connected net. Two types of crystallographically inequivalent Ni(II) sites have been investigated in **2**, namely, one five-coordinated distorted tetragonal pyramidal geometry (Ni1) and six-coordinated distorted octahedral environment (Ni2). As shown in Fig. S3, a pair of Ni1 atoms are bridged by four carboxylate groups in *syn-syn* coordination mode to form a paddlewheel dinuclear  $[\text{Ni}_2(\text{R-COO})_4]$  unit with  $\text{Ni1}\cdots\text{Ni1A}$  (A: x, 1-y, 1-z) separation of 2.650(6) Å. Each fully deprotonated  $\text{L}^{4-}$  ligand coordinates to four Ni atoms, with four carboxylate groups adopting  $\mu_1\text{-}\eta^1\text{:}\eta^1$ ,  $\mu_2\text{-}\eta^1\text{:}\eta^1$ ,  $\mu_2\text{-}\eta^1\text{:}\eta^1$  and  $\mu_1\text{-}\eta^1\text{:}\eta^1$  modes (Fig. S1, ESI†), resulting in the formation of a 2D sheet (Fig. S4, ESI†). Furthermore, the  $\text{L}^{4-}$  and *bpy* ligands linked the Ni(II) atoms to form a complex 3D self-penetrating network (Fig. 2a). Topologically, the dinuclear  $[\text{Ni}_2(\text{R-COO})_4]$  unit,  $\text{L}^{4-}$  and Ni2 are denoted as 4-connected, 3-connected and 4-connected nodes, respectively (Fig. S5). Thus, the 3D structure exhibits an new trinodal (3,4,4)-connected net of

$\{6^2.10^3.12\}\{6^3\}_2\{6^4.8.10\}_2$  topology (Fig. 2b) with self-penetrating feature, in which shortest 6-membered and 12-membered rings are interlocked (Fig. 2c, 2d). Such 3D topology net is confirmed to be unprecedented among MOFs *via* searching in the latest TTD database according to the TOPOS program.<sup>11</sup> More interestingly, two networks are interpenetrated into a 2-fold interpenetrating net, as shown in Fig. 2e and 2f. Due to interpenetration, the channels in a single 3D motif are mainly filled by another 3D motif. PLATON analysis revealed that the 3D framework structure was composed of voids of 952.3 Å<sup>3</sup> which represent 14.0% per unit cell volume.<sup>12</sup>



**Fig. 2** (a), (b) The view of 3D self-penetrating network along the *a* axis; (c), (d) The view of self-penetrating feature: 6-membered and 12-membered rings are interlocked; (e), (f) The packing and topological view of the 2-fold interpenetrating (3,4,4)-connected net with  $\{6^2.10^3.12\}\{6^3\}_2\{6^4.8.10\}_2$  topology.

Interestingly, if PEG-400 and  $\text{NaC}_8$  were replaced by other kinds of surfactants such as sodium dodecyl sulfate (SDS), hexadecyltrimethyl ammonium bromide (CTAB), or ethylene glycol (EG), mixed phases **1** and **2** were still investigated. However, if poly(vinylpyrrolidone) (PVP) and/or PEG-1500 was employed as the surfactants, no crystals were observed. It was worth noting only non-ionic PEG-400 or anionic  $\text{NaC}_8$  can easily give pure **1** or **2**. The results indicate that the surfactant properties (*e.g.* neutral, acidic, basic, cationic, anionic, or zwitterionic) and the degree of polymerization (DP) may play a key role to direct the crystallization of MOFs.

In order to confirm the phase purity of as-prepared compounds, PXRD pattern have been studied for **1** and **2**. The experimental PXRD patterns of compounds **1** and **2** are in good agreement with the simulated ones calculated from the single-crystal diffraction data, indicating that they are in a pure phase (Fig. S6, ESI†). To examine the thermal stability of these compounds, the thermogravimetric (TG) measurements (Fig. S7, ESI†) were performed in an air atmosphere. For **1**, the first step of weight loss from 30 to 230 °C,

accounts for 2.46% of mass loss, which is ascribed to water molecules (calcd. 2.82%), and the frameworks start to decompose from approximately 330 °C. For **2**, no weight loss is observed until 410 °C, indicating the high stability of compound **2**.

The temperature dependence of magnetic susceptibility of **1** and **2** were recorded between 300 and 2 K in an applied field of 1.0 kOe. The plots of  $\chi_M$  and  $\chi_M T$  versus  $T$  are shown in Fig.3. The  $\chi_M T$  value of **1** is 0.79 cm<sup>3</sup> K mol<sup>-1</sup> per Ni<sub>2</sub> paddlewheel units, and that of **2** is 3.01 cm<sup>3</sup> K mol<sup>-1</sup> for Ni<sub>4</sub>. Those are significantly lower than the expected spin-only values for isolated Ni(II) ions, suggesting the presence of dominant and strong antiferromagnetic exchange. As the temperature is lowered, the  $\chi_M$  value of **1** decreases constantly to a minimum of  $5.6 \times 10^{-4}$  cm<sup>3</sup> K mol<sup>-1</sup> at 80 K, typical of the presence of antiferromagnetic interaction. Then the increase of  $\chi_M$  may be attributed to a small amount of impure substance. A strong deviation of the experimental data from the Curie-Weiss law is also suggestive of a strong antiferromagnetic coupling of the nickel ions.<sup>13</sup> The  $\chi_M T$  product decreases rapidly upon cooling to a value of  $\sim 0.06$  cm<sup>3</sup> K mol<sup>-1</sup> at 100 K and then decreases smoothly until 2 K.

As shown in Fig. 3a, the best fitting for **1** in the whole range of temperature was obtained with  $J = -190.03$  cm<sup>1</sup>,  $g = 2.26$ ,  $\rho = 1.7\%$ , and  $zJ = -6.5$  cm<sup>-1</sup> (S7, ESI†). For **2**, the  $\chi_M T$  value decreases continuously to 2.44 at 18 K. and then, the  $\chi_M T$  value drops rapidly to 1.89 at 2K. The temperature dependence  $\chi_M$  in the range of 2-190 K followed the Curie-Weiss equation  $1/\chi_M = (T-\theta)/C$  with  $C = 1.25$  cm<sup>3</sup> K mol<sup>-1</sup>,  $\theta = -0.80$  K. As stated in the structure section, compound **2** consists of dinuclear [Ni<sub>2</sub>(R-COO)<sub>4</sub>] dimmers with Ni1...Ni1A separation of 2.650(6) Å, and then L<sup>4</sup> and bpy ligands link them and octahedral Ni2 atoms resulting in the formation of a 3D network. As shown in Fig.3b, the best fitting for **2** in the whole range of temperature was obtained with  $J = -196.23$  cm<sup>-1</sup>,  $g = 2.24$ , and  $zJ = -0.18$  (S7, ESI†).

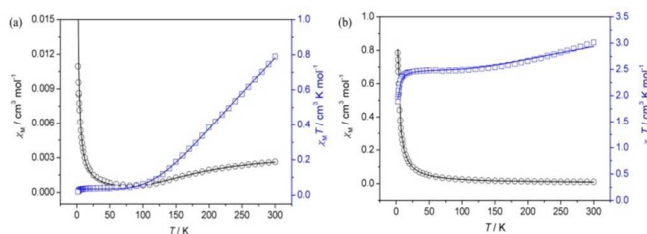


Fig.3 Temperature dependence of  $\chi_M T$  and  $\chi_M$  for **1** and **2** (a for **1**, b for **2**).

In summary, we presented here a new facile strategy for the separation of two mixed phases of MOFs. By introducing the non-ionic PEG-400 or anionic NaC<sub>8</sub> surfactants into the same reaction system, the pure phase of compounds **1** or **2** is individually crystallized. Interestingly, **1** shows a paddlewheel dinuclear [Ni<sub>2</sub>(R-COO)<sub>4</sub>] unit, which is linked by the hydrogen bonds to form a (3,8)-connected 3D supramolecular network, while **2** features a 3D 2-fold interpenetrating framework with a self-penetrating (3,4,4)-connected net. In addition, temperature-dependent magnetic susceptibility measurements indicated that both **1** and **2** display antiferromagnetic coupling among the adjacent Ni(II) centers. Our results confirmed that surfactant-directed crystal growth can effectively separate the mixed-phase crystals. Our success makes us believe that this new synthetic strategy could offer a new opportunity in purifying mixed phases of inorganic crystalline materials.

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## Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental details, Tables S1 and S2, Thermal analysis and PXRD patterns, crystallographic data and CIF files. For ESI and crystallographic data in cif or other electronic format see DOI: 10.1039/c000000x/

Crystallographic data for **1**: C<sub>62</sub>H<sub>42</sub>Ni<sub>2</sub>N<sub>6</sub>O<sub>18</sub>,  $M_r = 1276.44$ , Monoclinic,  $P2_1/n$ ,  $a = 13.142(6)$  Å,  $b = 12.337(5)$  Å,  $c = 17.656(8)$  Å,  $\beta = 108.5(1)^\circ$ ,  $V = 2715(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.562$  g cm<sup>-3</sup>,  $\mu = 0.780$  mm<sup>-1</sup>, 28282 total reflections, 6191 observed ( $I > 2\sigma(I)$ ),  $R_1 = 0.0458$ ,  $wR_2 = 0.1236$ , GOF = 1.017.

Crystallographic data for **2**: C<sub>36</sub>H<sub>21</sub>Ni<sub>2</sub>N<sub>4</sub>O<sub>8</sub>,  $M_r = 754.99$ , Orthorhombic,  $Cmca$ ,  $a = 31.395(15)$  Å,  $b = 13.702(7)$  Å,  $c = 15.808(8)$  Å,  $V = 6800(6)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.475$  g cm<sup>-3</sup>,  $\mu = 1.165$  mm<sup>-1</sup>, 35013 total reflections, 3985 observed ( $I > 2\sigma(I)$ ),  $R_1 = 0.0859$ ,  $wR_2 = 0.2111$ , GOF = 1.100.

CCDC 1039310 (**1**), 1039313 (**2**) contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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