

# Control of the topologies and packing modes of three 2D coordination polymers through variation of the solvent ratio of a binary solvent mixture†

Fang-Kuo Wang,<sup>a</sup> Shi-Yao Yang,<sup>\*a</sup> Rong-Bin Huang,<sup>a</sup> Lan-Sun Zheng<sup>a</sup> and Stuart R. Batten<sup>b</sup>

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By tuning the ratio of solvents in a binary solvent mixture, the coordination geometries of the metal centers were controlled and three 2D coordination polymers,  $[\text{Zn}(\text{bdc})(\text{dma})]_n$  **1**,  $[\text{Zn}_3(\text{bdc})_3(\text{dma})_2]_n$  **2** and  $\{[\text{Zn}(\text{bdc})(\text{H}_2\text{O})] \cdot (\text{DMA})\}_n$  **3**, were synthesized from zinc(II) nitrate and  $\text{H}_2\text{bdc}$  in water/DMA solvents ( $\text{H}_2\text{bdc}$  = benzene-1,4-dicarboxylic acid, DMA = *N,N*-dimethylacetamide). As the ratio of water/DMA increases, the number of DMA ancillary ligands coordinated to the zinc ion decreases, until all the DMA are substituted by water. The change in the ratio of solvents (which also act as ancillary ligands) affords a means to adjust the local coordination environment of the zinc ion, leading to three types of SBUs, which further determine the topologies and the packing modes of the coordination polymers.

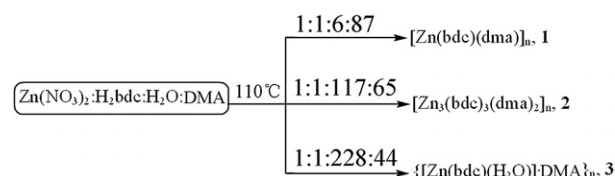
## Introduction

The assembly of coordination polymers by design is one aim of crystal engineering because of their outstanding bulk properties that are intimately related to their structures.<sup>1–6</sup> Significant effort has been expended towards this aim, resulting in important developments in recent years.<sup>7–10</sup> However, it is still a great challenge to synthesize a predicted structure because there are numerous influences that can have decisive roles in determining the structure and crystal packing.<sup>9–27</sup> In particular, when the solvents or the anions can compete with the ligands, the coordination environment adopted by the metal centre, and therefore the structure of the coordination polymer, can be very variable and unpredictable.<sup>7–13</sup> Fortunately, these uncertainties can be reduced by the use of well designed ligands that bind metals at chelating sites, such as carboxylate linkers that have the ability to aggregate metal ions into secondary building units (SBUs).<sup>28–34</sup> Nevertheless the true engineering of crystal structures is still a distant aim which demands more extensive and intensive investigations. Herein, we report three 2D coordination polymers  $[\text{Zn}(\text{bdc})(\text{dma})]_n$  **1**,  $[\text{Zn}_3(\text{bdc})_3(\text{dma})_2]_n$  **2**, and  $\{[\text{Zn}(\text{bdc})(\text{H}_2\text{O})] \cdot (\text{DMA})\}_n$  **3** ( $\text{H}_2\text{bdc}$  = benzene-1,4-dicarboxylic acid, DMA = *N,N*-dimethylacetamide) prepared in a binary solvent mixture. Our study shows that the change in the ratio of solvents can influence the subtle variables that lead to coordination polymers with different structures (Scheme 1).

## Experimental procedure

### Materials and methods

All chemicals and solvents used in the syntheses were analytical grade and used without further purification. Infrared spectra



**Scheme 1** The assembly of **1**, **2** and **3** tuned by the solvent ratio.

were recorded with a Nicolet AVATAR FT-IR360 spectrometer using the KBr pellet technique. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. X-Ray powder diffractions were measured on a Panalytical X-Pert Pro diffractometer with Cu  $\text{K}\alpha$  radiation. TGA was measured between 30 and 800 °C on a NETZSCH TG 209 F1 instrument under nitrogen gas flow.

### Syntheses

**$[\text{Zn}(\text{bdc})(\text{dma})]_n$  1.**  $\text{H}_2\text{bdc}$  (benzene-1,4-dicarboxylic acid, 0.17 g, 1.0 mmol) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.30 g, 1.0 mmol) were dissolved in DMA (*N,N*-dimethylacetamide, 8.0 ml). The solution was placed in a 25 ml conical flask, heated to 110 °C at the rate of 0.2 °C  $\text{min}^{-1}$ , and kept at 110 °C for 3 d, then slowly cooled down to room temperature at the rate of 0.1 °C  $\text{min}^{-1}$ . Colorless block crystals (0.26 g, yield 83%) suitable for X-ray diffraction were separated by filtration, washed with deionized water and dried in the air. Elemental Analysis.  $\text{ZnC}_{12}\text{H}_{13}\text{NO}_5$ : found (calc.) C 44.96 (45.52), H 4.05 (4.11), N 4.34 (4.42)%. FTIR (KBr,  $\text{cm}^{-1}$ ): 3422 (m), 2925 (w), 1627 (vs), 1504 (w), 1389 (vs), 1017 (m), 889 (w), 824 (s), 753 (vs), 607 (w), 549 (s).

**$[\text{Zn}_3(\text{bdc})_3(\text{dma})_2]_n$  2.**  $\text{H}_2\text{bdc}$  (0.17 g, 1.0 mmol) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.30 g, 1.0 mmol) were dissolved in a mixture of DMA (6.0 ml) and  $\text{H}_2\text{O}$  (2.0 ml). Then the solution was treated as that for **1** and colorless block crystals (0.20 g, yield 71%) were obtained. Elemental analysis.  $\text{Zn}_3\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_{14}$ : found (calc.) C 44.21 (44.55), H 3.41 (3.48), N 3.19 (3.25)%.

<sup>a</sup>State Key Laboratory of Physical Chemistry of Solid Surface, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. E-mail: syyang@xmu.edu.cn; Fax: +86-592-2183047; Tel: +86-592-2186175

<sup>b</sup>School of Chemistry, Monash University, 3800, Australia

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**Table 1** Crystallographic data for **1**, **2** and **3**

|   | <b>1</b>  | <b>2</b>   | <b>3</b>  |
|---|---|--|---|
| Formula   | ZnC <sub>12</sub> H <sub>13</sub> NO <sub>5</sub> | Zn <sub>3</sub> C <sub>32</sub> H <sub>30</sub> N <sub>2</sub> O <sub>14</sub> | ZnC <sub>12</sub> H <sub>15</sub> NO <sub>6</sub> |
| <i>M</i>  | 316.60  | 862.69   | 334.62  |
| <i>T/K</i>  | 297(2)  | 298(2)   | 295(2)  |
| Crystal system  | Monoclinic  | Monoclinic   | Triclinic   |
| Space group   | <i>C2/c</i>                                       | <i>C2/c</i>  | <i>P-1</i>  |
| <i>a/Å</i>  | 18.2323(8)  | 23.2531(11)  | 6.9787(3)   |
| <i>b/Å</i>  | 10.8209(5)  | 10.6100(5)   | 10.1257(5)  |
| <i>c/Å</i>  | 13.0970(6)  | 15.9768(7)   | 10.8955(5)  |
| $\alpha/^\circ$   | 90  | 90   | 70.436(1)   |
| $\beta/^\circ$  | 93.552(1)   | 111.641(1)   | 74.018(1)   |
| $\gamma/^\circ$   | 90  | 90   | 76.750(1)   |
| <i>V/Å<sup>3</sup></i>                                      | 2578.9(2)   | 3663.9(3)  | 689.41(6)   |
| <i>Z</i>  | 8   | 4  | 2   |
| <i>D<sub>c</sub>/g cm<sup>-3</sup></i>                      | 1.631   | 1.564  | 1.612   |
| $\mu/\text{mm}^{-1}$  | 1.920   | 2.015  | 1.805   |
| <i>F</i> (000)  | 1296  | 1752   | 344   |
| Ref. unique   | 3082  | 4331   | 3152  |
| Ref. ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                  | 14421   | 15360  | 7767  |
| <i>R</i> <sub>int</sub>                                     | 0.0277  | 0.0261   | 0.0220  |
| <i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | 0.0292  | 0.0344   | 0.0320  |
| <i>wR</i> <sub>2</sub> (all data)                           | 0.0837  | 0.0972   | 0.0822  |
| GOF( <i>S</i> )   | 1.078   | 1.060  | 1.055   |
| $\Delta\rho/e \text{ \AA}^{-3}$                             | 0.419, -0.355                                     | 0.602, -0.342  | 0.896, -0.397                                     |

FTIR (KBr, cm<sup>-1</sup>): 3415 (s), 1956 (w), 1590 (s), 1503 (m), 1384 (s), 1294 (w), 1018 (s), 971 (w), 887 (m), 825 (vs), 749 (vs), 594 (m), 531 (s).

**{[Zn(bdc)(H<sub>2</sub>O)]·(DMA)}<sub>n</sub> 3.** H<sub>2</sub>bdc (0.17 g, 1.0 mmol) and Zn(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (0.30 g, 1.0 mmol) were dissolved in a mixture of DMA (4.0 ml) and H<sub>2</sub>O (4.0 ml). Then the solution was treated as that for **1** and colorless block crystals (0.18 g, yield 55%) were obtained. Elemental analysis. ZnC<sub>12</sub>H<sub>15</sub>NO<sub>6</sub>: found (calc.) C 42.56 (43.07), H 4.43 (4.48), N 4.11 (4.18)%. FTIR (KBr, cm<sup>-1</sup>): 3257 (m), 2931 (w), 1963 (w), 1836 (w), 1627 (vs),

1504 (s), 1387 (vs), 1299 (w), 1191 (w), 1151 (w), 1017 (s), 890 (w), 854 (m), 824 (s), 752 (vs), 607 (w), 548 (s).

## X-Ray crystallography

Data collections were performed on Bruker SMART Apex CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation at room temperature for **1**, **2** and **3**. Absorption corrections were applied by using the multi-scan program SADABS.<sup>35</sup> Structural solutions and full-matrix least-square refinements based on *F*<sup>2</sup> were performed with the SHELXS-97<sup>36</sup> and SHELXL-97<sup>37</sup> program packages, respectively. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions and included in the refinement in the riding model approximation. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table 1, and selected bond lengths and angles are shown in Table 2. CCDC 669582–669584 are for **1**, **2** and **3**, respectively. Simulated and experimental X-ray powder diffraction patterns for **1**, **2** and **3** are shown in Fig. 1.

## Results and discussion

### Description of the crystal structures

In **1**, [Zn(bdc)(dma)]<sub>n</sub>, the zinc ion is in slightly distorted square-pyramidal coordination environment, coordinated by four oxygen atoms from four bdc ligands in the basal plane, and one oxygen atom from a DMA ligand at the apex. Pairs of zinc ions are bridged by four carboxylates to form a common paddle-wheel SBU (Fig. 2a), then the SBU expands to form a 2D (4,4) net (Fig. 2b). The 2D nets pack along the *c* axis of the crystal, with the bulky axial DMA ligand protruding into the voids of the adjacent nets. Each quadrangular void in the (4,4) net accommodates two DMA from the adjacent layers above and below. In

**Table 2** Selected bond lengths and angles for **1**, **2** and **3**

|  |            |             |           |              |           |
|--|------------|-------------|-----------|--------------|-----------|
| <b>[Zn(bdc)(dma)]<sub>n</sub> 1</b>  |            |             |           |              |           |
| Zn1–O1   | 2.0360(12) | O1–Zn1–O3   | 87.69(5)  | O4b–Zn1–O3   | 156.95(7) |
| Zn1–O2a  | 2.0069(12) | O1–Zn1–O4b  | 86.59(5)  | O5–Zn1–O1    | 105.02(5) |
| Zn1–O3   | 2.0506(13) | O2a–Zn1–O1  | 156.59(7) | O5–Zn1–O2a   | 98.38(5)  |
| Zn1–O4b  | 2.0487(13) | O2a–Zn1–O3  | 89.12(5)  | O5–Zn1–O3    | 99.48(6)  |
| Zn1–O5   | 1.9765(15) | O2a–Zn1–O4b | 87.33(5)  | O5–Zn1–O4b   | 103.56(6) |
| Symmetry codes: a <i>x</i> , <i>y</i> + 1, <i>z</i> ; b $-x$ , <i>y</i> , $-z$ + 1/2.  |            |             |           |              |           |
| <b>[Zn<sub>3</sub>(bdc)<sub>3</sub>(dma)<sub>2</sub>]<sub>n</sub> 2</b>  |            |             |           |              |           |
| Zn1–O1   | 1.949(2)   | O1–Zn1–O7   | 103.94(8) | O5–Zn1–O7    | 93.23(8)  |
| Zn1–O4a  | 1.935(2)   | O3a–Zn2–O2b | 88.09(7)  | O6–Zn2–O2    | 90.77(6)  |
| Zn1–O5   | 1.942(2)   | O3a–Zn2–O2  | 91.91(7)  | O6–Zn2–O2b   | 89.23(6)  |
| Zn1–O7   | 1.965(2)   | O3c–Zn2–O2  | 88.09(7)  | O6–Zn2–O3a   | 93.19(6)  |
| Zn2–O2   | 2.088(2)   | O3c–Zn2–O2b | 91.91(7)  | O6–Zn2–O3c   | 86.81(6)  |
| Zn2–O2b  | 2.088(2)   | O3c–Zn2–O3a | 180.00(9) | O6–Zn2–O6b   | 180.00(8) |
| Zn2–O3a  | 2.076(2)   | O4a–Zn1–O1  | 106.99(8) | O6b–Zn2–O2   | 89.23(6)  |
| Zn2–O3c  | 2.076(2)   | O4a–Zn1–O5  | 120.55(8) | O6b–Zn2–O2b  | 90.77(6)  |
| Zn2–O6   | 2.052(1)   | O4a–Zn1–O7  | 107.60(8) | O6b–Zn2–O3a  | 86.81(6)  |
| Zn2–O6b  | 2.052(1)   | O5–Zn1–O1   | 121.18(8) | O6b–Zn2–O3c  | 93.19(6)  |
| Symmetry codes: a <i>x</i> , $-y$ + 1, $z$ – 1/2; b $-x$ + 1/2, $-y$ + 3/2, $-z$ ; c $-x$ + 1/2, <i>y</i> + 1/2, $-z$ + 1/2. |            |             |           |              |           |
| <b>{[Zn(bdc)(H<sub>2</sub>O)]·(DMA)}<sub>n</sub> 3</b>   |            |             |           |              |           |
| Zn1–O1   | 2.041(2)   | O1–Zn1–O4a  | 85.29(10) | O3–Zn1–O4a   | 157.95(9) |
| Zn1–O2a  | 2.019(2)   | O2a–Zn1–O1  | 158.28(9) | O1 w–Zn1–O1  | 102.94(8) |
| Zn1–O3   | 2.018(2)   | O2a–Zn1–O4a | 88.00(11) | O1 w–Zn1–O2a | 98.47(8)  |
| Zn1–O4a  | 2.061(2)   | O3–Zn1–O1   | 87.46(11) | O1 w–Zn1–O3  | 103.35(8) |
| Zn1–O1 w   | 1.960(2)   | O3–Zn1–O2a  | 91.15(10) | O1 w–Zn1–O4a | 98.56(8)  |
| Symmetry codes: a $-x$ + 1, $-y$ + 1, $-z$ + 1.  |            |             |           |              |           |

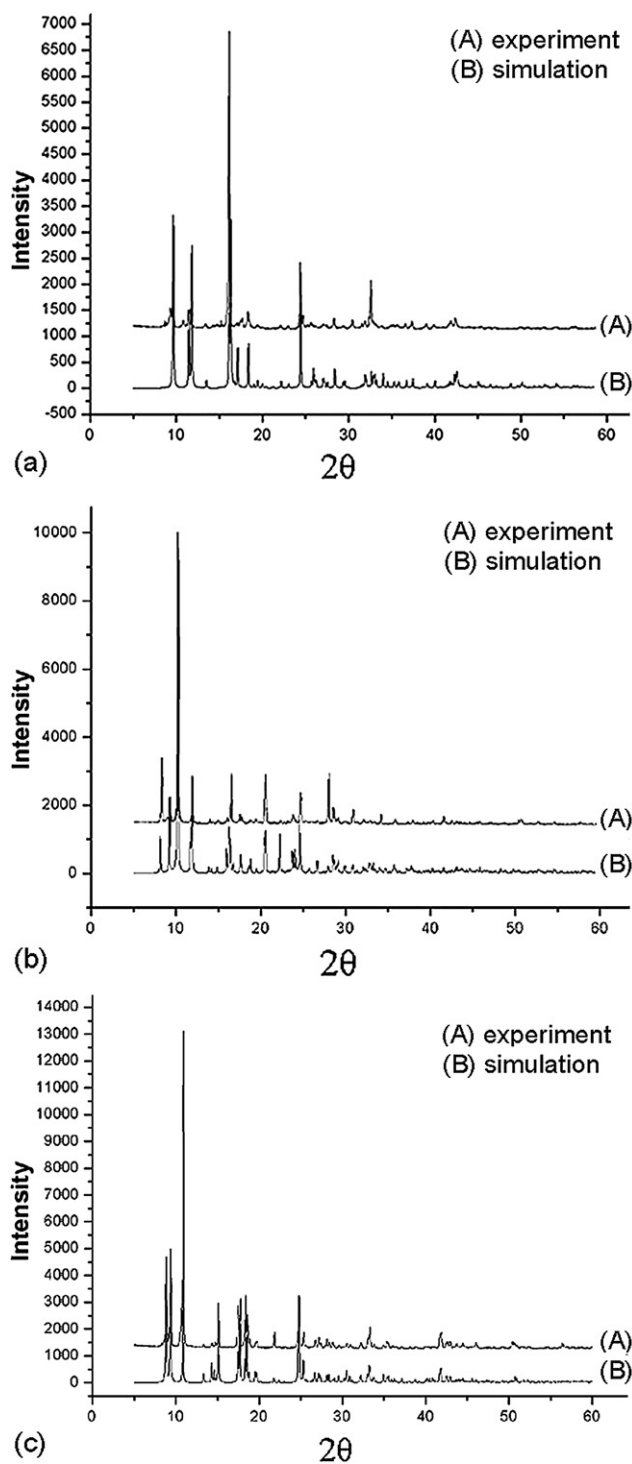


Fig. 1 Simulated and experimental X-ray powder diffraction pattern for 1 (a), 2 (b) and 3 (c).

order to fill the voids more efficiently, the two square-pyramid in the SBU twist at an angle of  $15.6^\circ$ , and the benzene rings also deviate from the mean plane of the 2D net at the angles of  $58.3$  and  $71.8^\circ$ . The interplanar distance between two adjacent 2D nets is  $5.417 \text{ \AA}$ .

In **2**,  $[\text{Zn}_3(\text{bdc})_3(\text{dma})_2]_n$ , the 2D layered structure is a (3,6) net propagated from trinuclear zinc SBUs. (Fig. 3) Three zinc ions

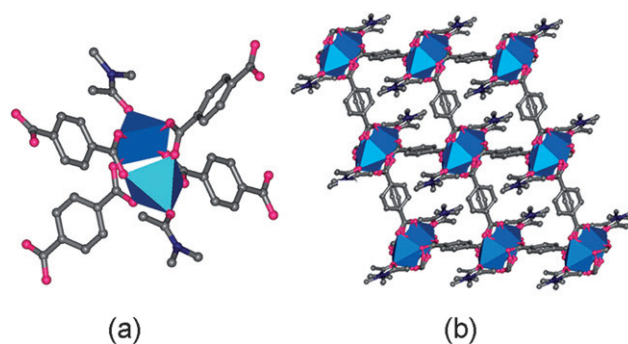


Fig. 2 (a) The building block, and (b) the interdigitated (4,4) net of **1**. Hydrogen atoms are omitted for clarity.

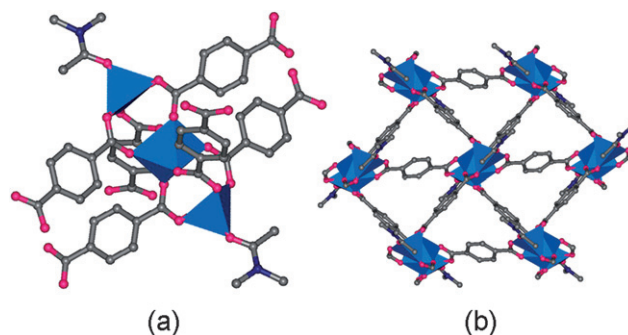


Fig. 3 (a) The building block, and (b) the (3,6) net of **2**. Hydrogen atoms are omitted for clarity.

are bridged by six bdc ligands to form each SBU; one octahedral zinc sandwiched between two tetrahedral zinc atoms. Each of the tetrahedral zinc atom binds to one ancillary DMA ligand. The (3,6) nets in **2** also display an interdigitated structure, with the interplanar distance between adjacent nets being  $10.807 \text{ \AA}$ . The coordinated DMA ligands of each net occupy the voids of the adjacent (3,6) nets.

Like **1**, coordination polymer **3**,  $\{[\text{Zn}(\text{bdc})(\text{H}_2\text{O})] \cdot (\text{DMA})\}_n$ , also contains paddle-wheel SBUs, but the axial ancillary ligand is water instead of DMA (Fig. 4). The (4,4) nets pack along the  $a$  axis and are connected *via*  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds ( $\text{O} \cdots \text{O} = 2.601(3) \text{ \AA}$ ,  $\text{O}-\text{H} \cdots \text{O} = 164.4^\circ$ ) between the coordinated water ligands and carboxyl groups from adjacent nets. The interplanar

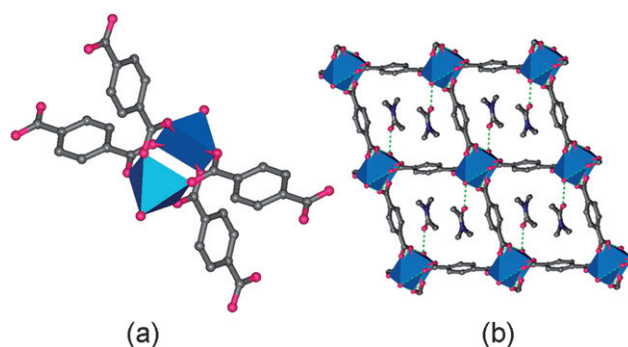


Fig. 4 (a) The building block, and (b) the (4,4) net, with guest solvent molecules, of **3**. Hydrogen atoms are omitted for clarity.

distance between adjacent nets is 5.860 Å. As the water molecule is much smaller than the cavities inside the (4,4) net, it is impossible to fill the voids by interdigitation of the nets (as seen in **1**). Thus, in order to minimise the empty space, DMA guest molecules are included through O–H...O hydrogen bonds between the water ligands and the DMA carbonyl groups (O...O = 2.872(3) Å, O–H...O = 166.0°). Each quadrangular void in the (4,4) net accommodates two DMA molecules.<sup>38</sup>

The TGA/DTA analysis of **3** indicates that H<sub>2</sub>O and DMA are lost in continuous steps at the range of 90–300 °C, with weight loss of 31.20 wt% (calc: 31.74 wt%), and it is difficult to assign each weight loss separately. (Sup 1) The decomposition of the zinc terephthalate occurs at >350 °C. Powder X-ray diffraction measurements at different temperatures show that the framework of **3** is stable only below 100 °C.

X-Ray powder diffraction patterns (Fig. 1) and elemental analyses show that **1**, **2** and **3** are obtained, respectively, by tuning the ratio of solvents in the binary solvent mixture of DMA and water. The syntheses are also carried out at 110 °C and the products are separated at once directly from the hot solutions before cooling down. The X-ray powder diffraction patterns of **1**, **2** and **3** are measured and compared with their corresponding calculated patterns (Sup 2). The results show again that **1**, **2** and **3** are obtained separately, nevertheless, **1** is always contaminated with a small amount of **3** because it is difficult to avoid the presence of water in the solution.

## Discussion

When we compare the structures and the synthetic conditions of the three coordination polymers, we find that there is a definite relationship between the ratio of solvents and the composition of the products (Table 3). When the ratio of water/DMA increases, the number of DMA ancillary ligands coordinated to the zinc ions decreases, until all the DMA are substituted by water. The number of coordinated DMA per zinc ion changes from 1 to 0.67 to 0, and the number of coordinated water changes from 0 to 0 to 1. The change in the ratio of solvents (which also act as ancillary ligands) affords a means to adjust the local coordination environment of the zinc ion, leading to a variety of SBUs which further determine the topologies and the packing modes of the coordination polymers.<sup>28,29</sup> In **1**, when DMA coordinates to the zinc ions, the framework of the coordination polymer is hydrophobic in nature, which is different from the polar water molecule and the amphiphilic DMA molecule. Therefore the (4,4) nets of **1** expel all the solvent molecules and interdigitate closely together with each other.

In the structure of **2**, the formation of the less common trinuclear zinc SBU<sup>28,30</sup> may be caused by the fact that neither of

the solvents (*i.e.* the ancillary ligands) dominates the solvent mixture (although water is in excess, Table 3). The (3,6) nets pack together through interdigitation in the crystal structure, similar to the packing mode of **1**.

In **3**, the waters coordinated to the zinc ions provide hydrogen bond donor on the framework. Thus in the structure of **3** the (4,4) nets pack together by hydrogen bonds between water and carboxyl oxygen atom and leave large voids in the crystal (45.1%). Unlike **1** and **2**, it is impossible to fill the voids in **3** by interdigitation because the water molecule is far too small to fill the space within the net. This leaves interpenetration of the framework or intercalation of guests as the only method by which the space can be filled.<sup>15</sup> Significantly, there are both hydrophobic and hydrophilic parts in the structure of the (4,4) net, as there are for the DMA molecules. Furthermore, the volume of two DMA molecules is also approximately the same as that of the cavity in the (4,4) net. Therefore both the structural similarities between the (4,4) net and the DMA molecule, and the geometric match in the volume lead the crystal to include DMA as guest molecules within the cavities. In order to further fill the space more efficiently, the paddle-wheel SBU distorts with the angle between two paddles deviating from 90 to 77.4° in **3** (82.7° in **1**). As has been previously seen, the paddle-wheel SBU formed by metal ion and carboxyl groups is not only a robust node, but also a versatile tecton in the construction of metal–organic-frameworks.<sup>29,30</sup>

## Conclusion

In summary, we have successfully synthesized three 2D coordination polymers: the interdigitated (4,4) net of [Zn(bdc)(dma)]<sub>n</sub> **1**, the interdigitated (3,6) net of [Zn<sub>3</sub>(bdc)<sub>3</sub>(dma)<sub>2</sub>]<sub>n</sub> **2**, and the solvent clathrate (4,4) net of {[Zn(bdc)(H<sub>2</sub>O)]·(DMA)}<sub>n</sub> **3**. By changing the ratio of the solvents, which also act as ancillary ligands, the coordination environments of the metal ions can be tuned, giving control over the topologies of the coordination polymers. Multi-point recognition between the coordination polymer nets and between the nets and the guest solvent molecules determine the packing mode of the 2D coordination polymers.

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**Table 3** Relation between ratio of reactants and composition of **1**, **2** and **3**

|          | Zn : bdc : H <sub>2</sub> O : DMA<br>in reactants | Zn : bdc : H <sub>2</sub> O : DMA<br>(guest) in products |
|----------|---|--|
| <b>1</b> | 1 : 1 : 6 : 87                                    | 1 : 1 : 0 : 1  |
| <b>2</b> | 1 : 1 : 117 : 65                                  | 1 : 1 : 0 : 0.67   |
| <b>3</b> | 1 : 1 : 228 : 44                                  | 1 : 1 : 1 : 0(1)   |

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