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## Nanosheet-assembled microflower-like coordination polymers by surfactant-assisted assembly with enhanced catalytic activity<sup>†</sup>

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Tuning the morphology and size of coordination polymers (CPs) is an effective strategy to enable crystalline materials for desired applications. Herein, two CPs, named  $[Cd_2(DBTP)(H_2O)_2]_n$  (1) and  $\{[Zn_2(DBTP)(H_2O)]\cdot 2.5H_2O\}_n$  (2), were prepared by employing a rigid V-shaped and multidentate N-heterocyclic ligand 2,6-di(1*H*,2'*H*-[3,3'-bi(1,2,4-triazol)]-5'-yl)pyridine (H<sub>4</sub>DBTP) under solvothermal conditions. Their crystal morphologies and sizes were controlled by varying the type and the amount of surfactants. The morphology can be changed from bulk blocks to microflower-like hierarchical spheres assembled by nanosheets and the mean size of the microflowers is approximately 2 µm. Nanoscale 1a and 2a were further evaluated as heterogeneous catalysts for the conversion reactions of nitromethylbenzenes into benzoic acids. The results showed that nanoscale 2a is a more efficient catalyst than nanoscale 1a and their corresponding bulk counterparts.

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### Introduction

With the rapid development of nanoscience, an increased number of research studies been focused on the synthesis of micro- and nanosized materials, which can provide unique possibilities for strengthening the physical and/or chemical properties of their corresponding bulk counterparts,<sup>1</sup> or even for producing new properties for novel applications.<sup>2</sup> Hierarchical architectures, usually referred to as twodimensional (2D) or three-dimensional (3D) structures assembled from sub-nanostructures with specific dimensions, have aroused great interest because of the cooperative combination of the advantages of nanostructures and microstructures. However, compared to the numerous developments made on the design of hierarchical structures in some inorganic materials, such as metal oxides or sulfides,<sup>3</sup> noble metals,<sup>4</sup> chalcogenides,<sup>5</sup> etc., relatively few examples have been reported on the fabrication of hierarchically structured coordination polymers (CPs).<sup>6</sup>

CPs, as a fascinating class of tunable and functionalizable crystalline materials assembled from metal ions or clusters and

organic ligands *via* coordination bonds, are perfect candidates for various applications including luminescence, catalysis, adsorption, sensing, and so on.<sup>7</sup> Recently, the use of CPs or CP composites as catalysts for synergistic catalysis and tandem reactions has attracted increasing attention due to their tunable open metal centers, functional organic linkers, and active guest species in their pores.<sup>8</sup> Through careful design of the inorganic nodes and the organic linkers, the active sites within CPs can be rationally manipulated to create materials with unique catalytic properties. Except for the active sites in the pores of CP materials, the morphology and size also play an important role in the catalytic process.<sup>9</sup> Generally, nanosized CP crystals as heterogeneous catalysts outperform their corresponding bulk crystals owing to their larger surface area, lower diffusion barriers and/or shorter diffusion distances.<sup>10</sup>

In the past few decades, many synthetic strategies have been developed to scale down CPs from bulk to micro- and nanometer regimes, including solvothermal, microwave, microemulsion, surfactant-mediated methods and so on.<sup>2b,11</sup> Recently, we have successfully downsized large crystals of Zn-based CPs to nanoscale with an octahedral geometry and nanosized strips by surfactant-assisted assembly. CPs with hierarchical architectures composed of smaller nano-substructures can be fabricated using this method and further provide a catalytic system with good conversions. Thus, we report here the control of the morphology and size of two new CPs with different structures and dimensionalities, namely  $[Cd_2(DBTP)(H_2O)_2]_n$  (1) and  $\{[Zn_2(DBTP)(H_2O)] \cdot 2.5H_2O\}_n$  (2) (H<sub>4</sub>-DBTP = 2,6-di(1H,2'H-[3,3'-bi(1,2,4-triazol]) - 5'-yl)pyridine), which

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were synthesized under solvothermal conditions. Crystals with different morphologies and sizes were achieved by using different types of surfactants or by varying their concentrations. Nanosheet-assembled microflower-like spheres were obtained and used as catalysts for the tandem reactions from nitroalkanes to carboxylic acids, showing much more efficient catalytic performance than that of the corresponding bulk ones.

## **Experimental section**

#### Materials and physical measurements

All the reagents and solvents were commercially available and used without further purification. A series of characterization techniques, including infrared (IR) spectroscopy, powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA), adsorption and desorption measurements, and elemental analysis of complexes **1–2a**, were performed using the corresponding instruments (ESI†).

Synthesis of  $[Cd_2(DBTP) \cdot 2H_2O]_n$  (1).  $Cd(NO_3)_2 \cdot 4H_2O$  (0.046 g, 0.15 mmol), H<sub>4</sub>DBTP (0.017 g, 0.05 mmol), dimethylamine (Me<sub>2</sub>NH, 3 mL), acetonitrile (MeCN, 2 mL), and *N*,*N*-dimethylformamide (DMF, 3 mL) were placed in a 25 mL Teflon-lined stainless steel container, heated at 165 °C for 3 days, and cooled to ambient temperature at a rate of 5 °C h<sup>-1</sup>. Colorless samples of 1 were achieved (yield, 58%, based on Cd). Elemental analysis calcd for  $C_{13}H_9Cd_2O_2N_{13}$ : C, 25.85%; H, 1.50%; N, 30.14%. Found: C, 25.67%; H, 1.51%; N, 30.12%. IR (KBr, cm<sup>-1</sup>): 3355 (s), 3090 (m), 2171 (vw), 2039 (w), 1618 (s), 1584 (s), 1431 (vs), 1188 (vs), 1085 (s), 832 (s), 795 (m), 757 (w), 735 (vw).

**Synthesis of {**[**Zn**<sub>2</sub>(**DBTP**)(**H**<sub>2</sub>**O**)]·2.5**H**<sub>2</sub>**O**}<sub>*n*</sub> (2). ZnSO<sub>4</sub>·7**H**<sub>2</sub>**O** (0.057 g, 0.2 mmol), H<sub>4</sub>DBTP (0.035 g, 0.1 mmol), H<sub>2</sub>O (3 mL), MeCN (3 mL), and DMF (3 mL) were placed in a 25 mL Teflon-lined stainless steel container, heated at 165 °C for 3 days, and cooled to ambient temperature at a rate of 5 °C h<sup>-1</sup>. Colorless samples of 2 were achieved (yield, 62%, based on Zn). Elemental analysis calcd for C<sub>13</sub>H<sub>12</sub>Zn<sub>2</sub>N<sub>13</sub>O<sub>3.5</sub>: C, 29.07%; H, 2.25%; N, 33.90%. Found: C, 29.11%; H, 2.28%; N, 33.73%. IR (KBr, cm<sup>-1</sup>): 3401 (m), 2165 (vw), 2052 (w), 1668 (vs), 1619 (vs), 1581 (s), 1434 (s), 1180 (vs), 1046 (w), 829 (m), 791 (s), 756 (m), 731 (w).

Syntheses of microflower-like spheres 1a with 0.10 g CTAB.  $Cd(NO_3)_2$ ·4H<sub>2</sub>O (0.046 g, 0.15 mmol) and CTAB (0.10 g) were mixed in MeCN (2 mL) and sonicated for 30 min, followed by the addition of the solution of H<sub>4</sub>DBTP (0.017 g, 0.05 mmol) in DMF (3 mL) and Me<sub>2</sub>NH (3 mL). The resulting solution was further sonicated for another 30 min and then transferred into Teflon-lined autoclaves for solvothermal synthesis at 165 °C for three days. After cooling to room temperature, the particles were collected by centrifugation, washed with deionized water and ethanol three times, respectively, and dried in a vacuum at 60 °C overnight.

Syntheses of microflower-like spheres 2a with 0.15 g CTAB.  $ZnSO_4$ -7H<sub>2</sub>O (0.057 g, 0.2 mmol) and CTAB (0.15 g) were mixed in H<sub>2</sub>O (3 mL) and sonicated for 30 min, followed

by the addition of the solution of  $H_4DBTP$  (0.035 g, 0.1 mmol) in DMF (3 mL) and MeCN (3 mL). The resulting solution was further sonicated for another 30 min and then transferred into Teflon-lined autoclaves for solvothermal synthesis at 165 °C for three days. After cooling to room temperature, the particles were collected by centrifugation, washed with deionized water and ethanol three times, respectively, and dried in a vacuum at 60 °C overnight.

The procedure for the conversion of nitrobenzyl compounds into benzoic acids catalyzed by the nanosized 2a. The synthesis of benzoic acids from nitrobenzyl compounds was conducted using the nanosized 2a samples as catalysts. In a typical reaction, a mixture of nitroalkane (1.0 mmol), TBAI (0.05 mmol) and nanosized 2a catalysts (0.1 mmol, 0.1 equiv. based on zinc ions) was dispersed in water (10 mL). The mixture was stirred at 80 °C and monitored by thin-layer chromatography (TLC). After the reaction finished, the mixture was cooled down to room temperature, acidified and The organic lavers were extracted. collected and dichloromethane was removed under reduced pressure.

**Crystal data collection and refinement.** Single-crystal X-ray diffraction (SCXRD) data of complexes **1** and **2** were collected on a Bruker D8 Venture diffractometer with Mo-Kα radiation ( $\lambda = 0.71073$  Å) at room temperature. The structure was solved by direct methods and refined by a full-matrix least-squares method on  $F^2$ . All calculations were carried out with the SHELXTL<sup>12</sup> program as shown in the ESI.† Crystal data, data collection, and structure refinement details are summarized in Table S1.†

### Results and discussion

#### Crystal structure of 1

In order to obtain stable and adjustable heterogeneous catalysts, H<sub>4</sub>DBTP was chosen as a rigid multidentate organic linker that bridges metal ions in many coordination modes, assisting in generating CPs containing multinuclear secondary building units (SBUs) as the active sites to improve the catalytic performance. Successfully, the mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and H<sub>4</sub>DBTP in Me<sub>2</sub>NH/MeCN/DMF was kept at 165 °C for three days to afford complex 1 as colorless single crystals. Meanwhile, the crystals of 2 were obtained by the direct reaction of  $ZnSO_4 \cdot 7H_2O$  with  $H_4DBTP$  in  $H_2O/$ MeCN/DMF under the same conditions. Complexes 1 and 2 were fully characterized by IR, elemental analysis, and TGA (Fig. S1 and S2<sup>†</sup>), and their structures were unambiguously determined by SCXRD. SCXRD analysis demonstrated that complex 1 crystallized in the orthorhombic system with the Pbca space group. As shown in Fig. 1a, the asymmetric unit of 1 consisted of two crystallographically unique Cd<sup>II</sup> ions, two coordinated water molecules and one DBTP<sup>4-</sup> ligand. The Cd1 ion was embedded in the middle tridentate binding site of the DBTP<sup>4-</sup> ligand (N1, N2, and N8), together with one terminal triazole N atom (N6<sup>i</sup>) from another DBTP<sup>4-</sup> ligand [symmetry code: (i) 1/2 - x, -1/2 + y, z], one O atom (O1) and one coordinated H<sub>2</sub>O molecule to produce a five-coordinated

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Fig. 1 Crystal structure of 1: (a) the asymmetric unit of 1. Hydrogen atoms and free solvent molecules are omitted for clarity. (b) View of the pentanuclear [Cd<sub>5</sub>(DBTP)] SBU in 1. (c) The 1D zigzag chain of 1. (d) The 2D framework of 1.

mode. The Cd2 ion was six-coordinated by two pairs of terminal bidentate combining sites from two DBTP<sup>4–</sup> ligands (N3 and N7; N9<sup>ii</sup> and N11<sup>ii</sup>) [symmetry code: (ii) x, 1/2 - y, 1/2 + z], one O atom (O2) from one coordinated H<sub>2</sub>O molecule and one terminal triazole N atom (N12<sup>iii</sup>) from another DBTP<sup>4–</sup> ligand [symmetry code: (iii) 1/2 - x, 1 - y, 1/2 + z].

In 1, the dihedral angles of the triazole rings with the adjacent pyridine were 2.57(16) and 6.21(16)°, respectively. Meanwhile, the four triazole rings in the H<sub>4</sub>DBTP ligand were completely deprotonated and adopted a chelating/bridging bidentate coordination mode to bridge five Cd ions, giving the  $[Cd_5(DBTP)(H_2O)_2]^{6+}$  unit (Fig. 1b). The Cd2 ions in the unit were fixed by the terminal bidentate combining sites of the adjacent triazole rings (N3 and N7; N9<sup>ii</sup> and N11<sup>ii</sup>) in two DBTP<sup>4-</sup> ligands to form a one-dimensional (1D) zigzag chain structure (Fig. 1c), which was extended into a 2D framework *via* the coordination bonds of the terminal triazole-N atoms (N6 and N12) and Cd ions (Cd1 and Cd2) (Fig. 1d). Finally, the weak  $\pi \cdots \pi$  interactions between the adjacent triazole and pyridine rings with a distance of *ca.* 3.6 Å further expanded the 2D framework into a 3D supermolecular architecture (Fig. S3<sup>+</sup>).

#### Crystal structure of 2

SCXRD study indicated that complex 2 crystallized in the tetragonal space group  $I\bar{4}$  and possessed a three-dimensional (3D) "condenser" framework. The asymmetric unit of 2 contained two Zn<sup>II</sup> ions, one coordinated water molecule and one DBTP<sup>4-</sup> ligand. As shown in Fig. 2a, the Zn1<sup>II</sup> ion was located in the central tridentate binding site of the DBTP<sup>4-</sup> ligand (N1, N4, and N10), along with one terminal triazole N atom (N12<sup>i</sup>) from another DBTP<sup>4-</sup> ligand [symmetry code: (i) 3/2 - x, -1/2 + y, 3/2 - z] and one O atom (O1) from one coordinated H<sub>2</sub>O to give the five coordinated tetragonal configuration ligated by two pairs of terminal bidentate bindings sites of two DBTP<sup>4-</sup> ligands (N3<sup>ii</sup> and N14<sup>ii</sup>; N9 and



Fig. 2 Crystal structure of 2. (a) The asymmetric unit of 2. Hydrogen atoms and free solvent molecules are omitted for clarity. (b) View of the pentanuclear [ $Zn_5(DBTP)$ ] SBU in 2. (c) 2D framework of 2. (d) 3D framework of 2.

N13) [symmetry code: (ii) 1/2 - x, 3/2 - y, -1/2 + z] and one bridged N atom (N6<sup>i</sup>) from another DBTP<sup>4-</sup> ligand.

Similarly, the triazole rings in the H<sub>4</sub>DBTP ligand in 2 were also completely deprotonated and took a chelating/ bridging bidentate coordination mode to link five Zn ions, generating the  $[Zn_5(DBTP)H_2O]^{6+}$  unit (Fig. 2b). Compared to 1, the triazole rings on both sides of pyridine in the same ligand in 2 are more seriously bent to the same direction with the dihedral angles of 7.57(22)° and 16.35(22)°, respectively, leading to a 1D wave-like infinite chain structure connected by the linkage of Zn ions and the N^N chelating sites from two neighbouring DBTP<sup>4-</sup> ligands (Fig. S4<sup>†</sup>). Two wave-like chains are connected vertically by the coordination bonds of the terminal triazole-N atoms and Zn ions, forming a 2D framework (Fig. 2c). Furthermore, the residue sites on chelated Zn ions lie almost perpendicular to the plane where the ligand is located, which expanded the 2D structure into a 3D "condenser" framework (Fig. 2d).

To examine the phase purity of complexes **1** and **2**, PXRD experiments of the large samples were performed (Fig. 3a and b). The results demonstrated that the PXRD patterns of the synthesized bulk samples of **1** and **2** matched well with the simulated ones, revealing the high purity of the crystalline samples.

## Controllable fabrication of CP-based microflower-like hierarchical spheres 1a and 2a

Considering the effect of morphology and size on the various applications, cetyltrimethylammonium bromide (CTAB) was first introduced into the system as a soft template. As we expected, different nanosized particles of 1 and 2 with diverse morphologies were achieved through a surfactant-assisted



Fig. 3 The PXRD patterns, photographs and SEM images of the 1 and 2 samples prepared without and with CTAB. (a and b) PXRD and the corresponding simulated patterns for (a) 1 and (b) 2 prepared with and without CTAB. (c) Photograph of the 1 sample without CTAB. (d and e) SEM images of 1a with 0.10 g CTAB in different magnifications. (f) Photograph of the 2 sample without surfactants. (g and h) SEM images of 2a with 0.15 g CTAB in different magnifications.

solvothermal reaction. Originally, the colorless crystals of 1 and 2 were crystallized as typical blocks with the dimensions of about  $0.8 \times 0.5 \times 0.4$  and  $1.1 \times 0.4 \times 0.3$  mm<sup>3</sup>, respectively (Fig. 3c and f). After the addition of 0.10 g CTAB to the synthesis solution as a surfactant, the particle morphology of 1 changed to microflower-like hierarchical spheres 1a with a size of 2 µm assembled by nanosheets (Fig. 3b and c). When the amount of CTAB was increased or decreased, it is difficult to observe the uniform morphology distribution. For 2, microflower-like crystals 2a with sub-nanostructures could also be achieved by the assistance of 0.15 g CTAB under hydrothermal reaction conditions. However, synthesis with another surfactant (polyvinylpyrrolidone (PVP)) resulted in a crystal morphology and size that were similar to those of complex 1, whereas microspheres were achieved for 2 when 0.15 g PVP was added to the reaction solution (Fig. S5 and S6<sup>†</sup>).

Calculations using PLATON showed that **1** has no free void volume, while **2** possesses a free void volume ratio of 28.2%. In addition, the nitrogen sorption experiments of **1** and **2** further indicated that they are nonporous materials (Fig. S7 and S8†). However, the adsorption isotherms of the as-synthesized microflowers **1a** and **2a** gave Brunauer-Emmett-Teller (BET) surface areas of 8.99 and 14.25 m<sup>2</sup> g<sup>-1</sup>, respectively, which are higher than those of their bulk analogues (3.94 and 5.64 m<sup>2</sup> g<sup>-1</sup>). Accordingly, the 3D hierarchical microflowers composed of sub-nanostructures were expected to be effective catalysts to improve the catalytic performance of organic transformation reactions due to the more easily accessible active sites.

# The catalytic performances of microflower-like hierarchical spheres 2a

The nitro to carbonyl conversion (Nef reaction) has been widely applied in the total synthesis of complex natural products and most of Nef reactions have been conducted in the presence of stoichiometric amounts of reductants (e.g., TiCl<sub>3</sub>, SnCl<sub>2</sub>, Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, etc.) or oxidants (e.g., KMnO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, etc.) under basic conditions, but yielded the desired products in low yield and low selectivity.13 Lately, several methods have been described to improve the harsh reaction conditions and give good conversions.<sup>10b,14</sup> Given the unique advantages of coordination polymers as heterogeneous catalysts and the characteristics of nanosized materials, microflower-like 1a and expected to execute the conversion 2awere of nitromethylbenzenes into carboxylic acids in high yields.

Stability is a key factor in the catalytic process, so compounds 1 and 2 were kept in boiling water to evaluate their stability. The results demonstrated that the crystallinity of both 1 and 2 was retained after the immersion in boiling water for 48 h. After widespread screening of various reaction conditions including catalyst loading, temperature, and reaction time, we found that at 10 mol% loading, the nanoscale 2a samples could catalyze the conversion reaction of nitrobenzyl compounds to carboxylic acids in 87% yield in H<sub>2</sub>O at 80 °C after 15 h (Table S2,† entry 5). It was also observed that the catalytic activity of 2a is better than that of nanoscale 1a, as well as the related homogeneous catalysts, such as metal salt  $Zn(OTf)_2$ , ligand H<sub>4</sub>DBTP, and their mixture in a ratio of 1:1 under identical conditions (Table S2,† entries 10-12). In contrast to the bulk crystals 1 and 2 as heterogeneous catalysts, the nanosized 1a and 2a showed much higher catalytic activity under the same reaction conditions (Table S2,† entry 13). The activated nanocrystals 1a and 2a formed by heating to remove the coordinated H<sub>2</sub>O molecules were also used to catalyze the conversion reaction, but the results showed that there was no significant difference in catalytic performance compared with that before activation (Table S2,† entry 14). Prolonging the reaction time and increasing the amount of the catalyst had little effects on the yield of the desired products.

substituted Subsequently, а diverse range of nitromethylbenzenes was examined to estimate the generality of this reaction system after the reaction conditions were optimized. It was found that all the substrates either with electron-donating (3a, 3b, 3e and 3h) or with electronwithdrawing groups (3c, 3d, 3g, 3h and 3i) screened undergo the conversion reaction to afford their respective carboxylic acids in good or moderate yields (Table 1). However, when the homogeneous catalyst Zn(OTf)2 was used, a mixture of the carboxylic acid, benzaldehyde and acetophenone products under the same reaction conditions was obtained, showing much lower selectivity. The high catalytic performance of the microflower-like 2a was ascribed to its unique structural characteristics and nanosized morphologies, providing more readily accessible active sites in the nanoscale particles by decreasing the diffusion distance.

Table 1 Conversion of nitrobenzyl compounds into benzoic acids catalyzed by nanoscale 2a in H<sub>2</sub>O<sup>4</sup>



Entry	Catalysts	Nitrobenzyl <b>3a-i</b>	Yield% of 4a-i <sup>b</sup>
1	2a		87
2	$Zn(OTf)_2$		34
3	2a		85
4	$Zn(OTf)_2$		33
5	2a		88
6	$Zn(OTf)_2$		34
7	2a	NC	91
8	$Zn(OTf)_2$	NO <sub>2</sub>	36
9	2a		87
10	$Zn(OTf)_2$	)=/ NO <sub>2</sub>	29
11	2a		84
12	$Zn(OTf)_2$		32
13	2a		90
14	$Zn(OTf)_2$		31
15	2a		89
16	$Zn(OTf)_2$		33
17	2a	F	84
18	$Zn(OTf)_2$		30
		NO₂	

 $^{a}$  Reaction conditions: **3a-i** (1.0 mmol), TBAI (0.05 mmol), nanoscale catalyst **2a** (0.1 mmol), H<sub>2</sub>O (10 mL), AcOH (60  $\mu$ L), 80 °C (15 h).  $^{b}$  Isolated yield after 15 h.

Moreover, the reusability experiments were performed to evaluate the robustness and recyclability of the nanoscale catalyst **2a**. The results indicated that it could be readily recycled after simple centrifugation from the reaction system and reused without obvious loss of activity even after ten reaction cycles (Fig. S9†). The crystallinity of the recovered solid catalyst retained and the structure remained intact as demonstrated by PXRD (Fig. S10†). In addition, a hot filtration test was executed to demonstrate the heterogeneity of nanosized catalyst **2a**. After the removal of nanoscale **2a** by hot filtration for 2 h, the reaction was completely shut down, suggesting no leaching of the active catalyst in the supernatant to promote the reaction.

## Conclusions

In conclusion, by tuning the types and the concentration of surfactants, the morphologies and sizes of two d<sup>10</sup> CPs with different structures and dimensionalities were controlled precisely. The particle size was reduced from a large scale to micro- or nanoscale in some attempts. The uniform 3D

microflowers assembled by nanosheets were successfully fabricated and exhibited a much higher surface area. With the advantage of easily accessible active sites in the nanosized particles, microflower Zn-CPs as heterogeneous catalysts remarkably outperformed their corresponding bulk crystals in the conversion reactions. This work further proved that the control of the shape and size of CP particles is very useful for improving their applications in catalysis. Further experiments for the applications of the generated nanoscale structures, in membranes, building blocks for nano-device assembly, *etc.*, are ongoing in our lab.

## Conflicts of interest

There are no conflicts to declare.

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#### CrystEngComm

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