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Introduction

The tandem Nef reaction to convert nitroalkanes into carboxylic acids has stimulated synthetic strategies to develop economical and environmental catalysts to selectively promote conversion reactions owing to their distinct roles in various disciplines, such as organic chemistry, materials science, and pharmaceutical science.¹ Current methodologies indicate that the tandem Nef reaction is an extremely versatile way of precisely regulating the conversion of nitroalkanes into carboxylic acid derivatives in one step with transition or noble metals (*e.g.*, SnCl₂, Al₂O₃, TiCl₃, Rh, Pd(OAc)₂, Ru(acac)-(C₂H₄)₂) as homogeneous catalysts.^{1*c*,²} Meanwhile, introducing these catalysts under various catalytic conditions usually generates the benzaldehyde and acetophenone frameworks along with a few of the desired benzoic acid derivatives since these catalysts cannot completely restrain multiple-component oxidative reac-

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Surfactant-assisted assembly of nanoscale zinc coordination compounds to enhance tandem conversion reactions in water†

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Precise control over the morphology and size of coordination polymers (CPs) is crucial for extending these inorganic–organic materials to many advanced applications, in particular for heterogeneous catalysis. In this work, two Zn-based CPs, $\{[Zn_3(idbt)_2(4,4'-dmbpy)_2]\cdot H_2O\}_n$ (1) and $\{[Zn_3(idbt)_2(H_2O)_3]\cdot H_2O\}_n$ (2) (H₃idbt = 5,5'-(1*H*-imidazole-4,5-diyl)-bis-(2*H*-tetrazole), 4,4'-dmbpy = 4,4''-dimethyl-2,2'-bipyridine), were synthesized through solvothermal reactions. The morphologies and particle sizes of 1 and 2 could be controlled from large scale to nanoscale by regulating the amount of poly(vinyl alcohol) (PVA). Furthermore, for the conversion reactions of nitromethylbenzenes into benzoic acids, the catalytic properties of nanoscale 1 and 2 were much more efficient than those of large size of 1 and 2, because of the benefit of readily accessible active sites in the nanoscale sized particles, which provide a tunable and functionalizable platform for the conversion reaction by minimizing the diffusion distance but do little for the selectivity.

tions to provide aldehydes, ketones, or amines as primary byproducts.^{1*c*,2,3} Thus, an alternative strategy is to make use of a modular and well-defined catalyst platform involving fixation of atomistically well-established homogeneous catalysts and uniformly dispersed active sites to construct a stable solid support, which can restrain the undesired approaches by eliminating multimolecular catalyst deactivation pathways.

Coordination polymers (CPs) have emerged as a welldefined platform to mimic the competencies of natural enzymes and immobilize molecular catalysts for many important organic transformations.⁴ Owing to their diversity and the tunability of the central metal coordination environments, CPs provide unique opportunities as synergistic or single-site heterogeneous catalysts to execute tandem or site-selective reactions.4,5 Meanwhile, the catalytic performance of CPs relies not only on the chemical structure of a material but also on their microstructure, morphology, and size.⁶ Tailored fabrication of well-defined CP crystallites in the submicrometer size regime is extremely desirable to improve their remarkable catalytic activity and relieve the diffusional constraint by reducing the single dimension of large CP crystals to the nanoregime to generate nanoscale CP materials.7 In addition, the particle morphology and size and the high loading capacity of nanoscale CPs can be easily regulated to maximize their sieving effects and build multi-active platforms to improve the overall permeability but this does little for their selectivity.8 Despite the ordered structures of nanoscale CPs catalysts inheriting



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[†]Electronic supplementary information (ESI) available: Experimental information; characterization data for all compounds, including figures for PXRD, TG, CIF files and crystal data. CCDC 1943115 and 1944008 for 1–2. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c9dt03145f

the heterogeneous characteristic and providing a promising platform to exert exquisite control over selectivity,^{8,9} rational synthetic strategies are required to assemble better solid catalysts to execute tandem conversion reactions and minimize the diffusional constraints in a predictable way.

Herein, we demonstrate a strategy for precise control of the size and morphology of uniform nanoscale CPs as catalysts to explore the tandem conversion reactions of nitroalkanes into carboxylic acids. Two Zn-based CPs, {[Zn₃(idbt)₂(4,4'- $(\text{mbpy})_2$ $(H_2O)_n$ (1) and $([Zn_3(idbt)_2(H_2O)_3] (H_2O)_n$ (2) $(H_3idbt =$ 5,5'-(1*H*-imidazole-4,5-diyl)-bis-(2*H*-tetrazole), 4,4'-dmbpy 4,4'-dimethyl-2,2'-bipyridine), were synthesized under solvothermal conditions. Subsequently, nanoscale Zn-based CPs 1 and 2 of different morphologies and particle sizes were constructed by using poly(vinyl alcohol) (PVA) as the surfactant. Furthermore, large scale and nanoscale 1 and 2 were demonstrated to be effective heterogeneous catalysts to facilitate the tandem conversion reactions of nitromethylbenzenes into benzoic acids. In particular, with the benefit of readily accessible active sites in the particles, nanoscale 1 and 2 provide a well-defined platform to efficiently promote the conversion reactions by decreasing the diffusion distance but do little for their selectivity.

Experimental section

Materials and physical measurements

H₃idbt ligand (5,5'-(1*H*-imidazole-4,5-diyl)-bis-(2*H*-tetrazole)) was prepared according to a method described in the literature.^{8b} Other reagents and solvents were obtained commercially and used without further purification. Elemental analysis, FT-IR spectroscopy, powder X-ray diffraction (PXRD), ¹H NMR, scanning electron microscopy (SEM) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were employed using various instruments (ESI†).

Synthesis of {[Zn₃(idbt)₂(4,4'-dmbpy)₂]-H₂O}_n (1). Zn(NO₃)₂· 6H₂O (0.030 g, 0.1 mmol), H₃idbt (0.02 g, 0.1 mmol), 4,4'dmbpy (4,4'-dmbpy = 4,4'-dimethyl-2,2'-bipyridine, 0.018 g, 0.1 mmol), DMF (3 mL) and H₂O (5 mL) were mixed and placed in a 25 mL Teflon-lined autoclave. The mixture was heated at 160 °C for three days, and colorless crystals of **1** were obtained with a yield of 65% (based on Zn). Anal. calcd for $C_{34}H_{28}Zn_3N_{24}O$: C, 41.46%; H, 2.87%; N, 34.13%. Found: C, 41.48%; H, 2.85%; N, 34.15%. IR (KBr, cm⁻¹): 3443 (s), 3062 (w), 2172 (w), 2108 (vs), 1981 (vw), 1653 (vs), 1459 (m), 1409 (s), 1135 (m), 1026 (m), 916 (w), 874 (vw), 761 (m), 728 (w).

Synthesis of $\{[Zn_3(idbt)_2(H_2O)_3]\cdot H_2O\}_n$ (2). $Zn(NO_3)_2\cdot 6H_2O$ (0.030 g, 0.1 mmol), H_3idbt (0.01 g, 0.05 mmol), $NH_3\cdot H_2O$ (4 mL) and EtOH (4 mL) were mixed and placed in a 25 mL Teflon-lined autoclave. The mixture was heated at 180 °C for three days, and colorless crystals of 2 were obtained with a yield of 54% (based on Zn). Anal. calcd for $C_{10}H_{10}Zn_3N_{20}O_4$: C, 17.91%; H, 1.50%; N, 41.78%. Found: C, 17.93%; H, 1.49%; N, 41.76%. IR (KBr, cm⁻¹): 3423 (s), 3061 (w), 2162 (w), 2115 (vs), 1976 (vw), 1636 (vs), 1440 (s), 1440 (s), 1245 (m), 1021 (w), 982 (vw), 874 (w), 763 (m), 722 (w).

Synthesis of nanocrystals of 1 with PVA. A mixture of $Zn(NO_3)_2$ ·6H₂O (0.059 g, 0.2 mmol), poly(vinyl alcohol) (PVA, 1788, 0.150 g), and H₂O (5 mL) was sonicated for 20 min. A solution of DMF (3 mL), H₃idbt (0.04 g, 0.2 mmol) and 4,4'-dmbpy (0.036 g, 0.2 mmol) was added to the mixture of PVA/H₂O and sonicated for another 30 min. Then, the solution was transferred to a Teflon-lined stainless-steel container at 160 °C for three days to afford crystal growth. After cooling, the nanocrystals were obtained by centrifugation at 10 000 rpm for 15 min. The nanocrystals of 1 were washed by sonication after being re-dispersed in EtOH.

Synthesis of nanocrystals of 2 with PVA. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.059 g, 0.2 mmol), PVA (0.150 g), and EtOH (4 mL) was sonicated for 20 min. A solution of $NH_3 \cdot H_2O$ (4 mL) and H_3 idbt (0.02 g, 0.1 mmol) was added to the mixture of PVA/EtOH and sonicated for another 30 min. Then, the solution was heated at 180 °C for three days. After cooling, the nanocrystals were achieved by centrifugation at 10 000 rpm for 15 min. The nanocrystals of 2 were washed by sonication after being re-dispersed in EtOH.

Procedure for nanoscale 1 and 2-catalyzed conversion of nitrobenzyl compounds into benzoic acids. To a solution of nitroalkane (1.0 mmol) and TBAI (0.05 mmol) in water (10 mL) was added nanoscale 1 or 2 (0.1 mmol, 0.1 equiv. based on zinc ions). The resulting mixture was stirred at 80 °C and monitored by TLC. After the completion of the reaction (approximately 15 h), the mixture was cooled to room temperature, acidified and washed by dichloromethane (DCM). The organic phases were collected and concentrated *in vacuo*.

Crystal data collection and refinement

The data for **1** and **2** were collected on a Rigaku Saturn 724 CCD diffractometer (Mo-K α , $\lambda = 0.71073$) at room temperature. Absorption corrections were applied by using a numerical program. The detailed structures were solved in direct ways and refined by full-matrix least-squares on F^2 with the SHELXL, as described in the ESI.^{†10} The final formulas were decided by combing the single-crystal structures, TGA, elemental analysis, and the electron count of the SQUEEZE results. The crystal data of **1** and **2** are summarized in Tables S1 and S2.[†] The crystal data have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 1943115 and 1944008.[†]

Results and discussion

Crystal structure of 1

To design and construct environmentally friendly heterogeneous catalysts and adjust their catalytic activity and selectivity with high stability in water systems, we chose a clamp-like and rigid bis-tetrazole H_3 idbt ligand as the shape-persistent unit, which acted as a premade constructing part to tune the catalytic microenvironment in the CPs. Furthermore, by virtue

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of its multiple Lewis sites, chelating or bridging coordination modes could be adopted to bridge metal ions to build multinuclear secondary building units (SBUs) as the catalytic activity centers to promote the regioselective catalytic reaction. Therefore, direct reaction of Zn(NO₃)₂·6H₂O with H₃idbt in H₂O/DMF/4,4'-dmbpy at 160 °C for three days afforded $\{[Zn_3(idbt)_2(4,4'-dmbpy)_2] \cdot H_2O\}_n$ (1) as colorless single crystals with a two-dimensional (2D) framework. The formula of 1 was determined by single-crystal X-ray diffraction analysis (SCXRD), EA, TGA (Fig. S1a[†]), and charge-balance considerations. Furthermore, PXRD analysis of the prepared crystals showed that the synthesized samples were pure (Fig. S1b[†]). SCXRD study showed that 1 crystallized in the monoclinic space group $P2_1/n$ and demonstrated a 2D grid-like architecture. The asymmetric unit of 1 included three Zn^{II} ions, two idbt³⁻ ligands and two 4,4'-dmbpy ligands (Fig. S1c[†]). The Zn1 and Zn3 ions adopted analogous six coordination with six N atoms (Zn1: N4, N5, N18, N22, N23 and N24; Zn3: N6, N10, N11, N12, N13 and N17) from two idbt³⁻ ligands and one 4,4'dmbpy ligand, providing a slightly distorted octahedral geometry, while the Zn2 ion was a slightly distorted tetrahedral coordination geometry, which was coordinated by four N atoms (N1, N7, N16 and N19) from two idbt³⁻ ligands. The tetrazole and imidazole rings in the H₃idbt ligands were completely deprotonated and took the bridging/chelating coordination modes to bridge Zn^{II} ions, generating an octanuclear [Zn₈(idbt)₄] secondary building unit (SBU) (Fig. 1a). In the SBU, four imidazole rings of idbt^{3–} ligands linked four Zn ions (two Zn1 and two Zn3) to build a square-like tetranuclear Zn^{II} macrocycle as an inwall through the repetitive unit of -[-Zn1-imidazole-Zn3-]- connection, while two tetrazole rings of the idbt^{3–} ligands took the chelating coordination mode to bridge four Zn ions (four Zn2) adjacent to the square to construct another tetranuclear unit. Furthermore, the neighbouring $[Zn_8(idbt)_4]$ SBUs could be extended by tetrazole rings of the idbt³⁻ ligands via the coordination bonds of Zn2 ions and tetrazole-N atoms (N1 and N7) to construct a 2D infinite grid-like architecture (Fig. 1b). In addition, PLATON analysis provided a free void volume ratio of 23.0% in 1. Besides, nitrogen sorption measurements of 1 after supercritical SC-CO₂ activation indicated that the Brunauer-Emmett-Teller (BET) surface area was 9.57 m² g⁻¹. Owing to the low N₂ uptake, the pore size distribution (PSD) of 1 revealed a very narrow range. Therefore, these results demonstrated that 1 was nonporous.

Crystal structure of 2

In contrast with **1**, the building unit of **2** transformed enormously when the 4,4'-dmbpy ligand was removed. Complex **2** crystallized in the monoclinic space group C2/c and indicated a three-dimensional (3D) supermolecular architecture. The asymmetric unit of **2** consisted of three Zn^{II} ions, two idbt³⁻ ligands and three coordinated H₂O molecules (Fig. S2a†). The Zn1 and Zn2 ions demonstrated similar four coordination with three N atoms (Zn1: N6, N7 and N12; Zn2: N1, N16 and N17) from two idbt³⁻ ligands and one O atom (Zn1: O1; Zn2: O3) from the coordinated H₂O molecule, generat-



Fig. 1 Crystal structure of **1**: (a) View of the octanuclear $[Zn_8(idbt)_4]$ SBU in **1**. Hydrogen atoms are omitted for clarity. (b) The 2D infinite grid-like architecture of **1**. Symmetry codes: #1 = -0.5 + x, 2.5 - y, -0.5 + z; #2 = 2 - x, 2 - y, 1 - z; #3 = 2.5 - x, -0.5 + y, 1.5 - z.

ing a slightly distorted tetrahedral arrangement. The Zn3 ion was coordinated by four N atoms (N2, N10, N11, and N20) from two idbt^{3–} ligands and one O atom (O2) from one coordinated H_2O molecule, indicating a distorted square pyramidal arrangement, where the O2 atom lays on the top of the square pyramid and the four N atoms are located at the bottom.

In 2, the H₃idbt ligands were totally deprotonated and adopted the chelating/bridging coordination modes to link Zn^{II} ions, giving a pentanuclear $[Zn_5(idbt)_2]$ SBUs (Fig. 2a). In the SBU, two imidazole rings linked two Zn ions (Zn1A and Zn2) and four tetrazole rings bridged another two Zn ions (Zn1 and Zn2A) to construct a tetranuclear unit, while the imidazole and tetrazole rings adopted the chelating coordination modes to connect one Zn ion (Zn3) adjacent to the sides in $idbt^{3-}$ ligands to provide another mononuclear block. Subsequently, the [Zn₅(idbt)₂] SBUs were bridged by imidazole-N atoms (N1 and N12) and Zn ions (Zn1 and Zn2) through coordination bonds to build a 2D layer structure (Fig. 2b). Moreover, the adjacent 2D layers, stacked by hydrogen bonding interactions $[O2 \dots N8 = 2.97 \text{ Å}]$ between the uncoordinated N atom from the idbt^{3–} ligands and the coordination H₂O molecule, give a 3D supermolecular framework with a layered architecture (Fig. S2b[†]). In addition, PLATON analysis gave a free void volume ratio of 6.4% in 2, indicating that 2 was completely nonporous.



Fig. 2 Crystal structure of **2**: (a) View of the pentanuclear $[Zn_5(idbt)_2]$ SBU in **2**. Hydrogen atoms are omitted for clarity. (b) The 2D layer structure of **2**. Symmetry codes: #1 = x, 1 - y, 0.5 + z; #2 = x, -y, -0.5 + z.

Synthesis of 1 and 2 with different morphologies and particle sizes

Two important characteristics that affect the catalytic activity and product diffusion rates of heterogeneously catalyzed reactions are the morphology-dependent physical size and the particle size distribution of the solid catalysts.¹¹ This is especially true for nanosized heterogeneous catalysts, which hold much promise for affording well-defined platforms with characteristic control of reactivity and regioselectivity in chemical transformations. To utilize the advantages of nanosized heterogeneous catalysts, an effective strategy is to scale down the size of crystalline CPs to nanoscale CPs as solid catalysts, formulating CPs materials with a high density of readily accessible catalytically active sites. Therefore, with the introduction of the surfactant PVA as a soft template, different nanoscale particle sizes and morphologies of **1** and **2** were achieved through surfactant-templated solvothermal reaction.

Without surfactants, the dimensions of colorless crystals 1 and 2 were approximately $0.8 \times 0.8 \times 0.5 \text{ mm}^3$ and $1 \times 1 \times 0.6 \text{ mm}^3$, respectively (Fig. 3a and b). When PVA was employed as a surfactant, the particle size of 1 could be reduced drastically from the nanometer regime of nearly 500 nm in length to 50 nm in width for 1 (Fig. 3c and d and Fig. S3a†). Furthermore, also by using PVA as the surfactant, nanoscale crystals of 2 with octahedral geometry could also be achieved with 300 nm length by 200 nm width through hydrothermal reaction (Fig. 3e and f and Fig. S3b†). The reason for the diverse particle sizes and morphologies of 1 and 2 could be



Fig. 3 (a) The particle sizes of **1** without surfactant PVA. (b) The particle sizes of **2** without surfactant PVA. (c, d) SEM images for the morphologies and particle sizes of **1** induced by PVA with various magnifications. (e, f) SEM images for the morphologies and particle sizes of **2** induced by PVA with various magnifications.

ascribed to the influence of the surfactant PVA, which not only acted as a capping agent to control the synthesis of the crystalline particles but also stabilized the particle growth processes at an early stage.^{6b} Furthermore, PXRD analysis revealed that there were no remarkable differences between the synthesized nanoscale crystals and the bulk phase for 1 and 2, which demonstrated that the synthesized nanoscale samples of 1 and 2 were crystalline and had the same frameworks as those of 1 and 2 (Fig. S1b and S2c†).

Moreover, to clarify the effect of the concentration of PVA on the nanoscale particle size, multiple attempts were made at preparing nanoscale crystals of 1 and 2 with different particle sizes and morphologies by utilizing different concentrations of PVA (0.20, 0.15, 0.10, and 0.05 g) (Fig. S3c-h†). The results demonstrated that uniform and well-defined compositions, morphologies, and nanoscale particle size distributions of 1 and 2 were generated when the concentration of PVA was 0.15 g. In addition, other surfactants (e.g., polyvinylpyrrolidone, polyethylene glycol, hexadecyl trimethyl ammonium bromide, sodium dodecyl sulfate) and methods (e.g., water-inoil microemulsion, nanoprecipitation, high-temperature routes) usually resulted in the formation of amorphous CPs. Besides, nitrogen sorption experiments with nanoscale 1 and 2 indicated that the N_2 uptake was 47 and 78 $\mbox{cm}^3\mbox{ g}^{-1}$ at the saturation pressure, respectively (Fig. S4a and b⁺). The adsorption

isotherms indicated that the BET surface areas of nanoscale 1–2 were 175 and 293 m² g⁻¹, respectively, while the BET surface areas of the bulk crystals of 1 and 2 were 9.57 and 15.29 m² g⁻¹, respectively. Thus, the nanoscale crystals of 1 and 2 possess large BET surface areas to provide the benefit of readily accessible active sites to facilitate the heterogeneous reactions.

The catalytic performances of nanoscale 1 and 2

The Nef reaction converting nitromethylbenzenes into carboxylic acids holds great challenges in the exploration of applicable catalysts to selectively accomplish carboxylic acid products without the need to pre-form the nitronate species as the intermediate products derived from nitro groups, which are direct strategies to prepare some functional ligands and natural products. However, exploration of this conversion reaction under a series of catalytic conditions (e.g. TiCl₃, KMnO₄, oxone, NaNO3-AcOH, etc.) frequently afforded low yields with low chemo- and regioselectivity under a large excess of oxidant and harsh reaction conditions (strong acidic, complex reagents, and toxic solvents, etc.).^{1a,c,3a} Inspired by the high density of readily accessible active centers in nanosized heterogeneous catalysts, we were interested in testing whether nanoscale CPs as nanosized heterogeneous catalysts could furnish a well-defined platform for the conversion of nitromethylbenzenes into carboxylic acids as the single product.

To accomplish these stoichiometric experiments for converting nitromethylbenzenes into carboxylic acids by Nef reaction, the solvent resistance properties of 1 and 2 in H₂O were studied by immersing the samples in boiling H₂O for 48 h since H₂O was chosen as the reaction solvent for the conversion reaction. The results indicated that 1 and 2 could hold their original shapes and stayed stable in boiling H₂O for 36 h. Subsequently, the catalytic performances of nanoscale catalysts of 1 and 2 for the conversion of nitromethylbenzenes into carboxylic acids were optimized using nitromethylbenzene (3a) and tetrabutylammonium iodide (TBAI) (Table S3[†]). After widespread screening of temperatures and solvents, the standard conditions were found by taking advantage of nanoscale 1 and 2 as catalysts (10 mol%) at 80 °C, giving the desired carboxylic acid product (4a) in 82 and 94% yield, respectively. The results displayed that nanoscale 1 and 2 acted as excellent nanosized heterogeneous catalysts to control the conversion reaction with high selectivity, while Zn(OTf)2 as a homogeneous catalyst was less selective, providing a mixture of benzoic acid (4a, 36%), benzaldehyde and acetophenone products under the same reaction conditions (Table S3,† entry 14). The conversion reaction proceeded moderately selectively in toluene (4a, 53 and 68% yield for nanoscale 1 and 2, respectively) and CH₃CN (4a, 59 and 71% yield for nanoscale 1 and 2, respectively) (Table S3,[†] entries 1 and 3); however, DMF, EtOH and CHCl₃ were inappropriate solvents (Table S3,† entries 4-6). When the temperature was increased from 25 to 110 °C, the yield of benzoic acid 4a was distinctly improved (Table S3,† entries 7 and 8). Furthermore, considering the best conditions, the influence of the amount of nanoscale catalysts

1 and 2 (0.01, 0.05, 0.1, 0.15, and 0.2 mmol) for this conversion reaction was also evaluated (Table S3,† entries 2 and 10–13). An increase (0.1, 0.15, and 0.2 mmol) in the amount of nanoscale catalysts 1 and 2 did not generate a remarkable influence on the selectivity and yield (Table S3,† entries 2 and 12–13), but a decrease (0.1, 0.05, and 0.01 mmol) in the amount of nanoscale catalysts 1 and 2 had a significant effect on the yield (Table S3,† entries 2 and 10–11). In addition, the yield of 4a was not obviously changed by extending the reaction time (Table S3,† entry 9). Therefore, in consideration of environmental friendliness, stability, efficiency and selectivity, nanoscale 1 or $2/H_2O/80$ °C was selected as the standard reaction conditions to perform the conversion of nitrobenzyl compounds into carboxylic acids.

Subsequently, in order to explore the tolerability, diversity, and feasibility of diverse functionalities, different kinds of substituted nitromethylbenzene (3a-i) were studied to observe the conversion reactions of 3a-i into carboxylic acids (Table 1). In all situations, nanosized heterogeneous catalyst 1 moderately selectively generated the benzoic acid as the major product with yields ranging from 71 to 82% (4a-i), along with a small amount of by-products (<8%), whereas nanosized heterogeneous catalyst 2 demonstrated excellent selectivity for the benzoic acid (4a-i) as the major product with much higher vields (88-94%) than for nanosized catalyst 1 under the same reaction conditions. Furthermore, we were pleased to find that the existence of the electron-donating (3a, 3b, 3e and 3h) and electron-withdrawing groups (3c, 3d, 3g, 3h and 3i) was well tolerated at the ortho-, meta-, and para-positions of the nitromethylbenzenes, providing the corresponding benzoic acid derivatives (4a-i) with remarkable yields. Moreover, when the reaction was executed with 2,6-difluoro-(nitromethyl)benzene (3i), the 2,6-difluorobenzoic acid framework (4i) was obtained in moderate yield (4i, 71 and 88% for nanoscale 1 and 2, respectively). However, when the large-sized 1 and 2 were used as heterogeneous catalysts, the yields of 4a-i (45-67% for 1 and 2) were much lower than for nanoscale 1 and 2 as heterogeneous catalysts under the same reaction conditions (Table S4[†]), which demonstrated that the BET surface area plays an important role in controlling the diffusional rate in the reaction. Thus, the results obviously revealed that an improvement of the surface area resulted in the increased reaction rate but had no effect on the selectivity. In contrast, Zn (OTf)₂, which was used as a homogeneous catalyst for the conversion of nitromethylbenzenes into benzoic acids, provided mixtures of the carboxylic acid (4a-i, <36%), benzaldehyde and acetophenone products under the same reaction conditions.

The particularly high catalytic selectivity of the nanoscale **1** and **2** systems was attributed to their unique structural characteristics and nanosized morphologies. The atomistically well-defined active sites in the CPs were placed periodically with uniformly identical azimuths and distances throughout the frameworks, which endowed the CPs with integrated well-established platforms to control the catalytic reactivities with high-efficiency selectivity. Structural study indicated that **1** was a 2D infinite grid-like architecture with octanuclear

Table 1 Conversion of nitrobenzyl compounds into benzoic acids catalyzed by nanoscale 1 and 2 in H_2O^a



3c: $R_1=CN$, $R_2=R_3=R_4=H$; 3d: $R_1=CI$, $R_2=R_3=R_4=H$ 3e: $R_1=R_3=R_4=H$, $R_2=Me$; 3f: $R_1=R_3=R_4=H$, $R_2=CI$ 3g: $R_1=R_3=R_4=H$, $R_2=F$; 3h: $R_1=R_2=R_3=H$, $R_4=Me$ 3i: $R_1=R_2=H$, $R_3=R_4=F$ 1.0 mmol

| Entry | Catalyst | Nitrobenzyl | Yield % of $4a-i^b$ |
|-------|-------------|-----------------|---------------------|
| 1 | 1 | | 82 |
| 2 | 2 | NO ₂ | 94 |
| 3 | $Zn(OTf)_2$ | 3a - | 36 |
| 4 | 1 | | 82 |
| 5 | 2 | | 94 |
| 6 | $Zn(OTf)_2$ | 3b | 33 |
| 7 | 1 | | 81 |
| 8 | 2 | | 93 |
| 9 | $Zn(OTf)_2$ | 3c | 34 |
| 10 | 1 | | 80 |
| 11 | 2 | | 93 |
| 12 | $Zn(OTf)_2$ | 3d | 33 |
| 13 | 1 | | 78 |
| 14 | 2 | | 92 |
| 15 | $Zn(OTf)_2$ | 3e | 31 |
| 16 | 1 | | 77 |
| 17 | 2 |)=/ NO2 | 91 |
| 18 | $Zn(OTf)_2$ | CI' | 31 |
| 19 | 1 | | 76 |
| 20 | 2 | >=/ NO2 | 91 |
| 21 | $Zn(OTf)_2$ | F 3g | 30 |
| 22 | 1 | | 73 |
| 23 | 2 | | 90 |
| 24 | $Zn(OTf)_2$ | 36 | 29 |
| 25 | 1 | ۶. ۶ | 71 |
| 26 | 2 | | 88 |
| 27 | $Zn(OTf)_2$ | F 3i | 24 |

 a Reaction conditions: 3a-i (1.0 mmol), TBAI (0.05 mmol), nanoscale catalysts 1 or 2 (0.1 mmol), H₂O (10 mL), AcOH (60 µL), 80 °C (15 h). b Isolated yield after 15 h.

 $[Zn_8(idbt)_4]$ SBUs, which assured the unsaturated active sites of Zn2 ions were positioned in the grid-like architecture regularly with identical distance, while the Zn1 and Zn3 ions were coordination saturated and still existed in the SBUs. In contrast, single-crystal structural analysis showed that the structure of 2 contained the pentanuclear $[Zn_5(idbt)_2]$ SBUs, in which all of the Zn ions were unsaturated metal sites and had more accessible active sites with high site density and uniformly fixed azimuths. The results demonstrated that 1 and 2 could provide a platform to execute conversion reactions, and indicated shape-selective catalytic capabilities to realize an orientation that upholds the selectivity during the reaction process. Furthermore, SEM images demonstrated that the astructure of the selective that the astructure of the selective that the astructure of the selective that the astructure of a platform to execute conversion reactions, and indicated shape-selective catalytic capabilities to realize an orientation that upholds the selectivity during the reaction process.

synthesized particles were 500 nm in length by 50 nm in width for the rodlike nanoscale 1 and 300 nm in length by 200 nm in width for nanoscale 2 with octahedral geometry, which provided more readily accessible active centers in the nanoscale particles by decreasing the diffusion distance and improving the product turnover and substrate diffusion rates. Moreover, owing to the BET surface area of nanoscale 2 (293 $m^2 g^{-1}$) being larger than that of nanoscale 1 (175 m² g⁻¹), it could provide much more readily accessible active sites to tune the selectivity and increase the overall permeability of the octahedral geometry morphology to promote the conversion reactions and generate the benzoic acid derivatives as the single products. Meanwhile, to examine the impact of the coordinated water molecules on the tandem conversion reactions, nanocrystals of 2 were activated at 260 °C to remove the coordinated H₂O molecules and provide the activated nanocrystals 2a. Then, the conversion reaction of 3i and TBAI was executed with the activated nanocrystals of 2a, giving 4i in 93% vield under the same reaction conditions. The result distinctly revealed that the coordinated H2O molecules were good leaving groups and open metal sites with a high density of Lewis acid catalytic sites could be created to contact with organic substrates during the catalytic process. Thus, we hypothesized that the nitro groups could be first activated by the active sites (Zn ions) in nanocrystals of 1 or 2 to form the nitronate species (I). Then, the water attacked the α -position of I to give II. Subsequently, the corresponding (dihydroxyamino) (phenyl)methanol (III) was generated as the intermediate product, which was further converted to the aldehyde by a Nef reaction mechanism. Finally, the aldehyde could be evolved to the carboxylic acid under oxidizing conditions (Scheme S1⁺). In order to verify this hypothesis, XPS measurements were employed to observe the tuning of the active sites of nanocrystals 1 and 2 at various reaction times (0, 7, and 15 h) (Fig. S5a and b[†]). Accordingly, the obtained Zn 2p_{3/2} peaks at 1022.31, 1022.34, and 1022.37 eV for 1 and 1022.43, 1022.39, and 1022.49 eV for 2 in the XPS spectra revealed that Zn ions always stayed divalent at the different reaction times¹² (0, 7, and 15 h). This made them an extremely appropriate feature to construct nanosized heterogeneous catalysts with catalytic active sites to facilitate the conversion of nitromethylbenzenes into benzoic acids. Furthermore, to monitor the group changes on the catalysts, FTIR spectra were used to monitor the tandem conversion reactions. Owing to the distinct characteristic absorption peaks of the C=N and C=O groups in the FTIR spectra, 3c was selected as the substrate to give direct evidence for the changes to the catalysts and substrate at the different reaction times (0, 8, and 15 h). As shown in Fig. S5c and d,† the appearance of new vibration bands at 2232 and 2239 cm^{-1} on nanoscale 1 and 2, respectively, which corresponded to the $\nu_{C=N}$, were indicative of the presence of substrate 3c or product 4c on the catalysts during the reaction process (8 h). More importantly, another new vibration bands around 1702 and 1695 cm⁻¹ on nanoscale 1 and 2, respectively, were assigned to the C=O stretching vibration of the product 4c, which the nitro group in substrate 3c was con-

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verted to carboxyl group. This result revealed that the unique structural characteristics of nanoscale 1 and 2 endowed them with well-defined platforms to promote the tandem conversion reactions. In addition, controlled trials were also carried out with Zn(OTf)₂/H₃idbt (0.1 mmol/0.1 mmol) and H₃idbt ligand (0.1 mmol) as homogeneous catalysts under the same conditions (Table S4[†]). Substrates 3a-i when catalyzed by Zn (OTf)₂/H₃idbt generated a mixture of products with benzoic acid yields ranging from 31 to 45% (4a-i), while H₃idbt ligand produced no benzoic acids. These yields (4a-i, 31-45%) were much lower than the yields (4a-i, 71-82% and 88-94% for nanosized catalysts 1 and 2, respectively) obtained with nanosized catalysts 1 and 2 because homogeneous catalysts Zn(OTf)₂/H₃idbt might be relatively simple coordination complexes without well-established platforms to immobilize active centers in fixed azimuths and distances. Thus, these results unambiguously demonstrated that nanosized catalysts 1 and 2, especially nanosized catalyst 2, provide atomistically well-defined active sites to perform the Nef conversion reaction of nitromethylbenzenes into benzoic acids with good selectivity.

In contrast, the low catalytic activities of the large-sized catalysts 1 and 2 were attributed to the BET surface areas, particle sizes and morphologies, which not only restricted the diffusional distances and rates but also reduced the permeability to the transported products and substrates. Therefore, emphasizing the superiority of the small size effect induced by nanosized catalysts 1 and 2 over large samples 1 and 2 as catalysts, surface and boundary effect could be released to increase the reactivity but does little for their selectivity.

To further verify that the tandem conversion reactions occurred on the surface rather than the channels or pores of the crystalline samples, the conversion reaction of 3a and TBAI was performed with the large crystals of 1 $(0.8 \times 0.8 \times 0.5 \text{ mm}^3)$ and 2 $(1 \times 1 \times 0.6 \text{ mm}^3)$ without grinding or stirring, to exclude the potential of catalytic activity arising from the surface metal active sites of very tiny particles. The corresponding benzoic acid product (4a) was obtained as the sole product in 34 (large crystals of 1) or 46% (large crystals of 2) yield, which was much lower than the 82 or 94% yield obtained by the crystalline nanoscale 1 or 2. Meanwhile, the yields (34 or 46%) were also much lower than the yields obtained with grinding or stirring of large crystals of 1 (56%) or 2 (67%). Furthermore, the BET surface areas of nanoscale 1 and 2 were 175 and 293 m² g⁻¹, respectively, which were much larger than the large-sized 1 $(9.57 \text{ m}^2 \text{ g}^{-1})$ and 2 $(15.29 \text{ m}^2 \text{ g}^{-1})$. This distinctly revealed that the catalytic performances relied on the surface catalytic sites of the particles. Moreover, owing to the very low N2 uptake of 1 and 2, the PSDs of 1 and 2 could not be determined, which clearly demonstrated that there were no channels or pores in 1 and 2. Thus, these results provided clear evidence that the tandem conversion reactions proceeded on the surface rather than in the interior of catalysts 1 or 2.

To evaluate the heterogeneous traits of this catalyst system, we first assessed the leaching of soluble catalytically competent Zn^{II} by ICP-AES, and the results revealed low Zn concen-

trations (0.65 ppm and 0.57 ppm for nanoscale 1 and 2, respectively) corresponding to less than 1% leaching. Then, hot filtration experiments were carefully carried out. The filtrate obtained by centrifuging to remove nanoscale catalysts 1 or 2 after 1 h of conversion reactions went on reacting for 14 h. Negligible benzoic acids in the presence of these mother solutions provided evidence against the leaching of the dissolvable active catalysts. Therefore, these consequences particularly revealed that nanoscale catalysts 1 and 2 were actually heterogeneous catalysts. Moreover, the long-term robustness and recyclability of the nanoscale catalysts 1 and 2 were determined with 3a via reusability experiments. The nanoscale catalysts 1 and 2 were readily recovered by centrifugation from the reaction solution and remained stable after at least ten reaction cycles without significant loss of activity. Furthermore, the PXRD patterns of the regenerated samples after ten reaction cycles matched well with those of as-synthesized 1 and 2 and demonstrated no architecture collapse or decomposition, which showed that the nanoscale catalysts 1 and 2 could retain their catalytic activity after at least ten reaction cycles (Fig. S6[†]).

Conclusions

In summary, we reported a high-efficiency catalytic system for the conversion of nitroalkanes into carboxylic acids in the presence of stable and robust nanosized heterogeneous catalysts utilizing environmentally friendly and green H₂O as the reaction solution. Furthermore, different morphologies and particle sizes of Zn-based CPs 1 and 2, from the large scale to the nanoscale, could be achieved under surfactant-templated solvothermal reactions with PVA as the template. Moreover, with the benefit of readily accessible active sites in the nanoscale particles, nanosized 1 and 2 as excellent heterogeneous catalysts remarkably outperformed large crystals 1 and 2 in the conversion reactions, providing a tunable and atomistically well-defined platform for promoting the conversion of nitromethylbenzenes into benzoic acids by increasing the permeability and diffusional rate with the minimum diffusion distance, but this does little for their selectivity.

Conflicts of interest

There are no conflicts to declare.

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2 (a) S. Ghorban, E. Soleimanï and L. E. Kaim, *Tetrahedron Lett.*, 2017, 58, 4595–4597; (b) L. Ping, D. S. Chung, J. Bouffard and S. Lee, *Chem. Soc. Rev.*, 2017, 46, 4299–4328; (c) Y. Hayashi, A. Takikawa, S. Koshino and K. Ishida, *Chem. – Fur. L.* 2019, 25, 10319–10322; (d) L. Li, B. Su.

- J. Bouffard and S. Lee, *Chem. Soc. Rev.*, 2017, **46**, 4299– 4328; (c) Y. Hayashi, A. Takikawa, S. Koshino and K. Ishida, *Chem. – Eur. J.*, 2019, **25**, 10319–10322; (d) L. Li, B. Su, Y. Liu and Q. Wang, *Curr. Org. Synth.*, 2018, **15**, 989–994; (e) S. Ding, G. Jia and J. Sun, *Angew. Chem., Int. Ed.*, 2014, **53**, 1887–1180.
- 3 (a) M. Maečeková, P. Gerža, M. Šoral, J. Moncol, D. Berkeś,
 A. Kolarovič and P. Jakubec, Org. Lett., 2019, 21, 4580–4584;
 (b) N. Ono, The nitro group in organic synthesis, Wiley-VCH,
 New York, 2001.
- 4 (a) M. Zhao, K. Yuan, Y. Wang, G. Li, J. Guo, G. Lin, W. Hu, H. Zhao and Z. Tang, Nature, 2016, 539, 76-80; (b) T. Drake, P. Ji and B. Lin, Acc. Chem. Res., 2018, 51, 2129-2138; (c) Y. Huang, J. Liang, X. Wang and R. Cao, Chem. Soc. Rev., 2017, 46, 126-157; (d) M. Liu, J. Wu and H. Hou, Chem. – Eur. J., 2018, 25, 2935-2948; (e) F. D. Toste, M. S. Sigman and S. J. Miller, Acc. Chem. Res., 2017, 50, 609-615; (f) C. Huang, G. Li, L. Zhang, Y. Zhang, L. Mi and H. Hou, Chem. – Eur. J., 2019, 10366-10374; (g) Y. Shi, W. Zhang, B. F. Abrahams, P. Braunstein and J. Lang, Angew. Chem., 2019, 58, 9453-9458; (h) F. Hu, Y. Mi, C. Zhu, B. F. Abrahams, P. Braunstein and J. Lang, Angew. Chem., Int. Ed., 2018, 57, 12696-12701; (i) D. Liu, Z. Ren, H. Li, J. Lang, N. Li and B. F. Abrahams, Angew. Chem., Int. Ed., 2010, 49, 4767-4770.
- 5 (a) T. Zhang and W. Lin, Chem. Soc. Rev., 2014, 43, 5982-5993; (b) L. Sun, X. Liu and H. Zhou, Chem. Soc. Rev., 2015, 44, 5092-5147; (c) R. Ding, C. Huang, J. Lu, J. Wang, C. Song, J. Wu, H. Hou and Y. Fan, Inorg. Chem., 2015, 53, 1405-1413; (d) C. Huang, J. Wu, C. Song, R. Ding, Y. Qiao, H. Hou, J. Chang and Y. Fan, Chem. Commun., 2015, 51, 10353-10356; (e) C. Huang, X. Han, Z. Shao, K. Gao, M. Liu, Y. Wang, J. Wu, H. Hou and L. Mi, Inorg. Chem., 2017, 56, 4874-4884; (f) Y. Cui, B. Li, H. He, W. Zhou, B. Chen and G. Qian, Acc. Chem. Res., 2016, 49, 483-493; (g) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov and F. Verpoort, Chem. Soc. Rev., 2015, 44, 6804-6849; (h) X. Guo, C. Huang, H. Yang, Z. Shao, K. Gao, N. Qin, G. Li, J. Wu and H. Hou, Dalton Trans., 2018, 47, 16895-16901; (i) D. Liu, H. Wang, B. F. Abrahams and J. Lang, Chem. Commun., 2014, 50, 3173-3175; (j) F. Hu, H. Wang, D. Guo, H. Zhang, J. Lang and J. E. Beves, Chem. Commun., 2016, 52, 7990-7993.

- Notes and references
 - (*a*) R. Ballini and M. Petrini, *Tetranearon*, 2004, 60, 1017–1047; (*b*) P. Marcé, J. Lynch, A. J. Blacker and J. M. J. Williams, *Chem. Commun.*, 2016, 52, 1013–1016; (*c*) R. Ballini and M. Petrini, *Adv. Synth. Catal.*, 2015, 357, 2471–2402; (*d*) I. Yavari, J. Sheykhahmadi, H. Saffarian and M. R. Halvagar, *Synth. Commun.*, 2019, 49, 456–462; (*e*) W. Huang, A. Raja, B. Hong and G. Lee, *Org. Lett.*, 2017, 19, 3494–3497.
- 1 (a) R. Ballini and M. Petrini, *Tetrahedron*, 2004, **60**, 1017–

View Article Online

- 6 (a) M. Zhao, S. Ou and C. Wu, Acc. Chem. Res., 2014, 47, 1199–1207; (b) C. Huang, H. Wang, X. Wang, K. Gao, J. Wu, H. Hou and Y. Fan, Chem. Eur. J., 2016, 22, 6389–6396; (c) C. Huang, Y. Zhang, H. Yang, D. Wang, L. Mi, Z. Shao, M. Liu and H. Hou, Cryst. Growth Des., 2018, 18, 5674–5681; (d) B. Li, Z. Ju, M. Zhou, K. Su and D. Yuan, Angew. Chem., 2019, 58, 7687–7691; (e) L. Cao, Z. Lin, F. Peng, W. Wang, R. Huang, C. Wang, J. Yan, J. Liang, Z. Zhang, T. Zhang, L. Long, L. Sun and W. Lin, Angew. Chem., Int. Ed., 2016, 55, 4962–4966; (f) Y. Yamada, C. Tsung, W. Huang, Z. Huo, S. E. Habas, T. Soejima, C. E. Aliaga, G. A. Somorjai and P. Yang, Nat. Chem., 2011, 3, 372–376.
- 7 (a) Z. Lin, N. C. Thacker, T. Sawano, T. Drake, P. Ji, G. Lan, L. Cao, S. Liu, C. Wang and W. Lin, Chem. Sci., 2018, 9, 143-151; (b) H. Noh, Y. Cui, A. W. Peters, D. R. Pahls, M. A. Ortuño, N. A. Vermeulen, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, J. Am. Chem. Soc., 2016, 138, 14720-14726; (c) C. S. Diercks, Y. Liu, K. E. Cordova and O. M. Yaghi, Nat. Mater., 2018, 17, 301-307; (d) W. Shi, L. Cao, H. Zhang, X. Zhou, B. An, Z. Lin, R. Dai, J. Li, C. Wang and W. Lin, Angew. Chem., Int. Ed., 2017, 56, 9704-9709; (e) F. Li, Q. Shao, X. Huang and J. Lang, Angew. Chem., Int. Ed., 2018, 57, 1888–1892; (f) Y. Ding, Y. Chen, X. Zhang, L. Chen, Z. Dong, H. Jiang, H. Xu and H. Zhou, J. Am. Chem. Soc., 2017, 139, 9136-9139; (g) F. Li, P. Wang, X. Huang, D. J. Young, H. Wang, P. Braunstein and J. Lang, Angew. Chem., 2019, 58, 7051-7056; (h) W. Yao, W. Gong, H. Li, F. Li, J. Gao and J. Lang, Dalton Trans., 2014, 43, 15752-15759.
- 8 (a) G. Lan, K. Ni, R. Xu, K. Lu, Z. Lin, C. Chan and W. Lin, Angew. Chem., Int. Ed., 2017, 56, 12102-12106; (b) J. Wang, C. Huang, K. Gao, X. Wang, M. Liu, H. Ma, J. Wu and H. Hou, Chem. - Asian J., 2016, 11, 1856-1862; (c) M. H. Beyzavi, N. A. Vermeulen, K. Zhang, M. So, C. Kung, J. T. Hupp and O. K. Farha, ChemPlusChem, 2016, 81, 708–713; (d) Z. Niu, W. D. C. Bhagya Gunatilleke, Q. Sun, P. Lan, J. Perman, J. Ma, Y. Cheng, B. Aguila and S. Ma, Chem, 2018, 4, 2587–2599; (e) P. Ji, K. Manna, Z. Lin, A. Urban, F. X. Greene, G. Lan and W. Lin, J. Am. Chem. Soc., 2016, 138, 12234-12242; (f) Y. Huang, M. Zhao, S. Han, Z. Lai, J. Yang, C. Tan, Q. Ma, Q. Lu, J. Chen, X. Zhang, Z. Zhang, B. Li, B. Chen, Y. Zong and H. Zhuang, Adv. Mater., 2017, 29, 1700102; (g) F. Li, H. Li and J. Lang, CrystEngComm, 2016, 18, 1760–1767; (h) W. Yao, F. Li, H. Li and J. Lang, J. Mater. Chem. A, 2015, 3, 4578-4585.
- 9 (a) B. Ghalei, K. Sakurai, Y. Kinoshita, K. Wakimoto, A. P. Isfahani, Q. Song, K. Doitomi, S. Furukawa, H. Hirao, H. Kusuda, S. Kitagawa and E. Sivaniah, *Nat. Energy*, 2017,
 2, 17086; (b) A. Dhakshinamoorthy, A. M. Asiri and H. Garcia, *Chem. Commun.*, 2017, 53, 10851–10869;
 (c) Q. Wang, X. Zhang, L. Huang, Z. Zhang and S. Dong, *Angew. Chem., Int. Ed.*, 2017, 56, 16082–16085.
- 10 (a) G. M. Sheldrick, A short history of SHELX, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122;
 (b) G. M. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3–8.

Paper

- 11 (a) K. H. Park, K. Jang, S. U. Son and D. A. Sweigart, J. Am. Chem. Soc., 2006, 128, 8740–8741; (b) Y. Liu, W. Zhang, S. Li, C. Cui, J. Wu, H. Chen and F. Huo, Chem. Mater., 2014, 26, 1119–1125.
- 12 (a) P. Taheri, J. R. Flores, F. Hannour, J. H. W. de Wit, H. Terryn and J. M. C. Mol, *J. Phys. Chem. C*, 2013, 117, 3374–3382; (b) M. S. Killian, J. Gnichwitz, A. Hirsch, P. Schmuki and J. Kunze, *Langmuir*, 2010, 26, 3531–3538.