Electronic Supplementary Material (ESI) for RSC Advances.

Ligand geometry controlling Zn-MOFs' spatial structures for their catalytic performance in Knoevenagel condensation

Supporting Information

Zimo He,[b #] Xi Zhao,[a #] Xinbo Pan,[a] Yuanyuan Li,[a] XiaoXiao Wang,[a] Haitao Xu,*[a] Zhenliang Xu[a]

[a] State Key Laboratory of Chemical Engineering, Membrane Science and Engineering R&D Lab, Chemical Engineering Research Center, East China University of Science and Technology (ECUST), 130 Meilong Road, Shanghai 200237, China.

[b] School of Chemistry and Molecular Engineering, East China University of Science and Technology (ECUST), 130 Meilong Road, Shanghai 200237, China.

Contents

Reagents

The following chemicals were used as received without further purification. 3-acetylpyridine(98%), hydrazine hydrate(80%), 5-nitroisophthalic acid(98%), 1,4-cyclohexanedicarboxylic acid(99%) and malonitrile(99%) were purchased from Aladdin chemistry Co.Ltd. N, N-Dimethylformamide (DMF, 99.5%), EtOH(99.7%), MeOH(99.5%) and benzaldehyde(98.5%) were provide by Shanghai Titan Scientific Co., Ltd. Polyvinylpyrrolidone (PVP, MW=58000), 3-nitrophthalic acid(99%), 4-acetylpyridine(98%), 3-pyridinecarboxaldehyde(98%) and n-dodecane(99%) were provide from Shanghai Mclean Biochemical Technology Co., Ltd. Sodium acetate anhydrous(99%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. $Zn(NO_3)_2{\cdot}6H_2O$(99%) was provided from Alfa Aesar.

Characterization

The single crystal X-ray experiment was performed on Bruker APEX II CCD diffractometer equipped with graphite monochromaized Mo Kα radiation (λ=0. 71073Å) at room temperature (296K), diffraction data collected by ω scanning was integrated by SAINT program and corrected adsorption by SADABS, the crystal structure is solved by direct methods and refined F2 by full-matrix least-squares methods for all data by using SHELXTL-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically and their positions were generated geometrically.

PXRD was carried out using D8 Advance X-Ray Polycrystaline Diffractometer. Cu target, ceramic X-ray tube, 2.2kw.

Scanning electron microscope imaging was carried out using Phenom ProX field emission scanning electron microscope.

Methods

Synthesis of 3-bpdh, 4-bpdh, 3-bpd

N,N'-bis-(1-pyridine-3-yl-ethylidene)-hydrazine (3-bpdh) was synthesized according to the previous literature[S1] . (7.268g, 60 mmol) 3-acetylpyridine was dissolved in 25 mL ethanol, and then (1.877g, 30mmol) hydrazine dissolved in 25 mL ethanol was added into the above solution. Subsequently, The mixture was stirred under 108℃for 8 h. After that, the obtained yellow solution was evaporated to remove some of the solvent and then crystallized when cooling to the room temperature. Finally, the obtained yellow needle-like crystal was filtered and dried under vacuum.

4-bpdh[S2] and 3-bpd[S3] were synthesized with the same procedure expect that 3-acetylpyridine was replaced by 4-acetylpyridine, 3-pyridinecarboxaldehyde respectively.

Synthesis of 1Zn, 2Zn and 3Zn single-crystal

Firstly, NIA (0.3 mmol, 0.063 g), NaOH (0.024 g) and distilled water (15 ml) were mixed to obtain NIA alkali aqueous solution, and the test tube was marked as A. Then, 3-bpdh (0.3 mmol, 0.0714 g) was dissolved into methanol (20 ml) in another test tube, and the test tube was marked as B. In addition, 0.3mmol $Zn(NO_3)_2{\cdot}6H_2O$ (0.0892 g) was dissolved into distilled water (5ml) and marked as C. The mixture of A and C (4 ml) was added to another clean test tube. 2 ml methanol-water buffer solution (1:1) was added to it, and then 4 ml B. After inserting the plug and standing for two weeks , the white needle crystal on the test tube wall was collected and washed with methanol for 3 times, and the **1Zn** single crystal was obtained after drying.

The preparation of **2Zn** single crystal and **3Zn** single crystal is the same as that of **1Zn** single crystal, except for ligands.

Synthesis of 1Zn micro-sheet

First, a mixture of NIA (0.3 mmol, 0.063 g), NaOH (0.024 g), and the distilled water (15 ml) was stirred to obtain a NIA alkali aqueous solution, and mark this test tube as A. Next, some 3-bpdh (0.3 mmol, 0.0714 g) was added to methanol (20 ml) in another test tube and mark this test tube as B. Mixed A and B, then transfer to a conical bottle. While stirring constantly, slowly dropped aqueous solution (5 ml) containing 0.3 mmol $Zn(NO_3)_2{\cdot}6H_2O$ (0.0892 g) into the conical bottle. Two hours later, centrifugated and dried the product.

Synthesis of 2Zn micro-cluster and 3Zn micro-cluster

The synthesis of **2Zn** micro-cluster and **3Zn** micro-cluster is similar to **1Zn** micro-sheet except for organic acids and bridged ligands.

Synthesis of 1Zn nanosphere

$Zn(NO_3)_2{\cdot}6H_2O$(0.1mmol, 0.0297g), NIA(0.1mmol, 0.0211g), 3-bpdh(0.1mmol, 0.0238g) was dissolved in 10ml DMF in turn, and to stabilize microcrystals, a certain amount of active agent polyvinyl pyrrolidone(PVP) was added, then the mixture solution was transferred to a 30 ml autoclave lined with Teflon, sealed and heated to 100^{o}C for 24 hours. The product was collected by centrifugation at 5000 rpm for 3 min, washed several times with DMF and ethanol and dried at 100°C overnight.

Synthesis of 2Zn microstick

Methanol was selected as the solvent for the preparation of **2Zn** nanostick. 0.1mmol $Zn(NO_3)_2{\cdot}6H_2O$ (0.0297g), NPA (0.0211g) and 4-bpdh (0.0238g) were mixed in 10 ml methanol and put into a Teflon-lined autoclave, which was placed at 120^{o}C for 24 h. The product was collected by centrifugation at 5000 rpm for 3 min, washed several times with DMF and ethanol and dried at 100°C overnight.

Synthesis of 3Zn hollowsphere

Sodium acetate and $Zn(NO_3)_2{\cdot}6H_2O$, 3-bpd, CHDA of 0.1mmol were mixed together respectively. After half an hour ultrasound, they were static for 24 hours at room temperature. The product was then centrifuged for three minutes at a speed of 5000 rpm and washed several times with DMF and ethanol and dried at 100°C overnight.

Knoevenagel condensation

Malonitrile (1.1 mmol, 0.0727 g) and benzaldehyde (1 mmol, 102 μL) were added in 5 ml EtOH, and as an internal standard, n-dodecane were dissolved in the solution. Then poured the synthesized catalyst (10 mg) into the solution under stirring. GC analysis was used to monitor the reaction process and samples were collected at every 1 hour.

PXRD patterns

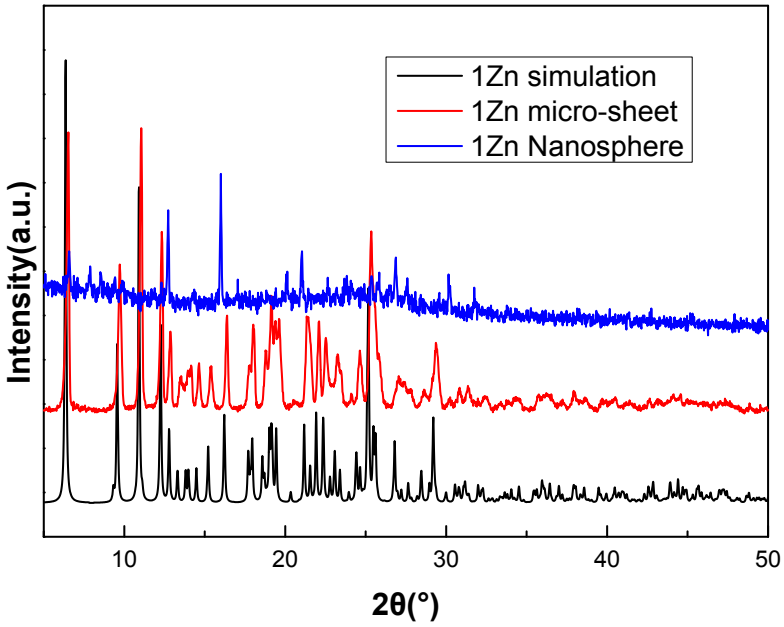

Figure S1 XRD patterns of **1Zn**

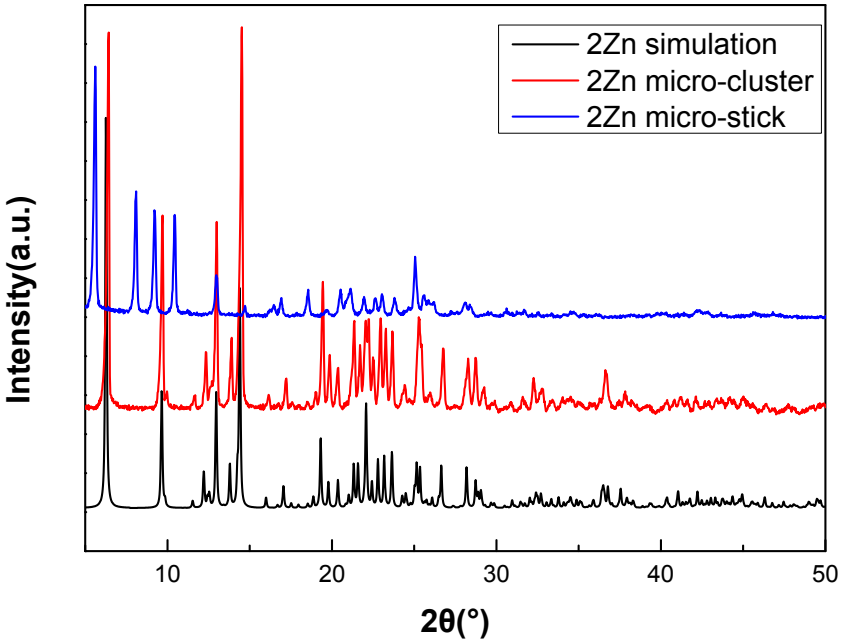

Figure S2 XRD patterns of **2Zn**

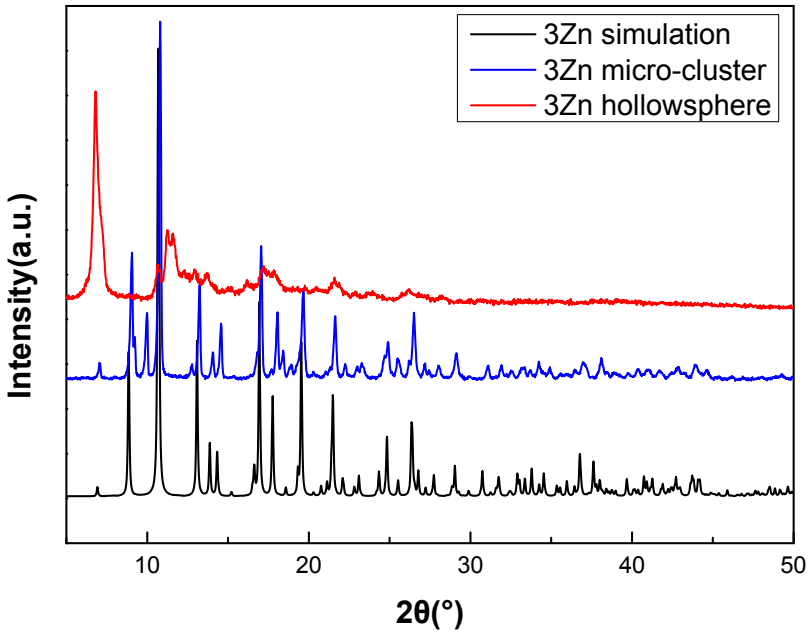

Figure S3 XRD patterns of **3Zn**

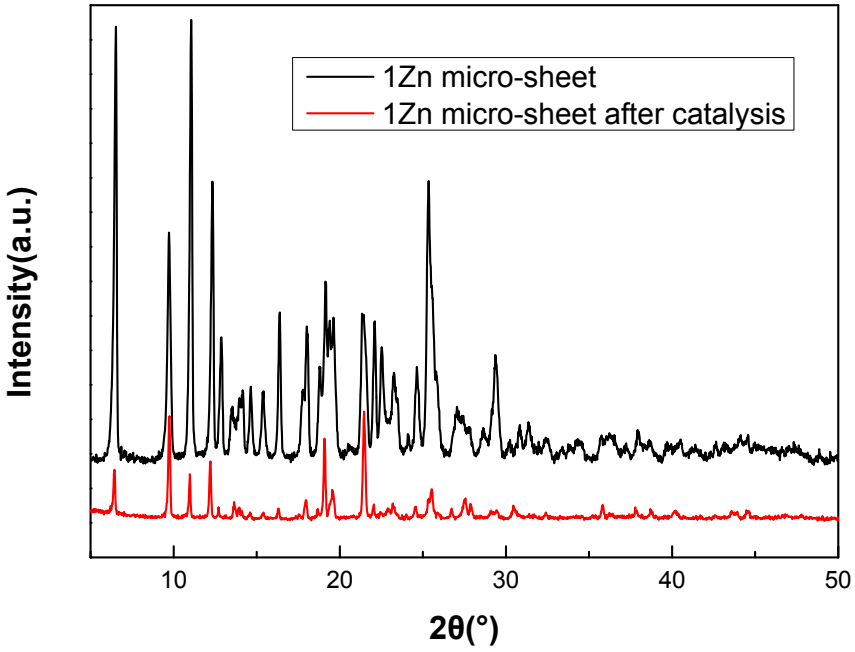

Figure S4 XRD patterns of **1Zn** microcluster before and after catalysis

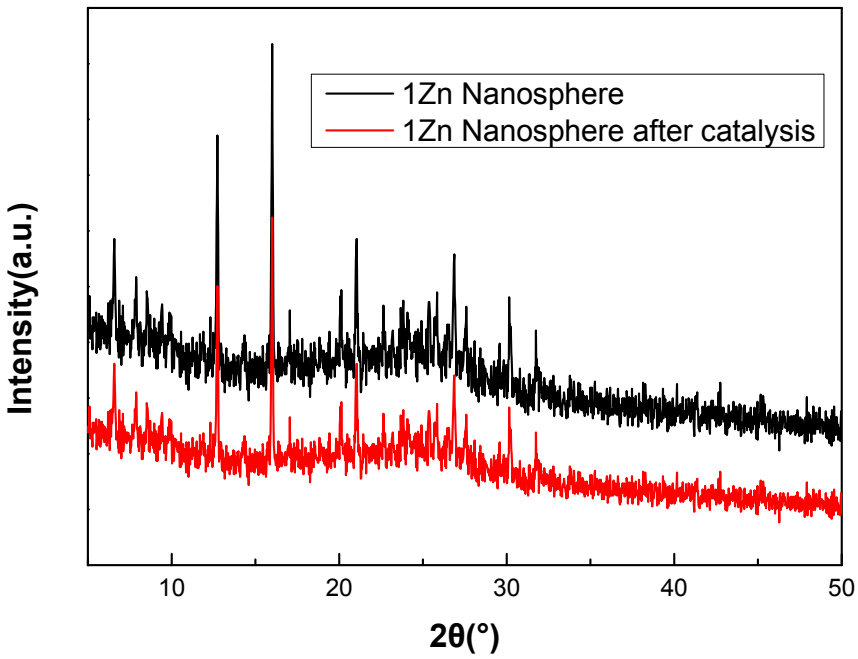

Figure S5 XRD patterns of **1Zn** nanosphere before and after catalysis

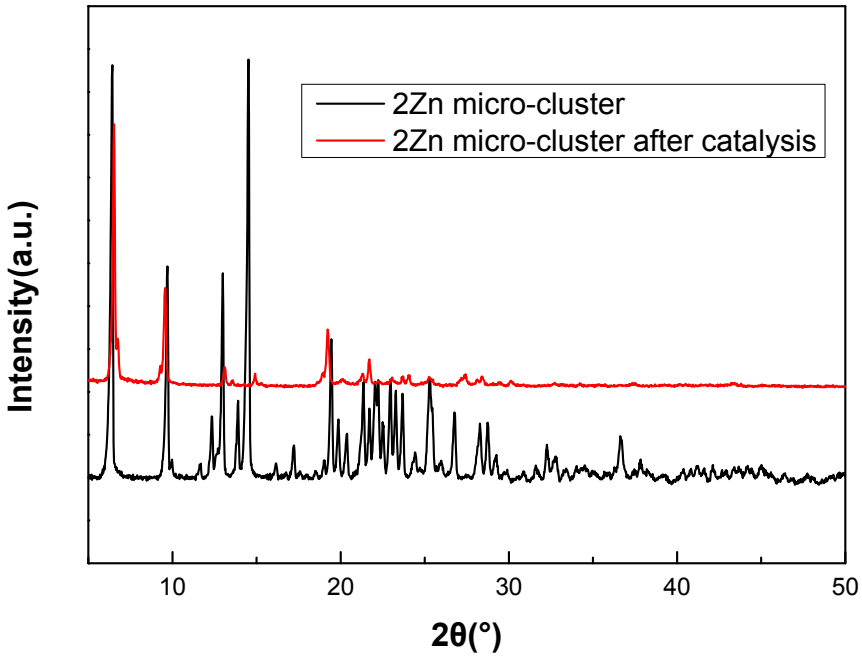

Figure S6 XRD patterns of **2Zn** micro-cluster before and after catalysis

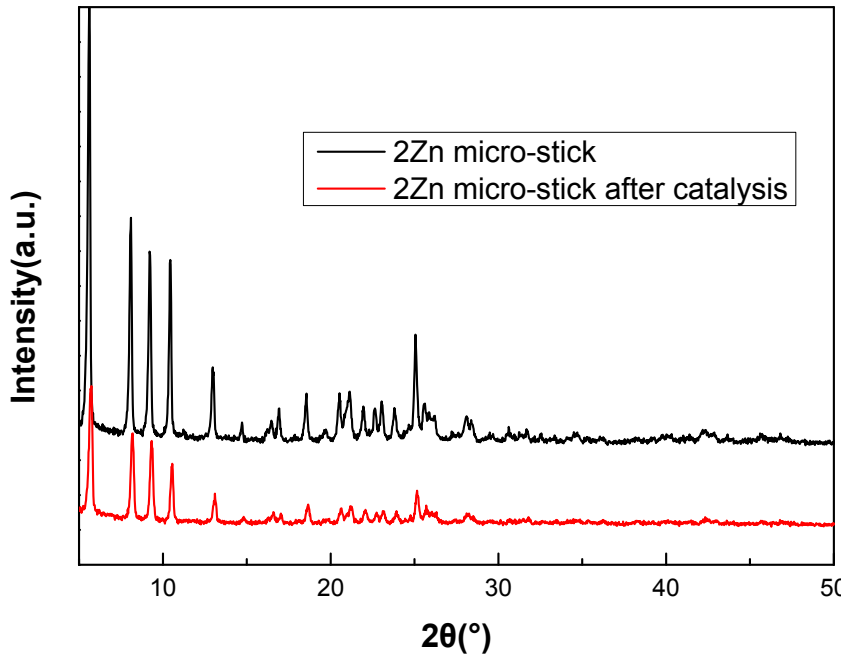

Figure S7 XRD patterns of **2Zn** micro-stick before and after catalysis

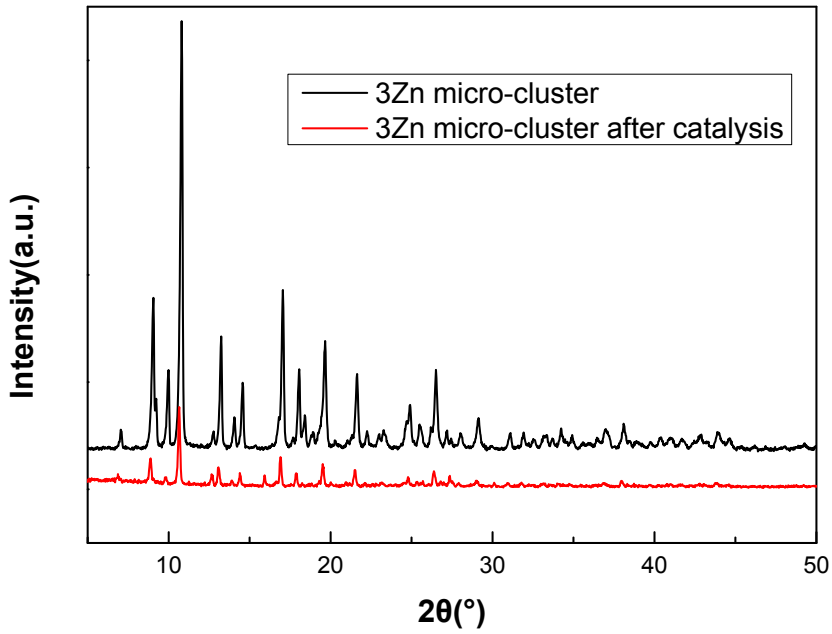

Figure S8 XRD patterns of **3Zn** micro-cluster before and after catalysis

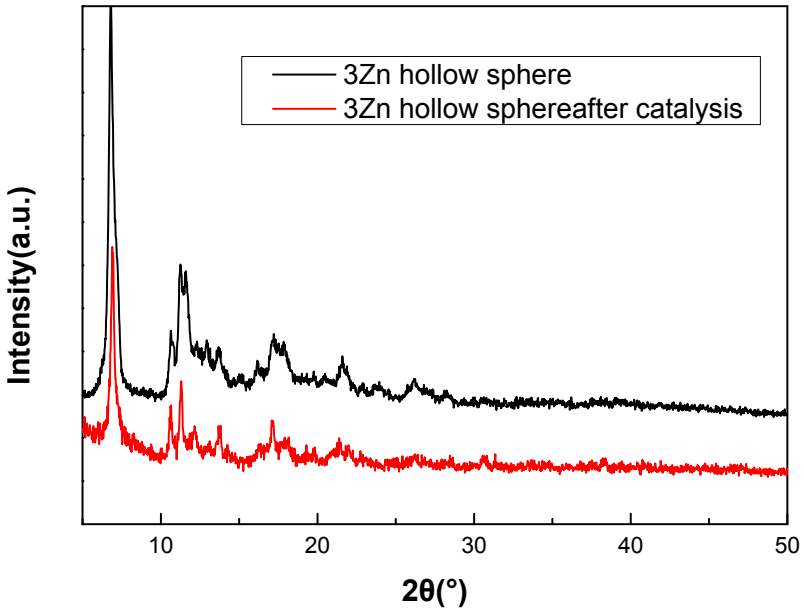

Figure S9 XRD patterns of **3Zn** hollow sphere before and after catalysis

SEM images

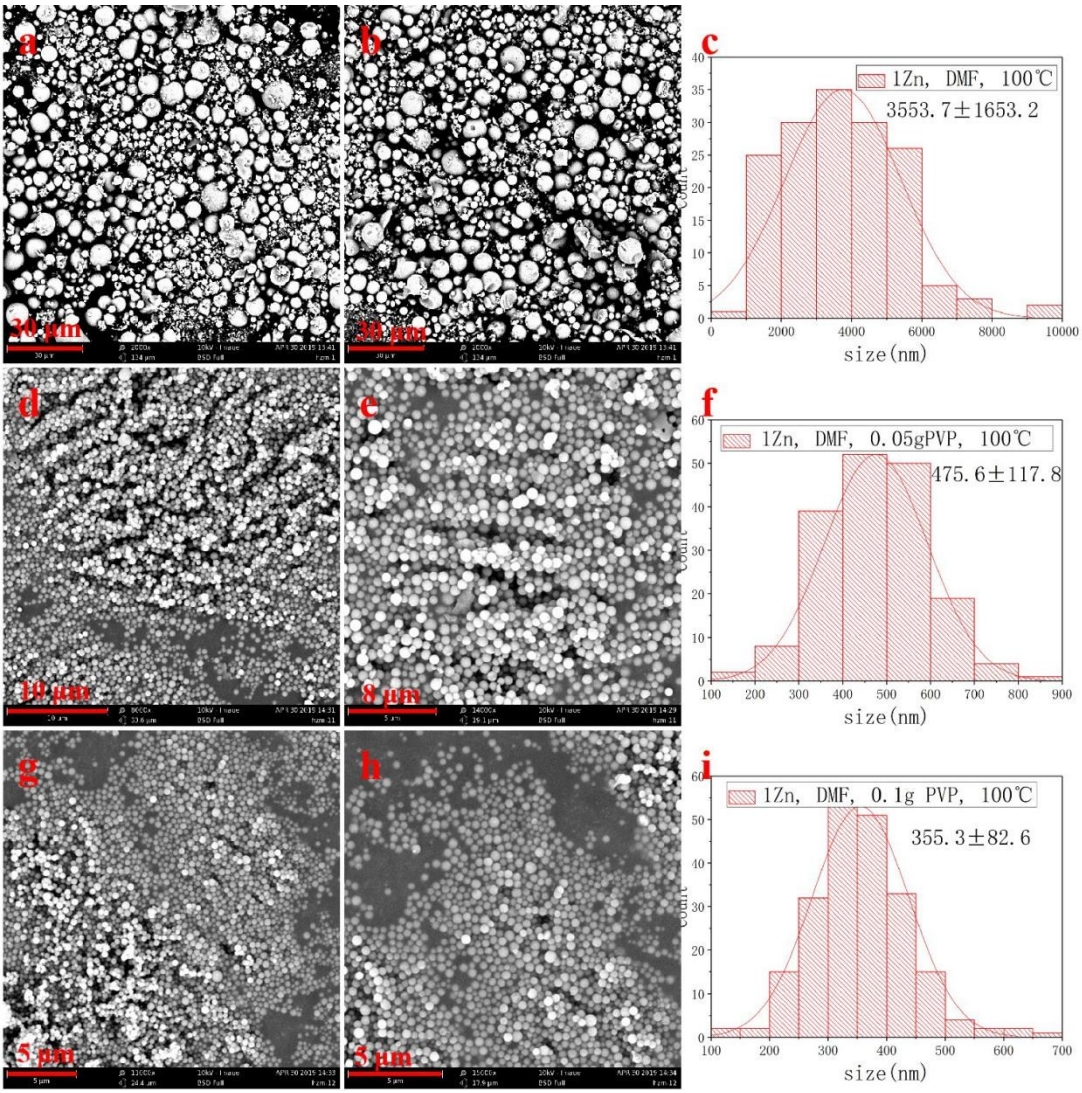

Figure S10 SEM images of **1Zn** nanospheres synthesized with different amounts of PVP. a-c) 0g; d-f) 0.05 g; g-i) 0.1 g

In the absence of PVP, **1Zn** spheres with uneven particle size were obtained, some of which were larger than 10 microns, and some of which were nano-sized; **1Zn** nanospheres with uniform size of about 476 nm were obtained by adding 0.05g of PVP to the precursor solution. When 0.1g PVP was added, the nanospheres became smaller (about 355 nm) and more uniform.

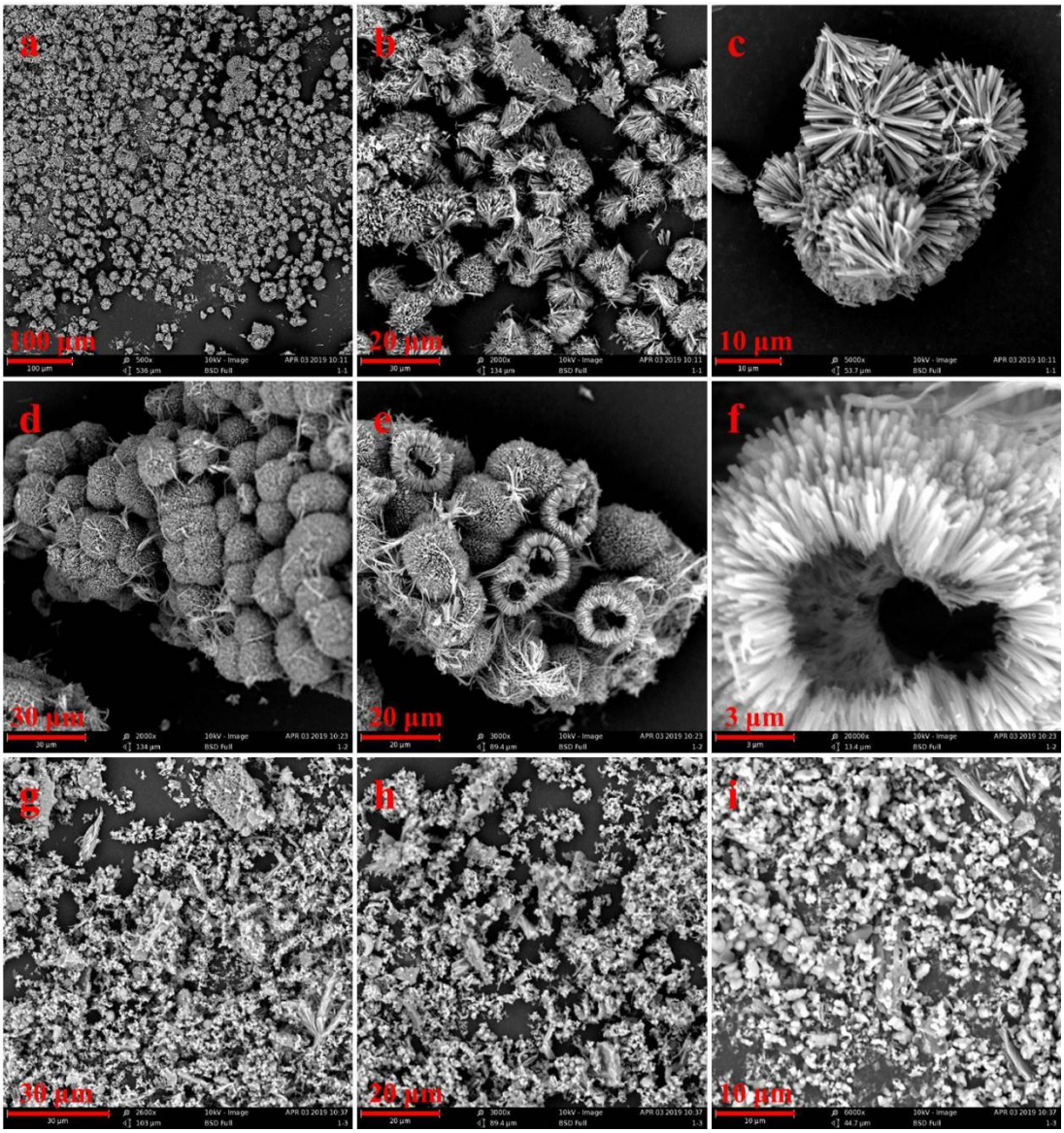

Figure S11 SEM images of **3Zn** hollowsphere synthesized with different amounts of NaAC a-c) 0.05 mmol; d-f) 0.1 mmol; g-i) 0.2 mmol

BET patterns

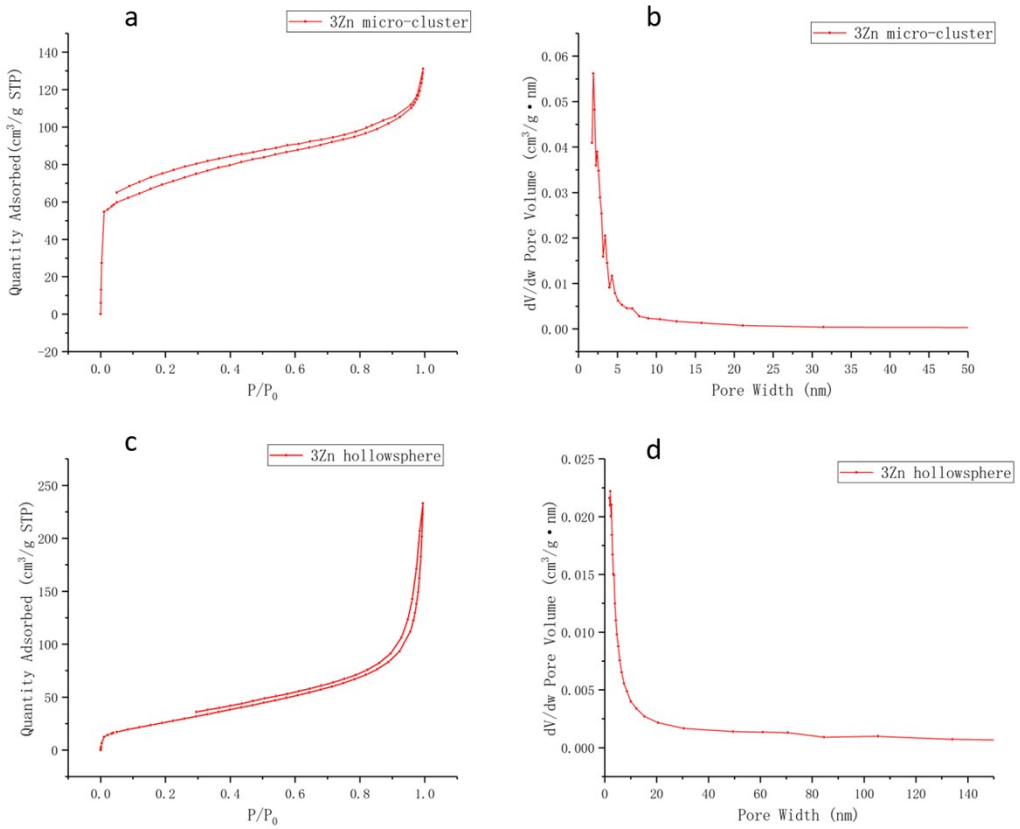

Figure S12 a-b) N_2 adsorption-desorption isotherms and the corresponding pore width of **3Zn** micro-cluster; c-d) N_2 adsorption-desorption isotherms and the corresponding pore width of **3Zn** hollowsphere. The existence of hollowsphere can be proved by the hysteresis between N_2 adsorption and desorption isotherms. And according to b) and d), the median pore width of **3Zn** hollowsphere and micro-cluster both are about 1 nm, but the hollowsphere has a considerable proportion of macropores. The BET surface area of **3Zn** micro-cluster and **3Zn** hollowsphere are 234.67 m^2/g and 99.59 m^2/g. The BJH Adsorption cumulative volume of pores of **3Zn** micro-cluster and **3Zn** hollowsphere are 0.15 cm^3/g and 0.33 cm^3/g.

Catalytic result

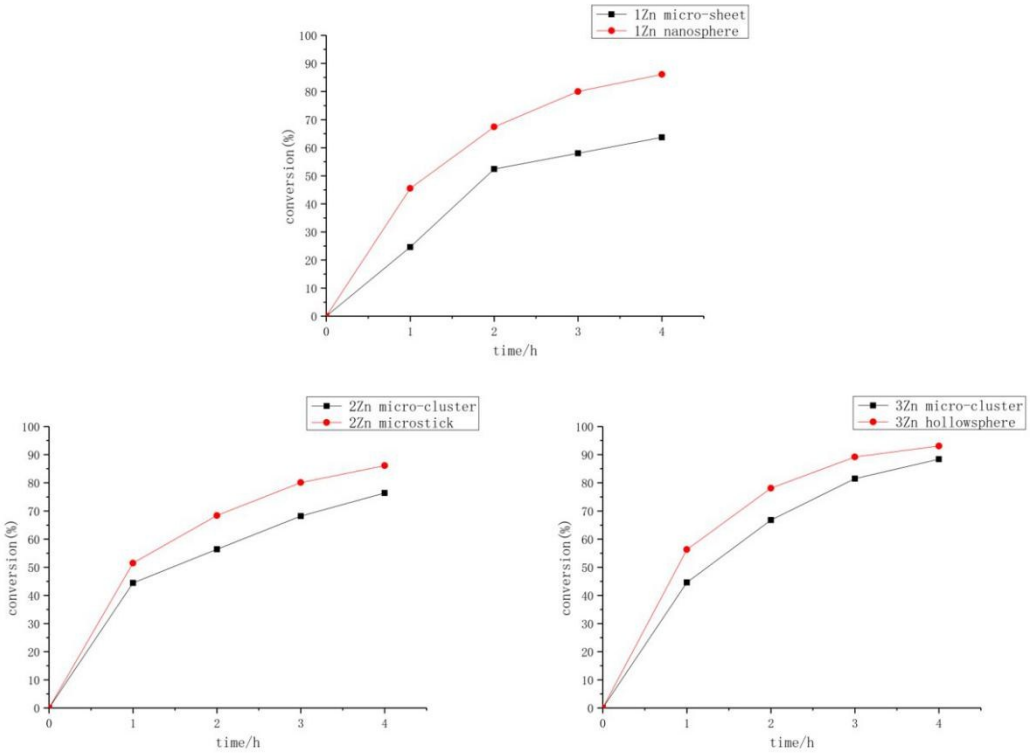

Figure S13 Effect of morphology on catalytic performance of **1Zn**, **2Zn**, **3Zn**

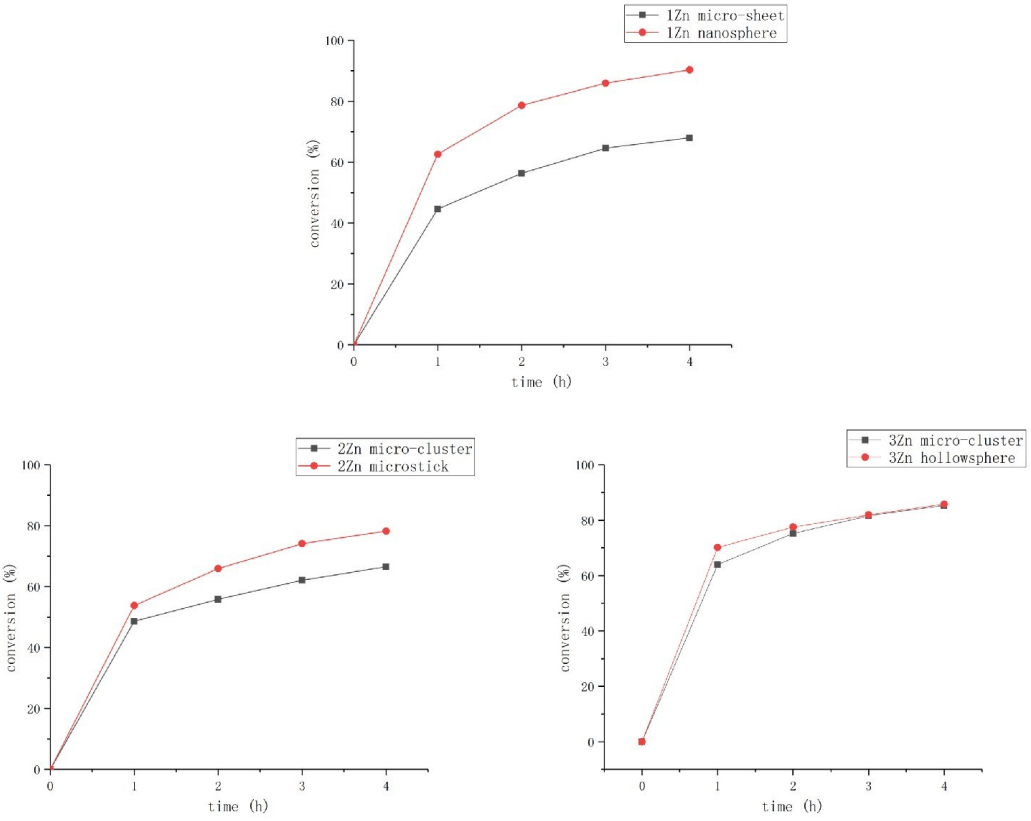

Figure S14 catalytic performance of **1Zn**, **2Zn**, **3Zn** as for n-heptanal

Table S1. Crystallographic data of the complex **1Zn**deposited in CCDC 1916896

Empirical formula	C_{23} H_{21} N_5O_7Zn
Formula weight	544.82
Space group	P-1
T (K)	293(2)
a (Å)	8.585(5)
b (Å)	10.181(6)
c (Å)	14.860(12)
α°	104.46(1)
β°	101.00(1)
γ°	102.35(1)
V (Å3)	1186.92(538)
Z	2
ρcal. Mg/m^3	1.524
λ(M_0-Kα)/Å	0.71073
R	0.0362
Rw	0.0949
GOF	1.001
Largest diff. Peak	0.818 eA^{-3}
Largest diff. Hole	-0.675 eA^{-3}
Crystal size(mm)	0.16 x 0.13 x 0.10 mm

Table S2. Selected bond lengths (Å) of the complex **1Zn**

Zn(1)-O(1)	1.968(2)	C(14)-N(2)	1.274(4)
Zn(1)-O(4)#1	1.977(2)	C(14)-C(15)	1.492(5)
Zn(1)-N(4)#2	2.041(3)	C(15)-H(15A)	0.96
Zn(1)-N(1)	2.069(3)	C(15)-H(15B)	0.96
C(1)-O(2)	1.235(3)	C(15)-H(15C)	0.96
C(1)-O(1)	1.280(3)	C(16)-N(3)	1.275(4)
C(1)-C(2)	1.497(3)	C(16)-C(18)	1.494(4)
C(2)-C(3)	1.388(4)	C(16)-C(17)	1.493(4)
C(2)-C(7)	1.387(4)	C(17)-H(17A)	0.96
C(3)-C(4)	1.383(4)	C(17)-H(17B)	0.96
C(3)-H(3)	0.93	C(17)-H(17C)	0.96
C(4)-C(5)	1.386(4)	C(18)-C(19)	1.376(4)
C(4)-C(8)	1.513(4)	C(18)-C(22)	1.387(4)
C(5)-C(6)	1.382(4)	C(19)-N(4)	1.344(3)
C(5)-H(5)	0.93	C(19)-H(19)	0.93
C(6)-C(7)	1.381(4)	C(20)-N(4)	1.336(4)
C(6)-N(5)	1.471(4)	C(20)-C(21)	1.381(4)
C(7)-H(7)	0.93	C(20)-H(20)	0.93
C(8)-O(3)	1.227(3)	C(21)-C(22)	1.384(4)
C(8)-O(4)	1.274(3)	C(21)-H(21)	0.93

C(9)-N(1)	1.339(3)	C(22)-H(22)	0.93
C(9)-C(10)	1.384(4)	C(23)-O(1W)	1.046(8)
C(9)-H(9)	0.93	C(23)-H(23A)	0.96
C(10)-C(11)	1.381(5)	C(23)-H(23B)	0.96
C(10)-C(14)	1.482(4)	C(23)-H(23C)	0.96
C(11)-C(12)	1.383(5)	N(2)-N(3)	1.392(3)
C(11)-H(11)	0.93	N(4)-Zn(1)#2	2.041(3)
C(12)-C(13)	1.359(5)	N(5)-O(6)	1.208(3)
C(12)-H(12)	0.93	N(5)-O(5)	1.212(3)
C(13)-N(1)	1.339(4)	O(4)-Zn(1)#3	1.977(2)
C(13)-H(13)	0.93	O(1W)-H(1W)	0.82

Table S3. Selected bond angles (°) of the complex **1Zn**

O(1)-Zn(1)-O(4)#1	101.08(9)	C(14)-C(15)-H(15B)	109.5
O(1)-Zn(1)-N(4)#2	116.34(9)	H(15A)-C(15)-H(15B)	109.5
O(4)#1-Zn(1)-N(4)#2	115.06(9)	C(14)-C(15)-H(15C)	109.5
O(1)-Zn(1)-N(1)	110.18(9)	H(15A)-C(15)-H(15C)	109.5
O(4)#1-Zn(1)-N(1)	103.05(9)	H(15B)-C(15)-H(15C)	109.5
N(4)#2-Zn(1)-N(1)	110.08(9)	N(3)-C(16)-C(18)	115.7(3)
O(2)-C(1)-O(1)	123.6(2)	N(3)-C(16)-C(17)	124.7(3)
O(2)-C(1)-C(2)	119.6(2)	C(18)-C(16)-C(17)	119.6(3)
O(1)-C(1)-C(2)	116.8(2)	C(16)-C(17)-H(17A)	109.5
C(3)-C(2)-C(7)	119.7(2)	C(16)-C(17)-H(17B)	109.5
C(3)-C(2)-C(1)	119.6(2)	H(17A)-C(17)-H(17B)	109.5
C(7)-C(2)-C(1)	120.7(2)	C(16)-C(17)-H(17C)	109.5
C(2)-C(3)-C(4)	121.1(2)	H(17A)-C(17)-H(17C)	109.5
C(2)-C(3)-H(3)	119.4	H(17B)-C(17)-H(17C)	109.5
C(4)-C(3)-H(3)	119.4	C(19)-C(18)-C(22)	117.3(3)
C(3)-C(4)-C(5)	119.8(2)	C(19)-C(18)-C(16)	120.7(2)
C(3)-C(4)-C(8)	118.7(2)	C(22)-C(18)-C(16)	122.0(3)
C(5)-C(4)-C(8)	121.5(2)	N(4)-C(19)-C(18)	123.7(3)
C(6)-C(5)-C(4)	118.2(2)	N(4)-C(19)-H(19)	118.2
C(6)-C(5)-H(5)	120.9	C(18)-C(19)-H(19)	118.2
C(4)-C(5)-H(5)	120.9	N(4)-C(20)-C(21)	121.4(3)
C(5)-C(6)-C(7)	123.0(2)	N(4)-C(20)-H(20)	119.3
C(5)-C(6)-N(5)	119.0(2)	C(21)-C(20)-H(20)	119.3
C(7)-C(6)-N(5)	118.1(2)	C(20)-C(21)-C(22)	119.6(3)
C(6)-C(7)-C(2)	118.2(2)	C(20)-C(21)-H(21)	120.2
C(6)-C(7)-H(7)	120.9	C(22)-C(21)-H(21)	120.2
C(2)-C(7)-H(7)	120.9	C(21)-C(22)-C(18)	119.4(3)
O(3)-C(8)-O(4)	124.3(2)	C(21)-C(22)-H(22)	120.3
O(3)-C(8)-C(4)	118.9(2)	C(18)-C(22)-H(22)	120.3
O(4)-C(8)-C(4)	116.7(2)	O(1W)-C(23)-H(23A)	109.5

N(1)-C(9)-C(10)	124.2(3)	O(1W)-C(23)-H(23B)	109.5
N(1)-C(9)-H(9)	117.9	H(23A)-C(23)-H(23B)	109.5
C(10)-C(9)-H(9)	117.9	O(1W)-C(23)-H(23C)	109.5
C(11)-C(10)-C(9)	116.9(3)	H(23A)-C(23)-H(23C)	109.5
C(11)-C(10)-C(14)	122.7(3)	H(23B)-C(23)-H(23C)	109.5
C(9)-C(10)-C(14)	120.4(3)	C(13)-N(1)-C(9)	117.6(3)
C(10)-C(11)-C(12)	119.3(3)	C(13)-N(1)-Zn(1)	119.19(19)
C(10)-C(11)-H(11)	120.4	C(9)-N(1)-Zn(1)	122.94(19)
C(12)-C(11)-H(11)	120.4	C(14)-N(2)-N(3)	116.3(2)
C(13)-C(12)-C(11)	119.9(3)	C(16)-N(3)-N(2)	115.9(2)
C(13)-C(12)-H(12)	120	C(19)-N(4)-C(20)	118.5(2)
C(11)-C(12)-H(12)	120	C(19)-N(4)-Zn(1)#2	119.58(19)
N(1)-C(13)-C(12)	122.2(3)	C(20)-N(4)-Zn(1)#2	121.67(19)
N(1)-C(13)-H(13)	118.9	O(6)-N(5)-O(5)	123.2(3)
C(12)-C(13)-H(13)	118.9	O(6)-N(5)-C(6)	118.3(2)
N(2)-C(14)-C(10)	115.6(3)	O(5)-N(5)-C(6)	118.5(2)
N(2)-C(14)-C(15)	124.2(3)	C(1)-O(1)-Zn(1)	107.17(17)
C(10)-C(14)-C(15)	120.2(3)	C(8)-O(4)-Zn(1)#3	110.94(17)
C(14)-C(15)-H(15A)	109.5	C(23)-O(1W)-H(1W)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x+2,-y+1,-z+2 #3 x,y+1,z

Table S4. Crystallographic data of the complex **2Zn**deposited in CCDC 1916895

Empirical formula	$C_{22}H_{21}N_5O_8Zn$
Formula weight	548.81
Space group	P2(1)/c
T (K)	293(2)
a (Å)	14.74(3)
b (Å)	8.444(15)
c (Å)	19.15(3)
$\alpha°$	90
$\beta°$	106.957(17)
$\gamma°$	90
V (Å3)	2280(7)
Z	4
ρcal. Mg/m^3	1.599
$\lambda(M_0\text{-}K\alpha)$/Å	0.71073
R	0.0372
Rw	0.1466
GOF	1.001
Largest diff. Peak	0.507 eA^{-3}
Largest diff. Hole	-0.581 eA^{-3}
Crystal size(mm)	0.20x 0.18 x 0.15 mm

Table S5. Selected bond lengths (Å) of the complex **2Zn**

Zn(1)-O(1W)	2.062(4)	C(13)-H(13)	0.93
Zn(1)-O(4)	2.099(4)	C(14)-N(2)	1.278(6)
Zn(1)-O(1)#1	2.102(4)	C(14)-C(15)	1.467(7)
Zn(1)-N(4)#2	2.147(4)	C(15)-H(15A)	0.96
Zn(1)-O(2)	2.153(4)	C(15)-H(15B)	0.96
Zn(1)-N(1)	2.175(4)	C(15)-H(15C)	0.96
C(1)-O(2)	1.243(4)	C(16)-N(3)	1.272(6)
C(1)-O(1)	1.261(4)	C(16)-C(18)	1.480(5)
C(1)-C(2)	1.514(5)	C(16)-C(17)	1.483(6)
C(2)-C(7)	1.379(5)	C(17)-H(17A)	0.96
C(2)-C(3)	1.405(5)	C(17)-H(17B)	0.96
C(3)-C(4)	1.402(5)	C(17)-H(17C)	0.96
C(3)-C(8)	1.514(5)	C(18)-C(22)	1.378(6)
C(4)-C(5)	1.373(6)	C(18)-C(19)	1.381(6)
C(4)-N(5)	1.474(5)	C(19)-C(20)	1.373(6)
C(5)-C(6)	1.377(6)	C(19)-H(19)	0.93
C(5)-H(5)	0.93	C(20)-N(4)	1.315(5)
C(6)-C(7)	1.388(6)	C(20)-H(20)	0.93
C(6)-H(6)	0.93	C(21)-N(4)	1.349(5)
C(7)-H(7)	0.93	C(21)-C(22)	1.366(6)
C(8)-O(3)	1.226(5)	C(21)-H(21)	0.93
C(8)-O(4)	1.260(5)	C(22)-H(22)	0.93
C(9)-N(1)	1.344(5)	N(2)-N(3)	1.383(5)
C(9)-C(10)	1.366(6)	N(4)-Zn(1)#3	2.147(4)
C(9)-H(9)	0.93	N(5)-O(5)	1.205(5)
C(10)-C(11)	1.381(6)	N(5)-O(6)	1.222(5)
C(10)-H(10)	0.93	O(1)-Zn(1)#4	2.102(4)
C(11)-C(12)	1.399(6)	O(1W)-H(1WA)	0.8468
C(11)-C(14)	1.486(6)	O(1W)-H(1WB)	0.8535
C(12)-C(13)	1.384(6)	O(2W)-H(2WA)	0.8501
C(12)-H(12)	0.93	O(2W)-H(2WB)	0.85
C(13)-N(1)	1.316(5)		

Table S6. Selected bond angles (°) of the complex **2Zn**

O(1W)-Zn(1)-O(4)	92.15(12)	C(12)-C(13)-H(13)	118.6
O(1W)-Zn(1)-O(1)#1	98.86(10)	N(2)-C(14)-C(15)	123.5(4)
O(4)-Zn(1)-O(1)#1	168.81(10)	N(2)-C(14)-C(11)	116.7(4)
O(1W)-Zn(1)-N(4)#2	95.88(12)	C(15)-C(14)-C(11)	119.8(4)
O(4)-Zn(1)-N(4)#2	91.90(18)	C(14)-C(15)-H(15A)	109.5
O(1)#1-Zn(1)-N(4)#2	84.97(18)	C(14)-C(15)-H(15B)	109.5
O(1W)-Zn(1)-O(2)	176.05(10)	H(15A)-C(15)-H(15B)	109.5

O(4)-Zn(1)-O(2)	88.81(11)	C(14)-C(15)-H(15C)	109.5
O(1)#1-Zn(1)-O(2)	80.35(10)	H(15A)-C(15)-H(15C)	109.5
N(4)#2-Zn(1)-O(2)	87.92(12)	H(15B)-C(15)-H(15C)	109.5
O(1W)-Zn(1)-N(1)	87.50(11)	N(3)-C(16)-C(18)	116.0(4)
O(4)-Zn(1)-N(1)	86.17(18)	N(3)-C(16)-C(17)	124.1(4)
O(1)#1-Zn(1)-N(1)	96.30(18)	C(18)-C(16)-C(17)	119.9(4)
N(4)#2-Zn(1)-N(1)	176.18(11)	C(16)-C(17)-H(17A)	109.5
O(2)-Zn(1)-N(1)	88.74(11)	C(16)-C(17)-H(17B)	109.5
O(2)-C(1)-O(1)	124.0(3)	H(17A)-C(17)-H(17B)	109.5
O(2)-C(1)-C(2)	119.3(3)	C(16)-C(17)-H(17C)	109.5
O(1)-C(1)-C(2)	116.5(3)	H(17A)-C(17)-H(17C)	109.5
C(7)-C(2)-C(3)	120.8(3)	H(17B)-C(17)-H(17C)	109.5
C(7)-C(2)-C(1)	117.9(3)	C(22)-C(18)-C(19)	117.4(4)
C(3)-C(2)-C(1)	121.2(3)	C(22)-C(18)-C(16)	120.3(4)
C(4)-C(3)-C(2)	115.7(3)	C(19)-C(18)-C(16)	122.3(4)
C(4)-C(3)-C(8)	123.2(3)	C(20)-C(19)-C(18)	119.5(4)
C(2)-C(3)-C(8)	121.0(3)	C(20)-C(19)-H(19)	120.3
C(5)-C(4)-C(3)	123.9(3)	C(18)-C(19)-H(19)	120.3
C(5)-C(4)-N(5)	116.9(3)	N(4)-C(20)-C(19)	123.8(4)
C(3)-C(4)-N(5)	119.2(3)	N(4)-C(20)-H(20)	118.1
C(4)-C(5)-C(6)	118.8(4)	C(19)-C(20)-H(20)	118.1
C(4)-C(5)-H(5)	120.6	N(4)-C(21)-C(22)	123.6(4)
C(6)-C(5)-H(5)	120.6	N(4)-C(21)-H(21)	118.2
C(5)-C(6)-C(7)	119.4(4)	C(22)-C(21)-H(21)	118.2
C(5)-C(6)-H(6)	120.3	C(21)-C(22)-C(18)	119.2(4)
C(7)-C(6)-H(6)	120.3	C(21)-C(22)-H(22)	120.4
C(2)-C(7)-C(6)	121.3(4)	C(18)-C(22)-H(22)	120.4
C(2)-C(7)-H(7)	119.4	C(13)-N(1)-C(9)	117.4(3)
C(6)-C(7)-H(7)	119.4	C(13)-N(1)-Zn(1)	123.7(3)
O(3)-C(8)-O(4)	126.9(4)	C(9)-N(1)-Zn(1)	116.5(3)
O(3)-C(8)-C(3)	114.9(4)	C(14)-N(2)-N(3)	115.8(4)
O(4)-C(8)-C(3)	118.2(3)	C(16)-N(3)-N(2)	118.4(4)
N(1)-C(9)-C(10)	123.9(4)	C(20)-N(4)-C(21)	116.4(3)
N(1)-C(9)-H(9)	118	C(20)-N(4)-Zn(1)#3	124.2(3)
C(10)-C(9)-H(9)	118	C(21)-N(4)-Zn(1)#3	119.1(3)
C(9)-C(10)-C(11)	119.0(4)	O(5)-N(5)-O(6)	123.6(4)
C(9)-C(10)-H(10)	120.5	O(5)-N(5)-C(4)	118.5(3)
C(11)-C(10)-H(10)	120.5	O(6)-N(5)-C(4)	117.9(4)
C(10)-C(11)-C(12)	117.1(3)	C(1)-O(1)-Zn(1)#4	127.9(2)
C(10)-C(11)-C(14)	120.7(4)	C(1)-O(2)-Zn(1)	146.5(2)
C(12)-C(11)-C(14)	122.1(4)	C(8)-O(4)-Zn(1)	115.2(2)
C(13)-C(12)-C(11)	119.5(4)	Zn(1)-O(1W)-H(1WA)	109.5
C(13)-C(12)-H(12)	120.2	Zn(1)-O(1W)-H(1WB)	119
C(11)-C(12)-H(12)	120.2	H(1WA)-O(1W)-H(1WB)	126.5

N(1)-C(13)-C(12)	122.8(4)	H(2WA)-O(2W)-H(2WB)	107.8
N(1)-C(13)-H(13)	118.6		

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+1/2 #2 x-1,-y+1/2,z-1/2

#3 x+1,-y+1/2,z+1/2 #4 -x,y+1/2,-z+1/2

Table S7. Crystallographic data of the complex **3Zn**deposited in CCDC 1916894

Empirical formula	$C_{14}H_{19}N_2O_6Zn$
Formula weight	376.68
Space group	C2/c
T (K)	296(2)
a (Å)	17.23(3)
b (Å)	19.96(3)
c (Å)	9.432(15)
$\alpha°$	90
$\beta°$	105.708(18)
$\gamma°$	90
V (Å3)	3123(8)
Z	8
ρcal. Mg/m^3	1.602
$\lambda(M_0\text{-}K\alpha)$/Å	0.71073
R	0.0443
Rw	0.1178
GOF	1.162
Largest diff. Peak	1.078 eA^{-3}
Largest diff. Hole	-1.022 eA^{-3}
Crystal size(mm)	0.25x 0.23 x 0.15 mm

Table S8. Selected bond lengths (Å) of the complex **3Zn**

Zn(1)-O(1)	2.047(4)	C(7)-H(7B)	0.97
Zn(1)-N(1)	2.048(4)	C(8)-O(4)	1.245(6)
Zn(1)-O(4)#1	2.053(4)	C(8)-O(3)	1.258(6)
Zn(1)-O(2)#2	2.054(4)	C(9)-N(1)	1.344(5)
Zn(1)-O(3)#3	2.061(4)	C(9)-C(10)	1.402(6)
Zn(1)-Zn(1)#2	2.903(4)	C(9)-H(9)	0.93
C(1)-O(2)	1.238(5)	C(10)-C(11)	1.393(6)
C(1)-O(1)	1.266(5)	C(10)-C(14)	1.466(6)
C(1)-C(2)	1.548(6)	C(11)-C(12)	1.385(7)
C(2)-C(3)	1.531(6)	C(11)-H(11)	0.93
C(2)-C(7)	1.536(6)	C(12)-C(13)	1.380(7)
C(2)-H(2)	0.98	C(12)-H(12)	0.93
C(3)-C(4)	1.533(6)	C(13)-N(1)	1.356(6)
C(3)-H(3A)	0.97	C(13)-H(13)	0.93
C(3)-H(3B)	0.97	C(14)-N(2)	1.270(6)

C(4)-C(5)	1.528(6)	C(14)-H(14)	0.93
C(4)-H(4A)	0.97	N(2)-N(2)#4	1.422(7)
C(4)-H(4B)	0.97	O(2)-Zn(1)#2	2.054(4)
C(5)-C(8)	1.530(6)	O(3)-Zn(1)#3	2.061(4)
C(5)-C(6)	1.537(6)	O(4)-Zn(1)#5	2.053(4)
C(5)-H(5)	0.98	O(1W)-H(1WA)	0.8487
C(6)-C(7)	1.524(6)	O(1W)-H(1WB)	0.849
C(6)-H(6A)	0.97	O(2W)-O(2W)#6	1.75(3)
C(6)-H(6B)	0.97	O(2W)-H(2WB)	0.85
C(7)-H(7A)	0.97	O(2W)-H(2WA)	0.85

Table S9. Selected bond angles (°) of the complex **3Zn**

O(1)-Zn(1)-N(1)	100.13(13)	C(5)-C(6)-H(6A)	109.5
O(1)-Zn(1)-O(4)#1	88.97(17)	C(7)-C(6)-H(6B)	109.5
N(1)-Zn(1)-O(4)#1	99.44(15)	C(5)-C(6)-H(6B)	109.5
O(1)-Zn(1)-O(2)#2	160.91(13)	H(6A)-C(6)-H(6B)	108.1
N(1)-Zn(1)-O(2)#2	98.96(14)	C(6)-C(7)-C(2)	111.7(3)
O(4)#1-Zn(1)-O(2)#2	87.91(16)	C(6)-C(7)-H(7A)	109.3
O(1)-Zn(1)-O(3)#3	88.35(17)	C(2)-C(7)-H(7A)	109.3
N(1)-Zn(1)-O(3)#3	99.74(14)	C(6)-C(7)-H(7B)	109.3
O(4)#1-Zn(1)-O(3)#3	160.81(15)	C(2)-C(7)-H(7B)	109.3
O(2)#2-Zn(1)-O(3)#3	88.44(16)	H(7A)-C(7)-H(7B)	107.9
O(1)-Zn(1)-Zn(1)#2	80.78(9)	O(4)-C(8)-O(3)	124.8(4)
N(1)-Zn(1)-Zn(1)#2	178.73(9)	O(4)-C(8)-C(5)	118.4(4)
O(4)#1-Zn(1)-Zn(1)#2	79.67(12)	O(3)-C(8)-C(5)	116.8(4)
O(2)#2-Zn(1)-Zn(1)#2	80.14(11)	N(1)-C(9)-C(10)	122.4(4)
O(3)#3-Zn(1)-Zn(1)#2	81.15(10)	N(1)-C(9)-H(9)	118.8
O(2)-C(1)-O(1)	125.2(4)	C(10)-C(9)-H(9)	118.8
O(2)-C(1)-C(2)	118.8(4)	C(11)-C(10)-C(9)	117.7(4)
O(1)-C(1)-C(2)	116.0(4)	C(11)-C(10)-C(14)	121.0(4)
C(3)-C(2)-C(7)	110.8(3)	C(9)-C(10)-C(14)	121.3(4)
C(3)-C(2)-C(1)	113.3(4)	C(12)-C(11)-C(10)	120.2(4)
C(7)-C(2)-C(1)	111.3(3)	C(12)-C(11)-H(11)	119.9
C(3)-C(2)-H(2)	107	C(10)-C(11)-H(11)	119.9
C(7)-C(2)-H(2)	107	C(13)-C(12)-C(11)	118.6(4)
C(1)-C(2)-H(2)	107	C(13)-C(12)-H(12)	120.7
C(2)-C(3)-C(4)	113.4(3)	C(11)-C(12)-H(12)	120.7
C(2)-C(3)-H(3A)	108.9	N(1)-C(13)-C(12)	122.4(4)
C(4)-C(3)-H(3A)	108.9	N(1)-C(13)-H(13)	118.8
C(2)-C(3)-H(3B)	108.9	C(12)-C(13)-H(13)	118.8
C(4)-C(3)-H(3B)	108.9	N(2)-C(14)-C(10)	121.6(4)
H(3A)-C(3)-H(3B)	107.7	N(2)-C(14)-H(14)	119.2

C(5)-C(4)-C(3)	111.9(4)	C(10)-C(14)-H(14)	119.2
C(5)-C(4)-H(4A)	109.2	C(9)-N(1)-C(13)	118.6(4)
C(3)-C(4)-H(4A)	109.2	C(9)-N(1)-Zn(1)	120.6(3)
C(5)-C(4)-H(4B)	109.2	C(13)-N(1)-Zn(1)	120.7(3)
C(3)-C(4)-H(4B)	109.2	C(14)-N(2)-N(2)#4	111.8(5)
H(4A)-C(4)-H(4B)	107.9	C(1)-O(1)-Zn(1)	126.3(3)
C(4)-C(5)-C(8)	114.2(4)	C(1)-O(2)-Zn(1)#2	127.4(3)
C(4)-C(5)-C(6)	109.4(3)	C(8)-O(3)-Zn(1)#3	125.9(3)
C(8)-C(5)-C(6)	112.0(3)	C(8)-O(4)-Zn(1)#5	128.5(3)
C(4)-C(5)-H(5)	106.9	H(1WA)-O(1W)-H(1WB)	44.2
C(8)-C(5)-H(5)	106.9	O(2W)#6-O(2W)-H(2WB)	109.1
C(6)-C(5)-H(5)	106.9	O(2W)#6-O(2W)-H(2WA)	62.8
C(7)-C(6)-C(5)	110.6(3)	H(2WB)-O(2W)-H(2WA)	76
C(7)-C(6)-H(6A)	109.5		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z-1/2 #2 -x+1/2,-y+1/2,-z+1

#3 -x+1,y,-z+3/2 #4 -x,-y+1,-z #5 x+1/2,-y+1/2,z+1/2

#6 -x+1,y,-z+1/2

[S1]. D. K. Maity, B. Bhattacharya, R. Mondal and D. Ghoshal, *Crystengcomm*, 2014, **16**, 8896-8909.

[S2]. M. Joharian and A. Morsali, *J. Solid State Chem.*, 2019, **270**, 135-146.

[S3]. C. M. Nagaraja and B. Ugale, *Polyhedron*, 2018, **155**, 433-440.