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Supplementary information

Nanosheets-assembled microflowers-like coordination polymers by surfactant-assisted assembly with enhanced catalytic activity

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1. Experimental Section

1.1 Materials and Physical Measurements. All the reagents were commercially available without further purification. The C, H, and N contents were determined by the FLASH EA 1112 elemental analyzer. Powder X-ray diffraction (PXRD) was recorded by the PANalyticalX'Pert PRO diffractometer on monochromated with Cu Kα_1 (λ = 1.5418 Å). The FT-IR spectra have been executed in 400-4000 cm^{-1} region with KBr tablets on the Bruker-ALPHA spectrophotometer. Thermal analyse (TGA) was recorded by the Netzsch STA 449C thermal analyzer at a heating rate of 10 °C·min^{-1} in air. NMR spectra were collected by Bruker Avance-400 spectrometers. A Cary 500 spectrophotometer equipped with a 110 nm diameter integrating sphere was used for collecting diffuse reflectivity spectra of the samples from 200 to 1200 nm. In the measurement process, $BaSO_4$ was selected as a standard with 100 % reflectance. The morphologies and sizes of the samples were observed by using Zeiss Merlin Compact field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. The adsorption and desorption measurements for the samples were measured on a Micromeritics ASAP2460 at 77 K after activating under vacuum at the optimized temperature for 24 h.

1.2 Characterizations for ligand 2,6-di(1H,2'H-[3,3'-bi(1,2,4-triazol)]-5'-yl)pyridine (H_4DBTP) and syntheses of 1 and 2 with and without CTAB

Characterizations for H_4DBTP: Elemental analysis calcd for $C_{13}H_9N_{13}$: C, 44.96 %; H, 2.61 %; N, 52.43 %. Found: C, 44.83 %; H, 2.69 %; N, 52.54 %. ^{1}H NMR (400 MHz, d$_6$-DMSO) δ: 14.69 (m, 2H), 8.72 (m, 1H), 8.22 (m, 2H).

Synthesis of [Cd_2(DBTP)·$2H_2O$]$_n$ (1). $Cd(NO_3)_2\cdot4H_2O$ (0.046 g, 0.15 mmol), H_4DBTP (0.017 g, 0.05 mmol), Dimethylamine (Me_2NH, 3 mL), acetonitrile (MeCN, 2 mL), N,N-Dimethylformamide (DMF, 3 mL) was placed in a 25 mL Teflon-lined stainless steel container, heated under 165 °C for 3 days, and cooled to ambient temperature at a rate of 5 °C/h. 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^{-1}): 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_2(DBTP)(H_2O)]·$2.5H_2O$}$_n$ (2). $ZnSO_4\cdot7H_2O$ (0.057 g, 0.2 mmol), H_4DBTP

(0.035 g, 0.1 mmol), H_2O (3 mL), MeCN (3 mL), DMF (3 mL) was placed in a 25 mL Teflon-lined stainless steel container, heated under 165 °C for 3 days, and cooled to ambient temperature at a rate of 5 °C/h. Colorless samples of **2** were achieved (yield, 62%, based on Zn). Elemental analysis calcd for $C_{13}H_{12}Zn_2N_{13}O_{3.5}$: C, 29.07 %; H, 2.25 %; N, 33.90 %. Found: C, 29.11 %; H, 2.28 %; N, 33.73 %. IR (KBr, cm^{-1}): 3401 (s), 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 microflowers-like spheres 1a with 0.10 g CTAB. $Cd(NO_3)_2 \cdot 4H_2O$ (0.046 g, 0.15 mmol), CTAB (0.10 g) were mixed in MeCN (2 mL) and sonicated for 30 min, followed by the addition of the solution of H_4DBTP (0.017 g, 0.05 mmol) in DMF (3 mL) and Me_2NH (3 mL). The resulting solution was further sonicated for another 30 min and then transferred into Teflon-lined autoclaves for solovothermal synthesis at 165 °C for three days. After cooling to room temperature, the particles were collected by centrifugation, washed with deionized water and ethanol for three times, respectively, and dried in vacuum at 60 °C overnight. Elemental analysis calcd for $C_{13}H_9Cd_2O_2N_{13}$: C, 25.85 %; H, 1.50 %; N, 30.14 %. Found: C, 25.95 %; H, 1.54 %; N, 29.91 %. IR (KBr, cm^{-1}): 3343 (s), 3077 (m), 2172 (vw), 2054 (w), 1607 (s), 1568 (s), 1433 (vs), 1185 (vs), 1071 (s), 821 (s), 788 (m), 750 (w), 723 (vw).

Syntheses of microflowers-like spheres 2a with 0.15 g CTAB. $ZnSO_4 \cdot 7H_2O$ (0.057 g, 0.2 mmol), CTAB (0.15 g) were mixed in H_2O (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 solovothermal synthesis at 165 °C for three days. After cooling to room temperature, the particles were collected by centrifugation, washed with deionized water and ethanol for three times, respectively, and dried in vacuum at 60 °C overnight. Elemental analysis calcd for $C_{13}H_{12}Zn_2N_{13}O_{3.5}$: C, 29.07 %; H, 2.25 %; N, 33.90 %. Found: C, 28.92 %; H, 2.32 %; N, 33.63 %. IR (KBr, cm^{-1}): 3409 (s), 2164 (vw), 1668 (vs), 1618 (vs), 1572 (s), 1438 (s), 1186 (s), 1046 (w), 820 (m), 799 (s), 750 (m), 725 (w).

1.3 The procedure for conversion of nitrobenzyl compounds into benzolic acids catalyzed by the nanosized 2a. The synthesis of benzolic acids from nitrobenzyl compounds was conducted using 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) were dispersed in water (10 mL). The resulting mixture was stirred at 80 °C and monitored by TLC. After the reaction finished, the temperature was cooled down to room temperature and acidified with 2 M HCl. The acidic solution was extracted by dichloromethane, and then the organic phase was collected and washed with a saturated solution of sodium bicarbonate. The organic layers were collected and dichloromethane was removed under reduced pressure.

1.4 Single-crystal structure determination.

Single-crystal X-ray diffraction (SCXRD) data of complex **1**-**2** was 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, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All calculations were carried out with the SHELXTL[1] program. Crystal data, data collection, and structure refinement details are summarized in Table S1. H atoms on C atoms were established with calculated positions (C-H = 0.93 Å or benzene and triazole rings) and refined with a riding model ($U_{iso}(H) = 1.2\ U_{eq}(C)$). The H atoms of water molecules were placed in a difference map. All H atoms were refined as riding on the parent atom.

2. Supplementary Figures

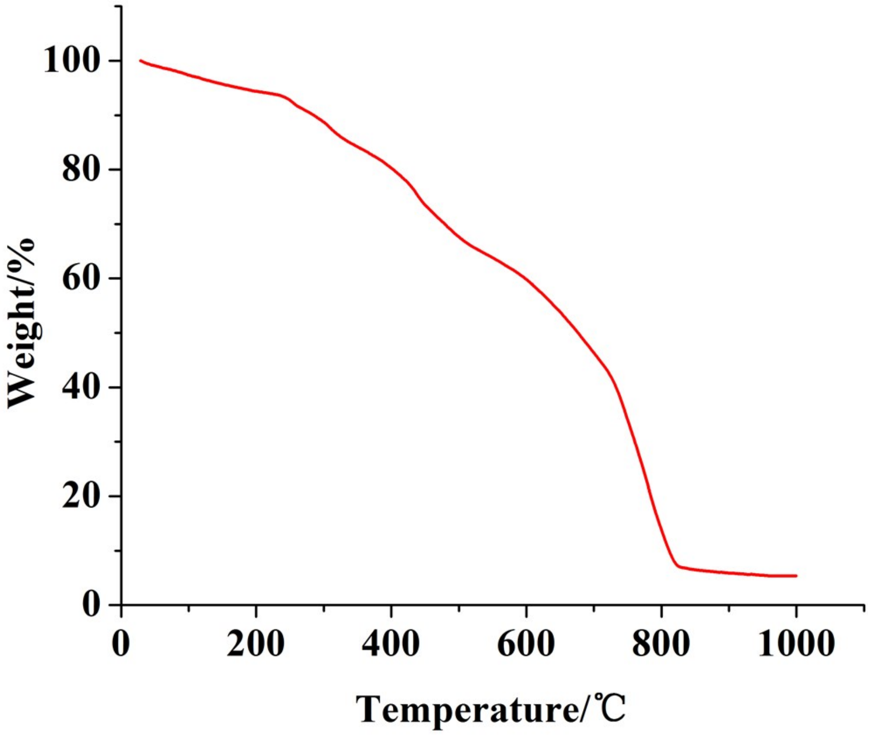


Fig. S1. TGA curve of **1**.

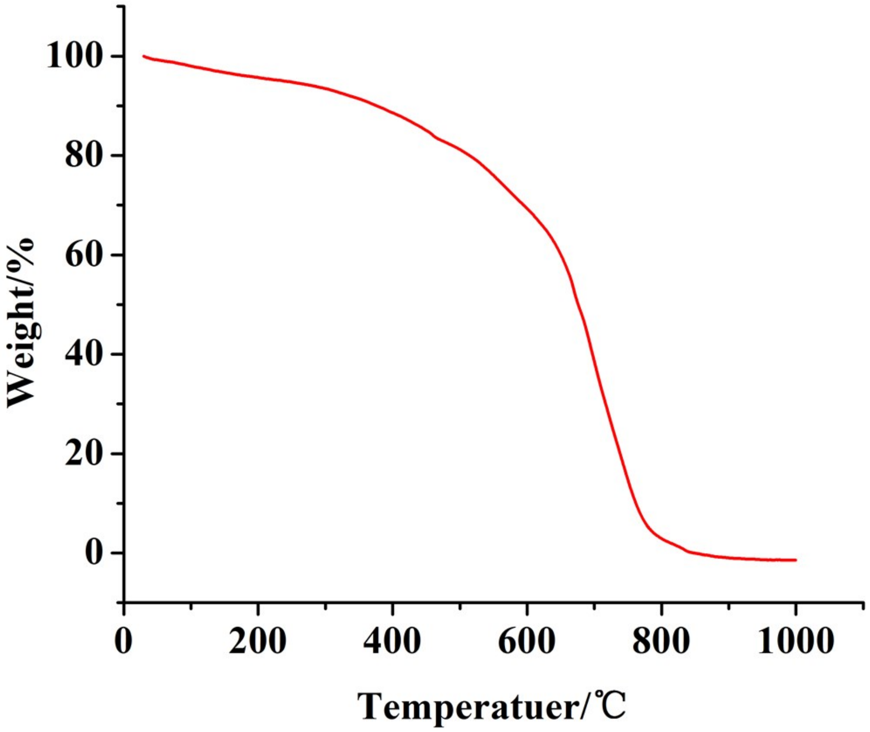


Fig. S2. TGA curve of **2**.

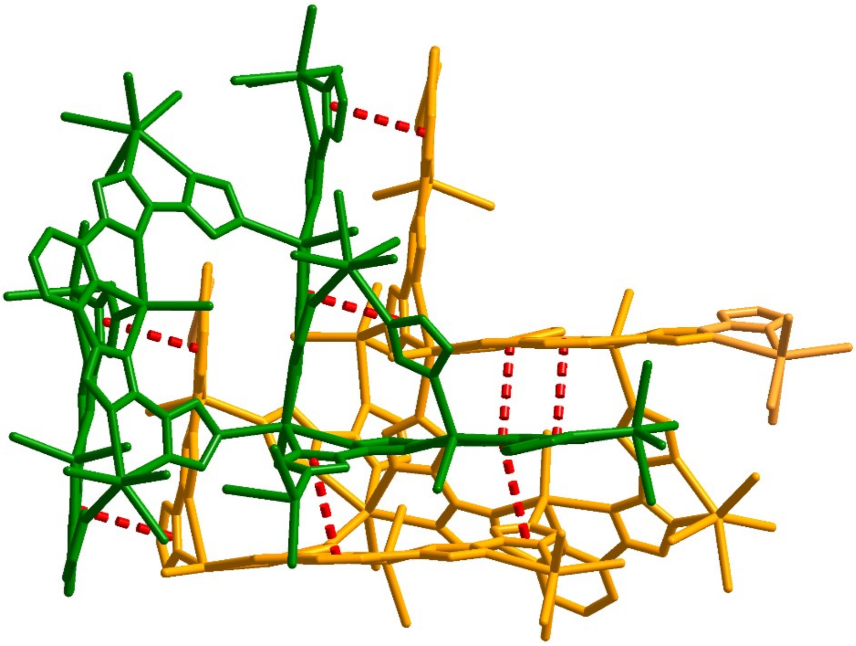


Fig. S3. The π···π interactions between the 2D layers of **1**.

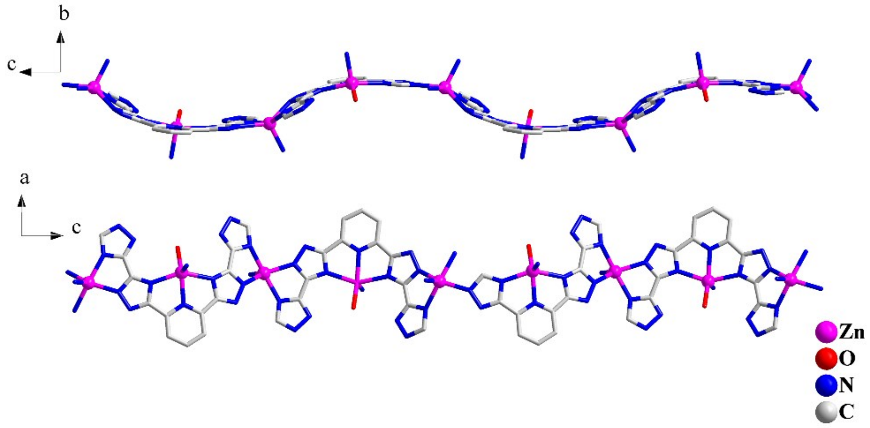


Fig. S4. The 1D wave-like chain of **2** viewed along *a* (top) and *b* (down) axis.

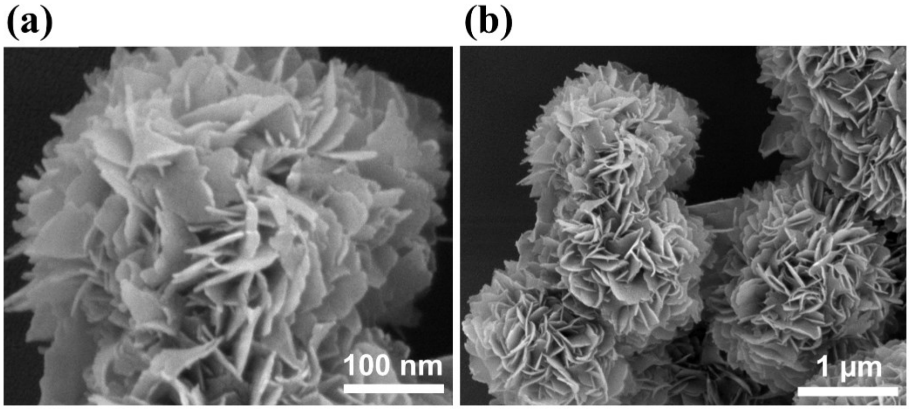


Fig. S5. SEM images for **1** prepared with 0.15 g PVP in different magnifications.

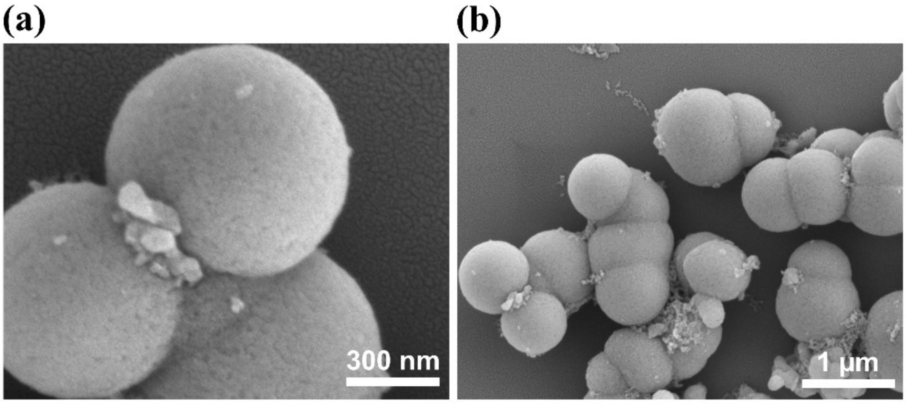


Fig. S6. SEM images for **2** with 0.15 g PVP in different magnifications.

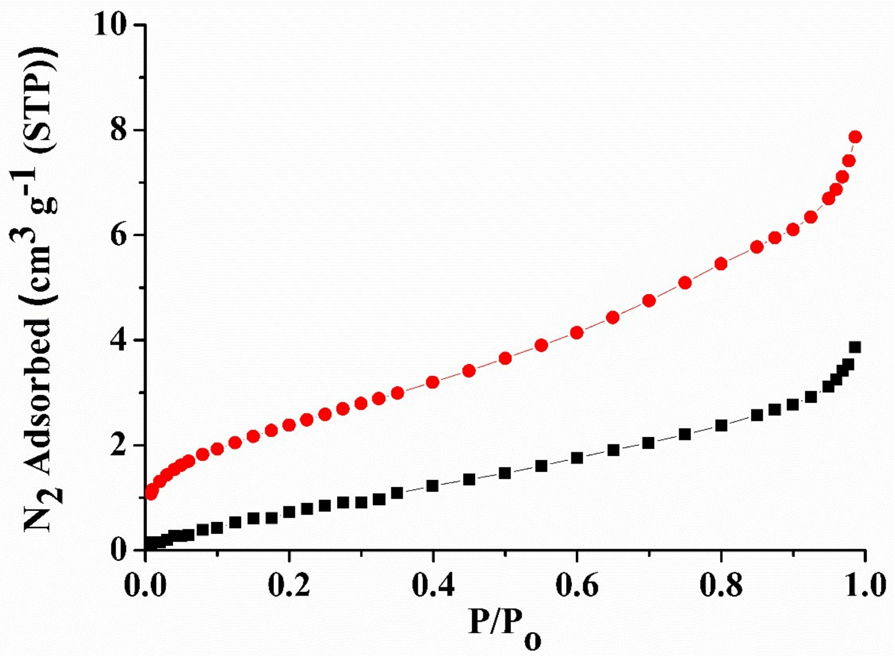


Fig. S7. N_2 adsorption isotherms of **1** samples prepared with 0.10 g CTAB (red line) and without CTAB (black line).

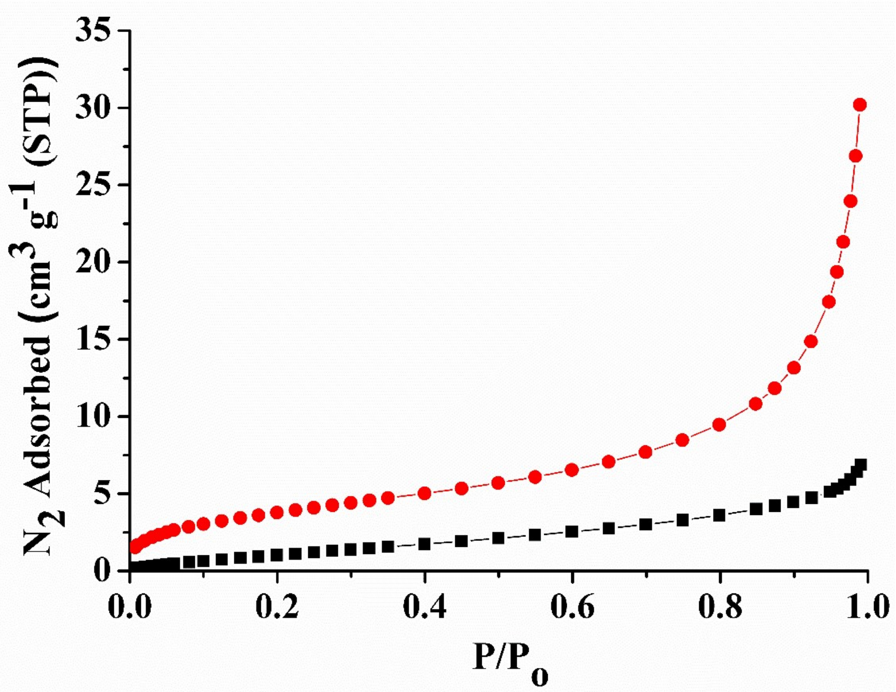


Fig. S8. N_2 adsorption isotherms of **2** samples prepared with 0.15 g CTAB (red line) and without CTAB (black line).

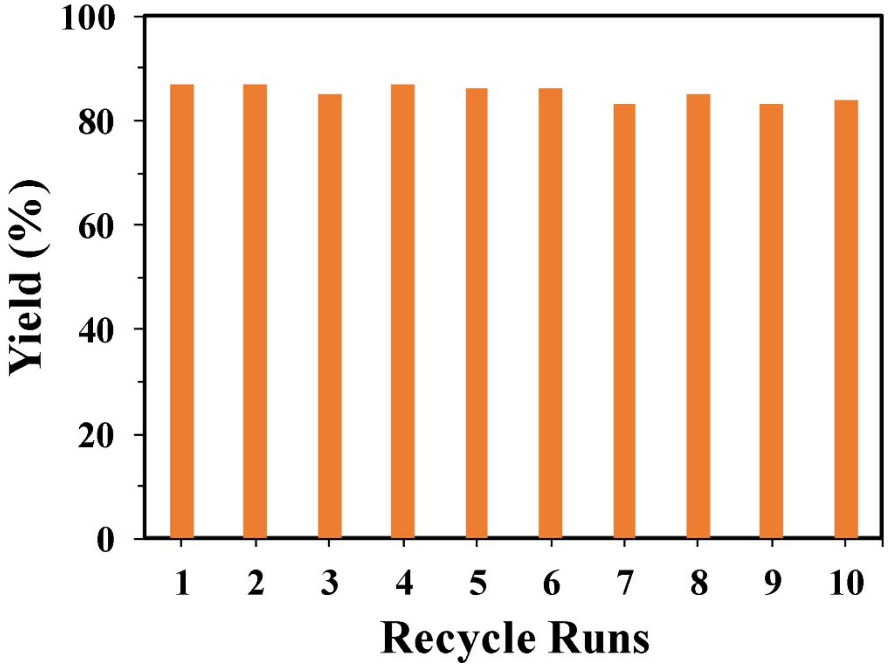


Fig. S9. Recycle results for nanoscale **2a** catalyzed the conversion of nitromethylbenzene into benzoic acid.

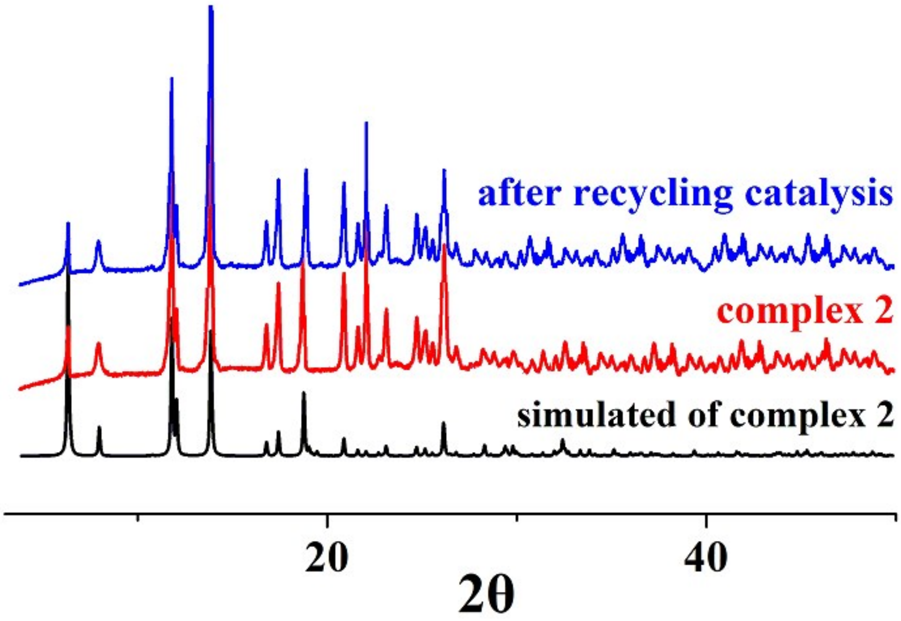


Fig. S10. PXRD and the corresponding simulated patterns for nanoscale **2a** after recycling catalysis.

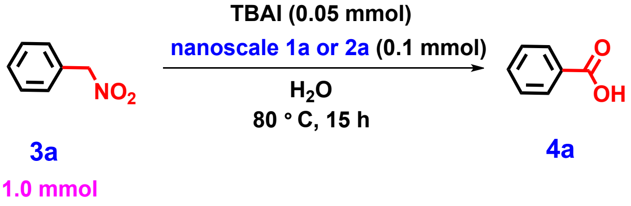
3. Supplementary Tables

Table S1. Crystallographic data and structure refinement parameters for complex **1** and **2**.

Complex	**1**	**2**
empirical formula	$C_{13}H_9Cd_2N_{13}O_2$	$C_{13}H_{12}Zn_2N_{13}O_{3.5}$
T[K]	273	273
M_r	604.13	537.10
crystal size [mm^3]	0.11 × 0.09 × 0.07	0.12 × 0.09 × 0.06
Cystal system	Orthorhombic	Tetragonal
space group	Pbca	I-4
a (Å)	16.8773(5)	13.8461(3)
b (Å)	10.5015 (3)	13.8461(3)
c (Å)	19.9631 (7)	23.3810(10)
α [°]	90	90
β (°)	90	90
γ [°]	90	90
V [Å^3]	3538.20(19)	4482.5(3)
Z	8	8
ρ_{calc} [g cm^{-3}]	2.268	1.592
μ [mm^{-1}]	2.450	2.185
F(000)	2320	2152
θ range [°]	2.502-27.544	2.714-25.499
limiting indices	$-21 \leq h \leq 21$	$-16 \leq h \leq 16$
	$-13 \leq k \leq 13$	$-16 \leq k \leq 16$
	$-25 \leq l \leq 24$	$-28 \leq l \leq 28$
collected reflns	78314	50639
unique reflns	4067	4166
max./min. transmission	0.687, 0.746	0.686, 0.743
data/restraints/parameters	4067/3/279	4166/6/268
goodness of fit	1.052	1.038
R_1/wR_2 [I >2σ(I)][a]	0.0364/0.1100	0.0829/ 0.2219
R_1/wR_2 (all data)[a]	0.0439/0.1148	0.0836/ 0.2240

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2=[\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2F_c^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S2. Optimization of reaction conditions for the conversion of nitromethylbenzene into benzoic acid[a].



Entry	Catalysts	Catalyst loading (mol%)	Temperature/ºC	Yield (%) **4a**[b]
1	**1a**	5	25	< 10
2	**1a**	5	80	31
3	**1a**	5	110	33
4	**1a**	10	25	< 10
5	**1a**	10	80	41
6	**1a**	10	110	43
7	**1a**	15	25	< 10
8	**1a**	15	80	42
9	**1a** **2a**	15	80	42[c] 89[c]
10	$Zn(OTf)_2$	10	80	34
11	H_4DBTP	10	80	n.o.[d]
12	$Zn(OTf)_2/H_4DBTP$	10	80	39
13	**1** **2**	15	80	32 69
14	**1a**[e] **2a**[e]	15	80	43 88

[a] Reaction conditions: **3a** (1.0 mmol), TBAI (0.05 mmol), nanoscale catalyst **1** or **2** (0.1 mmol), H_2O (10 mL), 80 ºC (15 h). [b] Isolated yield of the product after 15 h. [c] Isolated yield of the product after 24 h. [d] Not observed = n.o. [e] Activated nanocrystals formed by heating at 250 °C.

4. References

1. (a) G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **A64**, 112-122; (b) G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Cryst.,* 2015, **C71**, 3-8.