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## **Supporting Information**

### Surfactant-assisted Assembly of Nanoscale Zinc Coordination Compounds to

### **Enhance Tandem Conversion Reactions in Water**

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**1. General Method.** 5,5'-(1H-imidazole-4,5-diyl)-bis-(2H-tetrazole) (H<sub>3</sub>idbt) was synthesized according to a modified procedure from the literature.<sup>1</sup> The reagents and solvents were commercially available and used as received without further purification. <sup>1</sup>H spectra were obtained with Bruker Avance-400 spectrometers. FT-IR spectra were recorded on a Bruker-ALPHA spectrophotometer with KBr pellets in 400-4000 cm<sup>-1</sup> region. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. X-ray photoelectron spectroscopy (XPS) determination was measured in an ESCALAB 250Xi-type instrument. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses were carried out on a Thermo Scientic ICP 6000 spectrometry. Powder X-ray diffraction (PXRD) patterns were recorded using Cu K $\alpha_1$ radiation on a PANalyticalX'Pert PRO diffractometer. Thermal analyses were performed on a Netzsch STA 449C thermal analyzer at a heating rate of 10 °C·min<sup>-1</sup> in air.

#### 2. Synthesis

Synthesis of H<sub>3</sub>idbt ligand. A mixture of 4,5-dicyanoimidazole (4.00 g, 34.0 mmol), NaN<sub>3</sub> (13.20 g, 204 mmol), and triethylamine hydrochloride (49.4 g, 204 mmol) in 180 mL of toluene and 60 mL of methanol was heated at reflux in a 500 mL round-bottom flask for 3 days. Upon cooling to room temperature, an aqueous solution of NaOH (1 M, 300 mL) was added, and the mixture was stirred for 1 h. The aqueous layer was treated with dilute HCl (1 M, 350 mL) until no further white precipitate formed. The precipitate was then collected by filtration, and dissolved in aqueous NaOH (1 M). The resulting clear, colorless solution was titrated with dilute HCl (1 M) until the pH of the solution was approximately 3. The ensuing white precipitate was washed copiously with distilled water (1000 mL) and dried in air to afford 7.06 g (94 %) of product. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$ : 8.28 (S, 1H). ESI-TOF/MS for C<sub>5</sub>H<sub>4</sub>N<sub>10</sub>: calcd. 204.06, found 203.35 [M-H]<sup>-</sup>.

**Synthesis of** {[ $Zn_3(idbt)_2(4,4'-dmbpy)_2$ ]· $H_2O$ }<sub>*n*</sub> (1). Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.030 g, 0.1 mmol), H<sub>3</sub>idbt (0.02 g, 0.1 mmol), 4,4'-dmbpy (4,4'-dmbpy = 4,4'-dimethyl-2,2'-bipyridine, 0.018g, 0.1 mmol), DMF (3 mL) and H<sub>2</sub>O (5 mL) were mixed and placed in a 25 mL a 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<sub>34</sub>H<sub>28</sub>Zn<sub>3</sub>N<sub>24</sub>O: C, 41.46 %; H, 2.87 %; N, 34.13 %. Found: C, 41.48 %; H, 2.85 %; N, 34.15 %. IR (KBr, cm<sup>-1</sup>): 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<sub>3</sub>(idbt)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O}**<sub>*n*</sub> (2). Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.030 g, 0.1 mmol), H<sub>3</sub>idbt (0.01 g, 0.05 mmol), NH<sub>3</sub>·H<sub>2</sub>O (4 mL) and EtOH (4 mL) were mixed and placed in a 25 mL a Teflon-lined autoclave. The mixture was heated at 180 °C for three days, and the colorless crystals of 2 were obtained with a yield of 54 % (based on Zn). Anal. calcd for C<sub>10</sub>H<sub>10</sub>Zn<sub>3</sub>N<sub>20</sub>O<sub>4</sub>: C, 17.91 %; H, 1.50 %; N, 41.78 %. Found: C, 17.93 %; H, 1.49 %; N, 41.76 %. IR (KBr, cm<sup>-1</sup>): 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  $Zn(NO_3)_2 \cdot 6H_2O$  (0.059 g, 0.2 mmol), poly(vinyl alcohol) (PVA, 1788, 0.150 g), and H<sub>2</sub>O (5 mL) was sonicated for 20 min. A solution of DMF (3 mL), H<sub>3</sub>idbt (0.04 g, 0.2 mmol) and 4,4'-dmbpy (0.036g, 0.2 mmol) was added to the mixture of PVA/H<sub>2</sub>O and sonicated for another 30 min. Then, the solution was transferred to Teflon-lined stainless-steel container to afford crystal

growth at 160 °C for three days. After cooling, the nanocrystals were achieved by centrifugation at 10000 rpm for 15 min. The nanocrystals of **1** were washed by sonication after being redispersed 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  $H_3idbt$  (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 10000 rpm for 15 min. The nanocrystals of **2** were washed by sonication after being re-dispersed in EtOH.

## **3.** Procedure for the nanosacale 1 and 2-catalyzed conversion of nitrobenzyl compounds into benzolic acids frameworks

To a solution of water (10 mL) charged with nitroalkane (1.0 mmol) and TBAI (0.05 mmol) 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 and acidified with 2 M HCl. The acidic solution was washed with dichloromethane. The organic phases were collected and washed with a saturated solution of sodium bicarbonate. The aqueous washes were acidified with HCl<sub>conc</sub> and washed with dichloromethane. The organic layers were collected and concentrated under reduced pressure



**Benzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (100.4 mg, 82% for nanosacle 1; 114.7 mg, 94% for nanosacle 2). This compound had been reported.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ: 13.02 (s, 1H), 7.99-8.02 (m, 2H), 7.62-7.67 (m, 1H), 7.51-7.55 (m, 2H).



**4-Methylbenzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (111.5 mg, 82 % for nanosacle 1; 127.8 mg, 94 % for nanosacle 2). This compound had been reported.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$ : 12.85 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H).



**4-Cyanobenzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (119.0 mg, 81 % for nanosacle 1; 136.7 mg, 93 % for nanosacle 2). This compound had been reported.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$ : 13.62 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H).



4-Chlorobenzoic acid: Following the general procedure described above, benzoic acid was obtained as a white

solid (124.8 mg, 80 % for nanosacle 1; 145.1 mg, 93 % for nanosacle 2). This compound had been reported.<sup>21</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$ : 13.27 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H).



**3-Methylbenzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (106.1 mg, 78 % for nanosacle 1; 115.9 mg, 92 % for nanosacle 2). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ: 12.91 (s, 1H), 7.75-7.78 (m, 2H), 7.37-7.45 (m, 2H), 2.37 (s, 3H).



**3-Chlorobenzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (120.1 mg, 77 % for nanosacle 1; 142.0 mg, 91 % for nanosacle 2). This compound had been reported.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ: 13.36 (s, 1H), 7.90-7.92 (m, 2H), 7.70-7.73 (m, 1H), 7.54-7.58 (m, 1H).



**3-Fluorobenzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (106.4 mg, 76 % for nanosacle 1; 127.4 mg, 91 % for nanosacle 2). This compound had been reported.<sup>21</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$ : 13.33 (s, 1H), 7.79-7.82 (m, 1H), 7.65-7.69 (m, 1H), 7.55-7.61 (m, 1H), 7.47-7.53 (m, 1H).



**2-Methylbenzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (99.3 mg, 76 % for nanosacle 1; 122.4 mg, 90 % for nanosacle 2). This compound had been reported.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$ : 12.81 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.43-7.47 (m, 1H), 7.27-7.31 (m, 2H), 2.51 (s, 3H).



**2,6-Difluorobenzoic acid**: Following the general procedure described above, benzoic acid was obtained as a white solid (112.2 mg, 71 % for nanosacle 1; 139.0 mg, 88 % for nanosacle 2). This compound had been reported.<sup>2 1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$ : 7.55-7.64 (m, 1H), 7.19-7.25 (m, 2H).

4. Crystal Data Collection and Refinement. The data for 1-2 were collected on a Rigaku Saturn 724 CCD diffractomer (Mo-K $\alpha$ ,  $\lambda = 0.71073$ ) at room temperature, respectively. Absorption corrections were applied by using numerical program. The detailed structures were solved by direct ways and refined by full-matrix least-squares on  $F^2$  with the SHELXL.<sup>3,4</sup> All hydrogen atoms expect for H<sub>2</sub>O molecule were placed at geometrically calculated positions, and refined by riding. There are large solvent accessible void volumes in the samples of **2** which are occupied by highly disordered free water molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove these electron densities.<sup>5</sup> The number of solvent molecules were obtained by element analyses and TGA. The crystal data of **1-2** are summarized in Table S1and S2. The crystal data have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference number 1943115 and 1944008, respectively.

1	2
$C_{34}H_{28}Zn_3N_{24}O$	$C_{10}H_{10}Zn_3N_{20}O_4$
984.91	670.49
293(2)	293(2)
0.71073	0.71073
Monoclinic	Monoclinic
$P2_l/n$	C2/c
15.061(3)	20.348(4)
18.967(4)	12.590(3)
17.270(4)	19.354(4)
107.86(3)	117.33(3)
4695.6(18)	4404.6(19)
4	8
1.393	2.022
22220 / 8720	16900 / 4106
3223078730	10809/4100
1.575	3.310
1992	2656
1.51-25.50	1.97-25.50
1.067	1.138
0.0588	0.0495
0.1176	0.0912
	$\frac{1}{C_{34}H_{28}Zn_3N_{24}O}$ 984.91 293(2) 0.71073 Monoclinic P21/n 15.061(3) 18.967(4) 17.270(4) 107.86(3) 4695.6(18) 4 1.393 32230 / 8730 1.575 1992 1.51-25.50 1.067 0.0588 0.1176

Table S1. Crystallographic data and structure refinement details for complexes 1-2<sup>*a,b*</sup>

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| \sum / |F_{o}|. {}^{b}wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$ 

Complex 1				
Zn1-N4#1	2.219(4)	Zn2-N16	2.002(4)	
Zn1-N5#1	2.119(4)	Zn2-N19	1.985(4)	
Zn1-N18	2.122(4)	Zn3-N6	2.058(4)	
Zn1-N22	2.225(4)	Zn3-N10	2.307(4)	
Zn1-N23	2.167(4)	Zn3-N11	2.192(4)	
Zn1-N24	2.113(4)	Zn3-N12	2.118(4)	
Zn2-N1#2	2.005(4)	Zn3-N13	2.273(4)	
Zn2-N7#2	1.993(4)	Zn3-N17	2.125(4)	
N4#1-Zn1-N2#2	93.43(14)	N19-Zn2-N1#2	105.34(16)	
N5#1-Zn1-N4#1	78.13(14)	N19-Zn2-N7#2	117.79(16)	
N5#1-Zn1-N18	93.76(14)	N19-Zn2-N16	106.17(15)	
N5#1-Zn1-N22	90.97(15)	N6-Zn3-N10	76.93(14)	
N5#1-Zn1-N23	93.13(15)	N6-Zn3-N11	97.71(15)	
N18-Zn1-N4#1	167.70(14)	N6-Zn3-N12	165.79(15)	
N18-Zn1-N22	77.32(14)	N6-Zn3-N13	96.28(15)	
N18-Zn1-N23	93.48(14)	N6-Zn3-N17	95.62(14)	
N23-Zn1-N4#1	96.16(14)	N11-Zn3-N10	104.53(15)	
N23-Zn1-N22	170.17(14)	N11-Zn3-N13	158.43(14)	
N24-Zn1-N4#1	98.50(14)	N12-Zn3-N10	92.49(15)	
N24-Zn1-N5#1	168.81(14)	N12-Zn3-N11	75.54(16)	
N24-Zn1-N18	91.16(14)	N12-Zn3-N13	93.97(16)	
N24-Zn1-N22	99.92(15)	N12-Zn3-N17	96.34(15)	
N24-Zn1-N23	76.53(15)	N13-Zn3-N10	94.54(15)	
N7#2-Zn2-N12	104.94(15)	N17-Zn3-N10	167.67(15)	
N7#2-Zn2-N16	110.02(16)	N17-Zn3-N11	86.05(14)	
N16-Zn2-N1#2	112.65(16)	N17-Zn3-N13	76.33(14)	
Complex 2				

Table S2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1-2, and 2a

Zn1-O1	2.037(5)	Zn2-N17	1.999(3)
Zn1-N6	2.060(4)	Zn3-O2	2.002(5)
Zn1-N7	2.015(3)	Zn3-N2	2.119(4)
Zn1-N12#1	2.007(4)	Zn3-N10	2.134(4)
Zn2-O3	2.030(5)	Zn3-N11	2.153(4)
Zn2-N12	1.997(4)	Zn3-N20	2.110(3
Zn2-N16	2.101(4)	N17-Zn2-N16	99.00(14)
O1-Zn1-N6	97.8(2)	O2-Zn3-N2	102.95(17)
N7-Zn1-O1	111.6(2)	O2-Zn3-N10	110.67(17)
N7-Zn1-N6	99.21(14)	O2-Zn3-N11	104.29(17)
N12#1-Zn1-O1	111.63(19)	O2-Zn3-N20	108.32(17)
N12#1-Zn1-N6	101.20(15)	N2-Zn3-N10	76.93(14)
N12#1-Zn1-N7	128.59(16)	N2-Zn3-N11	152.69(16)
O3-Zn2-N16	100.2(2)	N10-Zn3-N11	95.14(14)
N1#2-Zn2-O3	106.9(2)	N20-Zn3-N2	92.95(14)
N1#2-Zn2-N16	101.24(15)	N20-Zn3-N10	140.98(16)
N1#2-Zn2-N17	130.39(16)		

Symmetry codes for 1: #1 = 2-x, 2-y, 1-z; #2 = 5/2-x, 1/2+y, 3/2-z. Symmetry codes for 2: #1 = x,-

y,1/2+z; #2 = x, 1-y, -1/2+z.





Figure S1. Crystal structure of 1: (a) The TG curve of 1. (b) A comparison of PXRD results of simulated, synthesized, and nanoscale crystals of 1. (c) Coordination environments of the  $Zn^{II}$  ions. Hydrogen atoms and water molecule are omitted for clarity.



**Figure S2**. Crystal structure of **2**: (a) Coordination environments of the Zn<sup>II</sup> ions. Hydrogen atoms and water molecule are omitted for clarity. (b) View of the 3D supermolecule framework through hydrogen bonding interactions. (c) A comparison of PXRD results of simulated, synthesized, and nanoscale crystals of **2**. (d) The TG curve of **2**.



**Figure S3**. (a) SEM images for the morphologies and particle sizes of **1** induced by PVA with various magnifications. (b) SEM images for the morphologies and particle sizes of **2** induced by PVA with various magnifications. (c) SEM images for the morphologies and particle sizes of **1** induced by PVA with concentrations of 0.05 g. (d) SEM images for the morphologies and particle sizes of **1** induced by PVA with concentrations of 0.10 g. (e) SEM images for the morphologies and particle sizes of **1** induced by PVA with concentrations of 0.20 g. (f) SEM images for the morphologies and particle sizes of **2** induced by PVA with concentrations of 0.05 g. (g) SEM images for the morphologies and particle sizes of **2** induced by PVA with concentrations of 0.05 g. (g) SEM images for the morphologies and particle sizes of **2** induced by PVA with concentrations of 0.10 g. (h) SEM images for the morphologies and particle sizes of **2** induced by PVA with concentrations of 0.10 g. (h) SEM images for the morphologies and particle sizes of **2** induced by PVA with concentrations of 0.10 g. (h) SEM images for the morphologies and particle sizes of **2** induced by PVA with concentrations of 0.20 g.



**Figure S4**. Crystal structure of **1**: (a) N<sub>2</sub> adsorption isotherm of nanoscale **1** at 77 K. (b) N<sub>2</sub> adsorption isotherm of nanoscale **2** at 77 K.

## 6. Optimization of reaction conditions for the conversion of nitromethylbenzene into benzoic acid<sup>[a]</sup>.

Table S3. Optimization of reaction conditions for the conversion of nitromethylbenzene into benzoic acid<sup>[a]</sup>.

TBAI (0.05 mmol)					
		H		УКон	
	3a	80 °C	C, 15h	4a	
	1.0 mmol				
Entry	Catalyst/mmol	Solvent	Temperature/°C	Yield (%) <b>4a</b> <sup>[b]</sup>	
1	<b>1</b> /0.1 mmol	. 1	00	53	
I	<b>2</b> /0.1 mmol	toluene	80	68	
2	<b>1</b> /0.1 mmol	H-O	80	82	
2	<b>2</b> /0.1 mmol	1120	00	94	
3	<b>1</b> /0.1 mmol	CH CN	80	59	
5	<b>2</b> /0.1 mmol	CHIJCH	00	71	
1	1/0.1 mmol	DMF	80	n.o. <sup>[c]</sup>	
4	<b>2</b> /0.1 mmol		00	n.o.	
5	1/0.1 mmol	FtOH	78	n.o.	
5	<b>2</b> /0.1 mmol	LIOII	70	n.o.	
6	1/0.1 mmol	CHCl <sub>3</sub>	62	n.o.	
-	<b>2</b> /0.1 mmol	5	-	n.o.	
7	<b>1</b> /0.1 mmol	H <sub>2</sub> O 25	25	< 10	
,	<b>2</b> /0.1 mmol		20	< 10	
8	<b>1</b> /0.1 mmol	H <sub>2</sub> O	110	85	
0	<b>2</b> /0.1 mmol		110	96	
9	<b>1</b> /0.1 mmol	ЦО	80	87 <sup>[d]</sup>	
)	<b>2</b> /0.1 mmol	1120	00	95 <sup>[d]</sup>	
10	1/0.01 mmol	H <sub>2</sub> O	80	51	
10	<b>2</b> /0.01 mmol			56	
11	1/0.05 mmol	$H_2O$	80	69	

	<b>2</b> /0.05 mmol			71
10	1/0.15 mmol	H <sub>2</sub> O	80	84
12	<b>2</b> /0.15 mmol		80	96
13	1/0.2 mmol	H <sub>2</sub> O	80	86
	<b>2</b> /0.2 mmol		80	97
14	Zn(OTf) <sub>2</sub> /0.1 mmol	H <sub>2</sub> O	80	36

<sup>a</sup>Reaction conditions: **3a-i** (1.0 mmol), TBAI (0.05 mmol), nanoscale catalysts **1** and **2** (0.1 mmol), H<sub>2</sub>O (10 mL), AcOH (60  $\mu$ L), 80 °C (15 h). <sup>b</sup>Isolated yield after 15 h. <sup>c</sup>Not observed = n.o. <sup>d</sup>Isolated yield of after 24 h.

# 7. Conversion of nitrobenzyl compounds into benzolic acids frameworks catalyzed by large size of 1-2, Zn(NO<sub>3</sub>)<sub>2</sub>/H<sub>3</sub>idbt and H<sub>3</sub>idbt in water.

Table S4. Conversion of nitrobenzyl compounds into benzolic acids frameworks catalyzed by large size of 1 and 2 under  $H_2O.a$ 



Entry	Catalysts/mmol	Nitrobenzyl	Yield % of <b>4a-i</b> <sup>b</sup>
1	<b>1</b> /0.1 mmol		56
2	<b>2</b> /0.1 mmol		67
3	$Zn(OTf)_2/H_3idbt/(0.$	Sa NO <sub>2</sub>	45
	I mmol/0.1 mmol)		
4	H <sub>3</sub> 1dbt/0.1 mmol		n.o. <sup>c</sup>
5	1/0.1 mmol		56
6	<b>2</b> /0.1 mmol		66
7	Zn(OTf) <sub>2</sub> /H <sub>3</sub> idbt/(0. 1 mmol/0.1 mmol)	3b	45
8	H <sub>3</sub> idbt/0.1 mmol		n.o.
9	<b>1</b> /0.1 mmol		54
10	<b>2</b> /0.1 mmol		63
11	Zn(OTf) <sub>2</sub> /H <sub>3</sub> idbt/(0.	NC-(-)-NO2	42
	1 mmol/0.1 mmol)	3c	43
12	H <sub>3</sub> idbt/0.1 mmol		n.o.
13	<b>1</b> /0.1 mmol		53
14	<b>2</b> /0.1 mmol		93
15	$Zn(OTf)_2/H_3idbt/(0.$ 1 mmol/0.1 mmol)	CI—∕NO₂ 3d	43
16	H <sub>3</sub> idbt/0.1 mmol		n.o.
17	<b>1</b> /0.1 mmol		53
18	<b>2</b> /0.1 mmol	Se NO2	63
10	Zn(OTf) <sub>2</sub> /H <sub>3</sub> idbt/(0.		42
19	1 mmol/0.1 mmol)		42
20	H <sub>3</sub> idbt/0.1 mmol		n.o.
21	<b>1</b> /0.1 mmol		51
22	<b>2</b> /0.1 mmol		62

22	$Zn(OTf)_2/H_3idbt/(0.$		39	
23	1 mmol/0.1 mmol)			
24	H <sub>3</sub> idbt/0.1 mmol		n.o.	
25	<b>1</b> /0.1 mmol		50	
26	<b>2</b> /0.1 mmol		59	
27	$Zn(OTf)_2/H_3idbt/(0.$	F NO <sub>2</sub>		26
27	1 mmol/0.1 mmol)	3g	30	
28	H <sub>3</sub> idbt/0.1 mmol		n.o.	
29	1/0.1 mmol		49	
30	<b>2</b> /0.1 mmol		57	
21	$Zn(OTf)_2/H_3idbt/(0.$	Sh NO₂	22	
51	1 mmol/0.1 mmol)		55	
32	H <sub>3</sub> idbt/0.1 mmol		n.o.	
33	<b>1</b> /0.1 mmol		45	
34	<b>2</b> /0.1 mmol	r, F	55	
25	$Zn(OTf)_2/H_3idbt/(0.$	F Si	21	
35	1 mmol/0.1 mmol)		3i	51
36	H <sub>3</sub> idbt/0.1 mmol		n.o.	

<sup>a</sup>Reaction conditions: **3a-i** (1.0 mmol), TBAI (0.05 mmol), large size of **1** and **2** (0.1 mmol) or  $Zn(NO_3)_2/H_3idbt$  (0.1 mmol/0.1 mmol) or  $H_3idbt$  (0.1 mmol),  $H_2O$  (10 mL), AcOH (60 µL) 80 °C (15 h). <sup>b</sup>Isolated yield after 15 h. <sup>c</sup>Not observed = n.o.

8. A plausible mechanism for the conversion of nitroalkanes into carboxylic acids.



Scheme S1. A plausible mechanism for the conversion of nitroalkanes into carboxylic acids.



**Figure S5**. (a) XPS spectrum of  $Zn^{II}$  ions in **1** during different reaction times (0, 7, and 15 h). (b) XPS spectrum of  $Zn^{II I}$  ions in **2** during different reaction times (0, 7, and 15 h). (c) The distinct characteristic absorption peak of NC group in FTIR spectrum changed on nanoscale **1** during the different reaction times (0, 8, and 15 h). (d) The distinct characteristic absorption peak of NC group in FTIR spectrum changed on nanoscale **2** during the different reaction times (0, 8, and 15 h).



### 9. Recycling test for conversion reactions with nanoscale 1 and 2.

Figure S6. (a) Recycling test for conversion reaction with nanoscale 1. (b) Recycling test for conversion reaction with nanoscale 2. (c) Comparison of the PXRD patterns of nanoscale 1 before and after catalysis. (d) Comparison of the PXRD patterns of nanoscale 2 before and after catalysis.



### 10. Spectral copies of MS and <sup>1</sup>H NMR of compounds obtained in this study.

















### 11. References

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