Electronic Supplementary Material (ESI)

Two new calix[4]resorcinarene-based coordination cages adjusted by metal ions for Knoevenagel condensation reaction

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Experimental section

Materials and methods.

All chemicals were purchased from commercial sources. A PerkinElmer TG-7 was used to determine thermogravimetric (TG) curves under nitrogen gas. PXRD patterns were conducted on a Rigaku Smart Lab X-ray diffractometer with graphite monochromatized CuK_α radiation (λ = 0.154 nm). C, H, and N elemental analyses were measured on a Euro Vector EA3000 CHN elemental analyzer. A Mattson Alpha-Centauri spectrometer was applied to record FT-IR spectra. ^{1}H NMR spectra were measured on a BRUKER AVANCE III HD 500 MHz. The field emission scanning electron microscope (FESEM, JEOLJSM-6700F field emission) was employed to record the morphologies of materials.

Synthesis of $[Zn_4(TPC4R)(PDC)_4]\cdot 2DMF\cdot 6H_2O$ (1-Zn).

The ligand tetra(2-(4H-pyrazol-3-yl)pyridine)calix[4]resorcinarene (**TPC4R**) was prepared with a method similar to the reported literature.[1,2] A mixture of **TPC4R** (10 mg, 0.008 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (15 mg, 0.05 mmol), H_2PDC (8 mg, 0.048 mmol), DMF (4 mL) and MeOH (4 mL) were placed into a Teflon reactor (15 mL) and kept at 100 ℃ for 1 day under autogenous pressure. Pale yellow crystals of **1-Zn** were achieved after naturally cooling the system to room temperature. The yield is 43% for **1-Zn** based on **TPC4R**. Element analysis (%) for $C_{106}H_{98}N_{18}O_{32}Zn_4$ (**1-Zn**): calculated C 53.10, H 4.12, N 10.52; found C 52.83, H 4.08, N 10.31. IR data (KBr, cm^{-1}): 450(w), 584(w), 646(w), 693(w), 741(m), 769(s), 921(m), 960(s), 986 (s), 1020(w), 1063(w), 1096(m), 1147(m), 1239(m), 1290(m), 1362(s), 1440(s), 1475(m), 1503(s), 1571(m), 1613(s), 2979(m), 3373(m).

Synthesis of $[In_{11}(TPC4R)_2(PDC)_{16}(\mu_2\text{-}OH)_2(H_2O)_2]\cdot[(CH_3)_2NH_2]\cdot 8DMF\cdot 20H_2O\cdot EtOH$ (2-In).

A mixture of **TPC4R** (10 mg, 0.008 mmol), $In(NO_3)_3\cdot 3H_2O$ (15 mg, 0.047 mmol) and H_2PDC (12 mg, 0.072 mmol) was added to a solution of DMF/EtOH (6 mL, 1/1, v/v) in a Teflon reactor (15 mL), to which 50 μL HCl aqueous solution (0.1 M) was added.

Then, the Teflon reactor were kept at 90 ℃ for 3 days. Yellow crystals of **2-In** were obtained after naturally cooling the system to room temperature. The yield is 21% for **2-In** based on **TPC4R**. Element analysis (%) for $C_{284}H_{282}N_{49}O_{113}In_{11}$ (**2-In**): calculated C 45.77, H 3.81, N 9.21; found C 45.36, H 3.82, N 9.08. IR data (KBr, cm^{-1}): 455(w), 584(w), 647(w), 660(w), 693(w), 739(w), 769(s), 854(w), 923(w), 961(m), 987(m), 1028(w), 1063(w), 1097(m), 1145(w), 1240(w), 1289(m), 1386(s), 1440(s), 1475(m), 1611(s), 1656(s), 2936(w).

X-ray crystallography.

Crystallographic data for **1-Zn** and **2-In** were determined on an Oxford diffraction Gemini R CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at room temperature. Crystal structures were solved by direct method and refined on F^2 by full-matrix least-squares using the *SHELXTL*-2018 program within WINGX.[3-5] All non-hydrogen atoms were found from the Fourier difference maps and refined anisotropically. Hydrogen atoms of the organic molecules were assigned geometrically. Highly disordered solvents were removed with the SQUEEZE routine in PLATON during the refinements of **1-Zn** and **2-In**.[6] Their formula units were established by diffuse electron density, the thermalgravimetric analysis and elemental analysis.

Catalytic experiments.

The samples of **1-Zn** and **2-In** were respectively soaked in methanol for 2 days and activated at 80 °C for 10 h under vacuum. The catalytic reactions were conducted in 15 mL pressure-tight tubes at 60 °C. The activated sample of **1-Zn** (7.0 μmol, 0.7%) or **2-In** (3.5 μmol, 0.35%) was added to the mixture of benzaldehyde derivatives (1.0 mmol) and malononitrile (2.0 mmol). The catalytic reaction times for **1-Zn** and **2-In** were 40 min and 60 min, respectively. After the catalytic reaction, 8 mL dichloromethane was added to the mixture and the catalyst was separated *via* filtration. Further, the catalyst was washed with methanol and dried at 80 ℃ for 10 h under vacuum for reuse. The catalytic yield was determined by GC or ^1H NMR.

References

1 Y.- J. Hu, J. Yang, Y. -Y. Liu, S. Y. Song and J.- F. Ma, *Cryst. Growth Des.*, 2015, **15**, 3822.

2 W.-Y. Pei, J. Yang, H. Wu, W. Zhou, Y.-W. Yang and J.-F. Ma, *Chem. Commun.*, 2020, **56**, 2491.

3 L. J. Farrugia, *WINGX: A Windows Program for Crystal Structure Analysis*; University of Glasgow: Glasgow, UK, 1988.

4 G. M. Sheldrick, *SHELXS-2018*, *Program for the crystal structure solution*; University of Göttingen: Göttingen, Germany, 2018.

5 G. M. Sheldrick, *SHELXL-2018*, *Program for the crystal structure refinement*; University of Göttingen: Göttingen, Germany, 2018.

6 A. L. Spek, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 9.

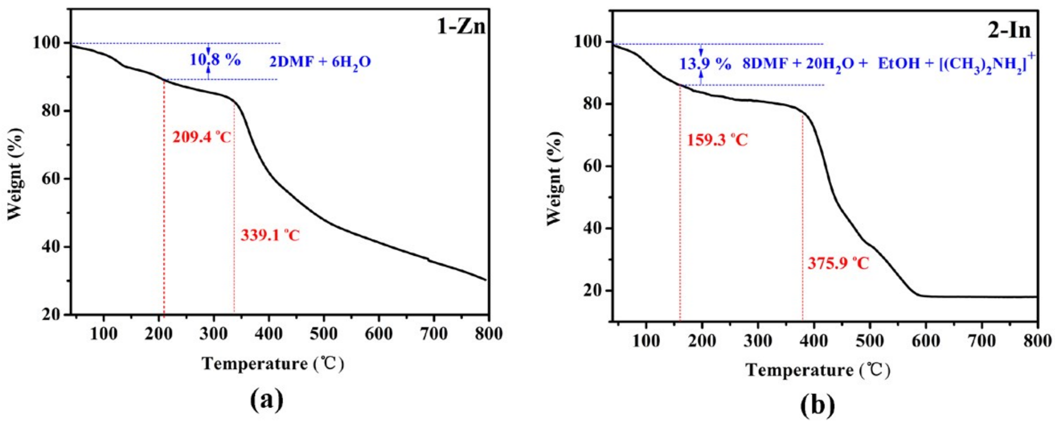


Fig. S1 TG curves for **1-Zn** and **2-In**.

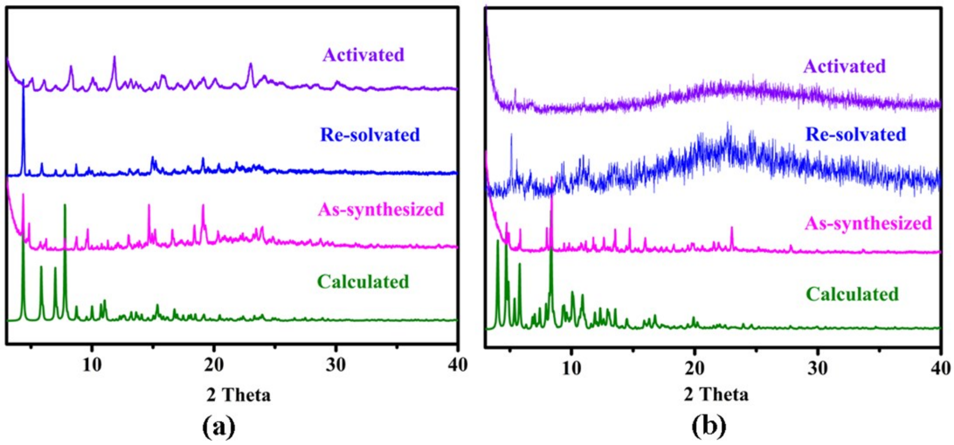


Fig. S2 PXRD patterns for **1-Zn (a)** and **2-In (b)**.

The 3D architectures of **1-Zn** and **2-In** are formed through non-coordinated intermolecular interactions, such as π-π interactions and hydrogen bonds. Therefore, the solvent molecules could play a key role in the structure construction. After losing partial solvents in the air, the supramolecular architectures may undergo the rotations, thus resulting in the changes of the as synthesized and the activated PXRD patterns (Fig. S2). Particularly, the peaks of the activated PXRD pattern of **1-Zn** moved to the high theta relative to the one of the as-synthesized sample. When the activated sample of **1-Zn** was soaked in the specific solvent (DMF: MeOH = 1:1/ DMF: EtOH = 1:1), the PXRD pattern of **1-Zn** can be recovered. While the sample of **2-In** is amorphous after activation.

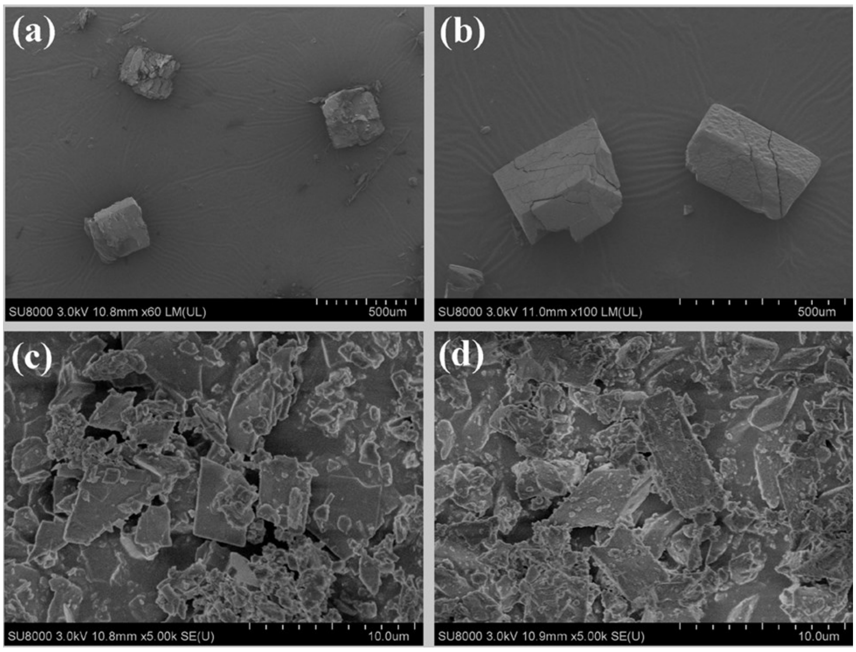
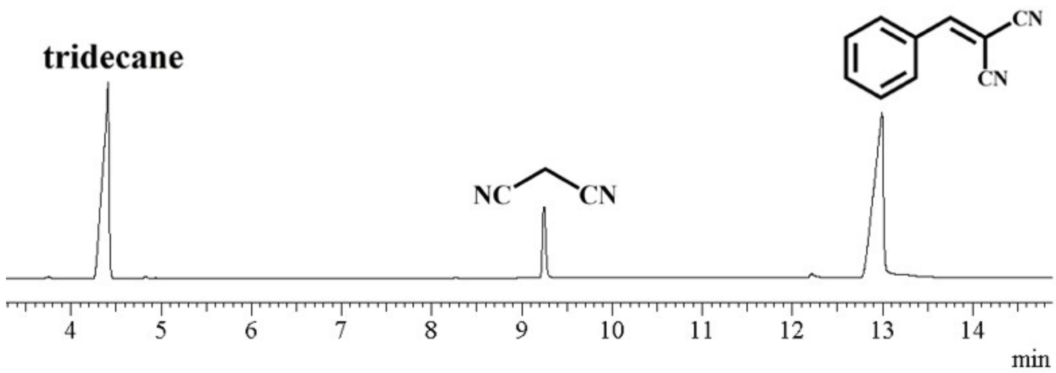


Fig. S3 SEM images of **1-Zn** (a), **2-In** (b), activated **1-Zn** (c) and activated **2-In** (d).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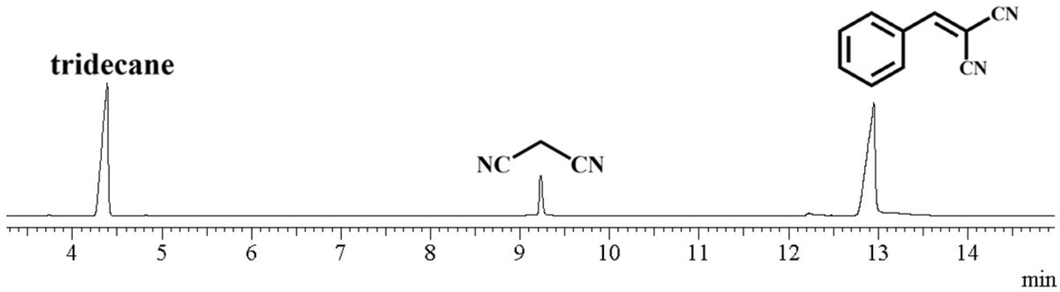
NC
CN
CN
CN
4 5 6 7 8 9 10 11 12 13 14
min

(a)


tridecane
NC
CN
CN
CN
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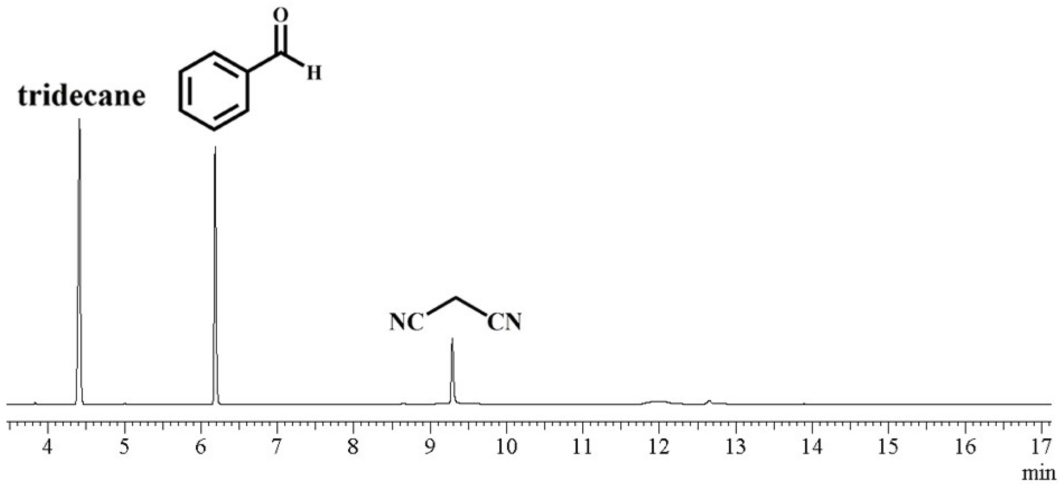
min

(b)


tridecane
O
H
NC
CN
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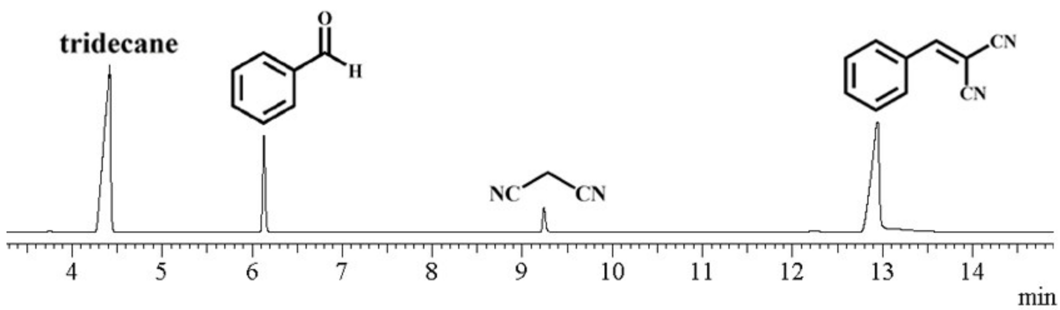
min

(c)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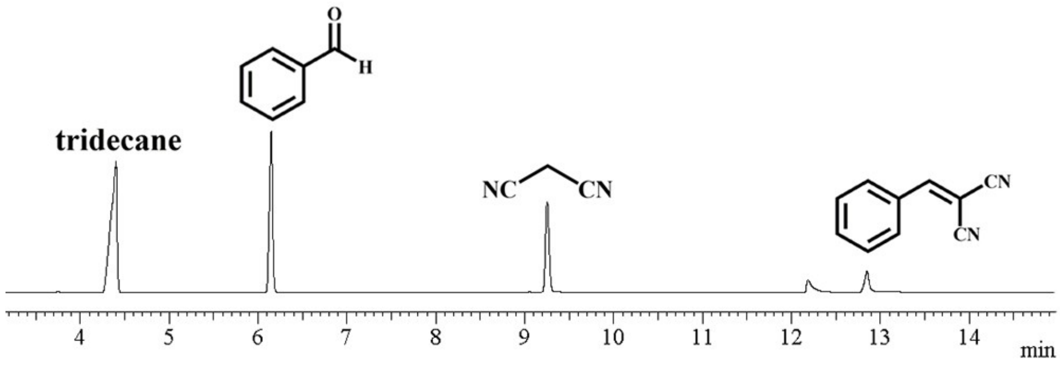
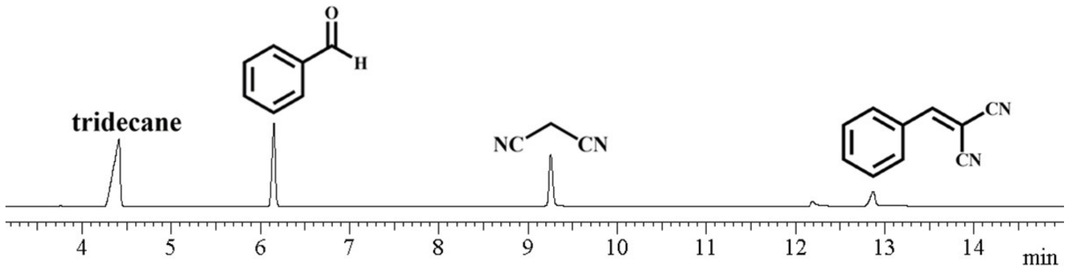
O
H
NC
CN
CN
CN
4 5 6 7 8 9 10 11 12 13 14
min

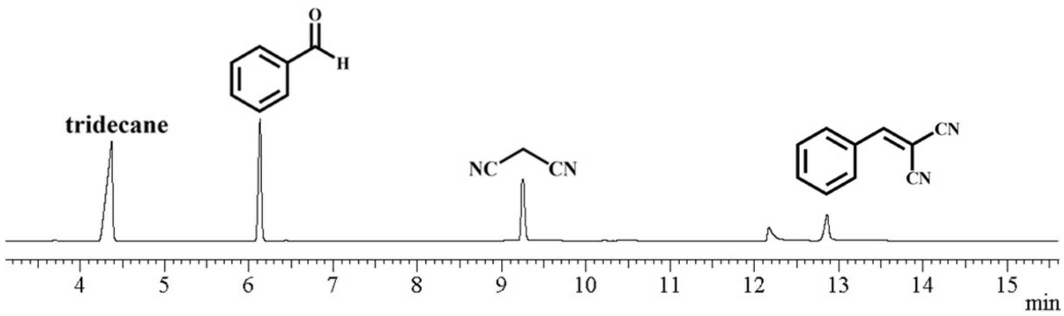
(d)



(e)

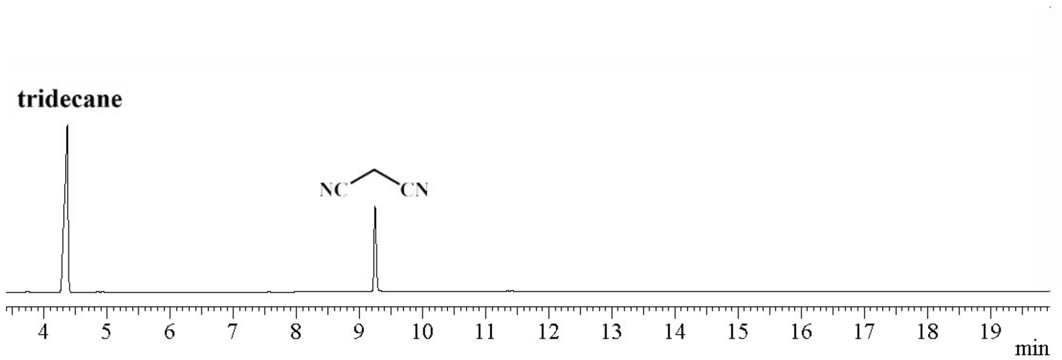


(f)

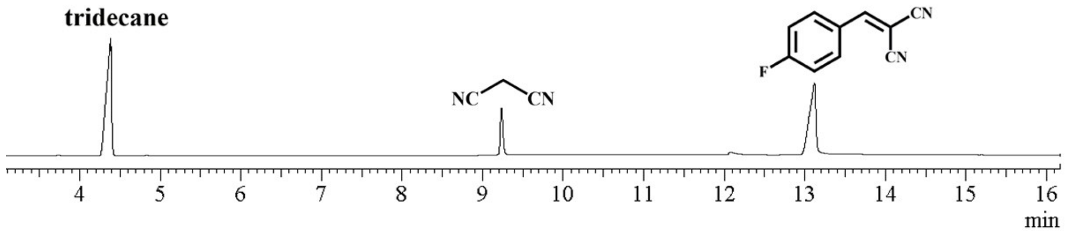


(g)

Fig. S4 GC for Knoevenagel condensation reaction of malononitrile and benzaldehyde: (a) with catalyst **1-Zn** after 40 min, (b) using **2-In** after 1 h, (c) without catalyst after 1 h, (d) with $Zn(NO_3)_2 \cdot 6H_2O$ after 40 min, (e) with $In(NO_3)_3 \cdot 3H_2O$ after 1 h, (f) with **H_2PDC** after 40 min, (g) with benzaldehyde catalyzed by **H_2PDC** after 1h.



(a)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F
CN
CN
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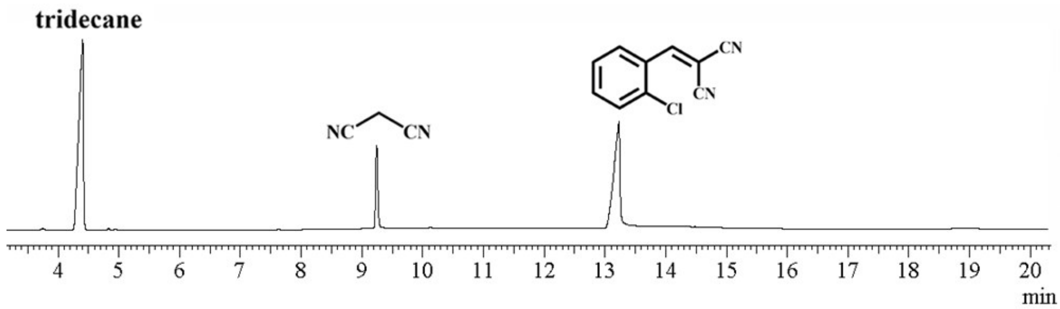
min

(b)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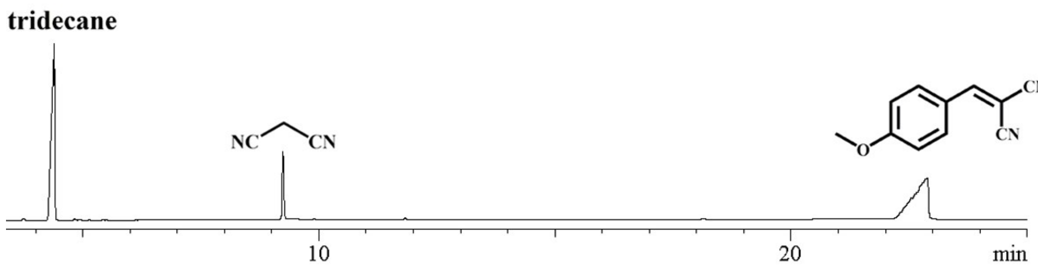
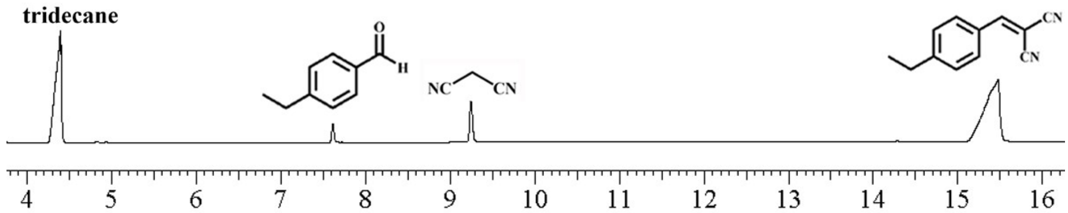
NC CN
Cl
CN
CN
4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
min

(c)


tridecane
NC CN
O
CN
CN
10
20
min

(d)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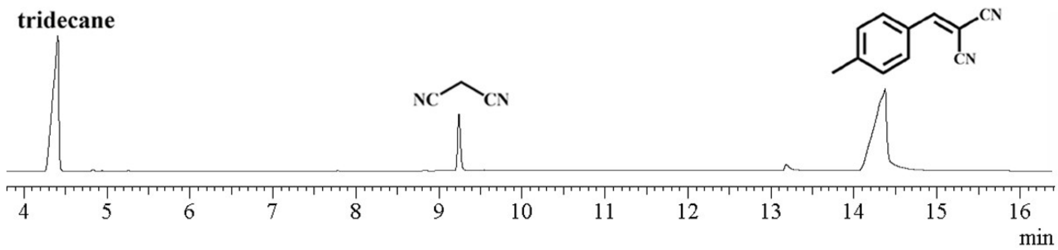
H
NC CN
CN
CN
4 5 6 7 8 9 10 11 12 13 14 15 16

(e)


tridecane
NC CN
CN
CN
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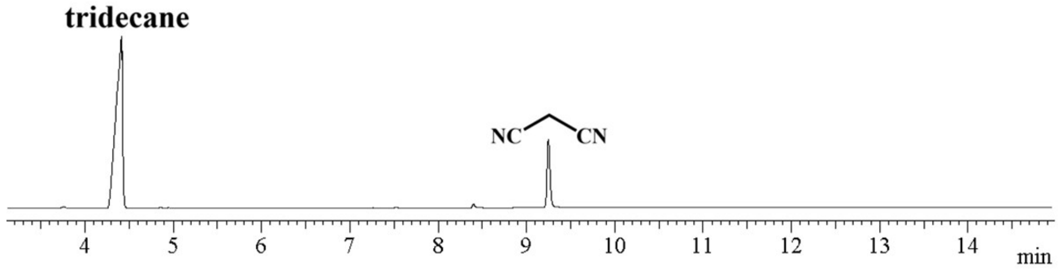
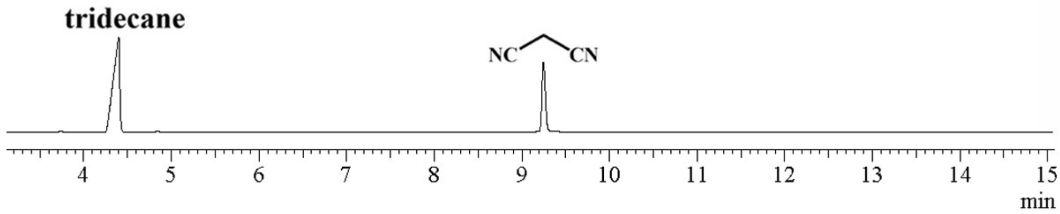
min

(f)

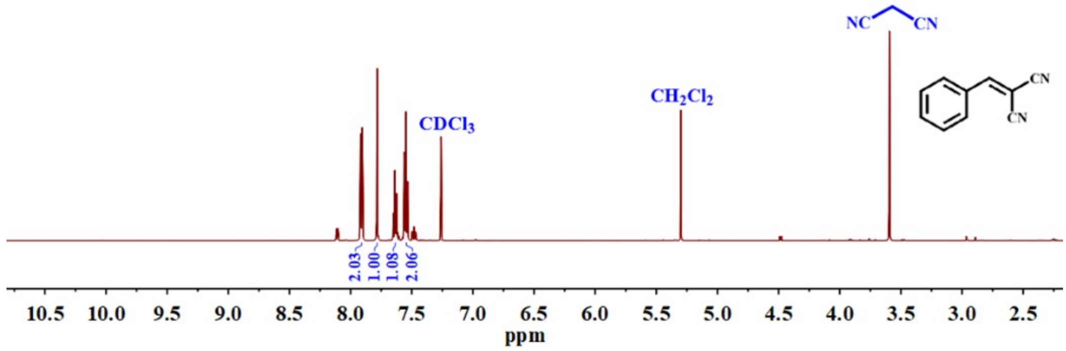


(g)

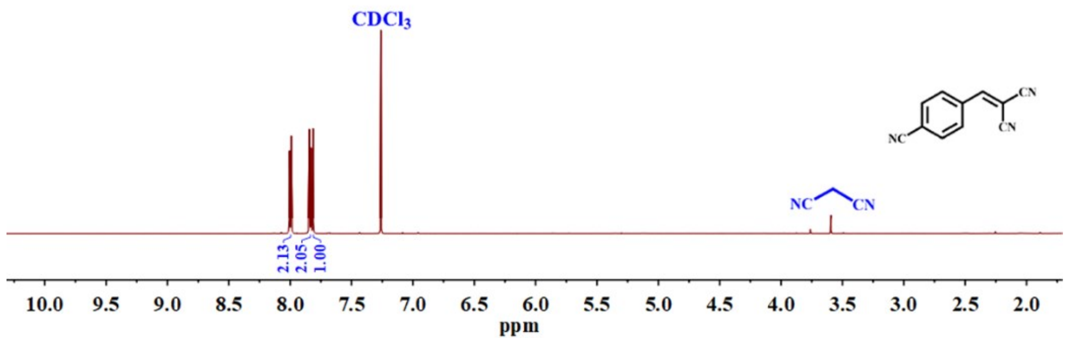


(h)

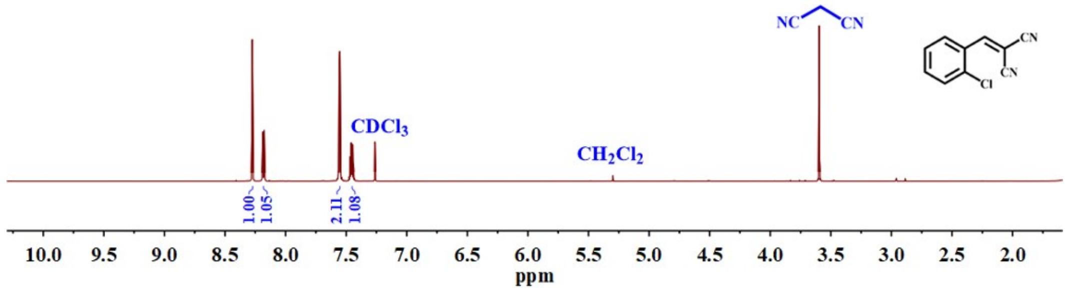
Fig. S5 GC for Knoevenagel condensation reaction of malononitrile and different benzaldehyde derivatives using catalyst **1-Zn** after 40 min: (a) 4-cyanobenzaldehyde, (b) 4-fluorobenzaldehyde, (c) 2-chlorobenzaldehyde, (d) 4-methoxybenzaldehyde, (e) 4-ethylbenzaldehyde, (f) 4-methylbenzaldehyde, (g) 2-naphthaldehyde and (h) 9-anthraldehyde.



(a)



(b)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CN
CN
Cl
CDCl3
CH2Cl2
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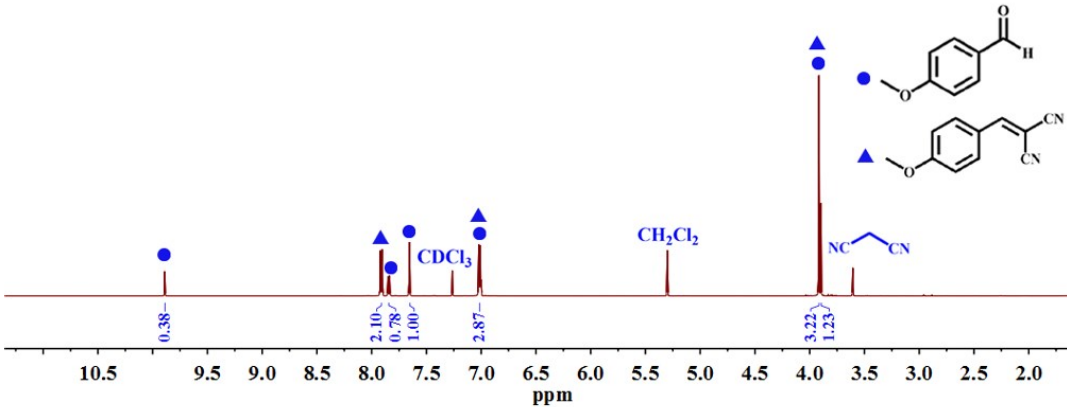
1.05
2.11
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
ppm

(c)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H
O
CN
CN
O
CDCl3
CH2Cl2
NC CN
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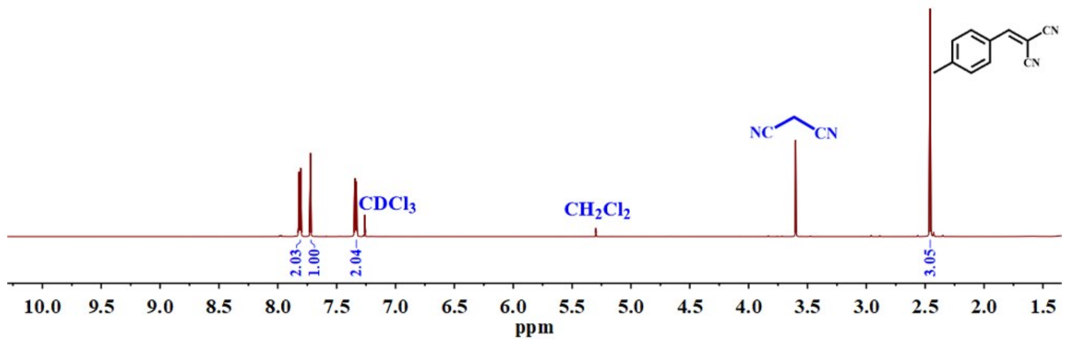
2.10
0.78
1.00
2.87
3.22
1.23
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
ppm

(d)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2.04
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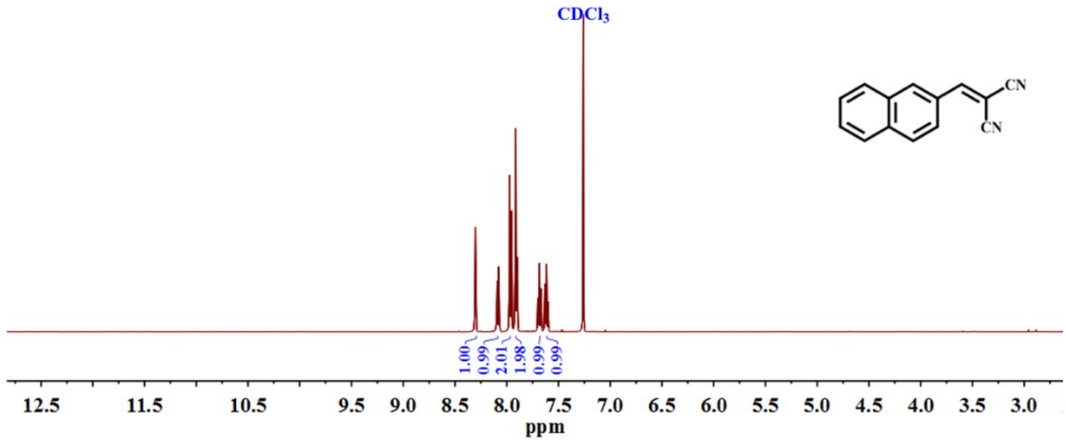
ppm

(e)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CN
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2.01
1.98
0.99
0.99
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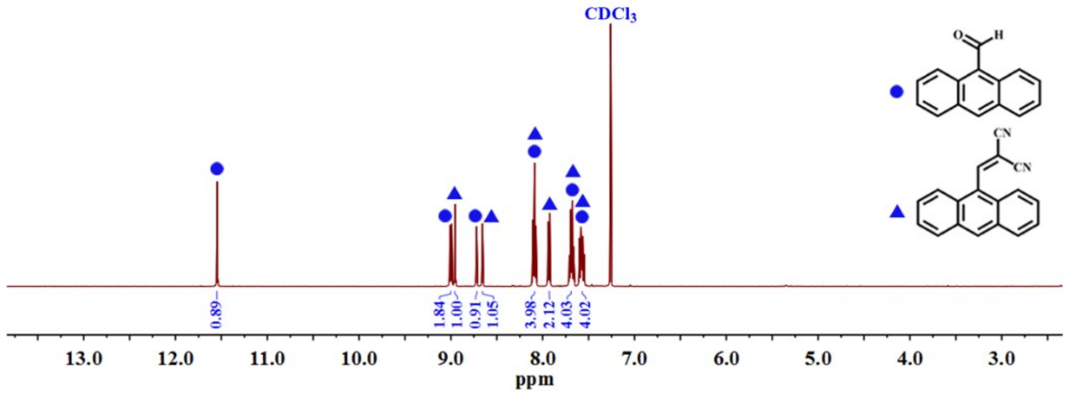
ppm

(f)



(g)

Fig. S6 ^{1}H NMR spectra for Knoevenagel condensation reaction of malononitrile and different benzaldehyde derivatives using catalyst **1-Zn** after 40 min: (a) benzaldehyde, (b) 4-cyanobenzaldehyde, (c) 2-chlorobenzaldehyde, (d) 4-methoxybenzaldehyde, (e) 4-methylbenzaldehyde, (f) 2-naphthaldehyde and (g) 9-anthraldehyde.

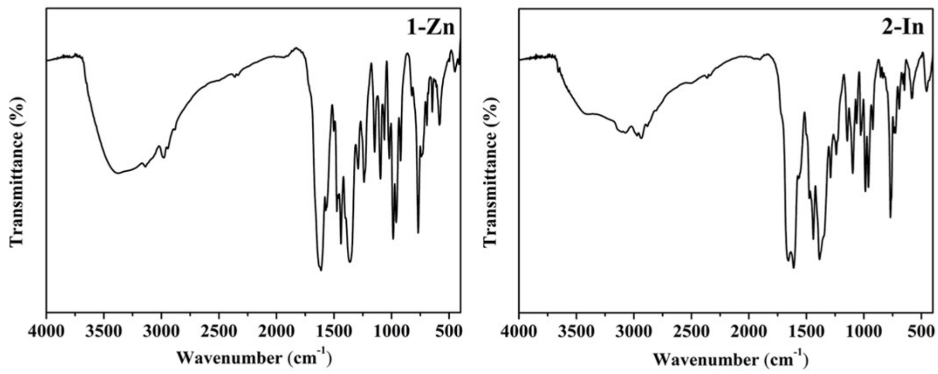
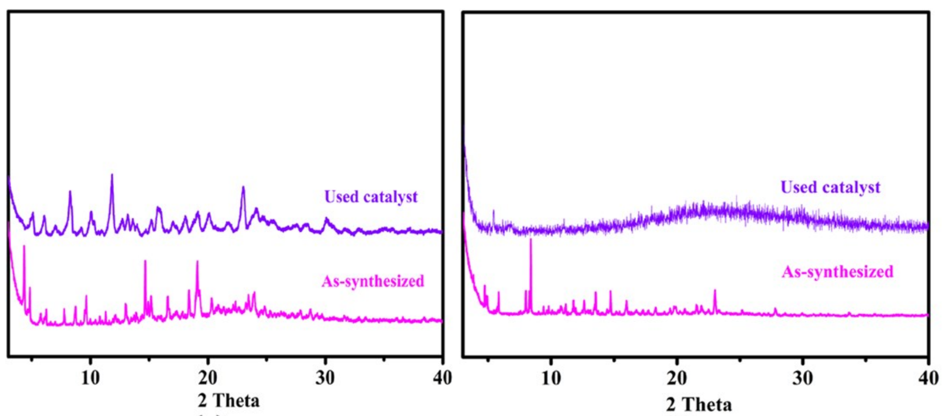


Fig. S7 FT-IR spectra for **1-Zn** and **2-In**.



(a) (b)

Fig. S8 PXRD patterns of the used catalysts and the as-synthesized samples of **1-Zn** (a) and **2-In** (b), respectively.

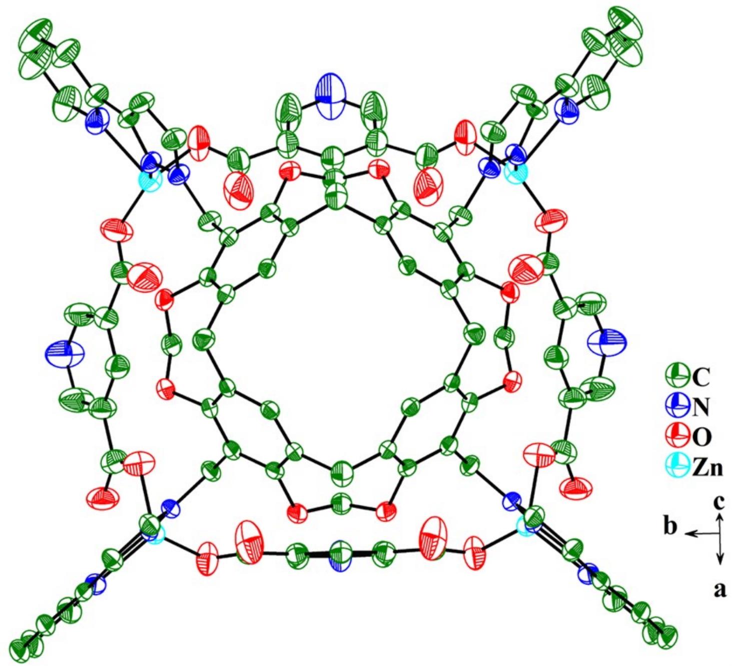
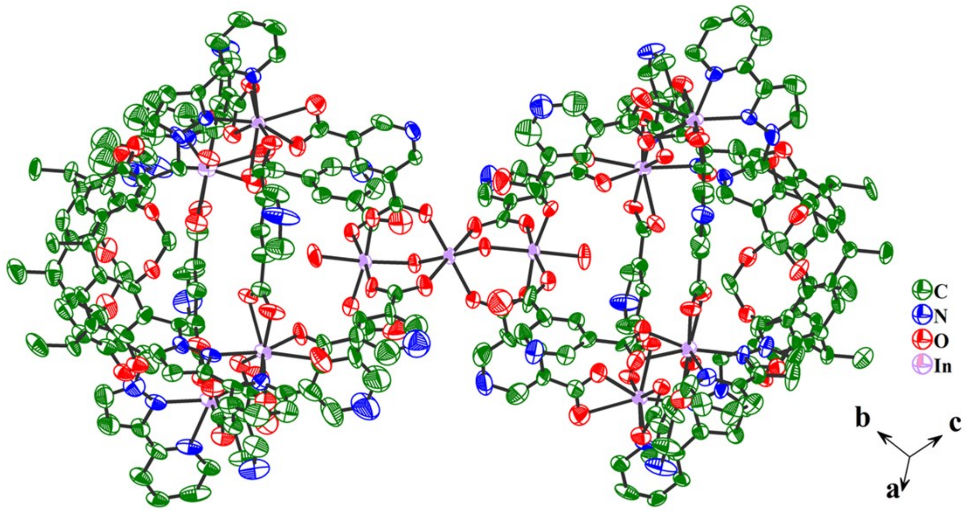
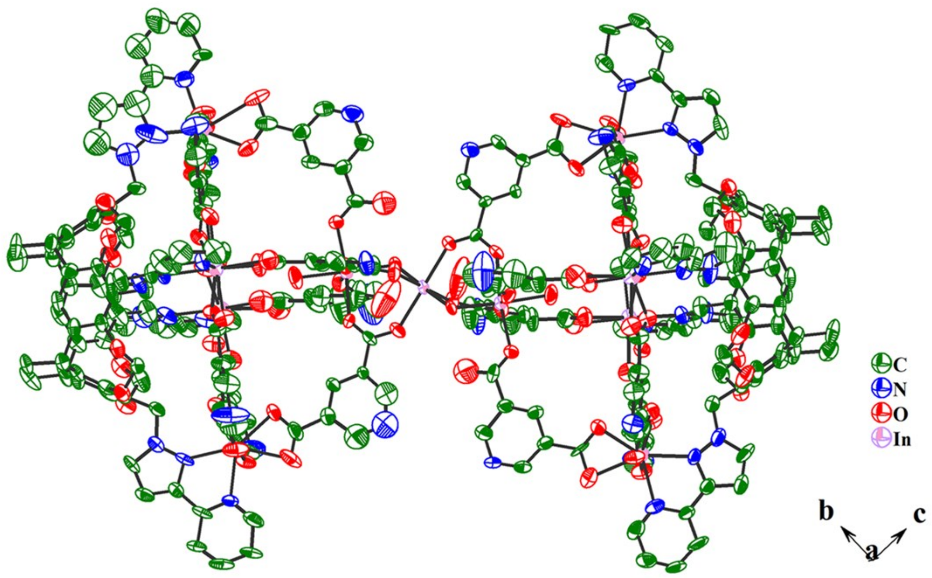


Fig. S9 Diagram showing anisotropic displacement parameters (ADPs) of **1-Zn**, with the thermal ellipsoids shown at a 30% probability level. All hydrogen atoms are omitted for clarity.



(a)



(b)

Fig. S10 Diagrams showing anisotropic displacement parameters (ADPs) of **2-In** in different directions, with the thermal ellipsoids shown at a 30% probability level. All hydrogen atoms are omitted for clarity.

Table S1. Crystallographic data for **1-Zn** and **2-In.**

Compound	**1-Zn**	**2-In**
Empirical formula	$C_{106}H_{98}N_{18}O_{32}Zn_4$	$C_{284}H_{282}N_{49}O_{113}In_{11}$
Formula weight	2397.50	7452.59
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic

Space group	*P* 21/m	*P* 21
a (Å)	14.8537(7)	22.1234(4)
b (Å)	22.6867(11)	36.2197(10)
c (Å)	20.3744(12)	28.4674(6)
α(°)	90	90
β(°)	96.555(6)	96.860(2)
γ(°)	90	90
V(Å^3)	6820.9(6)	22647.7(9)
Z	2	2
D_{calc} (g·cm^{-3})	1.167	1.093
F(000)	2472	7544
R_{int}	0.0501	0.0707
GOF on F^2	0.938	0.887
R_1, wR_2 [I>2σ(I)]	0.0593, 0.1446	0.0624, 0.1064
R_1, wR_2 (all data)	0.1264, 0.1803	0.1574, 0.1394

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$

Table S2. Specified hydrogen bonds for **1-Zn**.

D-H···A	D-H / Å	H···A / Å	D···A / Å	< (DHA) / °
C26-H26···O7	0.93	2.53	3.098(5)	119.5
C27-H27···O5	0.93	2.50	3.430(5)	174.8
C33-H33···O9	0.93	2.62	3.308(5)	131.1

Table S3. Selected bond distances (Å) and angles (deg) for **1-Zn.**

N(6)-Zn(2)	2.084(2)	O(7)-Zn(1)-N(3)	114.20(13)
N(2)-Zn(1)	2.053(3)	N(2)-Zn(1)-N(3)	79.09(12)
N(3)-Zn(1)	2.071(3)	O(9)-Zn(2)-N(5)	133.84(14)
N(5)-Zn(2)	2.040(3)	O(9)-Zn(2)-O(11)	105.9(3)
O(6)-Zn(1)	1.918(3)	N(5)-Zn(2)-O(11)	120.2(3)
O(7)-Zn(1)	1.964(3)	O(9)-Zn(2)-N(6)	103.17(14)
O(9)-Zn(2)	1.919(4)	N(5)-Zn(2)-N(6)	77.96(11)
O(11)-Zn(2)	2.195(10)	O(11)-Zn(2)-N(6)	91.8(2)

O(12)-Zn(2)	2.340(9)	O(9)-Zn(2)-O(12)	107.7(3)
O(6)-Zn(1)-O(7)	109.24(15)	N(5)-Zn(2)-O(12)	93.2(3)
O(6)-Zn(1)-N(2)	101.45(13)	O(11)-Zn(2)-O(12)	62.4(3)
O(7)-Zn(1)-N(2)	131.82(13)	N(6)-Zn(2)-O(12)	144.0(3)
O(6)-Zn(1)-N(3)	119.25(14)		

Table S4. Selected bond distances (Å) and angles (deg) for **2-In.**

N(8)-In(2)	2.132(12)	O(9)-In(3)	2.238(8)
N(1)-In(3)	2.299(9)	O(10)-In(3)	2.350(7)
N(2)-In(3)	2.242(10)	O(11)-In(3)	2.377(8)
N(4)-In(1)	2.351(9)	O(12)-In(3)	2.245(8)
N(5)-In(1)	2.280(11)	O(13)-In(3)	2.397(11)
N(7)-In(2)	2.287(11)	O(14)-In(3)	2.190(8)
N(10)-In(4)	2.297(7)	O(15)-In(1)	2.249(8)
N(11)-In(4)	2.248(8)	O(16)-In(1)	2.300(8)
N(21)-In(8)	2.301(10)	O(17)-In(1)	2.377(8)
N(22)-In(8)	2.257(9)	O(18)-In(1)	2.200(9)
N(24)-In(9)	2.246(8)	O(20)-In(1)	2.139(13)
N(25)-In(9)	2.269(10)	O(21)-In(2)	2.261(9)
N(27)-In(10)	2.266(9)	O(22)-In(2)	2.293(8)
N(28)-In(10)	2.310(9)	O(23)-In(2)	2.339(8)
N(30)-In(11)	2.308(7)	O(24)-In(2)	2.255(7)
N(31)-In(11)	2.265(9)	O(26)-In(2)	2.137(9)
O(1W)-In(5)	2.195(9)	O(27)-In(4)	2.295(8)
O(2W)-In(6)	2.051(7)	O(28)-In(4)	2.298(6)
O(2W)-In(5)	2.099(7)	O(29)-In(4)	2.397(7)
O(3W)-In(6)	2.056(6)	O(30)-In(4)	2.208(8)
O(3W)-In(7)	2.083(6)	O(31)-In(4)	2.482(10)
O(4W)-In(7)	2.234(8)	O(32)-In(4)	2.191(8)

O(33)-In(6)	2.145(7)	O(61)-In(10)	2.228(8)
O(34)-In(5)	2.152(8)	O(62)-In(10)	2.368(8)
O(36)-In(5)	2.151(9)	O(63)-In(10)	2.352(7)
O(38)-In(5)	2.153(7)	O(64)-In(10)	2.248(7)
O(39)-In(6)	2.133(8)	O(65)-In(10)	2.509(10)
O(40)-In(5)	2.200(8)	O(66)-In(10)	2.167(7)
O(49)-In(8)	2.235(7)	O(67)-In(11)	2.291(8)
O(50)-In(8)	2.381(7)	O(68)-In(11)	2.330(7)
O(51)-In(8)	2.411(7)	O(69)-In(11)	2.327(7)
O(52)-In(8)	2.232(8)	O(70)-In(11)	2.258(8)
O(53)-In(8)	2.440(9)	O(71)-In(11)	2.570(10)
O(54)-In(8)	2.190(8)	O(72)-In(11)	2.177(8)
O(55)-In(9)	2.221(8)	O(74)-In(7)	2.124(7)
O(56)-In(9)	2.408(7)	O(76)-In(7)	2.131(8)
O(57)-In(9)	2.329(7)	O(77)-In(6)	2.166(8)
O(58)-In(9)	2.259(8)	O(78)-In(7)	2.213(8)
O(59)-In(9)	2.511(11)	O(79)-In(6)	2.172(8)
O(60)-In(9)	2.199(8)	O(80)-In(7)	2.196(7)
O(20)-In(1)-O(18)	90.2(4)	N(7)-In(2)-O(23)	128.7(4)
O(20)-In(1)-O(15)	94.1(4)	O(22)-In(2)-O(23)	86.3(3)
O(18)-In(1)-O(15)	158.6(3)	O(14)-In(3)-O(9)	90.4(3)
O(20)-In(1)-N(5)	151.0(4)	O(14)-In(3)-N(2)	150.4(4)
O(18)-In(1)-N(5)	94.1(4)	O(9)-In(3)-N(2)	96.5(3)
O(15)-In(1)-N(5)	92.3(3)	O(14)-In(3)-O(12)	94.1(4)
O(20)-In(1)-O(16)	77.3(4)	O(9)-In(3)-O(12)	159.0(4)
O(18)-In(1)-O(16)	144.4(3)	N(2)-In(3)-O(12)	89.6(4)
O(15)-In(1)-O(16)	56.8(3)	O(14)-In(3)-N(1)	138.6(4)
N(5)-In(1)-O(16)	82.6(3)	O(9)-In(3)-N(1)	82.9(3)
O(20)-In(1)-N(4)	137.7(5)	N(2)-In(3)-N(1)	71.0(4)

O(18)-In(1)-N(4)	81.0(3)	O(12)-In(3)-N(1)	80.2(3)
O(15)-In(1)-N(4)	81.7(3)	O(14)-In(3)-O(10)	77.6(3)
N(5)-In(1)-N(4)	71.4(4)	O(9)-In(3)-O(10)	57.1(3)
O(16)-In(1)-N(4)	130.0(4)	N(2)-In(3)-O(10)	82.1(3)
O(20)-In(1)-O(17)	76.0(4)	O(12)-In(3)-O(10)	143.8(3)
O(18)-In(1)-O(17)	56.2(3)	N(1)-In(3)-O(10)	128.6(3)
O(15)-In(1)-O(17)	145.1(3)	O(14)-In(3)-O(11)	77.0(3)
N(5)-In(1)-O(17)	82.7(3)	O(9)-In(3)-O(11)	145.1(3)
O(16)-In(1)-O(17)	88.3(3)	N(2)-In(3)-O(11)	81.1(3)
N(4)-In(1)-O(17)	127.9(4)	O(12)-In(3)-O(11)	55.6(3)
N(8)-In(2)-O(26)	154.6(6)	N(1)-In(3)-O(11)	127.6(3)
N(8)-In(2)-O(24)	92.4(5)	O(10)-In(3)-O(11)	88.2(3)
O(26)-In(2)-O(24)	91.4(3)	O(14)-In(3)-O(13)	54.6(3)
N(8)-In(2)-O(21)	92.8(5)	O(9)-In(3)-O(13)	83.0(3)
O(26)-In(2)-O(21)	92.2(4)	N(2)-In(3)-O(13)	154.8(3)
O(24)-In(2)-O(21)	159.9(3)	O(12)-In(3)-O(13)	83.1(4)
O(26)-In(2)-N(7)	129.7(5)	N(1)-In(3)-O(13)	84.0(4)
N(8)-In(2)-N(7)	75.7(5)	O(10)-In(3)-O(13)	117.4(3)
O(24)-In(2)-N(7)	80.4(4)	O(11)-In(3)-O(13)	113.5(3)
O(21)-In(2)-N(7)	82.1(4)	O(32)-In(4)-O(30)	92.4(3)
O(26)-In(2)-O(22)	81.9(4)	O(32)-In(4)-N(11)	152.4(3)
N(8)-In(2)-O(22)	80.0(4)	O(30)-In(4)-N(11)	91.2(3)
O(24)-In(2)-O(22)	143.1(3)	O(32)-In(4)-O(27)	96.0(4)
O(21)-In(2)-O(22)	57.0(3)	O(30)-In(4)-O(27)	158.8(3)
N(7)-In(2)-O(22)	130.9(4)	N(11)-In(4)-O(27)	90.3(3)
O(26)-In(2)-O(23)	82.3(4)	O(32)-In(4)-N(10)	135.5(4)
N(8)-In(2)-O(23)	78.9(5)	O(30)-In(4)-N(10)	79.7(3)
O(24)-In(2)-O(23)	56.8(3)	N(11)-In(4)-N(10)	72.0(3)
O(21)-In(2)-O(23)	143.2(3)	O(27)-In(4)-N(10)	80.7(3)

O(32)-In(4)-O(28)	78.5(3)	O(36)-In(5)-O(40)	170.1(3)
O(30)-In(4)-O(28)	143.8(3)	O(34)-In(5)-O(40)	84.9(3)
N(11)-In(4)-O(28)	82.5(3)	O(38)-In(5)-O(40)	90.6(3)
O(27)-In(4)-O(28)	57.3(2)	O(1W)-In(5)-O(40)	82.7(3)
N(10)-In(4)-O(28)	130.5(3)	O(2W)-In(6)-O(3W	177.9(3)
O(32)-In(4)-O(29)	78.2(3)	O(2W)-In(6)-O(39)	91.3(3)
O(30)-In(4)-O(29)	56.1(3)	O(3W)-In(6)-O(39)	87.2(3)
N(11)-In(4)-O(29)	81.1(3)	O(2W)-In(6)-O(33)	92.3(3)
O(27)-In(4)-O(29)	144.9(3)	O(3W)-In(6)-O(33)	89.2(3)
N(10)-In(4)-O(29)	127.4(3)	O(39)-In(6)-O(33)	90.8(3)
O(28)-In(4)-O(29)	87.7(3)	O(2W)-In(6)-O(77)	86.2(3)
O(32)-In(4)-O(31)	54.9(3)	O(3W)-In(6)-O(77)	92.3(3)
O(30)-In(4)-O(31)	87.2(3)	O(39)-In(6)-O(77)	90.7(3)
N(11)-In(4)-O(31)	152.7(3)	O(33)-In(6)-O(77)	177.9(4)
O(27)-In(4)-O(31)	81.8(3)	O(2W)-In(6)-O(79)	87.5(3)
N(10)-In(4)-O(31)	80.9(3)	O(3W)-In(6)-O(79)	94.1(3)
O(28)-In(4)-O(31)	114.0(3)	O(39)-In(6)-O(79)	178.8(4)
O(29)-In(4)-O(31)	119.5(3)	O(33)-In(6)-O(79)	88.9(3)
O(2W)-In(5)-O(36)	97.2(3)	O(77)-In(6)-O(79)	89.5(3)
O(2W)-In(5)-O(34)	94.9(3)	O(3W)-In(7)-O(74)	97.4(3)
O(36)-In(5)-O(34)	90.0(4)	O(3W)-In(7)-O(76)	97.0(3)
O(2W)-In(5)-O(38)	93.5(3)	O(74)-In(7)-O(76)	90.4(3)
O(36)-In(5)-O(38)	93.2(3)	O(3W)-In(7)-O(80)	94.8(3)
O(34)-In(5)-O(38)	170.6(3)	O(74)-In(7)-O(80)	90.0(3)
O(2W)-In(5)-O(1W	174.5(3)	O(76)-In(7)-O(80)	168.0(3)
O(36)-In(5)-O(1W)	88.3(4)	O(3W)-In(7)-O(78)	92.1(3)
O(34)-In(5)-O(1W)	85.1(4)	O(74)-In(7)-O(78)	169.8(3)
O(38)-In(5)-O(1W)	86.1(4)	O(76)-In(7)-O(78)	92.0(3)
O(2W)-In(5)-O(40)	91.8(3)	O(80)-In(7)-O(78)	85.5(3)

O(3W)-In(7)-O(4W)	173.6(3)	N(22)-In(8)-O(53)	154.9(4)
O(74)-In(7)-O(4W)	87.4(3)	N(21)-In(8)-O(53)	81.9(4)
O(76)-In(7)-O(4W)	87.2(3)	O(50)-In(8)-O(53)	119.4(3)
O(80)-In(7)-O(4W)	80.9(3)	O(51)-In(8)-O(53)	112.3(3)
O(78)-In(7)-O(4W)	82.9(3)	O(60)-In(9)-O(55)	87.8(3)
O(54)-In(8)-O(52)	93.7(3)	O(60)-In(9)-N(24)	135.8(4)
O(54)-In(8)-O(49)	91.2(3)	O(55)-In(9)-N(24)	81.8(3)
O(52)-In(8)-O(49)	158.5(3)	O(60)-In(9)-O(58)	92.8(3)
O(54)-In(8)-N(22)	148.8(4)	O(55)-In(9)-O(58)	158.2(3)
O(52)-In(8)-N(22)	90.1(3)	N(24)-In(9)-O(58)	82.6(3)
O(49)-In(8)-N(22)	96.5(3)	O(60)-In(9)-N(25)	151.5(3)
O(54)-In(8)-N(21)	137.6(4)	O(55)-In(9)-N(25)	93.5(4)
O(52)-In(8)-N(21)	83.3(3)	N(24)-In(9)-N(25)	72.3(3)
O(49)-In(8)-N(21)	79.0(3)	O(58)-In(9)-N(25)	96.3(3)
N(22)-In(8)-N(21)	73.7(4)	O(60)-In(9)-O(57)	80.9(3)
O(54)-In(8)-O(50)	78.6(3)	O(55)-In(9)-O(57)	144.4(3)
O(52)-In(8)-O(50)	144.7(3)	N(24)-In(9)-O(57)	128.7(3)
O(49)-In(8)-O(50)	56.8(3)	O(58)-In(9)-O(57)	56.7(2)
N(22)-In(8)-O(50)	80.5(3)	N(25)-In(9)-O(57)	81.7(3)
N(21)-In(8)-O(50)	125.2(3)	O(60)-In(9)-O(56)	76.6(3)
O(54)-In(8)-O(51)	75.8(3)	O(55)-In(9)-O(56)	56.1(3)
O(52)-In(8)-O(51)	55.6(3)	N(24)-In(9)-O(56)	128.0(3)
O(49)-In(8)-O(51)	145.7(3)	O(58)-In(9)-O(56)	145.0(3)
N(22)-In(8)-O(51)	81.0(3)	N(25)-In(9)-O(56)	80.5(3)
N(21)-In(8)-O(51)	131.4(3)	O(57)-In(9)-O(56)	88.4(3)
O(50)-In(8)-O(51)	89.2(3)	O(60)-In(9)-O(59)	53.3(3)
O(54)-In(8)-O(53)	56.0(3)	O(55)-In(9)-O(59)	80.0(3)
O(52)-In(8)-O(53)	81.3(3)	N(24)-In(9)-O(59)	82.5(3)
O(49)-In(8)-O(53)	84.1(3)	O(58)-In(9)-O(59)	82.8(3)

N(25)-In(9)-O(59)	154.7(3)	O(63)-In(10)-O(65)	119.3(3)
O(57)-In(9)-O(59)	117.4(3)	O(62)-In(10)-O(65)	115.3(3)
O(56)-In(9)-O(59)	114.4(3)	O(72)-In(11)-O(70)	93.4(3)
O(66)-In(10)-O(61)	93.8(3)	O(72)-In(11)-N(31)	152.8(3)
O(66)-In(10)-O(64)	90.4(3)	O(70)-In(11)-N(31)	91.6(3)
O(61)-In(10)-O(64)	158.5(3)	O(72)-In(11)-O(67)	91.7(3)
O(66)-In(10)-N(27)	137.2(4)	O(70)-In(11)-O(67)	157.9(2)
O(61)-In(10)-N(27)	80.7(3)	N(31)-In(11)-O(67)	93.6(3)
O(64)-In(10)-N(27)	81.9(3)	O(72)-In(11)-N(30)	134.6(4)
O(66)-In(10)-N(28)	152.0(4)	O(70)-In(11)-N(30)	80.4(3)
O(61)-In(10)-N(28)	92.5(3)	N(31)-In(11)-N(30)	72.6(3)
O(64)-In(10)-N(28)	93.6(3)	O(67)-In(11)-N(30)	80.7(3)
N(27)-In(10)-N(28)	70.8(4)	O(72)-In(11)-O(69)	80.4(3)
O(66)-In(10)-O(63)	79.2(3)	O(70)-In(11)-O(69)	56.3(3)
O(61)-In(10)-O(63)	144.9(3)	N(31)-In(11)-O(69)	80.3(3)
O(64)-In(10)-O(63)	56.6(3)	O(67)-In(11)-O(69)	145.8(3)
N(27)-In(10)-O(63)	127.1(3)	N(30)-In(11)-O(69)	127.8(3)
N(28)-In(10)-O(63)	80.0(3)	O(72)-In(11)-O(68)	80.2(3)
O(66)-In(10)-O(62)	78.9(3)	O(70)-In(11)-O(68)	144.8(3)
O(61)-In(10)-O(62)	57.6(3)	N(31)-In(11)-O(68)	80.4(3)
O(64)-In(10)-O(62)	143.8(3)	O(67)-In(11)-O(68)	57.3(2)
N(27)-In(10)-O(62)	128.6(3)	N(30)-In(11)-O(68)	128.0(3)
N(28)-In(10)-O(62)	81.6(3)	O(69)-In(11)-O(68)	88.5(3)
O(63)-In(10)-O(62)	87.3(3)	O(72)-In(11)-O(71)	53.5(3)
O(66)-In(10)-O(65)	54.5(3)	O(70)-In(11)-O(71)	82.8(3)
O(61)-In(10)-O(65)	81.2(3)	N(31)-In(11)-O(71)	153.6(3)
O(64)-In(10)-O(65)	84.2(3)	O(67)-In(11)-O(71)	83.0(3)
N(27)-In(10)-O(65)	82.7(3)	N(30)-In(11)-O(71)	81.0(4)
N(28)-In(10)-O(65)	153.4(3)	O(69)-In(11)-O(71)	116.5(3)

O(68)-In(11)-O(71)	118.2(3)		