A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation

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Materials. Dichloromethane, dimethylformamide, and 1,4-biphenyldicarboxylic acid (**H_2bpdc**) were purchased from the Aldrich Chemical Company and used without further purification. Chloroform was distilled over calcium hydride and kept in a straus flass. 2-(*Tert*-butylsulfonyl)iodosylbenzene,[1] 2,2-dimethyl-*2H*-chromene,[2] 2,2-dimethyl-3,4-epoxychroman,[3] *(R,R)*-(-)-1,2-cyclohexanediamino-*N,N'*-bis(3-*tert*-butyl-5-(4-pyridyl)-salicylidene)$Mn^{III}Cl$ (**L**),[4] and dihydroxo-5,10,15,20-tetraphenylporphyrinatotin^{IV} ($Sn(TPP)(OH)_2$)[5] were synthesized according to literature procedures.

Characterization. Elemental analyses were performed by Atlantic Microlabs, Inc. (Norcross, GA). Powder X-ray diffraction patterns were recorded with a Rigaku XDS 2000 diffractometer using nickel-filtered Cu Kα radiation (λ = 1.5418 Å) over a range of 5° < 2θ < 30° in 0.1° steps with a 2-s counting time per step. ICP spectroscopy was conducted on a Thermo Jarrell Ash Atomscan Model 25 Sequential ICP spectrometer that is equipped with vacuum optics covering the spectral range from 160 to 850 nm. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 500 NMR spectrometer (500 MHz for ^{1}H NMR). NMR chemical shifts are reported in ppm against residual solvent resonance as the internal standard (: δ($CHCl_3$) = 7.27 ppm). ^{1}H NMR data are reported as follows: chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, assignment). Gas Chromatography/Mass Spectrometry (GC/MS) analyses were performed on a Hewlett-Packard 6890 GC/MSD interfaced to a HP 5972 Mass Selective Detector Quadrupole Mass Spectrometer. Electrospray-ionization mass spectrometry (ESIMS) was conducted on a Micromass Quattro II triple quadrupole HPLC/MS/MS mass spectrometer. UV-Vis spectra were obtained on a Varian Cary 500 spectrophotometer.

Quantitative analyses of 2,2-dimethyl-*2H*-chromene epoxidation were carried out on an HP 6890A gas chromatograph equipped with a FID detector and ChemStation software. The column used was a 30-m HP-5 (Crosslinked 5% PH ME Siloxane) capillary column with 0.32-mm inner diameter and 0.25-μm film thickness. Calibration curves were produced using analytically pure samples prepared and characterized by literature methods.[3] Product concentrations were determined with combined area of the epoxide and the ketone relative to undecane internal standard (approximately 30% of epoxide products were isomerized to ketone under the GC condition). Column head pressure was 9.3 psi. The column temperature was ramped from 80 to 250 °C at a rate of 5 °C/min. The retention time of the epoxide was 12.5 min and that of the ketone was 11.5 min. For determination of enantiomeric excess, a Supelco β–DEX 120 column was used on an HP 6890 gas chromatograph equipped with an FID detector and ChemStation software. Column head pressure was 23 psi. The column temperature was ramped from 140 to 175 °C at a rate of 1 °C/min and held at 175 °C for 20 min. The retention time of the first isomer [(3*R*,4*R*), minor] was 17.5 min and that of the second isomer [(3*S*,4*S*), major] was 18.5 min.

Single crystal X-ray structure determination. A brown block single crystal of **1** was coated with paraffin and mounted on a Bruker SMART CCD 1000 diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source in a cold nitrogen stream. All crystallographic data were corrected for Lorentz and polarization effects (SAINT) as well as face-index absorption. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 with appropriate software implemented in the SHELXTL program package. The refinement was constrained to fit the R,R structure. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions. One of the Mn atoms and its corresponding Cl atom are disordered over two positions. One coordinated DMF molecule can be reasonably modeled, while the other one cannot. Most of the DMF solvent molecules are severely disordered, which hindered satisfactory development of the model; therefore, the SQUEEZE routine (PLATON) was applied to remove the contributions of electron density from disordered solvent molecules.

(5,10,15,20-Tetraphenylporphyrinato)tin^{IV} bis(4-vinyl benzoate) ($Sn(TPP)(OCOC_6H_4$-*p*-$CH=CH_2)_2$) (2). Under a nitrogen atmosphere, $Sn(TPP)(OH)_2$ (236 mg, 0.309 mmol) and 4-vinyl benzoic acid (91.6 mg, 0.618 mmol) were added to a 50-mL round-bottom flask equipped with a magnetic stir bar. To this mixture were added dry $CHCl_3$ (20 mL). The mixture was stirred under nitrogen for 12 h at RT. The resulting solution was filtered through anhydrous $MgSO_4$ and evaporated to dryness *in vacuo* to give a bright purple solid (282 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.10 (m, 8H, *β*-pyrrole), 8.28 (m, 8H, *ortho*-Ar*H*), 7.82 (m, 12H, *meta,para*-Ar*H*), 6.37 (dd, 4H, J_1 = 8.2 Hz, J_2 = 9.7 Hz, 3' and 5'Ar*H*), 6.22 (m, 2H, CH=CH_2), 5.34 (m, 2H, CH=CH_2), 4.97 (d, 2H, *J* = 11 Hz, C*H*=CH_2), 4.84 (dd, 4H, J_1 = 8.2 Hz, J_2 = 26 Hz, 2' and 6'Ar*H*). UV-Vis (CH_2Cl_2): λ_{max} nm (log *ε*): 424 (5.79), 518 (3.50), 560 (4.33), 600 (3.98). ESIMS: Exact mass calcd. for $[C_{62}H_{42}N_4O_4Sn + H]^+$: 1027.2. Found: 1027.9.

Ethyl 4-vinyl benzoate (3). Under a nitrogen atmosphere, 4-vinyl benzoic acid (1.00 g, 6.75 mmol), 1,3-dicyclohexyl-carbodiimide (1.67 g, 8.10 mmol), and 4-dimethylaminopyridine (82.5 mg, 0.675 mmol) were added to a 100-mL round-bottom flask equipped with a magnetic stir bar. To this mixture were added CH_2Cl_2 (50 mL) and EtOH (2.90 g, 67.5 mmol). The resulting solution was stirred under nitrogen for 12 h at RT, filtered through a Celite pad, and evaporated to near dryness under vacuum. Chromatography of the crude product on silica (Hexane:EtOAc=30:1), followed by concentration gave a colorless oil (1.03 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d,

2H, J = 8.5 Hz, Ar*H*), 7.47 (d, 2H, J = 8.0 Hz, Ar*H*), 6.76 (dd, 1H, J_1 = 11 Hz, J_2 = 18 Hz, CH=CH_2), 5.87 (d, 1H, J = 18 Hz, CH=CH_2), 5.39 (d, 1H, J = 11 Hz, C*H*=CH_2), 4.38 (q, 2H, J = 7.5 Hz, C$H_2$$CH_3$), 1.405 (t, 3H, J = 7.0 Hz, CH_2CH_3). GC-MS(EI): m/z (%): 176 (23) [M^+], 148 (30), 131 (100), 103 (29), 77 (25).

General procedure for recycling study of 1. To a conical vial were added 2,2-dimethyl-2*H*-chromene (320 mg, 2.0×10^{-3} mol), undecane (19.1 mg), and dichloromethane (1 mL). **1** crystals (1.1 mg, containing 5.0×10^{-7} mol of **L**) were placed in the vial along with a micro stir bar. The oxidant, 2-(*tert*-butylsulfonyl)iodosylbenzene (170 mg, 5×10^{-4} mmol), was added to the solution to start the reaction. The same amount of the oxidant was added once more after 1 h. After 2-h vigorous stirring, the mixture was centrifuged on a Hermle Z230MA centrifuge at 12,000 rpm for 5 minutes. The supernatant solution was decanted and the remaining solid was washed with acetone (2×2 mL) followed by dichloromethane (2×2 mL). The solid was dried in air prior to being reused.

ICP spectrometric evaluation of manganese and zinc loss. In a typical procedure, the post-reaction supernatant solution was centrifuged, combined with acetone and dichloromethane washes, and passed through a Celite pad. The solvent was removed under reduced pressure and unreacted substrates and products were separated using a Kugelrohr distillation apparatus (Buchi). The remaining solid mixture was treated with conc. sulfuric acid (0.5 mL) to give a black viscous solution which was then heated to dryness.[6] To the resulting black solid was added hydrochloric and nitric acid (5.0 mL, 3/1 : v/v), and the whole mixture was heated at 120 ^oC until the total volume reached the 1–mL mark. The colorless solution was diluted volumetrically with doubly distilled water (a resistivity of 18 MΩ) to 10 mL, which was then evaluated by inductively coupled plasma (ICP) spectroscopy for Mn and Zn contents. The Mn and Zn contents were measured in ppm based on calibration curves obtained with a series of solution doped with different amount of Mn and Zn calibration standard solutions. The quantity of Mn lost from **1** after one cycle was calculated to be 0.020-0.035 μmol (4-7% of total Mn) and that of Zn was calculated to be 0.018-0.029 μmol (2-3% of total Zn).

General procedure for competitive substrate selectivity studies. To a Knotes brand thread NMR tube were added Sn(TPP)($OCOC_6H_4$-*p*-$CH=CH_2$)$_2$ (19.4 mg, 18.9 μmol), ethyl 4-vinyl benzoate (6.65 mg, 37.8 μmol), and **1** (0.42 mg, 0.189 μmol). The mixture was dissolved in $CDCl_3$ (1.0 mL) and the reaction was started by addition of 2-(*tert*-butylsulfonyl)iodosylbenzene (3.2 mg, 9.45 μmol). For a comparison, a solution with **L** (0.12 mg, 0.189 μmol) instead of **1** was set up in the same manner. The reaction was monitored by ^{1}H NMR for yield of each product (the epoxide peak of Sn(TPP)di-oxyranylbenzoate at δ 3.29 versus the epoxide peak of 4-oxyranyl benzoic acid ethyl ester at δ 3.82 which were integrated against *β*-pyrrole peak at δ 9.10).

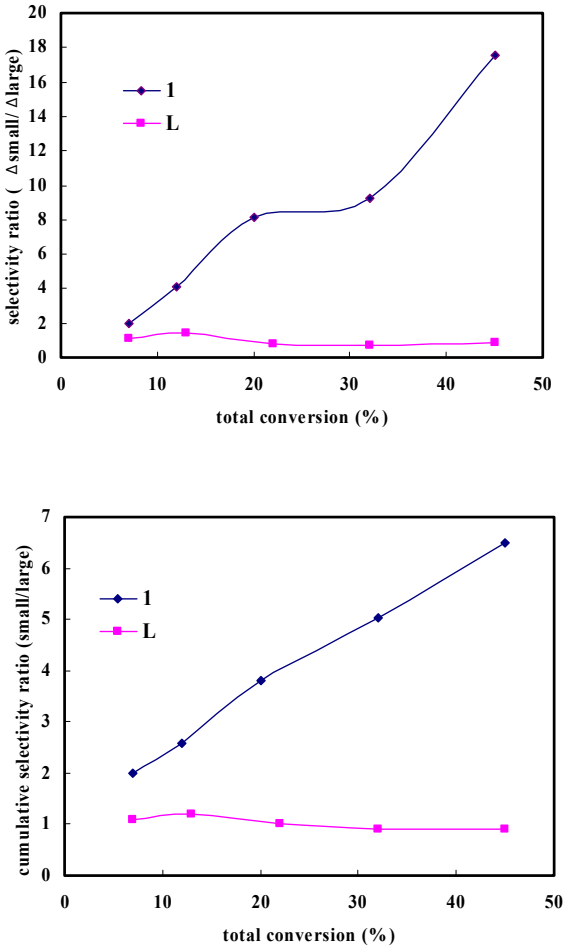


Fig. S1 Plots showing selectivity ratio (top) and cumulative selectivity ratio (bottom) for epoxidation of ethyl benzoate vs. Sn(TPP)($OCOC_6H_4$-*p*-$CH=CH_2)_2$ by **1** and **L**.

Table S1 Crystal data and structure refinement for **1**.

empirical formula	$C_{96}H_{144}ClMnN_{14}O_{28}Zn_2$
Fw	2163.38
T	153(2) K
crystal system	Triclinic
space group	P1
a, Å	15.1376(18)
b, Å	15.2092(18)
c, Å	26.300(3)
α,°	73.271(2)
β,°	77.508(2)
γ,°	82.596(2)
V, Å^3	5647.2(12)
Z	2
crystal size	0.33 x 0.30 x 0.22 mm
ρ_{calc}, Mg/m^3	1.272
μ, mm^{-1}	0.630
F(000)	2288
reflns collected	51451
reflns unique	44994
R_{int}	0.0515
Flack parameter	0.00(3)
GOF	0.798
R1/wR2 [$I > 2\sigma(I)$]	0.0634/0.1390
R1/wR2 (all data)	0.1258/0.1535
Largest diff. peak and hole	0.848 and -0.504

Table S2 Selected bond lengths [□] and angles [deg] for cavity.

Zn1-N4	1.9666 (17)	Zn1-O7#1	2.0070 (13)
Zn1-O2	2.0306 (14)	Zn1-O5	2.0782 (13)
Zn1-O4#2	2.0956 (13)	Zn1-Zn2	2.9721 (5)
Zn2-O8#1	2.0216 (13)	Zn2-O6	2.0287 (13)
Zn2-N1#3	2.0758 (16)	Zn2-O3#2	2.0849 (15)
Zn2-O1	2.0913 (13)	Zn3-O108#4	1.9948 (16)
Zn3-N101	2.0030 (18)	Zn3-O101	2.0179 (15)
Zn3-O106	2.0311 (17)	Zn3-O103#1	2.0506 (14)
Zn3-Zn4	2.9677 (5)	Zn4-O104#1	1.9691 (16)
Zn4-O105	2.0459 (15)	Zn4-N104#3	2.0529 (15)
Zn4-O107#4	2.0630 (14)	Zn4-O102	2.0763 (13)
Mn1-Mn10	0.8120 (11)	Mn1-Cl1	1.352 (3)
Mn1-O10	1.9065 (19)	Mn1-O9	1.973 (2)
Mn1-N3	2.1129 (18)	Mn1-N2	2.133 (2)
Mn10-Cl1	0.593 (3)	Mn10-O10	1.947 (2)
Mn10-O9	1.9880 (17)	Mn10-N3	1.999 (2)
Mn10-N2	1.999 (2)	Mn10-Cl10	2.408 (4)
Mn2-O109	1.891 (2)	Mn2-O110	1.952 (2)
Mn2-N102	2.026 (2)	Mn2-N103	2.0386 (18)
Mn2-Cl2	2.0849 (17)	Cl1-Cl10	1.882 (4)
Cl1-O9	1.912 (2)	Cl1-O10	2.067 (4)
O1-C1	1.225 (2)	O2-C1	1.321 (3)
O3-C14	1.275 (3)	O3-Zn2#4	2.0849 (15)
O4-C14	1.210 (2)	O4-Zn1#4	2.0956 (13)
O5-C15	1.288 (2)	O6-C15	1.289 (2)
O7-C28	1.239 (2)	O7-Zn1#5	2.0070 (13)
O8-C28	1.219 (3)	O8-Zn2#5	2.0216 (13)
O9-C37	1.250 (3)	O10-C57	1.279 (3)
O101-C101	1.328 (3)	O102-C101	1.270 (2)

O103-C114	1.215 (2)	O103-Zn3#5	2.0506 (14)
O104-C114	1.264 (3)	O104-Zn4#5	1.9691 (16)
O105-C115	1.223 (3)	O106-C115	1.250 (2)
O107-C128	1.261 (2)	O107-Zn4#2	2.0630 (14)
O108-C128	1.233 (3)	O108-Zn3#2	1.9948 (16)
O109-C137	1.398 (4)	O110-C157	1.322 (3)
N1-C33	1.333 (3)	N1-C29	1.400 (3)
N1-Zn2#6	2.0758 (16)	N2-C40	1.278 (3)
N2-C45	1.447 (3)	N3-C51	1.280 (3)
N3-C46	1.510 (3)	N4-C64	1.257 (3)
N4-C65	1.336 (3)	N101-C129	1.243 (3)
N101-C133	1.332 (3)	N102-C140	1.337 (3)
N102-C145	1.456 (3)	N103-C151	1.347 (4)
N103-C146	1.379 (3)	N104-C165	1.323 (3)
N104-C164	1.405 (3)	N104-Zn4#6	2.0529 (15)
C1-C2	1.466 (3)	C2-C3	1.317 (3)
C2-C7	1.350 (3)	C3-C4	1.494 (3)
C4-C5	1.338 (3)	C5-C6	1.437 (3)
C5-C8	1.462 (3)	C6-C7	1.339 (3)
C8-C9	1.380 (3)	C8-C13	1.473 (3)
C9-C10	1.334 (3)	C10-C11	1.410 (3)
C11-C12	1.354 (3)	C11-C14	1.478 (3)
C12-C13	1.482 (3)	C15-C16	1.477 (3)
C16-C17	1.282 (3)	C16-C21	1.399 (3)
C17-C18	1.448 (3)	C18-C19	1.389 (3)
C19-C20	1.284 (3)	C19-C22	1.392 (3)
C20-C21	1.478 (3)	C22-C27	1.329 (3)
C22-C23	1.402 (3)	C23-C24	1.433 (3)
C24-C25	1.370 (3)	C25-C26	1.375 (3)
C25-C28	1.586 (3)	C26-C27	1.299 (3)
C29-C30	1.480 (3)	C30-C31	1.375 (3)
C31-C32	1.333 (3)	C31-C34	1.449 (3)
C32-C33	1.421 (4)	C34-C39	1.355 (3)
C34-C35	1.405 (3)	C35-C36	1.508 (4)
C36-C37	1.339 (4)	C36-C40	1.547 (3)
C37-C38	1.517 (3)	C38-C39	1.365 (4)
C38-C41	1.580 (4)	C41-C44	1.410 (4)
C41-C42	1.540 (5)	C41-C43	1.586 (3)
C45-C46	1.440 (5)	C45-C50	1.541 (3)
C46-C47	1.443 (3)	C47-C48	1.614 (4)
C48-C49	1.513 (5)	C49-C50	1.474 (3)
C51-C52	1.443 (4)	C52-C53	1.472 (3)
C52-C57	1.497 (3)	C53-C54	1.439 (3)
C54-C62	1.417 (3)	C54-C55	1.475 (3)
C55-C56	1.329 (3)	C56-C57	1.397 (4)
C56-C58	1.540 (3)	C58-C61	1.389 (4)
C58-C60	1.401 (5)	C58-C59	1.442 (5)
C62-C66	1.333 (3)	C62-C63	1.417 (3)
C63-C64	1.444 (3)	C65-C66	1.371 (3)
C101-C102	1.422 (3)	C102-C107	1.388 (3)
C102-C103	1.436 (3)	C103-C104	1.332 (3)
C104-C105	1.418 (3)	C105-C106	1.481 (3)
C105-C108	1.547 (3)	C106-C107	1.461 (3)
C108-C113	1.411 (3)	C108-C109	1.411 (3)
C109-C110	1.368 (3)	C110-C111	1.433 (3)
C111-C112	1.378 (3)	C111-C114	1.539 (3)
C112-C113	1.335 (3)	C115-C116	1.512 (3)
C116-C117	1.422 (3)	C116-C121	1.459 (3)
C117-C118	1.316 (3)	C118-C119	1.317 (3)
C119-C120	1.326 (4)	C119-C122	1.549 (3)
C120-C121	1.422 (3)	C122-C127	1.256 (3)
C122-C123	1.450 (3)	C123-C124	1.415 (4)
C124-C125	1.331 (3)	C125-C126	1.358 (4)
C125-C128	1.585 (3)	126-C127	1.249 (4)
C129-C130	1.375 (3)	C130-C131	1.339 (4)

C131-C132	1.488 (4)	C131-C134	1.506 (4)
C132-C133	1.335 (4)	C134-C135	1.334 (4)
C134-C139	1.563 (4)	C135-C136	1.347 (4)
C136-C140	1.390 (3)	C136-C137	1.446 (4)
C137-C138	1.462 (4)	C138-C139	1.349 (4)
C138-C141	1.583 (5)	C141-C144	1.369 (7)
C141-C143	1.517 (5)	C141-C142	1.654 (5)
C145-C146	1.408 (3)	C145-C150	1.667 (5)
C146-C147	1.585 (3)	C147-C148	1.469 (4)
C148-C149	1.459 (4)	C149-C150	1.533 (4)
C151-C152	1.442 (4)	C152-C153	1.341 (3)
C152-C157	1.343 (3)	C153-C154	1.326 (4)
C154-C155	1.365 (3)	C154-C162	1.553 (3)
C155-C156	1.399 (4)	C156-C157	1.456 (4)
C156-C158	1.688 (4)	C158-C160	1.322 (6)
C158-C161	1.638 (9)	C158-C159	1.716 (5)
C162-C163	1.383 (3)	C162-C166	1.385 (3)
C163-C164	1.391 (3)	C165-C166	1.396 (3)

N4-Zn1-O7#1	102.05 (6)	N4-Zn1-O2	105.23 (6)
O7#1-Zn1-O2	88.00 (6)	N4-Zn1-O5	105.44 (6)
O7#1-Zn1-O5	152.36 (5)	O2-Zn1-O5	87.55 (6)
N4-Zn1-O4#2	96.14 (6)	O7#1-Zn1-O4#2	88.42 (5)
O2-Zn1-O4#2	158.61 (5)	O5-Zn1-O4#2	85.90 (6)
N4-Zn1-Zn2	166.98 (5)	O7#1-Zn1-Zn2	68.58 (4)
O2-Zn1-Zn2	83.95 (4)	O5-Zn1-Zn2	83.83 (4)
O4#2-Zn1-Zn2	75.11 (4)	O8#1-Zn2-O6	162.71 (6)
O8#1-Zn2-N1#3	102.98 (6)	O6-Zn2-N1#3	94.27 (6)
O8#1-Zn2-O3#2	89.01 (6)	O6-Zn2-O3#2	85.19 (6)
N1#3-Zn2-O3#2	105.57 (6)	O8#1-Zn2-O1	91.01 (6)
O6-Zn2-O1	88.15 (5)	N1#3-Zn2-O1	96.56 (6)
O3#2-Zn2-O1	157.28 (5)	O8#1-Zn2-Zn1	88.27 (4)
O6-Zn2-Zn1	74.86 (4)	N1#3-Zn2-Zn1	165.86 (5)
O3#2-Zn2-Zn1	82.85 (4)	O1-Zn2-Zn1	74.44 (4)
O108#4-Zn3-N101	108.81 (6)	O108#4-Zn3-O101	87.26 (6)
N101-Zn3-O101	101.48 (6)	O108#4-Zn3-O106	153.99 (6)
N101-Zn3-O106	97.05 (7)	O101-Zn3-O106	90.35 (6)
O108#4-Zn3-O103#1	89.38 (6)	N101-Zn3-O103#1	96.86 (6)
O101-Zn3-O103#1	161.46 (6)	O106-Zn3-O103#1	84.71 (6)
O108#4-Zn3-Zn4	80.93 (4)	N101-Zn3-Zn4	166.00 (5)
O101-Zn3-Zn4	88.76 (4)	O106-Zn3-Zn4	73.12 (4)
O103#1-Zn3-Zn4	72.71 (4)	O104#1-Zn4-O105	86.68 (6)
O104#1-Zn4-N104#3	104.30 (6)	O105-Zn4-N104#3	103.85 (6)
O104#1-Zn4-O107#4	89.49 (6)	O105-Zn4-O107#4	161.32 (6)
N104#3-Zn4-O107#4	94.82 (6)	O104#1-Zn4-O102	156.35 (6)
O105-Zn4-O102	88.96 (6)	N104#3-Zn4-O102	99.31 (6)
O107#4-Zn4-O102	87.25 (6)	O104#1-Zn4-Zn3	84.69 (4)
O105-Zn4-Zn3	84.52 (4)	N104#3-Zn4-Zn3	167.88 (5)
O107#4-Zn4-Zn3	76.92 (4)	O102-Zn4-Zn3	71.75 (4)
Mn10-Mn1-Cl1	13.36 (11)	Mn10-Mn1-O10	80.68 (10)
Cl1-Mn1-O10	76.66 (13)	Mn10-Mn1-O9	79.23 (10)
Cl1-Mn1-O9	67.23 (11)	O10-Mn1-O9	94.66 (8)
Mn10-Mn1-N3	70.81 (9)	Cl1-Mn1-N3	83.58 (11)
O10-Mn1-N3	87.81 (7)	O9-Mn1-N3	149.14 (10)
Mn10-Mn1-N2	69.48 (10)	Cl1-Mn1-N2	75.74 (13)
O10-Mn1-N2	149.33 (9)	O9-Mn1-N2	86.80 (9)
N3-Mn1-N2	76.10 (8)	Cl1-Mn10-Mn1	148.2 (2)
Cl1-Mn10-O10	93.2 (3)	Mn1-Mn10-O10	75.02 (10)
Cl1-Mn10-O9	74.0 (2)	Mn1-Mn10-O9	77.11 (9)
O10-Mn10-O9	92.91 (8)	Cl1-Mn10-N3	123.5 (2)
Mn1-Mn10-N3	86.63 (10)	O10-Mn10-N3	90.01 (9)
O9-Mn10-N3	162.10 (9)	Cl1-Mn10-N2	104.9 (3)
Mn1-Mn10-N2	88.16 (10)	O10-Mn10-N2	161.73 (10)
O9-Mn10-N2	90.18 (8)	3-Mn10-N2	81.78 (9)
Cl1-Mn10-Cl10	23.8 (2)	Mn1-Mn10-Cl10	170.19 (13)

O10-Mn10-Cl10	97.48 (12)	O9-Mn10-Cl10	97.25 (12)
N3-Mn10-Cl10	99.87 (11)	N2-Mn10-Cl10	99.99 (13)
O109-Mn2-O110	91.88 (9)	O109-Mn2-N102	93.56 (9)
O110-Mn2-N102	169.01 (8)	O109-Mn2-N103	157.25 (11)
O110-Mn2-N103	92.89 (8)	N102-Mn2-N103	78.50 (8)
O109-Mn2-Cl2	94.53 (9)	O110-Mn2-Cl2	94.36 (8)
N102-Mn2-Cl2	94.72 (7)	N103-Mn2-Cl2	107.26 (8)
Mn10-Cl1-Mn1	18.47 (15)	Mn10-Cl1-Cl10	148.8 (3)
Mn1-Cl1-Cl10	166.4 (2)	Mn10-Cl1-O9	88.6 (2)
Mn1-Cl1-O9	72.07 (11)	Cl10-Cl1-O9	121.56 (19)
Mn10-Cl1-O10	70.1 (3)	Mn1-Cl1-O10	63.81 (13)
Cl10-Cl1-O10	112.68 (18)	O9-Cl1-O10	91.52 (13)
Cl1-Cl10-Mn10	7.31 (8)	C1-O1-Zn2	135.11 (15)
C1-O2-Zn1	122.12 (11)	C14-O3-Zn2#4	120.03 (12)
C14-O4-Zn1#4	130.16 (14)	C15-O5-Zn1	119.60 (11)
C15-O6-Zn2	133.40 (12)	C28-O7-Zn1#5	140.72 (15)
C28-O8-Zn2#5	113.46 (12)	C37-O9-Cl1	129.55 (19)
C37-O9-Mn1	126.88 (16)	Cl1-O9-Mn1	40.70 (9)
C37-O9-Mn10	128.95 (16)	Cl1-O9-Mn10	17.34 (8)
Mn1-O9-Mn10	23.66 (4)	C57-O10-Mn1	138.17 (17)
C57-O10-Mn10	130.76 (17)	Mn1-O10-Mn10	24.30 (4)
C57-O10-Cl1	129.08 (18)	Mn1-O10-Cl1	39.52 (8)
Mn10-O10-Cl1	16.63 (7)	C101-O101-Zn3	115.54 (12)
C101-O102-Zn4	136.45 (15)	C114-O103-Zn3#5	131.52 (14)
C114-O104-Zn4#5	119.56 (12)	C115-O105-Zn4	118.29 (12)
C115-O106-Zn3	134.10 (16)	C128-O107-Zn4#2	124.99 (14)
C128-O108-Zn3#2	124.11 (13)	C137-O109-Mn2	128.61 (17)
C157-O110-Mn2	124.72 (16)	C33-N1-C29	126.30 (18)
C33-N1-Zn2#6	118.04 (13)	C29-N1-Zn2#6	115.00 (13)
C40-N2-C45	119.6 (2)	C40-N2-Mn10	127.69 (17)
C45-N2-Mn10	110.18 (15)	C40-N2-Mn1	123.78 (16)
C45-N2-Mn1	116.19 (17)	Mn10-N2-Mn1	22.36 (4)
C51-N3-C46	119.8 (2)	C51-N3-Mn10	126.18 (17)
C46-N3-Mn10	113.79 (17)	C51-N3-Mn1	124.14 (17)
C46-N3-Mn1	112.61 (14)	Mn10-N3-Mn1	22.56 (4)
C64-N4-C65	111.6 (2)	C64-N4-Zn1	125.14 (13)
C65-N4-Zn1	123.17 (16)	C129-N101-C133	110.9 (2)
C129-N101-Zn3	125.12 (15)	C133-N101-Zn3	123.00 (14)
C140-N102-C145	126.5 (2)	C140-N102-Mn2	123.44 (17)
C145-N102-Mn2	109.55 (17)	C151-N103-C146	125.3 (2)
C151-N103-Mn2	119.84 (17)	C146-N103-Mn2	114.62 (16)
C165-N104-C164	121.42 (18)	C165-N104-Zn4#6	118.88 (15)
C164-N104-Zn4#6	119.31 (11)	O1-C1-O2	121.6 (2)
O1-C1-C2	119.6 (2)	O2-C1-C2	118.56 (16)
C3-C2-C7	120.4 (2)	C3-C2-C1	115.51 (17)
C7-C2-C1	123.7 (2)	C2-C3-C4	117.50 (18)
C5-C4-C3	120.9 (2)	C4-C5-C6	118.3 (2)
C4-C5-C8	119.8 (2)	C6-C5-C8	121.90 (17)
C7-C6-C5	117.77 (19)	C6-C7-C2	124.9 (3)
C9-C8-C5	123.38 (19)	C9-C8-C13	116.1 (2)
C5-C8-C13	120.5 (2)	C10-C9-C8	124.62 (19)
C9-C10-C11	120.7 (2)	C12-C11-C10	120.8 (2)
C12-C11-C14	116.72 (17)	C10-C11-C14	122.22 (19)
C11-C12-C13	118.93 (19)	C8-C13-C12	118.4 (2)
O4-C14-O3	127.3 (2)	O4-C14-C11	119.83 (19)
O3-C14-C11	112.90 (16)	O5-C15-O6	123.95 (18)
O5-C15-C16	119.52 (16)	O6-C15-C16	116.42 (17)
C17-C16-C21	120.4 (2)	C17-C16-C15	121.98 (19)
C21-C16-C15	117.39 (18)	C16-C17-C18	119.4 (2)
C19-C18-C17	122.2 (2)	C20-C19-C18	117.2 (2)
C20-C19-C22	120.03 (19)	C18-C19-C22	122.8 (2)
C19-C20-C21	122.2 (2)	C16-C21-C20	118.0 (2)
C27-C22-C19	126.2 (2)	C27-C22-C23	114.5 (2)
C19-C22-C23	119.04 (17)	C22-C23-C24	122.06 (19)
C25-C24-C23	117.0 (2)	C24-C25-C26	118.4 (2)

C24-C25-C28	119.46 (19)	C26-C25-C28	122.10 (16)
C27-C26-C25	122.18 (18)	C26-C27-C22	125.3 (2)
O8-C28-O7	127.24 (19)	O8-C28-C25	116.19 (16)
O7-C28-C25	116.54 (18)	N1-C29-C30	111.77 (18)
C31-C30-C29	124.7 (2)	C32-C31-C30	114.9 (2)
C32-C31-C34	122.6 (2)	C30-C31-C34	122.11 (19)
C31-C32-C33	125.7 (3)	N1-C33-C32	115.5 (2)
C39-C34-C35	121.1 (2)	C39-C34-C31	120.35 (19)
C35-C34-C31	118.2 (2)	C34-C35-C36	112.6 (2)
C37-C36-C35	128.7 (2)	C37-C36-C40	124.2 (2)
C35-C36-C40	106.7 (2)	O9-C37-C36	126.2 (2)
O9-C37-C38	120.8 (2)	C36-C37-C38	112.2 (2)
C39-C38-C37	118.6 (2)	C39-C38-C41	124.9 (2)
C37-C38-C41	112.7 (2)	C34-C39-C38	125.1 (2)
N2-C40-C36	120.9 (2)	C44-C41-C42	100.9 (3)
C44-C41-C38	123.4 (3)	C42-C41-C38	107.0 (3)
C44-C41-C43	106.9 (3)	C42-C41-C43	108.2 (2)
C38-C41-C43	109.4 (2)	C46-C45-N2	112.4 (2)
C46-C45-C50	112.7 (2)	N2-C45-C50	116.34 (18)
C45-C46-C47	122.8 (3)	C45-C46-N3	108.2 (2)
C47-C46-N3	117.8 (2)	C46-C47-C48	107.6 (2)
C49-C48-C47	110.1 (2)	C50-C49-C48	115.2 (3)
C49-C50-C45	111.2 (2)	N3-C51-C52	122.3 (2)
C51-C52-C53	112.9 (2)	C51-C52-C57	128.7 (2)
C53-C52-C57	118.3 (2)	C54-C53-C52	119.72 (19)
C62-C54-C53	118.69 (18)	C62-C54-C55	124.2 (2)
C53-C54-C55	116.7 (2)	C56-C55-C54	124.1 (2)
C55-C56-C57	122.0 (2)	C55-C56-C58	119.9 (2)
C57-C56-C58	117.9 (2)	O10-C57-C56	125.7 (2)
O10-C57-C52	114.6 (2)	C56-C57-C52	118.6 (2)
C61-C58-C60	103.2 (3)	C61-C58-C59	101.6 (3)
C60-C58-C59	105.4 (3)	C61-C58-C56	118.0 (2)
C60-C58-C56	111.6 (3)	C59-C58-C56	115.5 (2)
C66-C62-C63	112.2 (2)	C66-C62-C54	124.80 (19)
C63-C62-C54	123.0 (2)	C62-C63-C64	116.3 (2)
N4-C64-C63	130.0 (2)	N4-C65-C66	123.5 (2)
C62-C66-C65	125.9 (2)	O102-C101-O101	124.94 (19)
O102-C101-C102	115.97 (19)	O101-C101-C102	119.09 (17)
C107-C102-C101	117.69 (17)	C107-C102-C103	120.87 (19)
C101-C102-C103	121.4 (2)	C104-C103-C102	121.6 (2)
C103-C104-C105	120.57 (19)	C104-C105-C106	120.77 (19)
C104-C105-C108	123.59 (18)	C106-C105-C108	115.53 (19)
C107-C106-C105	115.77 (19)	C102-C107-C106	120.07 (18)
C113-C108-C109	120.5 (2)	C113-C108-C105	121.24 (18)
C109-C108-C105	118.28 (18)	C110-C109-C108	117.10 (19)
C109-C110-C111	122.14 (19)	C112-C111-C110	118.2 (2)
C112-C111-C114	122.05 (18)	C110-C111-C114	119.60 (16)
C113-C112-C111	121.3 (2)	C112-C113-C108	120.8 (2)
O103-C114-O104	127.3 (2)	O103-C114-C111	115.12 (18)
O104-C114-C111	117.29 (16)	O105-C115-O106	127.3 (2)
O105-C115-C116	117.94 (15)	O106-C115-C116	114.66 (19)
C117-C116-C121	115.21 (19)	C117-C116-C115	125.38 (16)
C121-C116-C115	118.95 (19)	C118-C117-C116	119.8 (2)
C117-C118-C119	126.7 (3)	C118-C119-C120	117.1 (2)
C118-C119-C122	123.9 (2)	C120-C119-C122	117.99 (19)
C119-C120-C121	123.2 (2)	C120-C121-C116	116.9 (2)
C127-C122-C123	118.1 (2)	C127-C122-C119	125.0 (2)
C123-C122-C119	116.90 (19)	C124-C123-C122	116.0 (2)
C125-C124-C123	120.0 (2)	C124-C125-C126	116.4 (2)
C124-C125-C128	118.2 (2)	C126-C125-C128	125.31 (19)
C127-C126-C125	124.9 (2)	C126-C127-C122	123.7 (3)
O108-C128-O107	128.3 (2)	O108-C128-C125	117.45 (17)
O107-C128-C125	114.25 (19)	N101-C129-C130	131.6 (2)
C131-C130-C129	115.9 (2)	C130-C131-C132	116.8 (3)
C130-C131-C134	121.7 (3)	C132-C131-C134	121.4 (2)

C133-C132-C131	113.3 (2)	N101-C133-C132	129.5 (2)
C135-C134-C131	124.5 (3)	C135-C134-C139	113.2 (3)
C131-C134-C139	122.1 (2)	C134-C135-C136	127.6 (3)
C135-C136-C140	118.7 (2)	C135-C136-C137	115.7 (2)
C140-C136-C137	125.6 (2)	O109-C137-C136	121.4 (2)
O109-C137-C138	114.3 (2)	C136-C137-C138	123.2 (3)
C139-C138-C137	111.3 (3)	C139-C138-C141	114.5 (3)
C137-C138-C141	121.8 (3)	C138-C139-C134	124.3 (2)
N102-C140-C136	126.9 (3)	C144-C141-C143	99.7 (3)
C144-C141-C138	116.9 (3)	C143-C141-C138	111.6 (3)
C144-C141-C142	114.3 (3)	C143-C141-C142	123.2 (3)
C138-C141-C142	92.3 (2)	C146-C145-N102	109.1 (2)
C146-C145-C150	113.7 (2)	N102-C145-C150	114.1 (2)
N103-C146-C145	109.1 (2)	N103-C146-C147	120.5 (2)
C145-C146-C147	114.3 (2)	C148-C147-C146	115.8 (2)
C149-C148-C147	111.3 (2)	C148-C149-C150	116.7 (3)
C149-C150-C145	106.9 (3)	N103-C151-C152	129.5 (2)
C153-C152-C157	121.7 (2)	C153-C152-C151	117.1 (2)
C157-C152-C151	120.6 (2)	C154-C153-C152	124.8 (2)
C153-C154-C155	115.7 (2)	C153-C154-C162	125.7 (2)
`C155-C154-C162	118.4 (2)	C154-C155-C156	124.2 (3)
C155-C156-C157	115.7 (2)	C155-C156-C158	128.9 (3)
C157-C156-C158	114.9 (3)	O110-C157-C152	129.2 (2)
O110-C157-C156	113.2 (2)	C152-C157-C156	117.6 (2)
C160-C158-C161	129.6 (5)	C160-C158-C156	115.3 (4)
C161-C158-C156	99.3 (3)	C160-C158-C159	116.1 (4)
C161-C158-C159	93.2 (3)	C156-C158-C159	97.0 (3)
C163-C162-C166	117.8 (2)	C163-C162-C154	118.6 (2)
C166-C162-C154	123.17 (19)	C162-C163-C164	123.2 (2)
C163-C164-N104	116.24 (18)	N104-C165-C166	121.8 (2)
C162-C166-C165	119.2 (2)		

Symmetry transformations used to generate equivalent atoms:
(#1) x-1, y, z; (#2) x, y-1, z; (#3) x, y, 1+z; (#4) x, 1+y, z; (#5) 1+x, y, z; (#6) x, y, z-1.

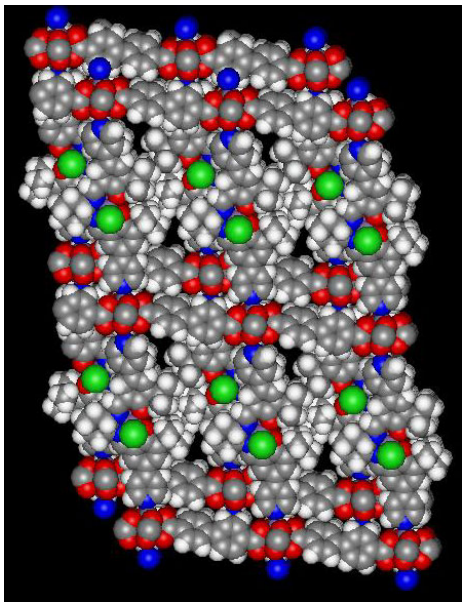
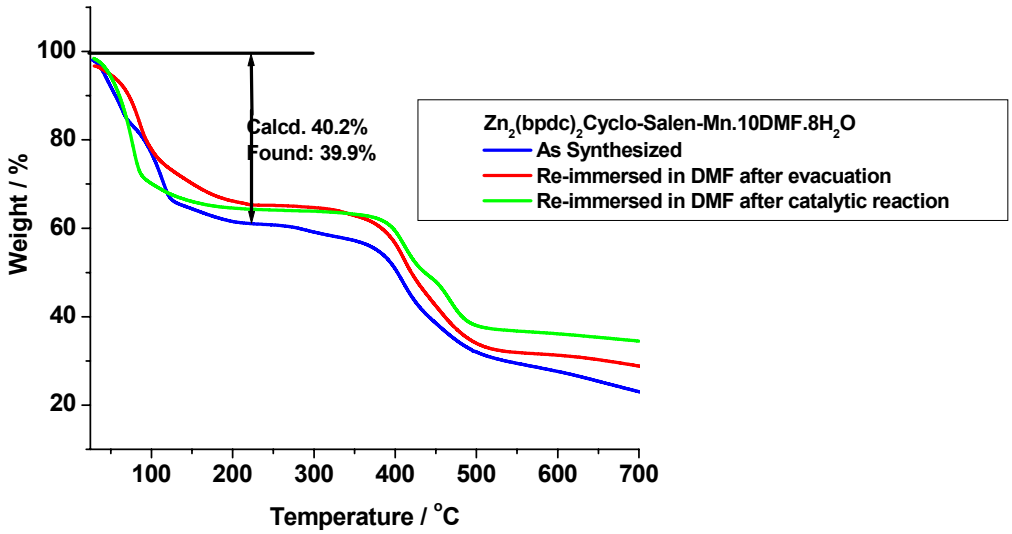


Fig. S2 Space filling diagram of compound **1** viewed along the [010] direction, illustrating the blocking of channel openings by network interpenetration.



1

Fig. S3 TGA compound **1** under different conditions: freshly prepared sample (blue line); the sample immersed in DMF for 2 days after evacuation at 100 °C overnight (red line); the evacuated sample immersed in DMF for 2 days after catalytic reaction (green line).

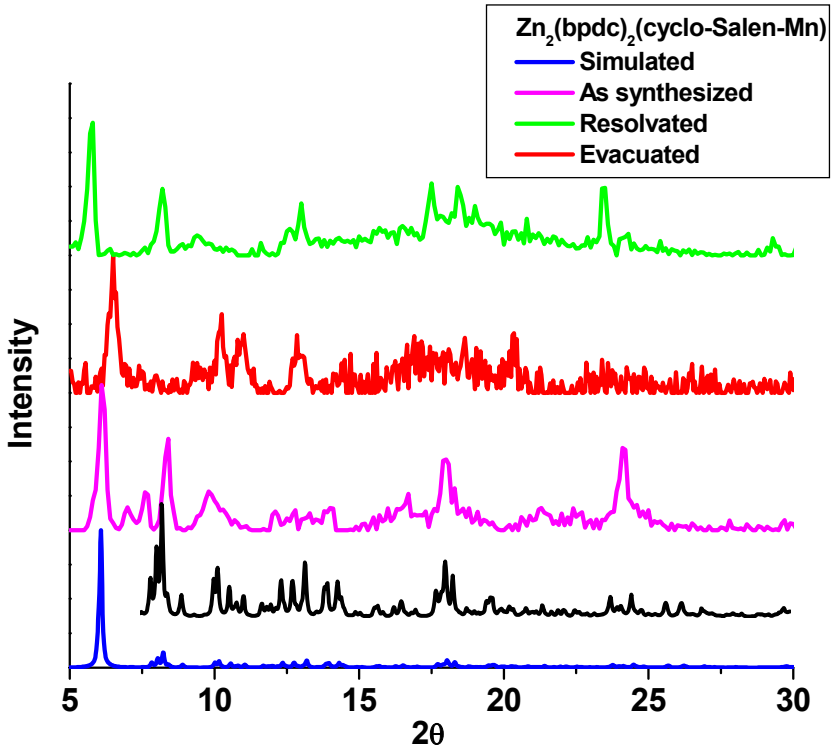


Fig. S4 XRD patterns for compound **1** (the black curve is a magnified version of the blue curve).

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