A cobalt –based 3D porous framework with excellent catalytic ability for the selective oxidation of *cis*-cyclooctene

(Supplementary Information)

X-ray crystallography

Suitable single crystal with dimensions of 0.12 × 0.12 × 0.10 mm for **1** was glued on a glass fiber. Diffraction intensity data were collected on a Bruker Smart Apex-II CCD diffractometer with Mo K*α* mono-chromated radiation (λ= 0.71073 Å) at 296 K. Absorption corrections were applied using the multiscan technique. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the *SHELXL*-97 software.[1] All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The aqua hydrogen atoms were located from difference Fourier maps. A summary of crystal data and structure refinement for **1** is provided in Table S2. Selected bond lengths and angles are listed in Table S3.

Reference

(1) (a) Sheldrick, G. M. *SHELXS*-97, Program for Crystal Structure Solution. University of Göttingen, Germany, **1997**; (b) Sheldrick, G. M. *SHELXL*-97, Program for Crystal Structure Refinement. University of Göttingen,Germany, **1997**.

Materials and General Methods

All materials were reagent grade obtained from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed using an EA1110 elemental analyzer. The IR spectra were recorded in the range of 400–4000 cm^{-1} on a Fourier transform IR spectrometer as KBr pellets. The thermogravimetric analysis (TG) was carried out by Universal Analysis 2000 thermogravimetric analyzer in N_2 with a heating rate of 10 ºC/min. Powder X-ray diffraction (PXRD) data were collected on an X'Pert-ProMPD (Holand) D/max-γA X-ray diffractometer with Cu K*α* radiation in a flat plate geometry. All the gas sorption isotherms were measured with ASAP 2020M adsorption equipment.

Thermal stability analysis for 1

Thermal gravimetric analyses (TG) of **1** was performed to investigate its thermal stabilities. The TG curve exhibits two steps of weight losses (**Fig. S4**). The first weight loss of 9.13 % from 50 to 300 ºC is corresponding to the loss of water molecules (calcd 9.81 %). The second weight loss of 49.05 % from 310 to 880 ºC is correspond to the release of organic ligands hypoxanthine (calcd 49.40 %). The remaining weight is 39.42 % indicating the residue is CoO (calcd 40.79 %).

X-ray Powder diffraction for 1

In order to check the phase purity of compound **1**, the X-ray powder diffraction was checked at room temperature. As shown in **Fig. S6,** the peak positions of simulated and experimental XRPD patterns are in agreement with each other, indicating the good phase purity of **1**. The differences in intensity may be due to the preferred orientation of the crystalline powder sample. Furthermore, the compound **1** was found to be stable after five cycles.

CCDC-917476 for **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Figures

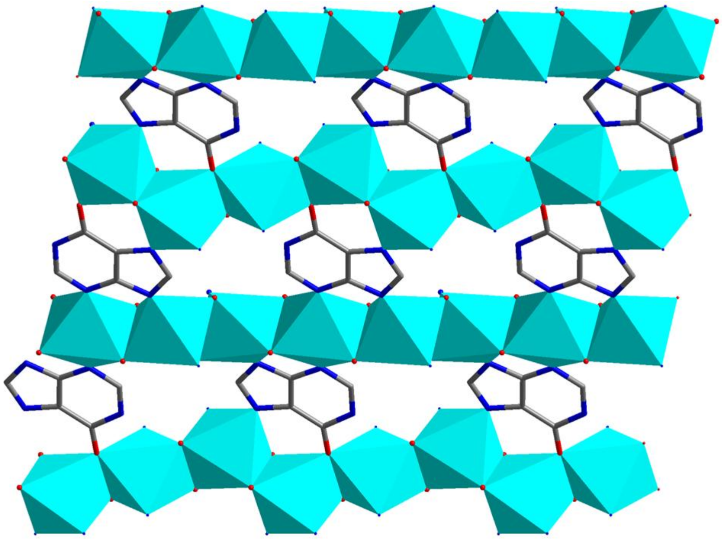


Fig. S1 The 2D layer in the *bc* plane of **1**. For clarity, the hydrogen atoms and lattice water molecules are omitted.

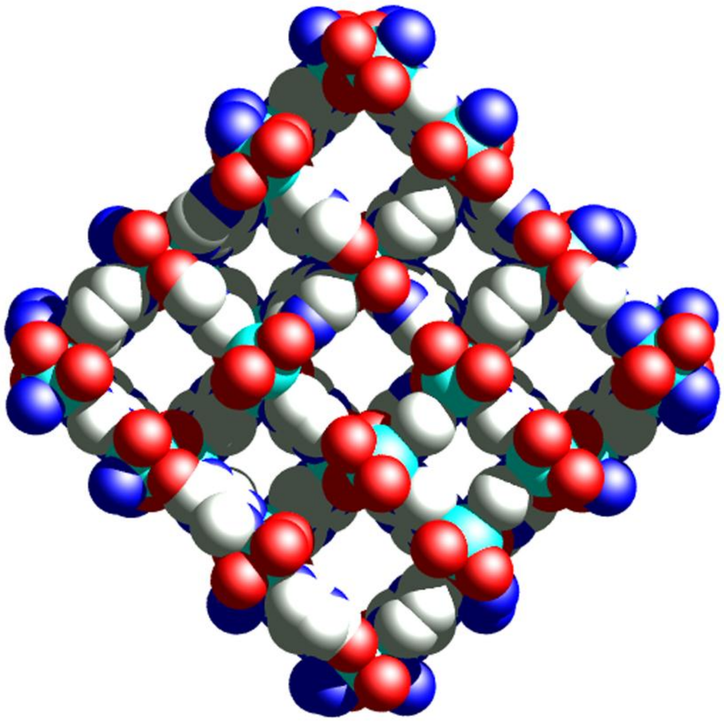


Fig. S2 Space-filling view of the 3D framework of **1.**

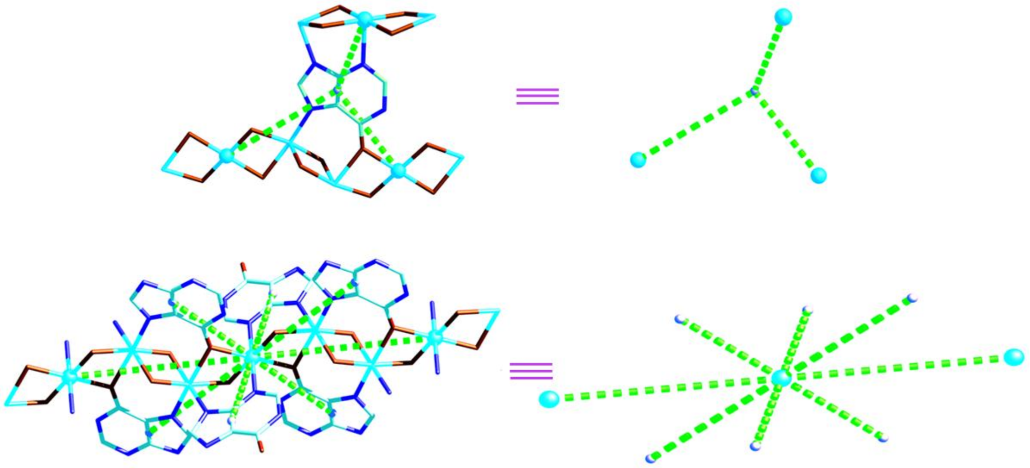


Fig. S3 Perspective views of the three-connected (hypoxanthine ligand) and eight-connected (the trinuclear cobalt cluster) nodes in **1**. Green dashed lines illustrate the three-connected and eight-connected circumstance of hypoxanthine ligand and the trinuclear cobalt cluster, respectively.

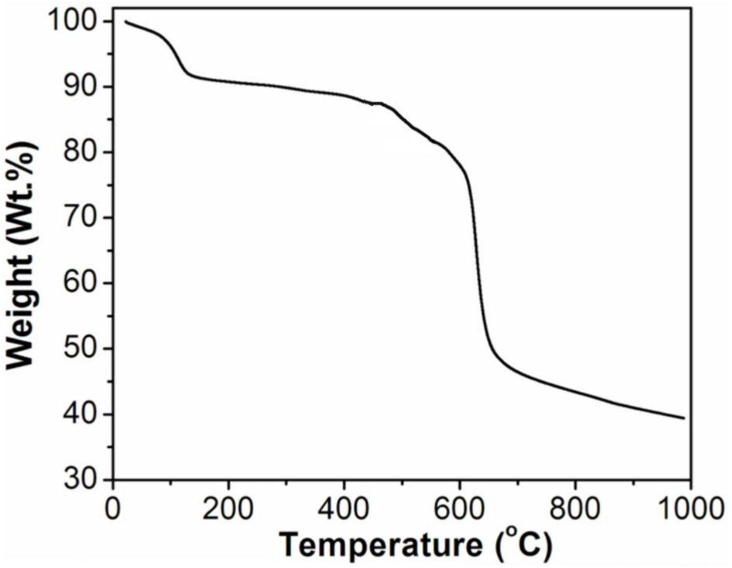


Fig. S4 The TG curve of **1** under N_2 atmosphere.

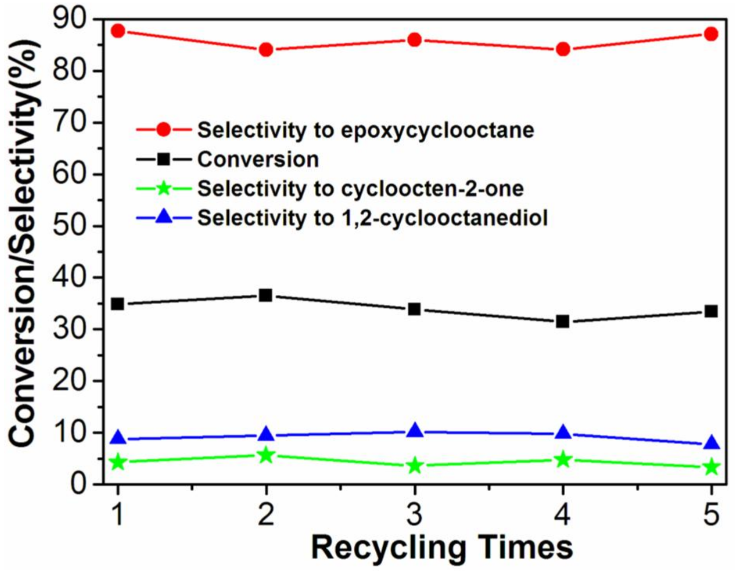


Fig. S5 The relationship between the conversion of *cis*-cyclooctene/selectivity of different products and recycling times with compound **1** as catalyst.

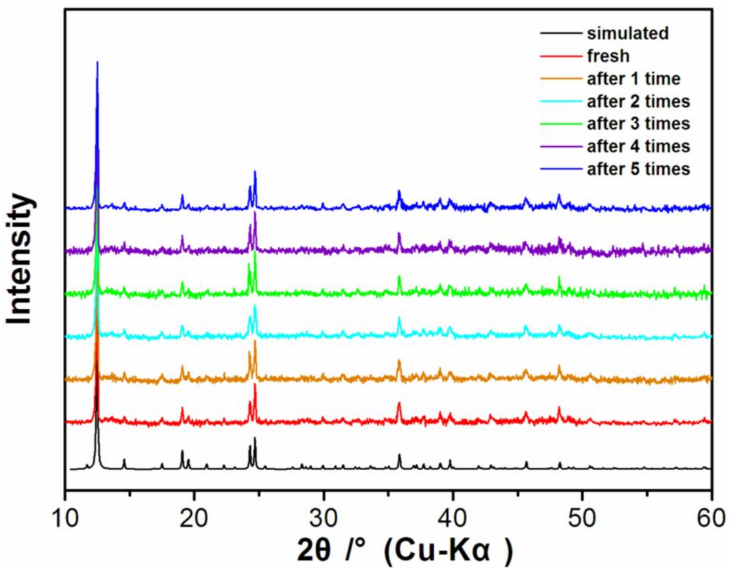


Fig. S6 The XRPD patterns based on the single-crystal structure of **1**: simulated one (dark line)，fresh one (red line), after 1(brown line), 2 (cyan line), 3 (green line), 4 (purple line), and 5 (blue line) times recycling.

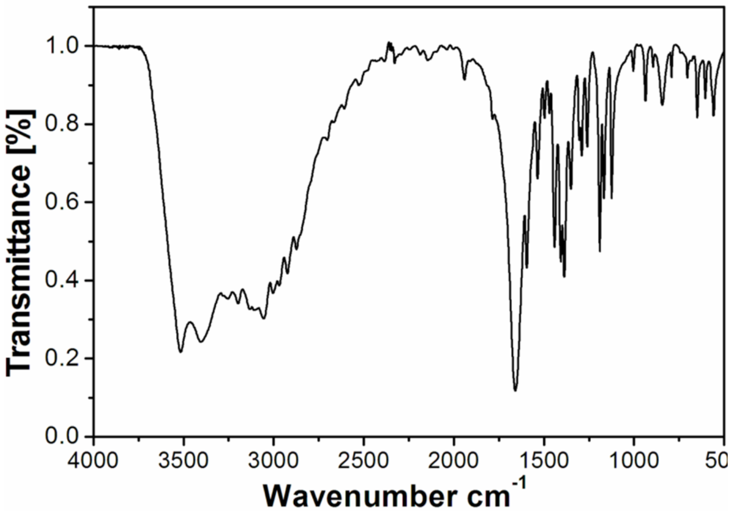
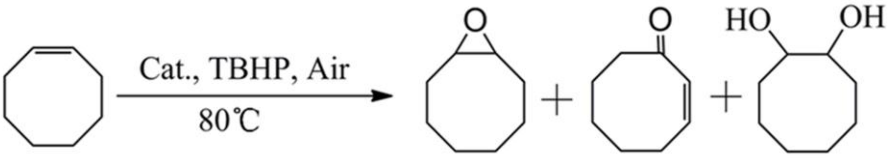
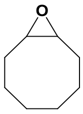
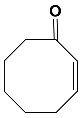
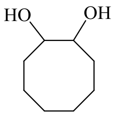


Fig. S7 IR spectrum of **1**.



Scheme S1 The equation of *cis*-cyclooctene epoxidation.

Table S1. Effect of variety of reaction time on selective oxidation of *cis*-cyclooctene using compound **1** as catalyst.

Reaction time (h)	Product Selectivity (%)			Conversion (%)	$\Sigma_{sel}C_8$[§]
					
0	0	0	0	0	0
4	74.11	14.41	11.47	6.88	99.99
8	77.44	13.00	9.23	13.65	99.67
12	80.78	11.31	7.54	17.97	99.63
16	82.80	10.70	5.84	25.40	99.34
20	84.76	9.23	5.35	29.93	99.34
24	87.71	7.82	3.71	34.84	99.24

Reaction conditions: compound **1** (20 mg), *cis*-cyclooctene (10 mL), TBHP (0.5 mL), 80 ºC, 24 h, atmospheric pressure.

§Total selectivity to C_8 partial oxidation products.

Table S2. Crystal data and structure refinement for **1**.

Complex	**1**
Chemical formula	$C_{10}H_{14}Co_3N_8O_8$
Formula weight	551.08
T (K)	296(2)
λ (Å)	0.71073
Crystal system	Tetragonal
Space group	$I4_1/a$
a (Å)	20.7387(5)
b (Å)	20.7387(5)
c (Å)	8.4495(4)
α (˚)	90
β (˚)	90
γ (˚)	90
V (Å^3)	3634.1(2)
Z	8

Dc (g/cm^3)	2.014
μ (mm^{-1})	2.767
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0371
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.1510
R_1 (all data)	0.0427
wR_2 (all data)	0.1592

[a]$R_1 = \sum||F_0|-|F_C||/\sum|F_0|$; [b]$wR_2 = \sum[w(F_0{}^2-F_C{}^2)^2]/\sum[w(F_0{}^2)^2]^{1/2}$

Table S3. Selected bond lengths [Å] and angles [°] for **1**.

Compound **1**			
Co(1)-O(1)	2.101(2)	Co(2)-O(1)	2.240(2)
Co(1)-O(1)#1	2.101(2)	Co(2)-N(1)	2.093(3)
Co(1)-O(1W)	2.0062(18)	Co(2)-N(2)#3	2.059(3)
Co(1)-O(1W)#1	2.0062(18)	Co(2)-O(1W)	2.0632(19)
Co(1)-N(3)	2.141(3)	Co(2)-O(2W)	2.0158(19)
Co(1)-N(3)#1	2.141(3)	Co(2)-O(2W)#2	2.0460(19)
O(1W)-Co(1)-O(1)	81.90(8)	O(2W)-Co(2)-O(1W)	96.15(8)
O(1W)-Co(1)-O(1)#1	98.10(8)	O(1W)-Co(2)-O(1)	77.35(8)
O(1W)#1-Co(1)-O(1)	98.10(8)	O(2W)-Co(2)-O(1)	84.41(9)
O(1W)#1-Co(1)-O(1W)	180.00(9)	N(1)-Co(2)-O(1)	169.34(10)
O(1W)#1-Co(1)-O(1)#1	81.90(8)	O(2W)#2-Co(2)-O(1W)	169.82(8)
O(1)-Co(1)-O(1)#1	180.000(1)	O(2W)-Co(2)-O(2W)#2	83.48(8)
O(1W)-Co(1)-N(3)	88.71(9)	N(2)#3-Co(2)-O(1W)	89.32(10)
O(1)-Co(1)-N(3)	90.53(11)	O(2W)#2-Co(2)-O(1)	92.50(8)
O(1W)#1-Co(1)-N(3)	91.29(9)	N(2)#3-Co(2)-O(1)	88.57(10)
O(1)#1-Co(1)-N(3)	89.47(11)	O(1W)-Co(2)-N(1)	94.40(9)
O(1W)#1-Co(1)-N(3)#1	88.71(9)	O(2W)-Co(2)-N(1)	89.84(10)
O(1W)-Co(1)-N(3)#1	91.29(9)	O(2W)#2-Co(2)-N(1)	95.77(10)
O(1)-Co(1)-N(3)#1	89.47(11)	N(2)#3-Co(2)-N(1)	98.18(11)
O(1)#1-Co(1)-N(3)#1	90.53(11)	O(2W)-Co(2)-N(2)#3	169.93(10)
N(3)-Co(1)-N(3)#1	180.0	O(2W)#2-Co(2)-N(2)#3	89.64(10)

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