Supporting information

Mixed Cu(II)-Bi(III) Metal Organic Framework with a 2-D inorganic subnetwork and its catalytic activity

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Experimental

2.1 Materials

All reagents are commercially available and were used without further purification. Copper(II) hydroxide carbonate ($CuCO_3{\cdot}Cu(OH)_2$, ≥ 99%, Panreac), bismuth (III) nitrate pentahydrates ($Bi(NO_3)_3{\cdot}5H_2O$, ≥ 98%, Panreac), 4,4’-bipyridine (4,4’-bpy, $C_{10}H_8N_2$, ≥ 98%, Alfa Aesar), 3,5-pyrazoledicarboxylic acid monohydrate (H_3pdc, $C_5H_5N_2O_4{\cdot}H_2O$, ≥ 98%, Alfa Aesar).

2.2 synthesis of $Bi_3O_2Cu(OH)$(3,5-pdc)$_2$, **1**

0.0317 g (0.14 mmol) of $CuCO_3{\cdot}Cu(OH)_2$, 0.1272 g (0.26 mmol) of $Bi(NO_3)_3{\cdot}5H_2O$, 0.0413 g (0.26 mmol) of 4,4´-bpy and 0.0622 g (0.36 mmol) of 3,5-pdc were added into 10.2 g of distilled water under magnetic stirring. The mixture was transferred into a 25 mL Teflon-lined autoclave and heated at 200 °C in an oven for 3 days. After natural cooling, the sample was filtered and washed with 3×50 mL distilled water. Intense blue crystals of **1** were harvested as a pure phase and air-dried at ambient conditions (0.070 g, yield ca. 76% based on $Bi(NO_3)_3{\cdot}5H_2O$). IR data (ν/cm^{-1}, Fig. S1): 3556 (w), 3106 (w), 1634 (s), 1565 (s), 1534 (s), 1509 (m), 1381 (m), 1340 (s), 1291 (s), 1267 (m), 1056 (m), 1005 (m), 846 (m), 789 (m), 603 (w), 531 (s), 454 (w). Anal. Calcd for (**1**) $C_{10}H_3Bi_3CuN_4O_{11}$ (MW = 1045.64): Bi, 59.96; Cu, 6.08; C, 11.48; H, 0.29; N, 5.36. Found: Bi, 59.88; Cu, 6.17; C, 11.32; H, 0.22; N, 5.21.

2.3 Instrumentation

Elemental analysis (EA) on CHN was performed with a TruSpec 630-200-200 CNHS Analyser at the Microanalysis Laboratory at the Department of Chemistry, University of Aveiro. FTIR spectra were collected using KBr pellets (Aldrich, 99%+, FTIR grade) on a Mattson 7000 FTIR spectrometer.

Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50, between room temperature and 700 °C with a heating rate of 5 °C/min, under an air atmosphere. Scanning electron microscopy (SEM) was performed using a Hitachi Su-70 and energy dispersive analysis of X-rays spectroscopy (EDS) was carried out on a Bruker QUANTAX 400 instruments working at 15 kV. Samples were prepared by deposition on aluminum sample holders by carbon coating. Powder X-ray diffraction data (PXRD) were collected at ambient temperature (*ca.* 298 K) on a X'Pert MPD Philips diffractometer (Cu-Kα radiation, $\lambda = 1.54056$ Å), equipped with a X'Celerator detector, curved graphite monochromated radiation and a flat-plate sample holder, in a Bragg–Brentano para-focusing optics configuration (40 kV, 50 mA). Intensity data were collected in the continuous scanning mode in the range ca. $5° < 2\theta < 50°$. The variable temperature experiment performed on **1** was conducted on the same instrument using a high-temperature Antoon Parr HKL 16 chamber, controlled by a Antoon Parr 100 TCU unit. Intensity data were collected in the step mode (0.02 º, 5 s per step) in the range ca. $5 \leqq 2\theta\,(°) \leqq 40$ from room temperature to 450 ºC.

2.4 X-Ray crystallography

Complete single-crystal data was collected at 296(2) K on a Bruker X8 Kappa APEX II charge-coupled device (CCD) area-detector diffractometer (Mo-Kα graphite monochromated radiation, $\lambda = 0.7107$ Å) controlled by the APEX2 software package.[1] Images were processed using the software package SAINT+.[2] Absorption corrections were applied by the multiscan semiempirical method implemented in SADABS.[3] The structure was solved by direct method using SHELXS-97 and refined using SHELXL-97.[4] All non-hydrogen atoms were successfully refined with anisotropic displacement parameters. Hydrogen atoms bound to carbon were located at their idealized positions by employing the HFIX 43 instruction in SHELXL-97 and included in subsequent refinement cycles in riding motion approximation with isotropic thermal displacement parameters (Uiso) fixed at 1.2Ueq of the carbon atom to which they were attached. The hydrogen atom associated with hydroxyl group was visible in the last difference Fourier maps synthesis. This atom has been included in the final structural model with the O-H distance perfectly refined to 0.8210(1) Å without adding any restraint. Complete crystallographic data (without including structure factors) for the structure reported in this paper has been deposited in the CIF format with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 871627. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

2.5 Catalytic experiments

2.5.1 Chemicals

Benzaldehyde (≥99%), cyclohexanone (≥99.5%) and chlorobenzene (≥99.5%) were from Aldrich. *N*-propylamine (≥98.0%) from BDH and dichloromethane was HPLC grade and from Romil.

2.5.2 Catalysis experiments

To 1.00 mmol of benzaldehyde, 3.00 mmol of cyclohexanone, 0.50 mmol of chlorobenzene (internal standard) and 0.0241 g of **1** in 5.00 mL of dichloromethane 1.00 mmol of *n*-propylamine was added. The reaction mixture was stirred at 1300 rpm and room temperature. Aliquots of 0.1 mL were periodically withdrawn, filtered through Nylon syringe filters of 0.2 µm, and analysed by Varian 450 GC-FID. The obtained products, depicted as *E*-**2** and *Z*-**2** in Scheme 1, were confirmed by Finnigan Trace GC-MS.

Control experiments without addition of catalyst and also in the presence of 0.01 mmol of $Bi(NO_3)_3\cdot5H_2O$ were also performed.

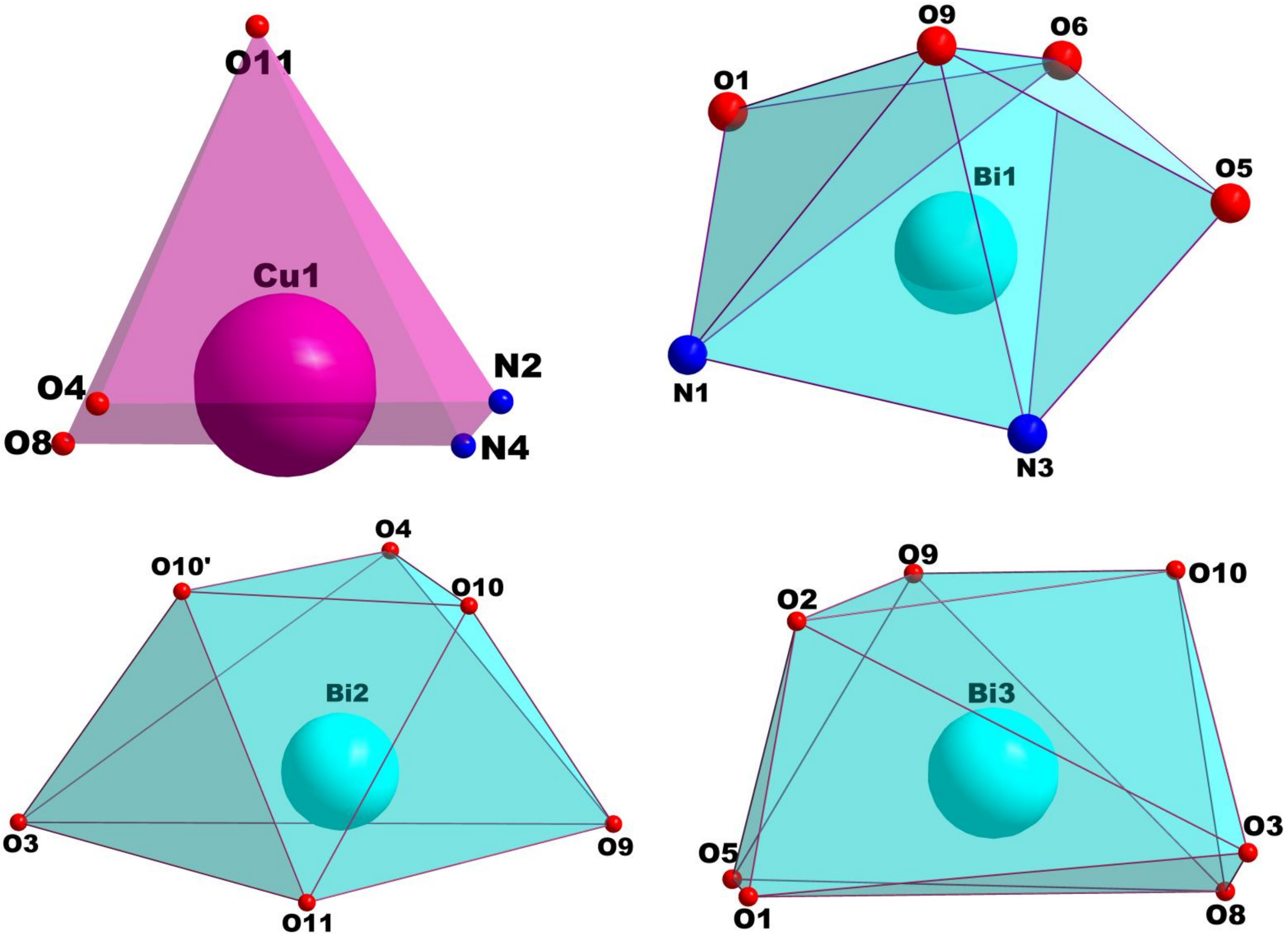


Figure S1 Polyhedral view of the coordination environment of metal atoms (Cu(1), Bi(1), Bi(2) and Bi(3)) in compound **1**.

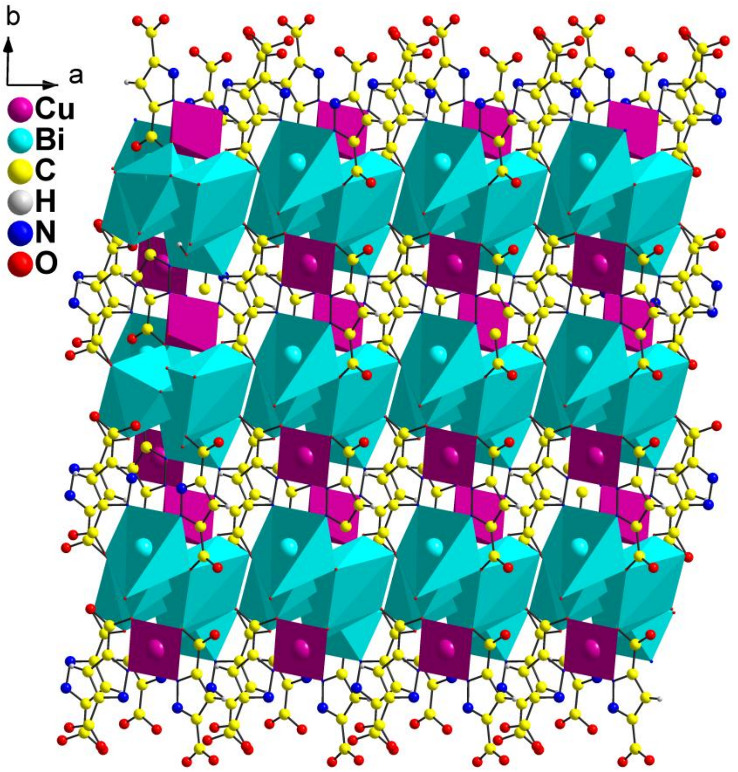


Figure S2: Polyhedron view of the super cell (2×2×2) structure of **1** along the *c* axis

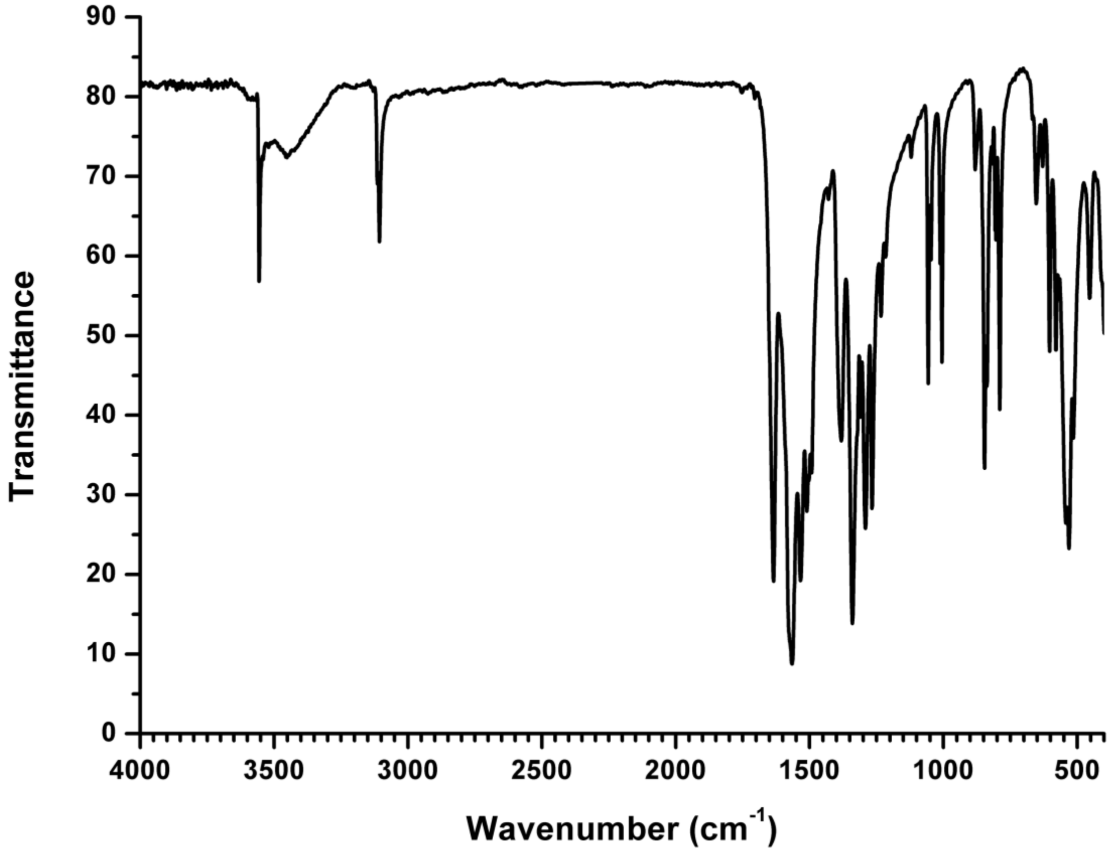


Figure S3: FT-IR spectrum of compound **1**

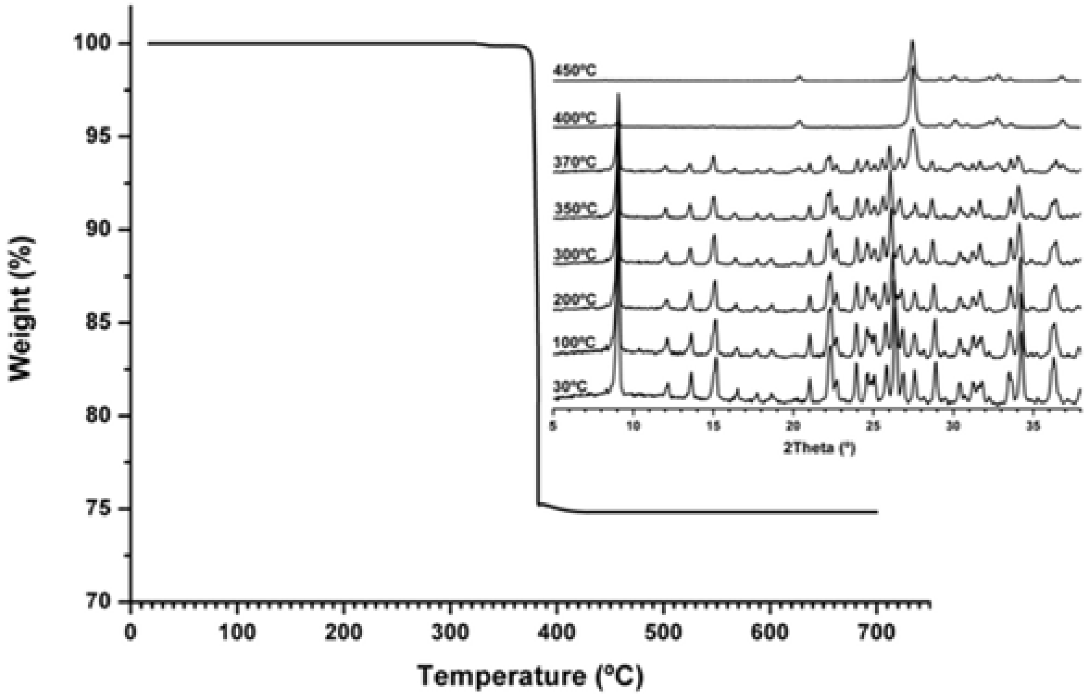
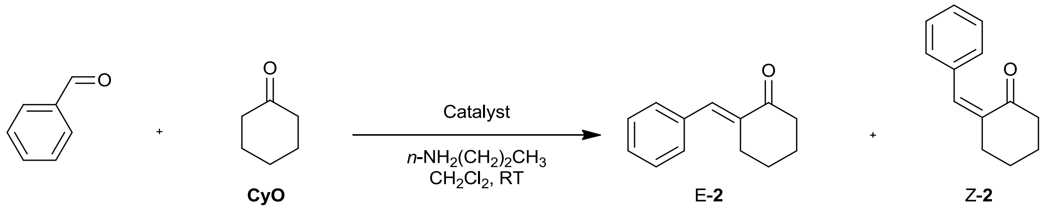


Figure S4 TGA plot and *in situ* powder XRD patterns (inset) of **1** in air show that **1** is stable up to 370 ºC.



Scheme 1 Synthesis of an (*E*)-*α*,*β*-unsaturated ketones (**2**) from the cross-condensation of benzaldehyde and cyclohexanone in the presence of *n*-propylamine.

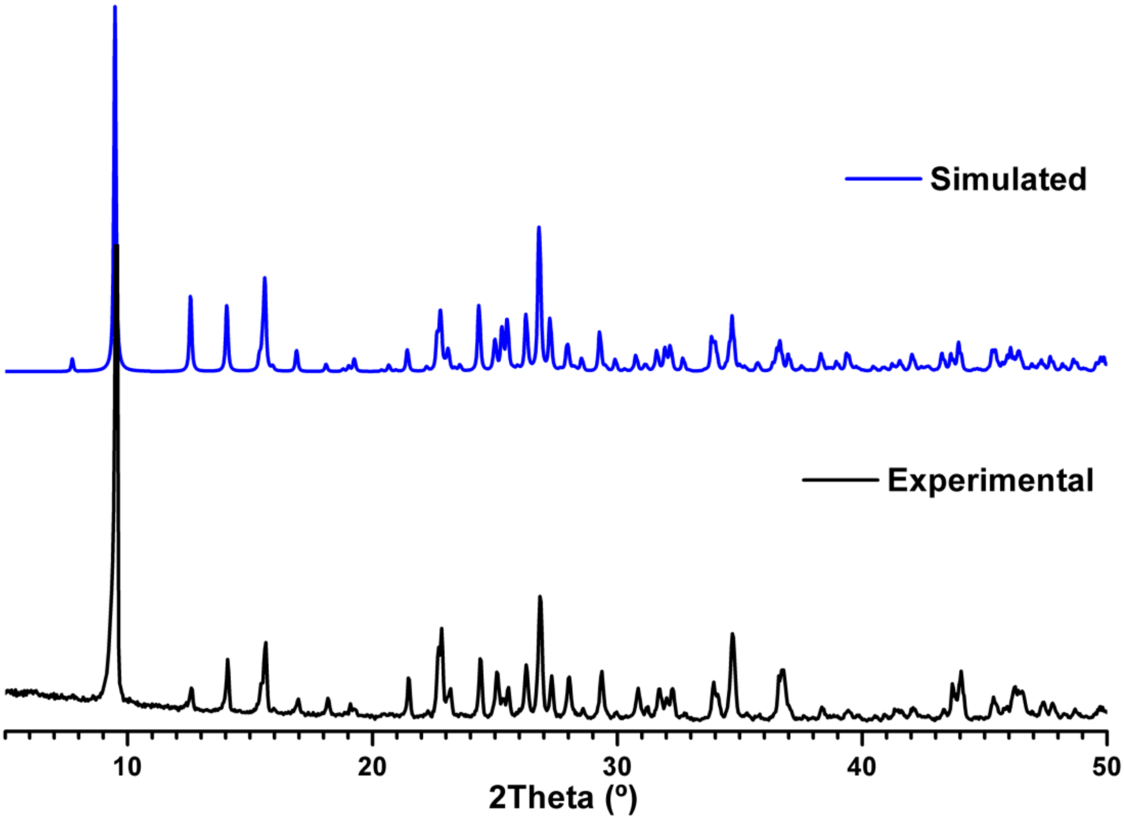


Figure S5 Experimental and simulated (from single-crystal structure) powder XRD patterns of **1** show that this is a pure phase.

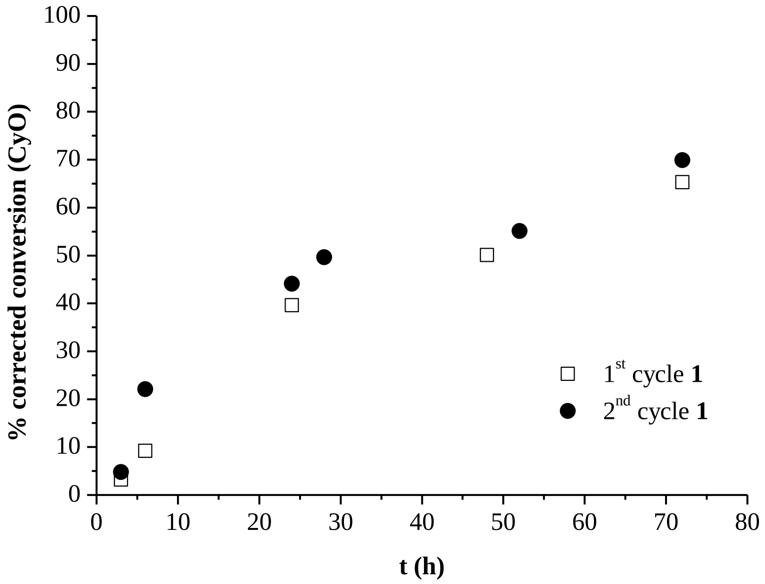


Figure S6. Recycling experiment of MOF **1** in the cross-condensation of cyclohexanone and benzaldehyde: 1st cycle (rectangles) and 2nd cycle (circles)

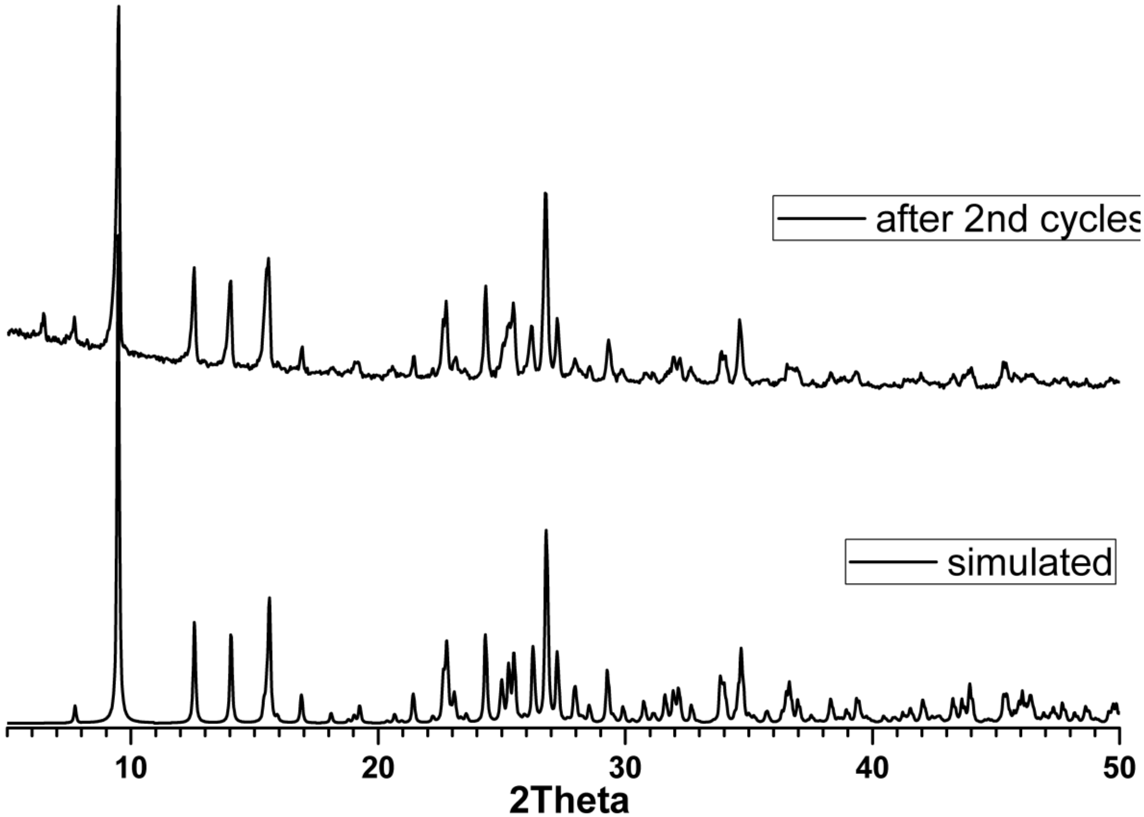


Figure S7 Powder and simulated XRD pattern of the material **1** after the 2nd cycle of catalysis.

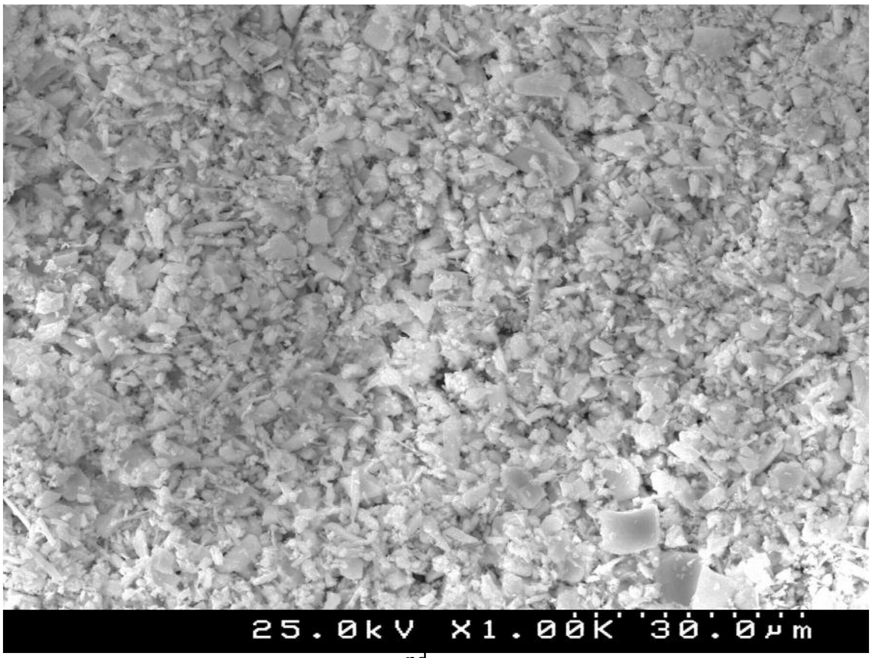


Figure S8 SEM image of the material **1** after the 2nd cycle of catalysis

Table S1 Crystallographic Data, Details of Data Collection, and Structure Refinement Parameters for **1**

chemical formula	$C_{10}H_3Bi_3CuN_4O_{11}$
M (g/mol)	1045.64
temperature (K)	296(2)
wavelength (Å)	0.71073
crystal size (mm^3)	0.17 × 0.05 × 0.03
crystal system	triclinic
space group	$P\bar{1}$
a (Å)	7.0862(5)
b (Å)	9.8582(7)
c (Å)	12.1267(8)
α (°)	71.132(4)
β (°)	83.785(4)
γ (°)	86.867(4)
V ($Å^3$)	796.73(10)
Z	2
*D*c (g/cm^3)	4.359
μ (mm^{-1})	34.424
F(000)	914
theta range for data collection (°)	3.54 to 30.03
reflections collected	21057
independent reflections	4619[R(int) = 0.0635]
completeness to theta = 30.61°	99.5%
data / restraints / parameters	4619 / 0 / 266
goodness of fit on F^2	1.044
final $R1$, $wR2[I > 2\sigma(I)]$	0.0414, 0.0887
$R1$, $wR2$ (all data)	0.0604, 0.0955
largest diff. peak and hole (e $Å^{-3}$)	3.420 and -3.096

Table S2 Selected bond distances (Å) and angles (°) for **1**

Cu(1)-N(2)	1.950(7)	Cu(1)-N(4)	1.956(8)
Cu(1)-O(8)	1.991(7)	Cu(1)-O(4)	2.003(7)
Cu(1)-O(11)	2.304(8)	Bi(1)-O(9)	2.067(6)
Bi(1)-O(1)	2.450(7)	Bi(1)-N(1)	2.467(8)
Bi(1)-N(3)	2.549(7)	Bi(1)-O(6)#1	2.566(7)
Bi(1)-O(5)	2.594(7)	Bi(2)-O(11)#2	2.153(8)
Bi(2)-O(10)	2.153(6)	Bi(2)-O(10)#3	2.191(6)
Bi(2)-O(9)	2.397(6)	Bi(2)-O(4)#4	2.739(7)
Bi(2)-O(3)	2.8608(7)	Bi(2)-Bi(2)#3	3.5415(7)
Bi(2)-Bi(3)	3.5938(5)	Bi(3)-O(10)	2.118(6)
Bi(3)-O(9)	2.154(6)	Bi(3)-O(2)#5	2.404(7)
Bi(3)-O(8)#4	2.504(7)	Bi(3)-O(5)	2.575(6)
Bi(3)-O(3)#6	2.709(7)	Bi(3)-O(1)#5	2.8666(7)
N(2)-Cu(1)-N(4)	97.5(3)	N(2)-Cu(1)-O(8)	165.9(3)
N(4)-Cu(1)-O(8)	81.2(3)	N(2)-Cu(1)-O(4)	81.9(3)
N(4)-Cu(1)-O(4)	165.1(3)	O(8)-Cu(1)-O(4)	95.8(3)
N(2)-Cu(1)-O(11)	94.2(3)	N(4)-Cu(1)-O(11)	106.4(3)
O(8)-Cu(1)-O(11)	99.6(3)	O(4)-Cu(1)-O(11)	88.4(3)
O(9)-Bi(1)-O(1)	77.8(2)	O(9)-Bi(1)-N(1)	93.3(3)
O(1)-Bi(1)-N(1)	65.9(2)	O(9)-Bi(1)-N(3)	93.8(2)
O(1)-Bi(1)-N(3)	142.1(2)	N(1)-Bi(1)-N(3)	78.0(3)
O(9)-Bi(1)-O(6)#1	85.0(3)	O(1)-Bi(1)-O(6)#1	70.4(2)
N(1)-Bi(1)-O(6)#1	135.6(2)	N(3)-Bi(1)-O(6)#1	146.5(2)
O(9)-Bi(1)-O(5)	71.3(2)	O(1)-Bi(1)-O(5)	142.6(2)
N(1)-Bi(1)-O(5)	135.2(2)	N(3)-Bi(1)-O(5)	62.1(2)
O(6)#1-Bi(1)-O(5)	86.1(2)	O(11)#2-Bi(2)-O(10)	87.7(3)
O(11)#2-Bi(2)-O(10)#3	90.5(3)	O(10)-Bi(2)-O(10)#3	70.8(3)
O(11)#2-Bi(2)-O(9)	92.1(3)	O(10)-Bi(2)-O(9)	67.8(2)
O(10)#3-Bi(2)-O(9)	138.3(2)	O(11)#2-Bi(2)-O(4)#4	167.3(3)
O(10)-Bi(2)-O(4)#4	80.7(2)	O(10)#3-Bi(2)-O(4)#4	80.7(2)
O(9)-Bi(2)-O(4)#4	88.4(2)	Bi(2)#3-Bi(2)-Bi(3)	67.926(12)
O(10)-Bi(3)-O(9)	73.2(2)	O(10)-Bi(3)-O(2)#5	90.5(2)
O(9)-Bi(3)-O(2)#5	81.4(2)	O(10)-Bi(3)-O(8)#4	81.0(2)
O(9)-Bi(3)-O(8)#4	95.2(2)	O(2)#5-Bi(3)-O(8)#4	171.4(2)
O(10)-Bi(3)-O(5)	143.3(2)	O(9)-Bi(3)-O(5)	70.5(2)
O(2)#5-Bi(3)-O(5)	88.9(2)	O(8)#4-Bi(3)-O(5)	97.4(2)
O(10)-Bi(3)-O(3)#6	68.4(2)	O(9)-Bi(3)-O(3)#6	141.5(2)
O(2)#5-Bi(3)-O(3)#6	100.4(2)	O(8)#4-Bi(3)-O(3)#6	77.3(2)
O(5)-Bi(3)-O(3)#6	147.4(2)	Bi(3)-O(5)-Bi(1)	92.9(2)
Cu(1)-O(4)-Bi(2)#7	126.9(3)	Bi(1)-O(9)-Bi(3)	125.1(3)
Cu(1)-O(8)-Bi(3)#7	134.1(3)	Bi(1)-O(9)-Bi(2)	129.3(3)
Bi(2)#2-O(11)-Cu(1)	128.6(3)	Bi(3)-O(9)-Bi(2)	104.2(2)
Bi(3)-O(10)-Bi(2)	114.6(3)	Bi(3)-O(10)-Bi(2)#3	135.4(3)
Bi(2)-O(10)-Bi(2)#3	109.2(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1 ; #2 -x+1,-y+1,-z ; #3 -x+1,-y,-z ; #4 x,y-1,z ; #5 x+1,y,z ; #6 x+1,y-1,z ; #7 x,y+1,z.

Table S3 hydrogen bonds for **1** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(11A)...O(10)#1	0.82(14)	2.33(14)	2.984(10)	138(13)
O(11)-H(11A)...O(9)#1	0.82(14)	2.58(15)	3.281(11)	144(12)

Symmetry transformation used to generate equivalent atoms: #1 -x+1,-y+1,-z

References

1 APEX2 (2006): Data Collection Software Version 2.1-RC13, Bruker AXS, Delft, The Netherlands
2 SAINT+(1997-2005): Data Integration Engine v. 7.23a. Bruker AXS, Madison, Wisconsin, USA
3 Sheldrick GM (1998) SADABS v. 2.01: Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA
4 (*a*) Sheldrick GM (1997) SHELXS-97: Program for Crystal Structure Solution, University of Göttingen; (*b*) Sheldrick GM (1997) SHELXL-97: Program for Crystal Structure Refinement, University of Göttingen