Electronic Supplementary Information for

Self-assembly of mixed-valent and heterometallic metallocycles: efficient catalyst for oxidation of alcohols to aldehydes with ambient air

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General Procedure

Starting materials, reagents, and solvents were purchased from commercial sources (Alfa Aesar, Engry, TCI and Sigma) and used without further purification. FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer (vs = very strong, s = strong, m = middle, w = weak). ^{1}HNMR Nuclear Magnetic Resonance spectra were measured using a Bruker AVANCE III HD 400 (400 MHz) equipment. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using Q50 TGA (TA) thermal analysis equipment with a heating rate of 10 °C min^{-1}. Gas chromatography mass spectrometry was carried out in Agilent 5977B GCMS. Powder X-ray diffraction (PXRD) patterns of the bulk samples were measured on a Rigaku Ultima IV X-ray Diffractometer (Cu Kα, λ = 1.5418 Å). Elemental analyses were carried out with an Elementar vario Micro Cube equipment. ESI-TOF mass spectra were recorded on an API-TOFMS II (China) mass spectrometer. Data analyses and simulations of ESI-TOF mass spectra were processed on an API-TOFMS II software.

1.1 Preparation of ligands.

Synthesis of H_2L1 A mixture of 1H-imidazole-4-carbaldehyde (3840 mg, 40 mmol), 1,4-butanediamine (1760 mg, 20 mmol) and 150 mL methanol into 300 mL Round bottom flask, The mixture was heated to 80 °C for 6 h, then vacuum-screwed and dried (Yield: 95.1%). ^{1}H NMR (CD_3OD, 25 °C, 400 MHz): δ 8.27 (s, 2H); δ 7.78 (s, 2H); δ 7.54 (s, 2H); δ 3.62 (s, 4H); δ 1.77 (s, 4H).

Synthesis of H_2L2 A mixture of 1H-imidazole-4-carbaldehyde (3840 mg, 40 mmol), propane-1,3-diamine (1480 mg, 20 mmol) and 150 mL methanol into 300 mL Round bottom flask, The mixture was heated to 80 °C for 6 h, then vacuum-screwed and dried (Yield: 94%). ^{1}H NMR (CD_3OD, 25 °C, 400 MHz): δ 8.21 (s, 2H); δ 7.70 (s, 2H); δ 7.28 (s, 2H); δ 3.55 (s, 4H); δ 1.89 (s, 4H).

1.2 Synthesis of the mononuclear complexes

Synthesis of $Cu(H_2L1)$ A mixed of H_2L1 (976 mg, 4 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (1480 mg, 4 mmol) and 50 mL methanol into erlenmeyer flask, and then stir at room temperature for 12 h, vacuum distillation, and dry to obtain blue powder. Yield: 98%. MS: *m/z*, Calcd for $C_{12}H_{15}N_6CuClO_4$ ($[(CuL1){\cdot}ClO_4]^+$) 405.01, found 404.90.

Synthesis of $Cu(H_2L2)$ A mixed of H_2L2 (920 mg, 4 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (1480 mg, 4 mmol) and 50 mL methanol into erlenmeyer flask, and then stir at room temperature for 12 h, vacuum distillation, and dry to obtain blue powder. Yield: 97%. MS: *m/z*, Calcd for $C_{11}H_{13}N_6CuClO_4$ ($[(CuL2){\cdot}ClO_4]^+$) 391.00, found 391.91.

2.1 Syntheses of the metallocycles

Synthesis of 1 A mixture of $Cu(H_2L1)$ (24.42 mg, 0.06 mmol), Cu_2O (8.58 mg, 0.06 mmol), and mixed solvent *of N*, *N*'-dimethylacetamide (DMA)/ ethanol (3 mL, 2:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 h. and then cooled to room temperature at a rate of 5 °C h^{-1}. Compound **1** can also be synthesized by using second method by direct using H_2L1. For example, the heating of a mixture of Cu $(ClO_4)_2{\cdot}6H_2O$ (11.12 mg, 0.03 mmol), Cu_2O (4.29 mg, 0.03 mmol), H_2L1 (7.3 mg, 0.03 mmol) and mixed solvent of DMA/ ethanol (3 mL, 2:1, v/v) also afforded metallocycle **1** under solvothermal conditions (at 100 °C for 72 h). Both methods given purple rod crystals with equal yield (yield: 88%). IR (KBr, cm^{-1}): 3126.55 (w), 2934.19 (w), 2862.87 (w), 1620.96 (vs), 1551.72 (m), 1470.78 (s), 1351.12 (m), 1252.76 (s), 1209 (s), 984.3 (m), 856.12 (m), 649.81 (vs), 620.27 (w); Elemental analysis (CHN) for $C_{36}H_{42}N_{18}Cl_3O_{12}Cu_6$: C 30.45, H 3.192, N 18.11; found (%): C 30.77, H 2.94, N 17.94.

Synthesis of 2 The purple rod crystals of metallocycle **2** were synthesized similarly to **1** by using Cu(H_2L2) instead of Cu(H_2L1) or H_2L2 instead of H_2L1 for second method. (yield: 94% based on Cu salt). IR (KBr, cm^{-1}): 3441.45 (w), 3126.92 (w), 2937.90 (w), 2446 (w), 1731 (w), 1615 (vs), 1551 (m), 1469 (s), 1334.35 (m), 1240.54 (s), 1094 (vs), 874 (m), 772 (m), 616 (vs), 466 (w); Elemental analysis (CHN) for $C_{33}H_{36}N_{18}Cl_3O_{12}Cu_6$: C 28.82, H 2.882, N 18.74; found (%): C 29.05, H 2.66, N 18.48.

Synthesis of 3 A solution containing a mixture of Cu(H_2L1) (24.42 mg, 0.06 mmol), $AgNO_3$ (10.2 mg, 0.06 mmol), and mixed solvent of DMA/ethanol (3 mL, 2:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 h, and then cooled to room temperature at a rate of 5 °C h^{-1}. Similarly, compound **3** can also be synthesized by using second method by direct using H_2L1. For example, the heating of a mixture of Cu $(ClO_4)_2 \cdot 6H_2O$ (11.12 mg, 0.03 mmol), $AgNO_3$ (5.1 mg, 0.03 mmol), H_2**L1** (7.3 mg, 0.03 mmol) and mixed solvent of DMA/ ethanol (3 mL, 2:1, v/v) also afforded metallocycle **3** under solvothermal conditions (at 100 °C for 72 h). Both methods given purple rod crystals with equal yield (yield: 36%). IR (KBr, cm^{-1}): 3116.07 (m), 2923.95 (w), 2851.90 (w), 1618.59 (vs), 1538.02 (w), 1452.81 (s), 1394.65 (s), 1291.97 (s), 1247.06 (s), 1122.33 (s), 1032.76 (vs), 960.76 (m), 818.92 (m), 634.46 (s); Elemental analysis (CHN) for $C_{36}H_{42}N_{21}O_9Cu_3Ag_3$: C 30.99, H 3.080, N 20.11; found (%): C 30.30, H 2.97, N 20.61.

Synthesis of 4 The purple rod crystals of metallocycle **4** were synthesized similarly to **3** by using Cu(H_2L2) instead of Cu(H_2L1) or H_2L2 instead of H_2L1 for second method. (yield: 94.5%). IR (KBr, cm^{-1}): 3116.45 (w), 3018.92 (w), 2937.46 (w), 2360.75 (m), 1618.59 (vs), 1533 (m), 1462.10 (s), 1390.42 (s), 1314.63 (s), 1256.37 (s), 1117.52 (vs), 1302.95 (s), 877 (m), 818.35 (m), 769 (m), 652.55 (s); Elemental analysis (CHN) for $C_{33}H_{36}N_{18}N_{2}O_{6}Cu_{3}Ag_{3}H_{6}O_{3}$: C 28.67, H 2.798, N 20.42; found (%): C 28.62, H 2.62, N 20.34.

General procedure for catalysis

Oxidation of alcohol The metallocycle **1** (5 mol% equiv. catalyst), benzyl alcohol (0.0925 mmol, 9.99 mg), 2,2,6,6-tetramethylpiperdine-1-oxyl (TEMPO, 10 mol% equiv. co-catalyst) and NMI (50 mol% equiv. base) were added to a glass bottle containing acetonitrile (HPLC, 2 mL). The glass bottle was exposed to air and stirred for 2 hours at room temperature. A green transparent solution was obtained. The reaction solution was filtered by using an organic filter. A certain amount of filtered reaction solution (100 μL) was diluted with acetonitrile (1.3 mL, HPLC). Then, the quantitative internal standard (100 μL, chlorobenzene) was added to the acetonitrile solution, which were analyzed by GCMS to give the conversion.

Knoevenagel condensation reaction Without treating the reaction solution of oxidation of benzyl alcohol, the malononitrile (12.95 mg, 2 equiv) was further added to the solution. The reaction was stirred at room temperature for additional 1.5 h by exposing in air. The reaction solution was filtered by using an organic filter. A certain amount of filtered reaction solution (100 μL) was diluted with acetonitrile (1.3 mL, HPLC). Then, the quantitative internal standard (100 μL, chlorobenzene) was added to the acetonitrile solution, which were analyzed by GCMS to give the conversion.

2.2 Characterization

2.2.1 Crystal Structure Analysis and Additional Characterization.

Crystallographic Studies

Single crystal structures of **1**, **2**, **3** and **4** were measured by X-ray diffraction. Data collection was performed on a XtaLab PRO MM007HF DW Diffractometer System equipped with a MicroMax-007DW MicroFocus X-ray generator and Pilatus 200K silicon diarray detector (Rigaku, Japan, Cu Kα, λ = 1.54184 Å). Crystals were measured at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares refinements based on F^2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were performed using the SHELXL-2014/7 programs. Crystal data and structure refinement were summarized in Table S1. CCDC nos. 1963369-1963370 and 1974814-1974815.

Table S1 Summary of Crystal Data and Structure Refinement Parameters for **1-4.**

Parameter	**1**	**2**
Chemical formula	$C_{36}H_{41}N_{18}Cl_3O_{12}Cu_6$	$C_{33}H_{36}N_{18}Cl_3O_{12}Cu_6$
Formula weight	1405.79	1364.39
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.33780(10)	9.4929(2)
b (Å)	16.3060(3)	14.9760(5)
c (Å)	17.6821(3)	17.9421(4)
α (deg)	112.780(2)	108.253(2)
β (deg)	93.5500(10)	97.505(2)
γ (deg)	102.5950(10)	106.236(3)
V (Å^3)	2390.32(7)	2258.22(11)
Z	2	2
D_{calcd}(g cm^{-3})	1.953	2.007
μ (mm^{-1})	5.151	5.428
Reflections collected	29277	27245
Unique reflections	9849	9307
R_{int}	0.0389	0.0397
Goodness-of-fit on F^2	1.092	1.125
$R_1{}^a$ [I > 2σ(I)]	0.0507	0.0552
$wR_2{}^b$ [I > 2σ(I)]	0.1417	0.1555
$R_1{}^a$ [all refl.]	0.0573	0.0665
$wR_2{}^b$ [all refl.]	0.1462	0.1612
CCDC number	1963370	1963369

^{a} $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; ^{b} $wR_2=[\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)$

Parameter	**3**	**4**
Chemical formula	$C_{36}H_{42}N_{21}O_9Cu_3Ag_3$	$C_{33}H_{36}N_{21}O_9Cu_3Ag_3$
Formula weight	1427.13	1385.06
Crystal system	Triclinic	Triclinic
Space group	P□	P□
a (Å)	9.4794(6)	9.5892(3)
b (Å)	15.6237(8)	14.4378(3)
c (Å)	17.3463(6)	17.4445(4)
α (deg)	109.865(4)	106.568(2)
β (deg)	96.933(4)	94.899(2)
γ (deg)	102.870(5)	107.855(3)
V (Å^3)	2300.8(2)	2163.47(10)
Z	2	2
D_{calcd}(g cm^{-3})	2.060	2.216
μ (mm^{-1})	12.226	12.976
Reflections collected	22359	20290
Unique reflections	9200	8817
R_{int}	0.0582	0.0549
Goodness-of-fit on F^2	1.099	1.080
R_1[a] [I > 2σ(I)]	0.0767	0.0667
wR_2[b] [I > 2σ(I)]	0.2203	0.1891
R_1[a] [all refl.]	0.0835	0.0717
wR_2[b] [all refl.]	0.2332	0.1939
CCDC number	1974814	1974815

[a] $R_1=\sum(||F_o|-|F_c||)/\sum|F_o|$; [b] $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)$

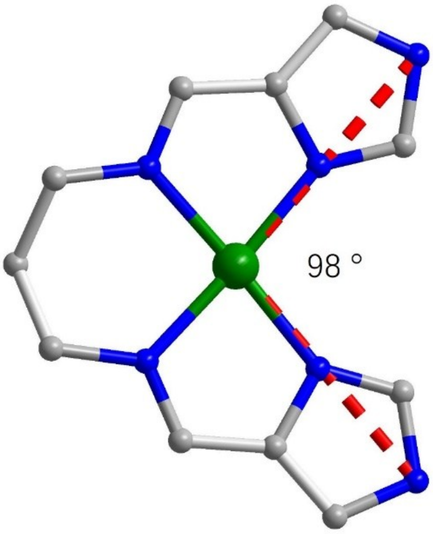
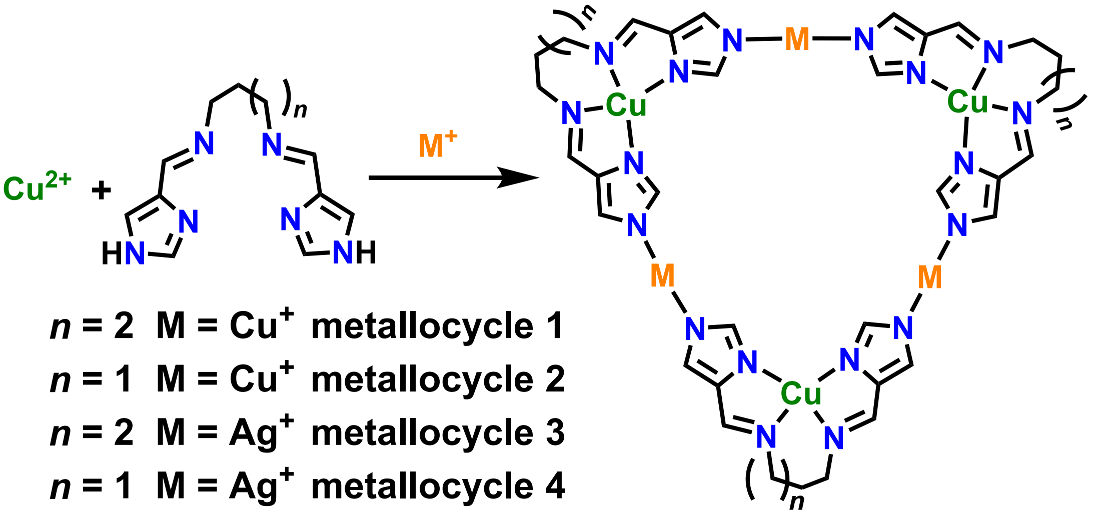


Fig S1, The structure of metalloligand. Color codes: Cu^{II}, Green; C, light gray; N, blue; H, omitted.



Scheme S1 Schematic of one-step synthesis of metallocycles **1-4**.

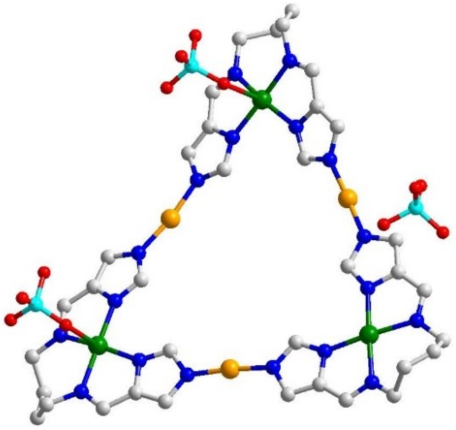


Fig. S2 The asymmetric unit of metallocycle **1**. Color codes: Cu^{II}, Green; Cu^{I}, orange; C, light gray; N, blue; O, red; Cl, turquoise, H, omitted.

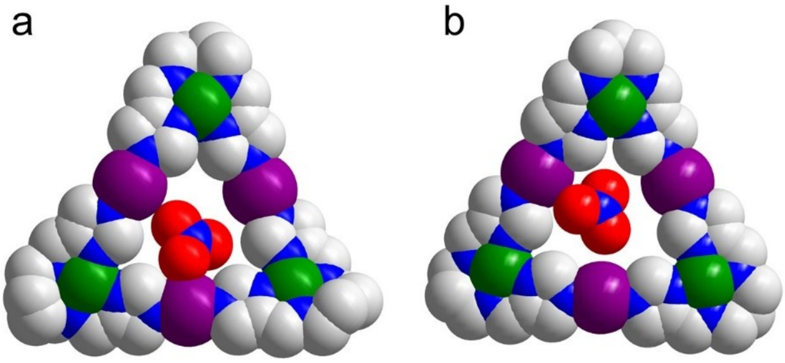


Fig. S3 The space-filling modes of metallocycles **3** (a) and 4 (b) filled with NO_3^- anions. Color codes: Cu^{II}, Green; Ag^{I}, orange; C, light gray; N, blue; O, red; H, omitted.

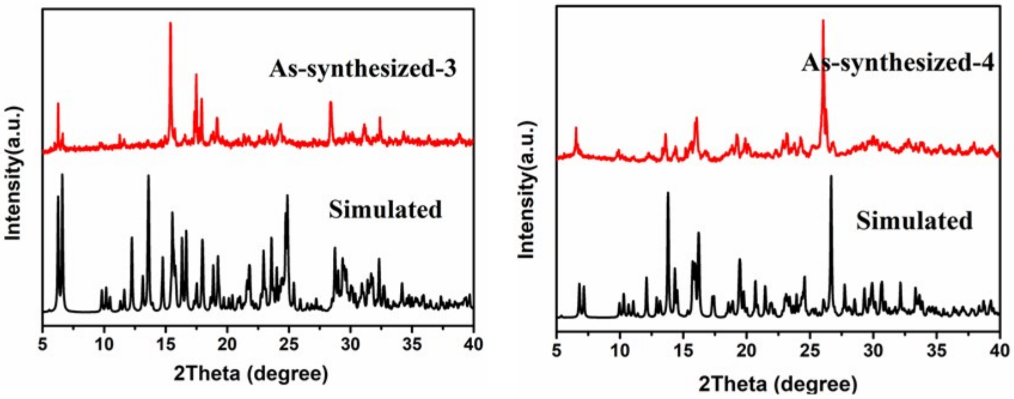


Fig. S4 The PXRD patterns of **3** and **4**.

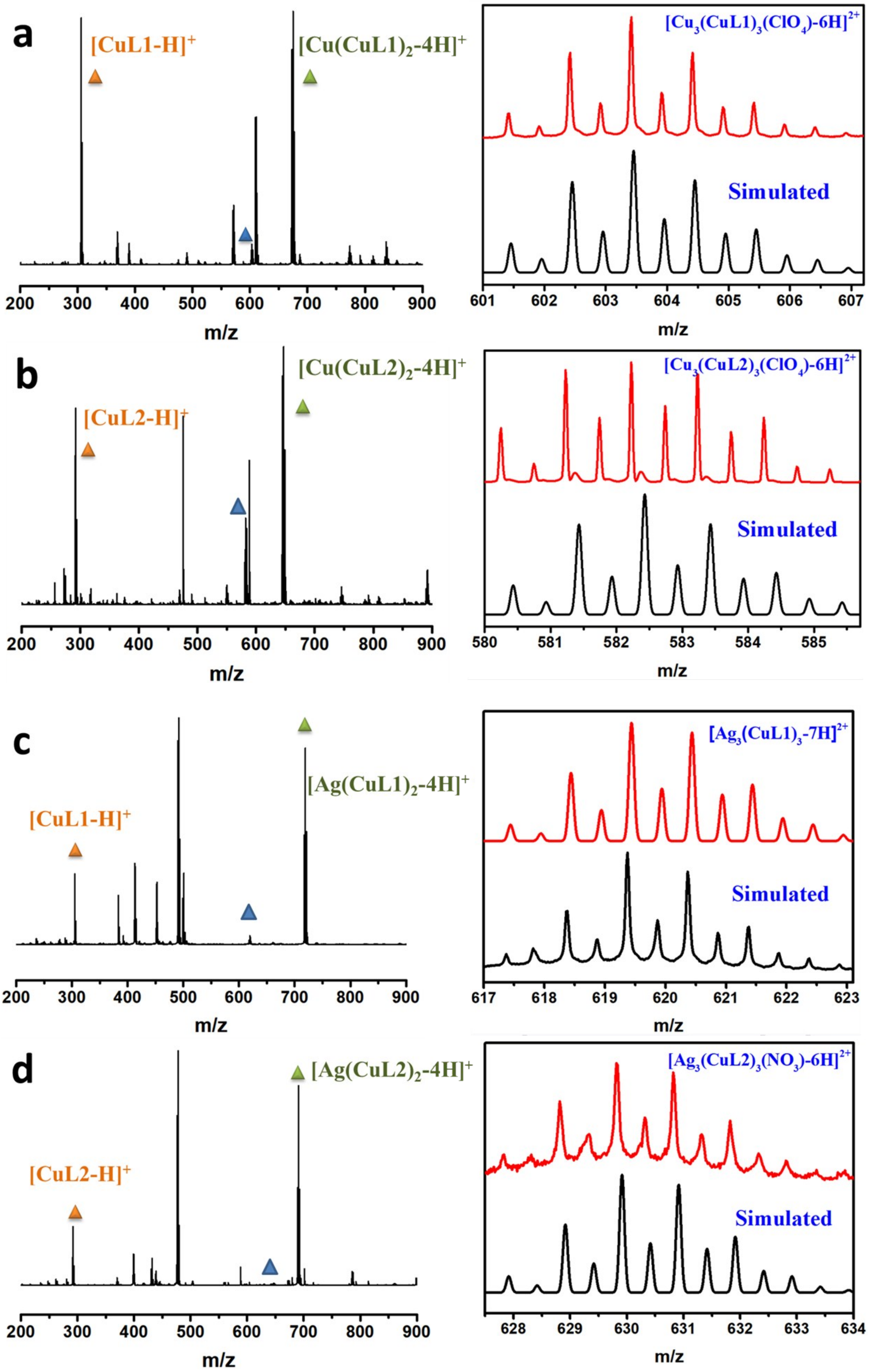


Fig. S5 ESI mass spectrum of **1** (a), **2** (b), **3** (c), and **4** (d) in a CH_3CN solution.

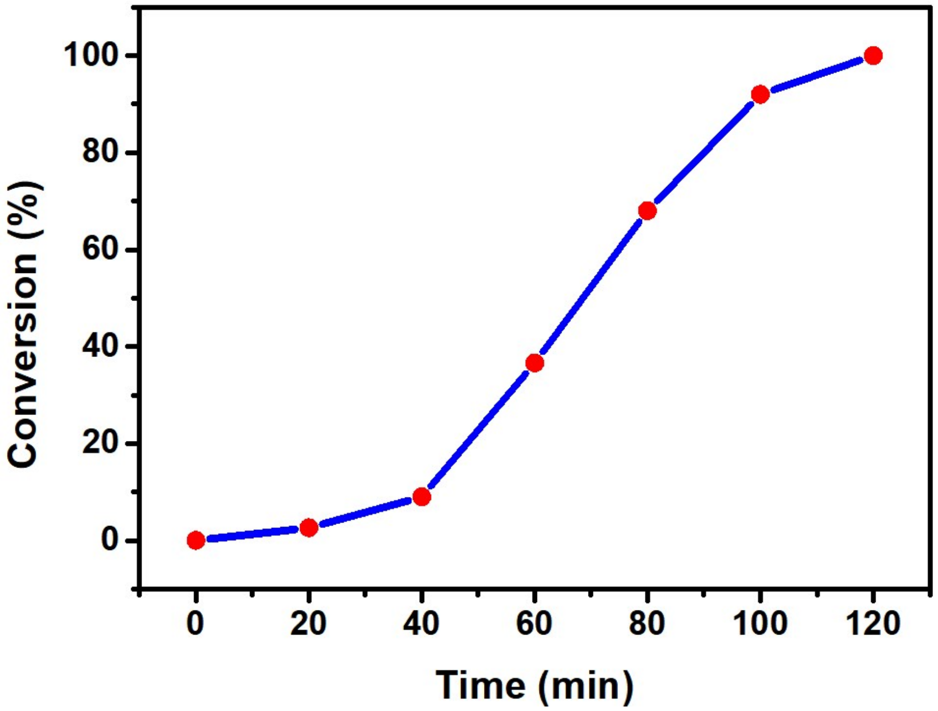
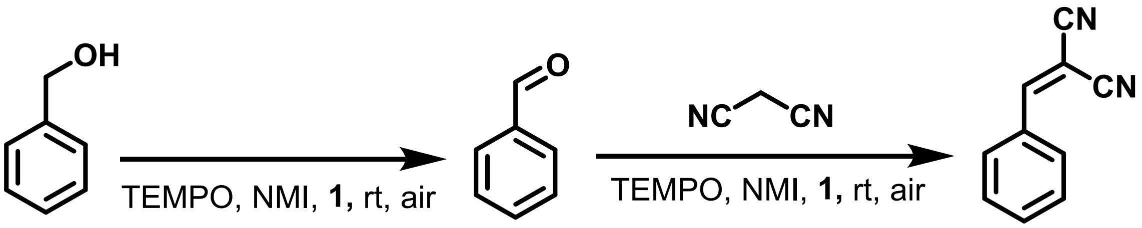


Fig. S6 Time conversion plot for the aerobic oxidation of benzyl alcohol to benzaldehyde catalyzed by **1.**



Scheme S2. The oxidation/Knoevenagel condensation reaction catalyzed by **1**.

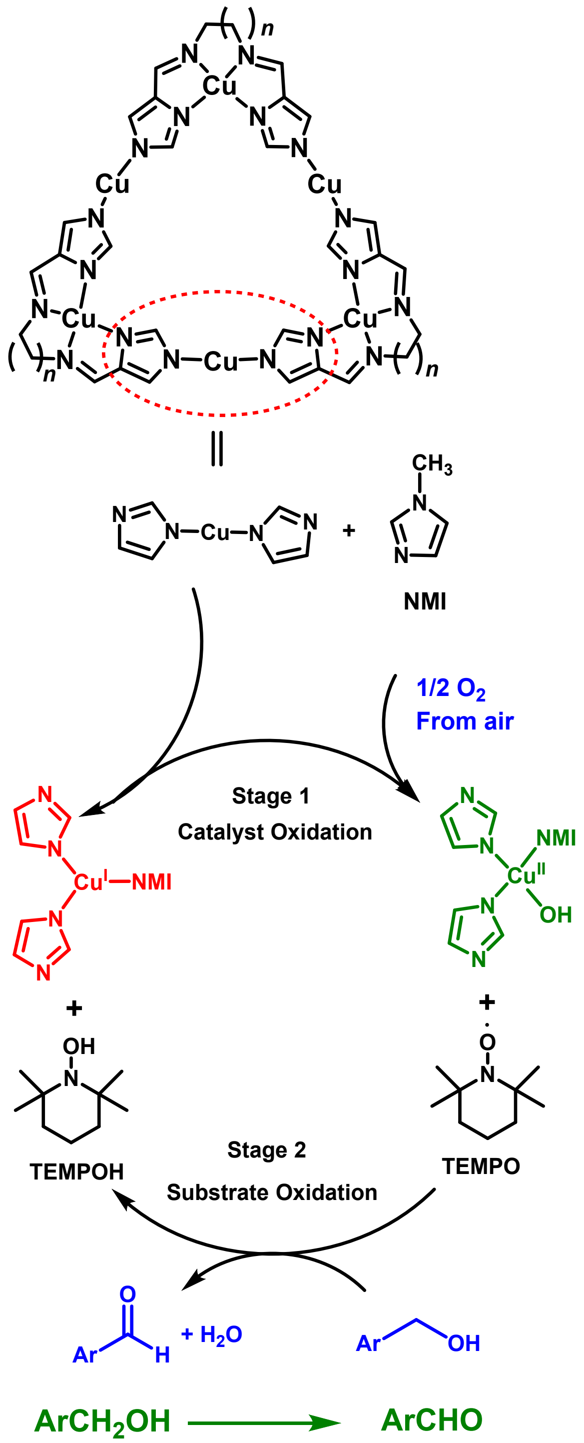


Fig. S7 Proposed mechanism of catalytic alcohol oxidation by **1** mediated by TEMPO.

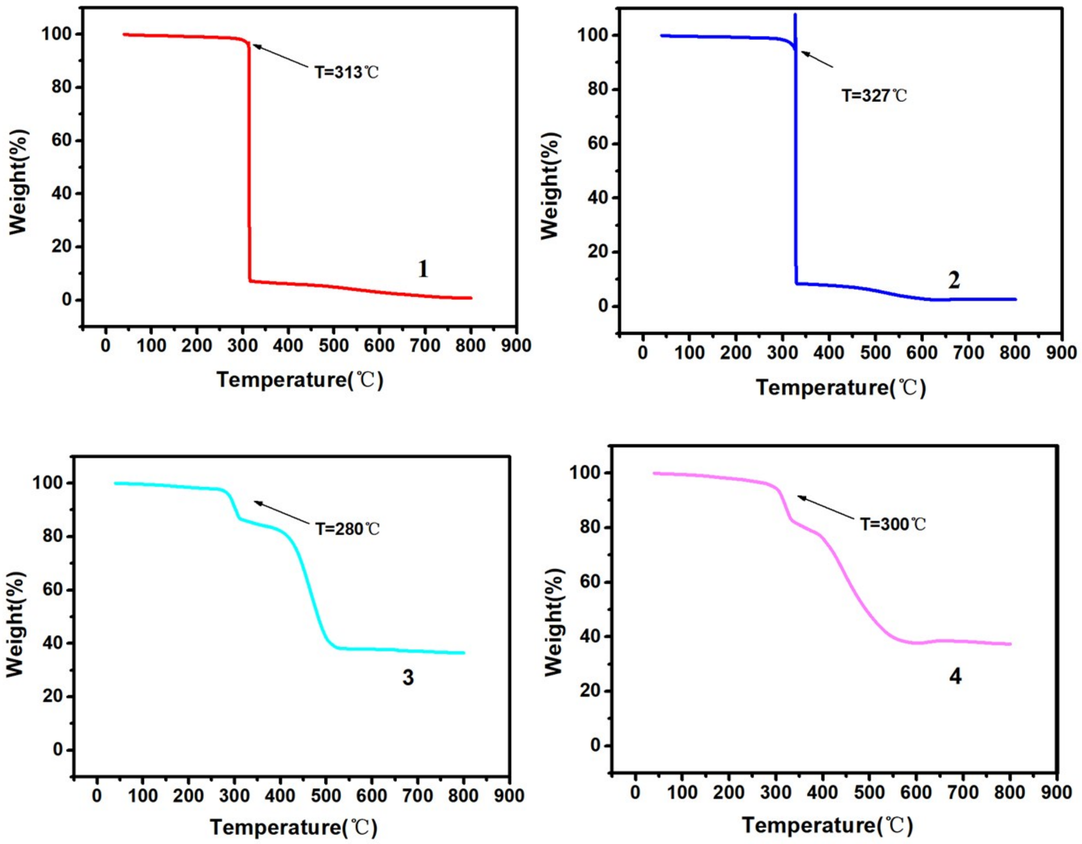


Fig S8 TGA plots of metallocycles **1** (a), **2** (b), **3** (c), and **4** (d). The rapid weight loss for **1** and **2** is probably due to the explosion of ClO_4^- anions.