Electronic Supplementary Information (ESI) for

## Facile preparation and dual catalytic activity of copper(I)-metallosalen coordination polymers

Yun-Long Hou,<sup>a</sup> Sheng-Xia Li,<sup>a</sup> Raymond Wai-Yin Sun,<sup>a</sup> Xin-Yuan Liu,<sup>b</sup> Seik Weng Ng<sup>c, d</sup> and Dan Li\*<sup>a</sup>

<sup>a</sup> Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Guangdong 515063, P. R. China.

<sup>b</sup> Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, P. R. China

<sup>c</sup> Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia.

<sup>d</sup> Chemistry Department, Faculty of Science, King Abdulaziz University, PO Box 80203 Jeddah, Saudi Arabia. \*E-mail: <u>dli@stu.edu.cn</u>

## SI 1 Experimental Section

General: All reagents and solvents employed were commercially available and used as received without further purification. Fourier transform Infrared spectra (FT-IR) were obtained in KBr disks on a Nicolet Avatar 360 FT-IR spectrometer in the range of 4000-400 cm<sup>-1</sup>. Elemental analyses (C, H, N) was performed using a Vario EL III CHNS elemental analyzer. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 Thermogravimetric Analyzer under nitrogen flow of (40 mL min<sup>-1</sup>) at a typical heating rate of 10 °C min<sup>-1</sup>. Powder X-ray diffraction (PXRD) experiments were performed on a D8 Advance X-ray diffractometer with Cu Ka radiation ( $\lambda = 1.5418$  Å). Diffuse Reflectance Spectra (DRS) were recorded on a Perkin Elmer UV/VIS spectrophotometer (Lambda 950) equipped with a integrating sphere in the range of 300-1000nm. UV-vis spectra were measured with a Bio-Logic MOS-450/AF-CD Spectrometer. <sup>1</sup>H-NMR spectra were determined using a 400 MHz Bruker NMR spectrometer. High Performance liquid chromatography (HPLC) experiments were performed on Agilent Technologies 1100 with a Hypersil ODS column. Atomic Absorption Spectroscopy (AAS) was performed on Solaar M6 MK2 equipment.

[Ni<sup>II</sup>(SalHImCy)](NO<sub>3</sub>)<sub>2</sub> (NiL-H<sub>2</sub>). A solution of 1S, 2S(+)-1, 2-cyclohexanediamine (0.924 g, 6 mmol) in MeOH (30mL) was added dropwise to a solution of 1H-imidazole-4-carbaldehyde (1.27 g, 13.2 mmol) in MeOH (50mL), and the resulting mixture was refluxed for 6h to form a clear light-brown solution. To this solution was added a solution of Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.75 g, 6 mmol) in MeOH (20mL), and the mixture was stirred for another 7 h at RT. The products were obtained as yellow precipitates with 78% yield that were collected by filtration, washed with MeOH, and dried in vacuum. IR (KBr, cm<sup>-1</sup>): 3134.1m, 2938.8m, 2863.1m, 1625.4s, 1517.3w, 1446.8m, 1384.1s, 1346.4s, 1276.8m, 1079.8m, 824.5w, 615.1m. Elemental analysis (%): Calcd. for Ni (SalHImCy)·(NO<sub>3</sub>)<sub>2</sub> (C<sub>14</sub>H<sub>18</sub>N<sub>8</sub>O<sub>6</sub>Ni): C, 37.12; H, 4.00; N, 24.73; Found: C, 36.82; H, 4.11; N, 24.35.

 $[Cu^{II}(SalHImCy)](NO_3)_2$  (CuL-H<sub>2</sub>).<sup>1</sup> A procedure similar to that utilized for the synthesis of NiL-H<sub>2</sub>. Blue precipitates of CuL-H<sub>2</sub> were collected with 82% yield. IR (KBr, cm<sup>-1</sup>): 3115.6m, 2851.1w, 2831.5w, 1649.4s, 1637.6s, 1527.2m, 1475.1m, 1384.1m, 1343.9m, 1261.8m, 1111.8s, 1042.4m, 874.8m, 800.2m, 788.9m, 650.1m. Elemental analysis (%): Calcd for Cu(SalHImCy)·(NO<sub>3</sub>)<sub>2</sub> (C<sub>14</sub>H<sub>18</sub>N<sub>8</sub>O<sub>6</sub>Cu): C, 36.72; H, 3.96; N, 24.47; Found: C, 36.67; H, 3.92; N, 24.00.

[Cu<sup>II</sup>(SalMImCy)](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (CuL-Me<sub>2</sub>). A procedure similar to that utilized for the synthesis of NiL-H<sub>2</sub>. Blue precipitates of CuL-Me<sub>2</sub> were collected with 79% yield. Single crystals of CuL-Me<sub>2</sub> suitable for X-ray crystallography were grown by slow-diffusion method at room temperature. IR (KBr, cm<sup>-1</sup>): 3207.2m, 3121.9m, 3033.5w, 2946.0w, 2857.2w, 1639.8s, 1513.9w, 1445.4m, 1384.1s, 1337.4m, 1315.9m, 1284.8m, 1239.1w, 1141.4w, 1105.7w, 979.6w, 841.0w, 635.5m. Elemental analysis (%): Calcd for Cu(SalMImCy)]·(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (C<sub>16</sub>H<sub>24</sub>N<sub>8</sub>O<sub>7</sub>Cu): C, 38.13; H, 4.80; N,

22.23; Found: C, 38.04; H, 4.85; N, 22.17.

 $\{[Ni^{II}(SalImCy)]_2(Cu^{I}CN)_9\}_n$  (1). A mixture of Ni (SalImCy) (NO<sub>3</sub>)<sub>2</sub> (0.0068 g, 0.015 mmol), CuCN (0.0067 g, 0.075 mmol) in DMF (4mL) and CH<sub>3</sub>CN (2mL) was sealed and heated in a 9 mL rigid glass tube at 120 °C for 72 h, and slowly cooled to room temperature at a rate of 5 °C /h. Red block crystals could be obtained (yield: 38% based on NiL-H<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 2932.7m, 2856.7w, 2125.4vs, 1605.1vs, 1551.7m, 1469.9m, 1384.5w, 1341.1w, 1278.2s, 1250.0m, 1120.1s, 1047.7m, 823.4m, 644.4m, 562.5w. 458.2w. Elemental analysis (%): Calcd for  $\{[Ni^{II}(SaIImCy)]_2(Cu^{I}CN)_9\}_n (C_{37}H_{32}N_{21}Cu_9Ni_2): C, 30.44; H, 2.21; N, 20.15; Found:$ C. 31.02: H. 2.58: N. 19.94.

 $\{[Cu^{II}(SaIImCy)]_2(Cu^{I}CN)_9\}_n$  (2). A mixture of Cu (SaIImCy) (NO<sub>3</sub>)<sub>2</sub> (0.0069 g, 0.015 mmol), CuCN (0.0067 g, 0.075 mmol) in DMF (3mL) and CH<sub>3</sub>CN (3mL) was sealed and heated in a 9 mL rigid glass tube at 120 °C for 72 h, and slowly cooled to room temperature at a rate of 5 °C/h. Red block crystals were obtained (yield: 32% based on CuL-H<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 2933.3m, 2856.9w, 2124.8vs, 1622.3vs, 1550.9m, 1470.3m, 1340.5w, 1280.1s, 1249.2m, 1118.1s, 1030.2m, 822.3m, 645.8m, 561.4w, 487.3w. Elemental analysis (%): Calcd for  $\{[Cu^{II}(SaIImCy)]_2(Cu^{I}CN)_9\}_n$  (C<sub>37</sub>H<sub>32</sub>N<sub>21</sub>Cu<sub>11</sub>): C, 30.24; H, 2.19; N, 20.01; Found: C, 29.62; H, 2.13; N, 20.41.

{[Ni<sup>II</sup>(SalImCy)](Cu<sup>I</sup>I)<sub>2</sub>·DMF}<sub>n</sub> (3). A mixture of Ni (SalImCy)(NO<sub>3</sub>)<sub>2</sub>(0.0092 g, 0.02 mmol), CuI (0.0095 g, 0.05 mmol) in DMF (3mL) and EtOH (1.5mL) was sealed and heated in a 9 mL rigid glass tube at 100 °C for 12 h. Red cuboid-like crystals were obtained (yield: 52% based on NiL-H<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 2927.8w, 2860.3w, 1615.1vs, 1547.6m, 1465.8m, 1337.7w, 1276.4m, 1242.6w, 1120.8s, 1032.8m, 822.9m, 640.5m, 559.6w, 437.7w. Elemental analysis (%): Calcd for {[Ni<sup>II</sup>(SalImCy)](Cu<sup>I</sup>I)<sub>2</sub>·DMF}<sub>n</sub> (C<sub>17</sub>H<sub>23</sub>N<sub>7</sub>OI<sub>2</sub>Cu<sub>2</sub>Ni): C, 26.14; H, 2.97; N, 12.55; Found: C, 25.75; H, 3.00; N, 12.57.

[L(Cu<sup>1</sup>I)<sub>2</sub>]<sub>n</sub> (L = 4,4'-Bis[(4-cyanophenyl)methyl]-3,5-dimethylpyrazole) (4). The ligand (4,4'-Bis[(4-cyanophenyl)methyl]-3,5-dimethylpyrazole) was prepared by the reported method<sup>2</sup> with revisions. Acetylacetone (5 g, 0.05mol) was added during a 30-minute period to a stirred, refluxing *tert*-butanol (80mL) solution of potassium *tert*-butoxide (11.2 g, 0.1mol). After 30 minutes, 4-cyanobenzyl bromide (19.6 g, 0.1mol) was slowly added. The reaction mixture was stirred and heated at reflux temperature of 90 °C for 24 h. After three-fourths of the solvent were distilled, the solid residue was washed thoroughly with water, filtered and dried (yield ca. 14 g). Then excess hydrazine hydrates were added to the ethanol solution of the above residue to PH~8. The solution was stirred and heated at reflux temperature of 80 °C for 12 h. The products were obtained as white precipitates (yield ca. 13 g) that were collected by filtration, washed with EtOH, and dried in vacuum. <sup>1</sup>H-NMR (400MHz, CD<sub>3</sub>Cl):  $\delta$ 7.54 (s, 2H, ArH),  $\delta$ 7.51 (s, 2H, ArH),  $\delta$ 7.04 (s, 2H, ArH),  $\delta$ 7.02 (s, 2H, ArH),  $\delta$ 3.18 (s, 4H, CH<sub>2</sub>),  $\delta$ 2.25 (s, 6H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 2974.4m, 2931.7m,

2865.8w, 2226.9vs, 1639.4m, 1608.5s, 1573.7m, 1505.7m, 1388.7m, 859.8s, 828.6s, 657.4m, 558.3m, 546.9w. Elemental analysis (%): Calcd for  $C_{21}H_{18}N_4$ : C, 77.28; H, 5.56; N, 17.17; Found: C, 77.20; H, 5.53; N, 17.35. The synthesis of complex 4: A mixture of CuI (0.012 g, 2.0 mmol), 4,4'-Bis[(4-cyanophenyl)methyl] -3,5-dimethylpyrazole (0.010 g, 1.0 mmol), CH<sub>3</sub>OH (4.0 mL) was stirred for 15 min in air. The mixture was then sealed and heated in a 9mL rigid glass tube at 140 °C for 72 h, and slowly cooled to room temperature at a rate of 5 °C/h. Purely yellowish block crystals were obtained (yield: 70% based on the prepared ligand). IR (KBr, cm<sup>-1</sup>): 2931.9m, 2908.1m, 2360.6vs, 2336.8s, 2235.7s, 1607.9s, 1590.1m, 1411.6s, 1384.8m, 852.2m, 834.4m, 819.5m, 679.7w, 551.7m. Elemental analysis (%): Calcd. for  $C_{21}H_{18}N_4I_2Cu_2$ : C, 35.66; H, 2.56; N, 7.92; Found: C, 35.30; H, 2.51; N, 7.77.

**Catalytic oxidation of aromatic alcohols and stability measurements.** The catalytic oxidation of aromatic alcohols by sample **1**, **2**, **3** was performed at 20 °C. The details of the reaction systems are given briefly as footnotes of Table 1 for each reaction. The typical procedure was as follows: An acetonitrile (5 mL) solution of alcohol (0.65 mmol), catalyst (1.5 mol %) and TBHP (0.975 mmol) were carefully added to a 10 mL flask under continuous stirring. Afterwards, 0.1 mL of the sample was diluted with 1.4 mL HPLC grade acetonitrile, centrifuged and filtered to recover the catalyst. The crystallinity of the powder was verified with powder X-ray diffraction (PXRD) (Figures S3-S4). The filtrates were allowed to evaporate to dryness, the residue was dissolved in 0.2% HNO<sub>3</sub> and afterwards analysed by Atomic Absorption Spectroscopy (AAS) to determine the amount of metal ion leaked in the solution.

(Photo-)catalytic degradation experiments and stability measurements. The (photo-)degradations of the organic dye (methylene blue, MB) by sample 1, 2, 3 and 4 were performed at ambient temperature (25 °C). A 500 W xenon arc lamp ( $\lambda > 400$ nm) surrounded with water cooling system was fixed in the center of the reaction cell (instrument: BL-GHX-V, Shanghai Binlon Instrument Co., Ltd, China). A 560 nm cutoff filter was placed between the lamp and the photoreactor to absorb the light below 560nm. The typical procedure was as follows: 0.012 g of sample 1 was dispersed into a temperature-controlled quartz photoreactor filled with 16 mL of MB aqueous solution (12 mg  $L^{-1}$ ) and stirred in the dark for 30 minutes to reach the adsorption equilibrium, followed by the addition of 0.1 mL of hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30%). The above solutions were illuminated under continuous stirring with visible light illumination. During the degradation process, the mixture was withdrawn regularly from the reactor at different time intervals and analyzed by UV/Vis spectroscopy. The amount of MB was determined on the basis of its characteristic optical absorption at 665 nm based on Lambert-Beer's law (Figure S22-28). The dispersed powders were recovered by centrifugation and verified with powder X-ray diffraction (Figure S31-32). Furthermore, Atomic Absorption Spectrophotometer (AAS) was applied to determine the amount of metal ion leaked in the solution.

**X-ray crystallography.** Suitable crystals of CuL-Me<sub>2</sub>, **1**, **2**, **3** or **4** were mounted with glue at the end of a glass fiber. Data collections were performed with Mo-Ka radiation ( $\lambda = 0.71073$  Å) on a Bruker-AXS SMART CCD diffractometer at 293(2) K. Empirical absorption corrections were carried out by utilizing the SADABS routine. The structures were solved by direct methods and on  $F^2$  using the SHELXTL program.<sup>3</sup> All non hydrogen atoms were anisotropically refined. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. The bridge C/N atoms of CN<sup>-</sup> in the asymmetric units of **1** and **2** are indistinguishable and were assigned randomly as a C or an N atom, but the terminal C/N atoms were refined with a 50% probability of being C- or N-labeled C/N. Crystal data, structure refinement details of **1**, **2**, **3** and **4** are given in Table S1.

## References:

- 1. J.-M. Xiao and W. Zhang, Inorg. Chem. Commun., 2009, 12, 1175.
- 2 G.-F. Gao, M. Li, S.-Z. Zhan, Z. Lv, G.-h. Chen and D. Li, *Chem. Eur. J.*, 2011, **17**, 4113.
- 3. G. M. Sheldrick, SHELXL-97, Program for the refinement of the crystal structures, University of Gottingen, Gottingen, Germany, 1997.

## SI 2 Tables and Figures:

Parameter	CuL-Me <sub>2</sub>	1	2	3	4
formula	$C_{16}H_{24}N_8O_7Cu$	$C_{37}H_{32}N_{21}Cu_9Ni_2$	$C_{37}H_{32}N_{21}Cu_{11}$	$C_{17}H_{23}N_7OI_2Cu_2Ni$	$C_{21}H_{18}N_{4}I_{2}Cu_{2} \\$
Mr	503.97	1460.12	1469.78	781.01	707.27
cryst syst	monoclinic	triclinic	triclinic	triclinic	orthorhombic
space group	P2(1)	P-1	P-1	P-1	Cmca
<i>a</i> (Å)	6.7015(3)	8.0519(6)	7.9826(4)	8.7755(9)	14.1911(3)
<i>b</i> (Å)	18.7764(8)	12.4494(9)	12.5733(5)	11.4427(6)	21.0436(5)
c (Å)	8.4556(5)	13.6971(10)	13.7208(5)	12.7640(8)	15.4097(3)
$\alpha$ (deg)	90.0	79.532(6)	79.779(3)	82.939(5)	90.0
$\beta$ (deg)	101.755(5)	83.882(6)	83.639(4)	70.893(7)	90.0
γ (deg)	90.0	82.718(6)	82.562(4)	88.924(6)	90.0
$V(\text{\AA}^3)$	1041.65(9)	1334.35(17)	1338.41(10)	1201.59(16)	4601.81(18)
Ζ	2	1	1	2	8
$D_C(\text{g cm}^{-3})$	1.607	1.817	1.824	2.159	2.042
$\mu(\text{mm}^{-1})$	1.107	4.243	4.321	5.121	4.546
reflections	2951	5954	5979	4390	2113
unique	2658	3309	4676	2645	1884
R <sub>int</sub>	0.0231	0.0698	0.0306	0.0589	0.0309
goodness-of-fit	1.006	1.054	1.162	1.083	0.999
$R_1[I \ge 2\sigma(I)]^a$	0.0358	0.0836	0.0715	0.0623	0.0245
$wR_2[I>2\sigma(I)]^b$	0.0868	0.2320	0.2117	0.1175	0.0587
$R_1$ [all data]	0.0419	0.1499	0.0910	0.1186	0.0297
wR <sub>2</sub> [all data]	0.0908	0.2707	0.2223	0.1401	0.0617

**Table S1.** Summary of the crystal data and structure refinement parameters for CuL-Me<sub>2</sub>, **1**, **2**, **3**, **4** 

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

 Table S2. Summary of the bond length data for the asymmetric unit of 1.



Atom	Atom	Length(Å)
Cul	N1	2.047(10)
Ni	N2	1.904(8)
Ni	N3	1.893(8)
Ni	N4	1.893(8)
Ni	N5	1.917(8)
Cu5	N6	1.864(10)
Cu5	Cu4	2.901(2)
Cu3	Cu4	2.778(3)





Atom	Atom	Length(Å)
Cu1	N1	2.033(7)
Cu6	N2	1.938(6)
Cu6	N3	1.950(7)
Cu6	N4	1.956(7)
Cu6	N5	1.956(6)
Cu5	N6	1.854(7)
Cu5	Cu4	2.8918(18)
Cu3	Cu4	2.798(3)

Photocatalyst	HOMO-LUMO gap		
	Wavelength(nm)	Photon energy (eV)	
1	785	1.6	
2	700	1.8	
3	700	1.8	
4	515	2.4	

 Table S4. HOMO-LUMO gap determination.

 Table S5.
 Oxidation of aromatic alcohols with different catalysts<sup>[a]</sup>



Entry	Time[h]	Substrate	Catalyst	Conv. <sup>[b]</sup> [mol%]	Select. <sup>[b]</sup> [mol%]
1	2	Н	NiL-H <sub>2</sub> , CuCN	24	18
2	2	Н	CuL-H <sub>2</sub> ,CuCN	20	33
3	8	Me	NiL-H <sub>2</sub> ,CuCN	24	65
4	8	Me	CuL-H <sub>2</sub> ,CuCN	28	77
5[c]	2	Н	1	32	87
6[d]	2	Н	1	29	84
7[c]	8	Me	1	90	97
8[d]	8	Me	1	95	99

[a] Reaction condition: aromatic alcohol (0.65mmol), catalyst (1.5mmol%), TBHP (0.975mmol), acetonitrile (5ml), 20 °C. [b] Conversion % and selectivity % were determined by HPLC analysis. [c] The second run. [d] The third run.



Figure S1 The PXRD patterns of synthesized 1.



Figure S2 The PXRD patterns of synthesized 2.



Figure S3 The PXRD patterns of synthesized 3.



Figure S4 The PXRD patterns of synthesized 4.



Figure S5 X-ray crystal analysis of CuL-Me<sub>2</sub>.



Figure S6 The 2D layers of 1 viewed along *b*-axis.



Figure S7 The stacking diagram of 2D layers in 1 viewed along *a*-axis.



Figure S8 The asymmetric unit of 2.



Figure S9 The 2D layers of 2 viewed along *a*-axis.



Figure S10 The 2D layers of 2 viewed along *b*-axis.



Figure S11 The 2D layers of 2 viewed along *c*-axis.



Figure S12 Thermogravimetric analysis of 1.



Figure S13 Thermogravimetric analysis of 2.



Figure S14 Thermogravimetric analysis of 3.



**Figure S15.** Conversion and selectivity as a function of reaction time in 1-catalyzed oxidation of benzyl alcohol at 323K (1 hour was able to get a conversion of 35%, with a selectivity of 83%, which further decreased dramatically to 61% after 6 h. Product analysis shows a mol ratio of 0.6 (benzoic acid to aldehyde) in the final reaction solution and indicates that higher temperature tends to give over-oxidation product of benzoic acid and hinders the selectivity of the oxidation reaction in our system).



**Figure S16** % degradation rates of MB over different catalysts. The samples were illuminated with different visible light wavelength range ( $\lambda > 400$ nm, up;  $\lambda > 560$ nm, down).



Figure S17. Time dependent UV/Vis spectra of MB over 1 in the absence of light.



Figure S18. Time dependent UV/Vis spectra of MB over 2 in the absence of light.



Figure S19. Time dependent UV/Vis spectra of MB over 3 in the absence of light.



Figure S20. Time dependent UV/Vis spectra of MB over 1 in the presence of light.



Figure S21. Time dependent UV/Vis spectra of MB over 2 in the presence of light.



Figure S22. Time dependent UV/Vis spectra of MB over 3 in the presence of light.



Figure S23. The asymmetric unit of 4 with labeled atoms.



Figure S24. A representative coordinative experiment of 4 along *a*-axis.



Figure S25. The 2D layers of 4 viewed along *b*-axis.



Figure S26. The 2D layers of 4 viewed along *a*-axis.



Figure S27. Thermogravimetric analysis of 4.



Figure S28. Time dependent UV/Vis spectra of MB over 4 in the presence of light.



**Figure S29.** Recycling test of **1** for MB degradation in the presence of light irradiation.



**Figure S30.** Recycling test of **2** for MB degradation in the presence of light irradiation.



Figure S31 The PXRD patterns of 1 for photodegradation of MB aqueous solution under three cycles.



Figure S32 The PXRD patterns of 2 for photodegradation of MB aqueous solution under three cycles.