

# A copper(I)/copper(II)–salen coordination polymer as a bimetallic catalyst for three-component Strecker reactions and degradation of organic dyes†

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**A copper(I)/copper(II)–salen coordination polymer prepared by solvothermal reactions shows prominent bimetallic catalytic activities towards three-component Strecker reactions and photo-degradation of organic dyes under visible-light illumination.**

Inspired by the fact that several multi-functional enzymes contain multiple metal-based catalytic units,<sup>1</sup> worldwide efforts have been made to employ different materials as novel classes of bi-/multi-metallic<sup>2</sup> and multi-functional catalysts.<sup>3</sup> Metal–organic frameworks (MOFs), a subcategory of coordination polymers (CPs) having structural flexibility to bear more than one catalytic unit resulting from the huge variations of metal nodes and organic linkers,<sup>4</sup> have recently been demonstrated to achieve bifunctional catalytic activities.<sup>5</sup> For instance, some site-isolated Lewis acid–Brønsted base MOFs have been employed in aldol-condensations,<sup>5a</sup> Knoevenagel reactions<sup>5b</sup> and one-pot tandem reactions,<sup>5c–e</sup> with coordinatively unsaturated metal sites (CUSs)<sup>4b,6</sup> and organic ligands serving as acidic and basic catalytic sites, respectively. Moreover, various MOFs/CPs are insoluble and stable in common organic solvents or aqueous solutions. These intrinsic properties thus render MOFs/CPs to be potentially used as green heterogeneous catalysts which could readily be reused. Nevertheless, preparation of bimetallic MOFs/CPs *via* integration of one type of CUS with another type of metal-based catalytic moiety remains a formidable challenge.<sup>7</sup> Limited examples include a bimetallic heterogeneous catalyst palladium(II)–copper(II) MOF which could be synthesized *via* post-synthetic modification (PSM)<sup>8</sup> with potent catalytic activity in a multi-component reaction.<sup>7a</sup> The reported PSM approach in preparing MOFs, however, is sometimes limited by its sophisticated modification steps, as well as the chemical and physical instabilities of the intermediates/products.<sup>8</sup>

Metalloligands have been widely employed as linkers for the preparation of MOFs/CPs,<sup>9</sup> since these ligands could feature in the straightforward immobilization of CUSs under solvothermal synthesis.<sup>6,9c–e</sup> A notable example of metalloligands is metallosalens, and the reported metallosalen-based MOF catalysts usually contain a single CUS.<sup>4b,10</sup> With the ease in structural modification, metallosalens indeed could be readily tuned to display a wide range of catalytic activity towards a number of organic transformations.

In the literature, several Cu<sup>I</sup><sub>2</sub>I<sub>2</sub> clusters have shown prominent catalytic activity in a multi-component reaction.<sup>11</sup> Moreover, various copper(I)-based CPs including these copper(I) clusters which may have potential to be used as effective heterogeneous catalysts have been structurally characterized and reviewed by others<sup>12</sup> and by us.<sup>13</sup> As an effort in exploring the catalytic applications of different kinds of polymeric materials,<sup>3</sup> we aim to design a novel bimetallic CP which could present multi-functional catalytic activities by combining catalytically active units of copper(I) and metallosalens. In this work, we develop a straightforward solvothermal approach for the preparation of a bimetallic CP,  $[\text{Cu}^{\text{II}}(\text{SalImCy})][\text{Cu}^{\text{I}}\text{I}_2\text{DMF}]_n$  (**1**, wherein SalImCy = *N,N'*-bis-[(imidazol-4-yl)methylene]cyclohexane-1,2-diamine, Fig. 1a), which contains copper(II)–salen-based catalysts Cu<sup>II</sup>(SalImCy) and copper(I) iodide clusters. Its bimetallic catalytic activities toward three-component coupling reactions and visible-light driven degradation of organic dyes have been examined.

The copper(II)–salen ligand [Cu<sup>II</sup>(SalHImCy)](NO<sub>3</sub>)<sub>2</sub> was prepared by a one-pot reaction of *in situ*-formed SalHImCy with Cu<sup>II</sup>(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in a molar ratio of 1 : 1 (see ESI†). This ligand exhibits a good solubility (>10 mg mL<sup>−1</sup>) in dimethylformamide (DMF), CH<sub>3</sub>CN and C<sub>2</sub>H<sub>5</sub>OH and is stable in air at 298 K, which in turn could be used as a precursor for subsequent solvothermal reactions.

CP **1** in the form of red cuboid-like crystals was obtained by a solvothermal reaction of [Cu<sup>II</sup>(SalHImCy)](NO<sub>3</sub>)<sub>2</sub> with Cu<sup>I</sup>I in a molar ratio of 1 : 2 in a DMF/C<sub>2</sub>H<sub>5</sub>OH mixture (v/v, 2 : 1) for 24 h (Fig. 1a). It has been formulated and characterized on the basis of elemental analysis, IR spectroscopy, and thermogravimetric and single-crystal X-ray diffraction analyses. The experimental details are given in the ESI† (Table S1 and Fig. S1). CP **1** can be readily prepared by either

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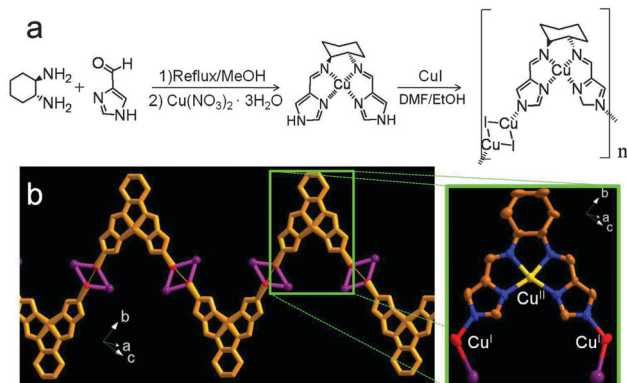


Fig. 1 (a) Schematic drawing of solvothermal synthesis of **1** from  $\text{Cu}^{\text{II}}(\text{SalImCy})$  and  $\text{Cu}^{\text{I}}$ . (b) A representative zigzag chain and the asymmetric unit of **1** viewed along the *a*-axis.

one of the four different forms of the 1,2-cyclohexanediamine (*i.e.*, 1*S*, 2*S* (+)-1,2-cyclohexanediamine); while all of them render **1** to form crystal lattices in the triclinic centro-symmetric  $P\bar{1}$  space group (Table S1, ESI†). The phase purity of the bulk sample has been established by comparing its observed and simulated powder X-ray diffraction (PXRD) patterns (Fig. S2, ESI†). CP **1** is found to be highly stable in air as well as in solvents including  $\text{H}_2\text{O}$ , DMF,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{CN}$  at 298 K.

Single-crystal X-ray diffraction analysis reveals that prominent structural features of **1** include the square-planar 4-coordinate  $\text{Cu}^{\text{II}}$  in the metallosalen units (Fig. 1b, yellow) and the 3-coordinate  $\text{Cu}^{\text{I}}$  in the rhomboid  $\text{Cu}_2\text{I}_2$  clusters (Fig. 1b, purple). The  $\text{Cu}^{\text{II}}$  ion, which embraces the CUS, is chelated by two imines [ $\text{Cu}^{\text{II}}\text{--N}_{\text{imine}}$ , 1.9571(12)–1.9613(14) Å] and two imidazols [ $\text{Cu}^{\text{II}}\text{--N}_{\text{imidazol}}$ , 1.9630(13)–1.9631(13) Å] (Fig. 1b). The copper(II)–salen linker, with an angle of 112.5° between two deprotonated imidazol N atoms, is bridged by two  $\text{Cu}^{\text{I}}_2\text{I}_2$  nodes to form a zigzag chain along the *a*-axis. Along the *b*-axis, 1D zigzag chains stack with each other to form tubular channels which could be used to trap DMF molecules (Fig. S3, ESI†).

Given that various metallosalens and  $\text{Cu}^{\text{I}}$  demonstrated potent catalytic activities on three-component Strecker reactions,<sup>11,14</sup> we first examined the catalytic activity of **1** in these reactions using aldehydes, trimethylsilyl cyanide and asymmetric amines as substrates. For instance, the reaction was carried out by mixing benzaldehyde, (*R*)-(+)-1-phenylethylamine and trimethylsilyl cyanide (TMSCN) in the presence of **1** at 0.5 mol% in  $\text{CD}_3\text{CN}$  at 283 K for 1 h. Two  $\alpha$ -aminonitriles (*R,R*)-(+)- $\alpha$ -phenyl- $\alpha$ -(1-phenylethyl)amino]acetonitrile and (*R,S*)-(+)- $\alpha$ -phenyl- $\alpha$ -(1-phenylethyl)amino]acetonitrile were the reaction products and were found in the mixture with a 99% conversion as determined by  $^1\text{H}$ -NMR spectrometry (Table 1, entry 1). The turnover frequency (TOF) of **1** was found to be 198  $\text{h}^{-1}$ . Apart from benzaldehyde, four other aromatic aldehydes have also been employed as substrates in the **1**-catalyzed Strecker reaction. Similar to that of **1**, up to 99% conversion can be obtained by using aromatic aldehydes substituted with a 4-methyl (entry 2) or a 4-*tert*-butyl (entry 3) group. Increasing the bulkiness by using 3,5-di-*tert*-butyl (entry 4) or 4-phenyl (entry 5) substitution may result in slightly changing the percentage conversions of  $\alpha$ -aminonitriles from 99% to

Table 1 Asymmetric three-component Strecker reaction catalyzed by **1**<sup>a</sup>

Entry	Substrate (R)	<i>t</i> <sup>b</sup> (h)	Conversion <sup>c</sup> (%)	<i>a</i> : <i>b</i> <sup>d</sup>	TOF <sup>e</sup> ( $\text{h}^{-1}$ )
1	H	1	99	67 : 33	198
2	4-Methyl	2	99	68 : 32	99
3	4- <i>tert</i> -Butyl	2	99	70 : 30	99
4	3,5-Di- <i>tert</i> -butyl	2	93	71 : 29	92
5	4-Phenyl	3	86	67 : 33	60
6	H	1	99 <sup>f</sup>	67 : 33	198
7	H	1	95 <sup>g</sup>	66 : 34	191

<sup>a</sup> Aromatic aldehydes (1 mmol), (*R*)-(+)-1-phenylethylamine (1 mmol), TMSCN (1.5 mmol),  $\text{CD}_3\text{CN}$  (2 mL), and **1** (0.5 mol%), sealed in a screw-cap vial were stirred at 283 K. <sup>b</sup> Reaction time *t*, hour. <sup>c</sup> % conversions were determined by GC. <sup>d</sup> Diastereoselectivity was determined by H-NMR. <sup>e</sup> TOF = turnover frequency (moles of reactants converted per moles of active sites per unit time),  $\text{h}^{-1}$ . <sup>f</sup> The second cycle. <sup>g</sup> The third cycle.

93% and 86%, respectively. The effect of the change of reaction temperature from 283 K to 273 K (Table S2, ESI†) and 298 K (Table S3, ESI†) has also been examined. We found that these temperature changes did not significantly affect the catalytic activities of **1** in the Strecker reaction in terms of the percentage conversion (86–99%) and diastereoselectivity (2–2.4) (Fig. S4, ESI†). Since changes in temperature as well as the size of the aldehyde substrate did not render a significant impact on the catalytic activity of **1** in terms of percentage conversions and diastereoselectivity, we reckon that the catalytically active metal centers on the solid exterior surface may be highly accessible, as evidenced by reports on efficient salen-based 1D CP catalysts.<sup>15</sup>

For comparison, the catalytic activities of two reference compounds  $\text{Cu}^{\text{I}}$  and  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$  have also been examined under similar experimental conditions. Both of them were found to display a much lower catalytic activity than **1**, in terms of the amount employed (10 mol% for  $\text{Cu}^{\text{I}}$  and 0.5 mol% for  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$ ) and the reaction time required (3 h), as well as the percentage conversions obtained (82% for  $\text{Cu}^{\text{I}}$  and 87% for  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$ ) for the  $\alpha$ -aminonitrile products (Table S4, ESI†). The superior catalytic activity of **1** indicates that a cooperative catalytic event is achieved by two different catalytically active sites (*i.e.*,  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$ ) of **1**. In this reaction, the  $\text{Cu}^{\text{I}}$ –Im moieties of **1** may function as Brønsted bases to activate the cyanides, while  $\text{Cu}^{\text{II}}$  ions act as Lewis acids to activate the imine intermediates in the Strecker reaction.<sup>7a,16</sup> Furthermore, the inductively-coupled-plasma spectroscopic analysis demonstrates the heterogeneity of **1** with less than 0.02% of copper content in the reaction mixture.<sup>9b,17</sup> A recycling test with three consecutive runs shows that **1** can be re-used without a significant loss of catalytic activity (the conversions can reach from 95 to 99%, see Table 1, entries 6 and 7). Solid residues of **1**, which were isolated from the reaction mixture *via* centrifugation, displayed the same PXRD pattern as that of the pristine solid of **1** (Fig. S2, ESI†). These results support that **1** has an adequate stability and recoverability to be used as an efficient bimetallic heterogeneous catalyst for the three-component reactions.

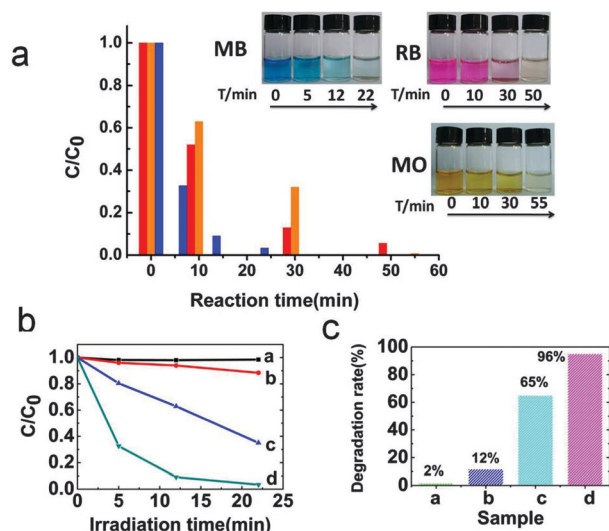


Fig. 2 Photocatalytic degradation of organic dyes catalyzed by **1** upon visible-light illumination. (a) Photographs of different dye solutions and concentrations in terms of absorbance changes of dyes as a function of time [blue pillar: methylene blue (MB); red pillar: rhodamine (RhB); orange pillar: methyl orange (MO)]. (b) Time-dependent concentration changes and (c) % degradation rates of MB under different conditions [**1**/visible-light illumination]: (a) [-/-]; (b) [-/+]; (c) [+/-]; (d) [+/+].

To further elucidate the bimetallic catalytic nature of **1** which contains two kinds of metal-based catalytic sites, catalytic degradation experiments of various organic dyes in the presence or absence of visible light have been carried out. The **1**-catalyzed (photo-)degradation of an aqueous solution (12 mg L<sup>-1</sup>) of methylene blue (MB) has been first examined by means of UV-vis spectrophotometry (Fig. S5, ESI<sup>†</sup>). In the absence of visible-light illumination, 65% of MB is decomposed in the solution (Fig. 2b and c). We reckon that the Cu<sup>II</sup> ions in **1** is crucial in decomposing MB, since various studies have shown that Cu<sup>II</sup> could play a major catalytic role in various oxidation reactions.<sup>18</sup> It should be noted that up to 96% of MB could be decomposed when the reaction was performed under visible-light illumination (Fig. 2b and c). We reckon that the enhanced degradation of MB is due to the cooperative decomposition achieved by photoactive Cu(i) moieties in **1**.<sup>19</sup> Apart from MB, the photodegradation of other organic dyes including rhodamine B (RhB) and methyl orange (MO) by **1** have also been examined. Similar high photocatalytic efficiencies (>95%) were observed in both cases after a ~50 min light illumination (Fig. 2a and Fig. S6–S9, ESI<sup>†</sup>). Furthermore, the stability and recoverability of **1** have also been examined. After repeating the photocatalytic degradation of MB three times, the solid residues left in the reaction mixture retained a similar PXRD pattern as that of the pristine solid of **1**. As expected, these residues also displayed a similar photocatalytic efficiency as that of **1** (Fig. S10 and S11, ESI<sup>†</sup>).

In summary, this work has described a feasible approach in preparing a copper(i)/copper(ii)-salen coordination polymer (**1**) having high bimetallic catalytic activity through the incorporation of two different metal-based catalytic moieties into a single framework. The CP **1** could be used as an efficient heterogeneous multifunctional catalyst for the synthesis of  $\alpha$ -aminonitriles *via* asymmetric

three-component Strecker reactions. Meanwhile, **1** has also been demonstrated to display promising visible-light-driven bimetallic catalytic activity in degrading various organic dyes. This work paves the way to the solvothermal synthesis of efficient heterogeneous multifunctional materials which could catalyze transformations through a bimetallic pathway.

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