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,[1] worldwide efforts have been made to employ different materials as novel classes of bi-/multi-metallic[2] and multi-functional catalysts.[3] 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,[4] have recently been demonstrated to achieve bifunctional catalytic activities.[5] For instance, some site-isolated Lewis acid–Brønsted base MOFs have been employed in aldol-condensations,[5a] Knoevenagel reactions[5b] and one-pot tandem reactions,[5c–e] with coordinatively unsaturated metal sites (CUSs)[4b,6] 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.[7] Limited examples include a bimetallic heterogeneous catalyst palladium(II)–copper(II) MOF which could be synthesized *via* post-synthetic modification (PSM)[8] with potent catalytic activity in a multi-component reaction.[7a] 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.[8]

Metalloligands have been widely employed as linkers for the preparation of MOFs/CPs,[9] since these ligands could feature in the straightforward immobilization of CUSs under solvothermal synthesis.[6,9c–e] A notable example of metalloligands is metallosalens, and the reported metallosalen-based MOF catalysts usually contain a single CUS.[4b,10] 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 $Cu^I_2I_2$ clusters have shown prominent catalytic activity in a multi-component reaction.[11] 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[12] and by us.[13] As an effort in exploring the catalytic applications of different kinds of polymeric materials,[3] 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, $\{[Cu^{II}(SalImCy)](Cu^II)_2 \cdot DMF\}_n$ (**1**, wherein SalImCy = N,N'-bis-[(imidazol-4-yl)methylene]cyclo-hexane-1,2-diamine, Fig. 1a), which contains copper(II)–salen-based catalysts $Cu^{II}(SalImCy)$ 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 $[Cu^{II}(SalHImCy)](NO_3)_2$ was prepared by a one-pot reaction of *in situ*-formed SalHImCy with $Cu^{II}(NO_3)_2 \cdot 3H_2O$ in a molar ratio of 1:1 (see ESI†). This ligand exhibits a good solubility (>10 mg mL^{-1}) in dimethylformamide (DMF), CH_3CN and C_2H_5OH and is stable in air at 298 K, which in turn could be used as a precursor for subsequent solvo-thermal reactions.

CP **1** in the form of red cuboid-like crystals was obtained by a solvothermal reaction of $[Cu^{II}(SalHImCy)](NO_3)_2$ with Cu^I in a molar ratio of 1:2 in a DMF/C_2H_5OH 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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a

b

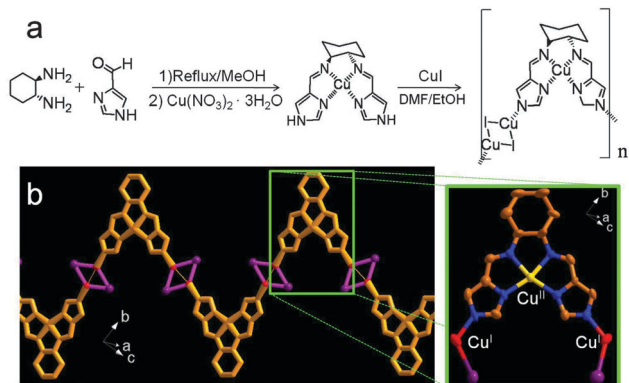**Fig. 1** (a) Schematic drawing of solvothermal synthesis of **1** from Cu^{II}(SalImCy) and Cu^{I}I. (b) A representative zigzag chain and the asymmetric unit of **1** viewed along the a-axis.

Table 1 Asymmetric three-component Strecker reaction catalyzed by **1**[a]

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

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

one of the four different forms of the 1,2-cyclohexanediamine (i.e., 1S, 2S (+)-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 H$_2$O, DMF, C$_2$H$_5$OH and CH$_3$CN at 298 K.

Single-crystal X-ray diffraction analysis reveals that prominent structural features of **1** include the square-planar 4-coordinate Cu^{II} in the metallosalen units (Fig. 1b, yellow) and the 3-coordinate Cu^I in the rhomboid Cu$_2$I$_2$ clusters (Fig. 1b, purple). The Cu^{II} ion, which embraces the CUS, is chelated by two imines [Cu^{II}–N$_{imine}$, 1.9571(12)–1.9613(14) Å] and two imidazols [Cu^{II}–N$_{imidazol}$, 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 Cu$_2$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 Cu^I demonstrated potent catalytic activities on three-component Strecker reactions,[11,14] 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 CD$_3$CN at 283 K for 1 h. Two α-aminonitriles (R,R)-(+)-α-phenyl-α-[(l-phenylethyl)amino]-acetonitrile and (R,S)-(+)-α-phenyl-α-[(l-phenylethyl)amino]-acetonitrile were the reaction products and were found in the mixture with a 99% conversion as determined by ^{1}H-NMR spectrometry (Table 1, entry 1). The turnover frequency (TOF) of **1** was found to be 198 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 α-aminonitriles from 99% to

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.[15]

For comparison, the catalytic activities of two reference compounds Cu^{I}I and [Cu^{II}(SalHImCy)](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 Cu^{I}I and 0.5 mol% for [Cu^{II}(SalHImCy)]-(NO$_3$)$_2$) and the reaction time required (3 h), as well as the percentage conversions obtained (82% for Cu^{I}I and 87% for [Cu^{II}(SalHImCy)](NO$_3$)$_2$) for the α-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., Cu^I and Cu^{II}) of **1**. In this reaction, the Cu^{I}I–Im moieties of **1** may function as Brønsted bases to activate the cyanides, while Cu^{II} ions act as Lewis acids to activate the imine intermediates in the Strecker reaction.[7a,16] Furthermore, the inductively-coupled-plasma spectroscopic analysis demonstrates the heterogeneity of **1** with less than 0.02% of copper content in the reaction mixture.[9b,17] 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.
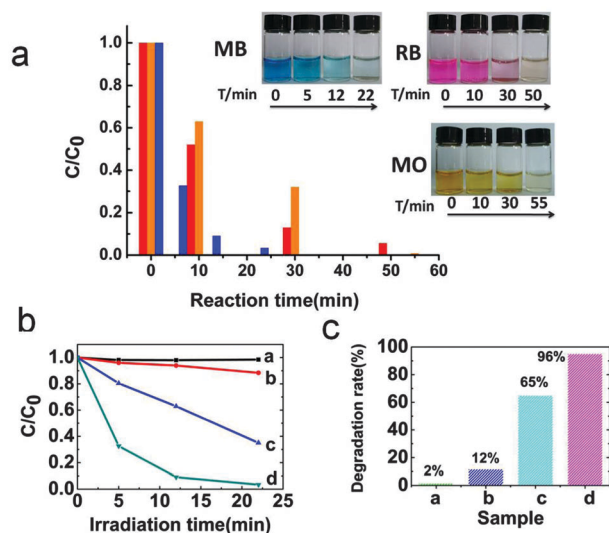
Fig. 2 Photocatalytic degradation of organic dyes catalyzed by **1** upon visible-light illumination. (a) Photographs of different dye solutions and concentrations in terms of absorbance changes of dyes as a function of time [blue pillar: methylene blue (MB); red pillar: rhodamine (RhB); orange pillar: 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^{-1}) of methylene blue (MB) has been first examined by means of UV-vis spectrophotometry (Fig. S5, ESI†). In the absence of visible-light illumination, 65% of MB is decomposed in the solution (Fig. 2b and c). We reckon that the Cu^{II} ions in **1** is crucial in decomposing MB, since various studies have shown that Cu^{II} could play a major catalytic role in various oxidation reactions.[18] 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**.[19] 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†). 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†).

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 α-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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