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

Yun-Long Hou, Raymond Wai-Yin Sun, Xiao-Ping Zhou, Jun-Hao Wang and Dan Li*

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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 photodegradation 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-metallic2 and multi-functional catalysts.3 Metal-organic frameworks (MOFs), a subcategory of coordination polymers (CPs) having structural flexibility to bear more than one catalytic units resulting from the huge variations of metal nodes and organic linkers,4 have recently been demonstrated to achieve bifunctional catalytic activities.5 For instances, some site-isolated Lewis acid-Bronsted base MOFs have been employed in aldol-condensations,6a,c Knoevenagel reactions7 and one-pot tandem reactions,b–e with coordinatively unsaturated metal sites (CUSs)4d,e and organic ligands served 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 CUSs 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.7d The reported PSM approach in preparing MOFs, however is sometimes limited by its sophisticated modification steps, as well as their chemical and physical instabilities of the intermediates/products.8

Metallogiandgs have been widely employed as linkers for the preparation of MOFs/CPs,9 since these ligands could feature in straightforward immobilization of CUSs under solvothermal synthesis.5a–e A notable example of metallogiands is metallosalen, and the reported metallosalen-based MOF catalysts usually contain single CUS.4g,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 literature, several Cu2I3 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 others12 and us.13 As a continuous effort in exploring the catalytic applications of different kinds of polymeric materials,7 we aim to design a novel bimetallc CP which could present multi-functional catalytic activities by combining catalytic active units copper(I) and metallosalens. In this work, we develop a straightforward solvothermal approach for the preparation of a bimetallic CP, [CuII(SalImCy)][CuI]2·DMF (1), wherein SalImCy = N,N′-bis-[[(imidazol-4-yl)methylene]cyclohexane-1,2-diamine], Fig. 1a), which contains copper(II)-salen-based catalysts CuII(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 [CuII(SalHImCy)](NO3)2 was prepared by a one-pot reaction of situ-formed SalHImCy with...
Cu(NO$_2$)$_3$·3H$_2$O in a molar ratio of 1:1 (see Electronic Supporting Information, ESI†). This ligand exhibits good solubility (>10 mg/ mL) in dimethylformamide (DMF), CH$_3$CN and C$_2$H$_5$OH and is stable in air at 298 K, which in turn could be used as a precursor for subsequent solvolithic reactions.

CP 1 in the form of red cuboid-like crystals was obtained by a solvolithic reaction of [Cu(NO$_2$)$_3$] with CuI in a molar ratio of 1:2 in a DMF/CH$_3$OH mixture (v/v, 2:1) for 24 h (Fig. 1a). It has been formulated and characterized on the basis of elemental analysis, IR, thermogravimetric and single-crystal X-ray diffraction analyses. The experimental details are given in ESI† (Table S1 & Fig. S1). CP 1 can be readily prepared by either one of the four different forms of the 1,2-$	ext{L}$phenyl-$	ext{L}$α[($	ext{L}$phenylethyl)amino]acetoni-trile and ($	ext{L}$phenyl)Im moieties of CuI (Table S1, ESI†) and reaction time required (3 h), as well as the percentage yields obtained (82% for CuI and 87% for Cu[SalHImCy](NO$_2$)$_3$) for the a-aminonitrile products (Table S4, ESI†). The superior catalytic activity of 1 indicates that there is a cooperative catalytic event achieved by two different active catalytic sites (i.e., Cu$^+$ and Cu$^{II}$) of 1. In this reaction, the Cu$^+$-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.16

For comparison, the catalytic activities of two reference compounds CuI and [Cu(NO$_2$)$_3$] with [Cu(NO$_2$)$_3$] 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 CuI, 0.5 mol% for [Cu(NO$_2$)$_3$] and reaction time required (3 h), as well as the percentage yields obtained (82% for CuI and 87% for [Cu(NO$_2$)$_3$]) for the a-aminonitrile products (Table S4, ESI†). The superior catalytic activity of 1 indicates that there is a cooperative catalytic event achieved by two different active catalytic sites (i.e., Cu$^+$ and Cu$^{II}$) of 1. In this reaction, the Cu$^+$-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.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.18 A recycling test with three consecutive runs shows that 1 can be re-used without a significant loss of catalytic activity (the yields 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 adequate stability and recoverability to be used as an efficient bimetallic heterogeneous catalyst for the three-component reactions.

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

![Table 1 Asymmetric three-component strecker reaction catalyzed by 1](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (R)</th>
<th>t (h$^*$)</th>
<th>Yield (%)</th>
<th>a:b</th>
<th>TOF (h$^{-1}$)</th>
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<td>H</td>
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<td>99</td>
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<tr>
<td>7</td>
<td>H</td>
<td>1</td>
<td>95$^*$</td>
<td>66.34</td>
<td>191</td>
</tr>
</tbody>
</table>

$^*$Aromatic aldehydes (1 mmol), (R)(+)-1-phenylethylamine (1 mmol), TMSCN (1.5 mmol) and CD$_3$CN (2 mL), 1 (0.5 mol%), sealed in a screw-cap vial were stirred at 283 K. $^*$Reaction time t, hour. $^*$% yields determined by GC. $^*$Diastereoselectivity were determined by H-NMR. $^*$TOF = turnover frequency (moles of reactants converted per moles of active sides unit time), h$^{-1}$. $^*$The second cycle. $^*$The third cycle.
(photo-)degradation of methylene blue (MB) aqueous solution (12 mg/L) has first been examined by means of UV-vis spectrophotometry (Fig. S5, ES†). In the absence of visible-light illumination, 65% of MB had been decomposed in the solution (Fig. 2b, 2c). We reckon that the CuII ions in I is crucial in decomposing MB, since various studies have shown that CuII could play major catalytic role in various oxidation reactions. It should be noted that up to 96% of MB could be decomposed when the reaction was performed under visible-light illumination (Fig. 2b, 2c). We reckon that the enhanced degradation of MB is due to the cooperative decomposition achieved by photactive Cu(I) moieties in I. Apart from MB, the photodegradation of other organic dyes including rhodamine B (RhB) and methyl orange (MO) by I 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, ES†). Furthermore, the stability and recoverability of I have also been examined. After repeating the photocatalytic degradation of MB three times, the solid residues left in the reaction mixture retained similar PXRD pattern as that of the pristine solid of I. As expected, these residues also displayed similar photocatalytic efficiency as that of I (Fig. S10–S11, ES†).

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 I could be used as an efficient heterogeneous multifunctional catalyst for the synthesis of α-aminoaldehydes via asymmetric three-component strecker reaction. Meanwhile, I 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.

Notes and references


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