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

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Three copper(I)-metallosalen coordination polymers (CPs), \{\text{[Ni}^\text{II}(\text{SalImCy})_2\text{Cu}^\text{II}(\text{CN})_n\} (1), \{\text{[Cu}^\text{II}(\text{SalImCy})_2\text{Cu}^\text{II}(\text{CN})_n\} (2) and \{\text{[Ni}^\text{II}(\text{SalImCy})_2\text{Cu}^\text{II}(\text{CN})_n\} (3) were prepared by direct combination of \text{Ni}^\text{II}/\text{Cu}^\text{II}(\text{salen}) motifs with \text{Cu}^\text{II}(\text{CN})_n chains and \text{Cu}_3\text{I}_2 clusters via the metalloligand strategy. The mixed-valence and mixed-metal CPs could effectively catalyze both the oxidation of aromatic alcohols to ketones and aldehydes under mild conditions and photocatalytic degradation of organic dye methylene blue (MB). This work demonstrates the effective integration of traditional metal catalytic \text{Ni}^\text{II}/\text{Cu}^\text{II}(\text{salen}) units and photoactive copper(I) species in a single solid polymer to meet the demand for catalytic materials with the dual catalytic property.

Introduction

In nature, various enzymes such as ureases and tyrosinase could bear more than one catalytic-active unit to achieve selective catalytic oxidations and specific chemical transformations.\(^1\) The obtained high conversion for specific chemical reactions is of fundamental importance for chemical industries and thus enormous efforts have been made in the development of these enzyme mimics.\(^2\) To this end, metal-based coordination polymers (CPs) and metal-organic frameworks (MOFs) have been regarded as novel classes of catalyst candidates,\(^3\) since more than one type of accessible coordinatively unsaturated sites (CUSs),^4^ chiral active sites^5^ and photoactive species^6^ could be present in these frameworks/polymers.\(^7\) In literature, some examples including site-isolated Lewis acid–Brønsted base MOFs^8^ and bimetallic palladium(II)–copper(II) MOFs,^9^ which were synthesized via post-synthetic modification (PSM)^10^ have been reported. Moreover, metalloligands can also be used as linkers of CUSs to construct MOFs and CPs under solvothermal conditions.\(^11\) Compared to the PSM, the metalloligand strategy has advantages in the immobilization of multiple metal sites into CPs/MOFs,\(^11\) and

\(^{12a\text{c}}\) separation of chiral and achiral small molecules\(^12\) \text{Mn}^\text{II}/\text{Ni}^\text{II}(\text{salen}) 1D CPs have also been reported to exhibit great heterogeneous catalytic activity in olefin epoxidation.\(^12\) More recently we have reported the successful preparation of a \text{Cu}^\text{II}/\text{Cu}^\text{II}(\text{salen})-based 1D CP showing promising biomimetic catalytic activity towards the three-component Strecker reaction.\(^13\) Nevertheless, studies on the synthesis of mixed-metal MOFs/CPs via the metalloligand strategy and the dual catalytic property of two metal sites, which may show the synergistic catalytic effect towards chemical transformations as enzyme mimics, remain sparse.

In an attempt to design heterogeneous catalytic materials for selective oxidation reactions,\(^2\) in this work we designed different 1D and 2D CPs containing two catalytically-active metal units by the immobilization of metallosalen and copper(I) into the framework of CPs via the metallosalen strategy. Copper(I) atom was chosen since copper is easily recoverable and copper(I)-based photoactive complexes and polymeric materials\(^14\) could be designed to display tunable electronic properties and long excited state lifetimes,\(^15\) rendering them to have enormous potentials in constructing heterogeneous photocatalytic materials.\(^16\) Furthermore, we previously have demonstrated that the use of different copper(I) halides and pseudohalides could readily modify the coordination networks of CPs/MOFs from zero-dimensional (0D) to three-dimensional (3D) geometry.\(^17\) On the other hand, \text{Ni}^\text{II}(\text{salen}) has been chosen to form another catalytically-active unit,\(^12\) since various 1D CPs and MOFs with nickel(II) atoms could be used as effective heterogeneous catalysts in olefin epoxidation,\(^12\) the oxidation of CO\(^18\) and photocatalytic degradation of organic dyes.\(^19\,\,3\) However, very few studies have been focused on the CP-based multifunctional catalysts for both selective oxidation reaction and photocatalysis in a single framework.

Herein we first report three copper(I)–metallosalen CPs which were prepared by the metalloligand strategy (Scheme 1) under solvothermal condition. The CPs have been utilized as heterogeneous catalysts for the efficient transition metal catalytic oxidation of aromatic alcohols to ketones and aldehydes and the...
visible-light-induced degradation of dye pollutant methylene blue (MB) using t-butyl hydroperoxide (TBHP) or hydrogen peroxide (H₂O₂) as a sacrificial oxidant.

**Results and discussion**

Three copper(I)-metallosalen CPs, [{Ni⁴(SalImCy)₂}(CuCN)ₙ] (1, wherein SalImCy = N,N'-bis-[(imidazol-4-yl)methylene]cyclohexane-1,2-diamine), [{Cu⁴}(SalImCy)₂](CuCN)ₙ (2) and [{Ni⁴(SalImCy)}(CuI)₃·DMF]ₙ (3), were prepared by the solvothermal synthesis of the metallosalen precursors and copper(I) halides and pseudohalides. 1 and 2 were prepared by Ni⁴/Cu⁴(salen) and CuCN in a molar ratio of 1:5 in a DMF/CH₃CN mixture (1, v/v, 2:1; 2, v/v, 1:1) at 120 °C for 72 h, 3 was prepared by Ni⁴(salen) and Cu in a molar ratio of 1:2 in a DMF/CH₃OH mixture (v/v, 2:1) at 100 °C for 12 h. For comparison, a copper(I) CP [4,4'-bis[(4-cyanophenyl)methyl]-3,5-dimethylpyrazole(CuI)₃] (4), which contains copper(I) iodine clusters, was also prepared by 4,4'-bis[(4-cyanophenyl)methyl]-3,5-dimethylpyrazole and Cu in a molar ratio of 1:2 in CH₃OH at 140 °C for 72 h. All of these complexes have been formulated and characterized on the basis of elemental analysis, IR, thermogravimetric analysis (TGA) and single-crystal X-ray diffraction analyses. The experimental details and characterization data are given in Electronic Supporting Information (ESI†).

Phase purity of the bulk samples was established by comparison of their observed and simulated PXRD patterns (Figures S1–S4, ESI†). CPs 1–4 are found to be stable in air for at least six months confirmed by powder X-ray diffraction (PXRD) analysis, and 1–3 have a poor solubility (<0.5 mg/mL) in water, dimethylformamide (DMF), C₂H₅OH and CH₃CN at room temperature. CP 4 is insoluble in water and C₂H₅OH but is soluble in DMF and CH₃CN.

The metallosalen precursors, [{Ni⁴(SalImCy)₂}(NO₃)₂](NiL₂H₂), [Cu⁴(SalImCy)₂](NO₃)₂(CuL₂H₂) and [Cu⁴(SalMImCy)₂](NO₃)₂·H₂O (CuL·Me₂), were in situ-prepared from 4-IH-imidazole-4-carbaldehyde, 1S, 2S (+)-1, 2-cyclohexanediimine and metal salts. X-ray crystal analysis of CuL·Me₂ reveals that the Cu⁴⁺ ion of this precursor is connected to two N-imine atoms and two N-imidazol to form a square-planar 4-coordinate geometry, with ligand bite angle between the two unprotonated N-imidazol atoms of 109.465(93)° (Figure S5, ESI†). Some N-donor-based angular linkers with bite angle around 120° in literature have been shown to display impressive coordination architectures such as polygons, zigzag chains, and helices. In addition to CuL·Me₂, NiL₂H₂ and CuL·H₂ drawing similar coordination geometry could also serve as angular linkers in forming CPs 1, 2 and 3.

Heterometallic CP 1 crystallized in the triclinic P-1 space group by single-crystal X-ray diffraction analysis (Table S1, ESI†). Each asymmetric unit of 1 contains one deprotonated Ni⁴(salen) ligand, five Cu⁺ ions and four and a half CN⁻ molecules. The Ni⁴⁺ ion adopts a square-planar chelating coordination geometry (Figure 1a). The two deprotonated imidazol N atoms of the Ni⁴⁺(salen) are coordinated to two separate Cu⁺ atoms (Cu1 and Cu5) from [Cu-CN], clusters. The Cu⁵⁺ atom (Cu5) adopts a linear coordination geometry to bridge two Ni⁴⁺(salen) [Cu5-N̵₉imine 1.864(0) Å]. The Cu⁺ atom with a 3-coordinated triangular geometry [Cu1-N̵₉imine 2.047(10) Å] is bound with two CN⁻ ligands of [Cu-CN] clusters to form 1D zigzag chains along the a-axis (Figure 1b), which are further extended by [Cu-CN] chains to furnish a 2D layer (Figure 1c and 1d, Figure S6, ESI†). There exists two different Cu⁺–Cu⁺ interaction in the layer with a distance of 2.778(3) Å (Cu3–Cu4) and 2.901(2) Å (Cu4–Cu5) in the two adjacent 2-coordinated
CuI atoms. The layers stack into a three-dimensional structure (Figure S7, ESI†). The Cu"(salen)-based CP 2 is isostructural to 1 based on the comparison of bond lengths of the asymmetric unit of 1 and 2 from X-ray diffraction parameters (Tables S2 and S3, ESI†) and structural analysis (Figures S8-S11, ESI†).

3 crystallized in a triclinic centro-symmetric P-1 space group (Table S1, ESI†). The asymmetric unit of 3 features a square-planar 4-coordinate NiII ion of the NiII(salen) (Figure 2a) and a triangular 3-coordinate CuI ion of the rhomboid CuII3I2 cluster (Figure 2b). The NiII(salen) linker, with a bite angle of 112.3(2)° between two N-imidazol atoms, is bridged by two CuII3I2 nodes to form a zigzag chain along the a-axis (Figure 2b). Along the b-axis, zigzag chains stack into a three-dimensional structure, forming tubular channels with dimension of 7.24(1) × 12.53(3) Å, where DMF molecules were located (Figure 2c).

As shown in the crystal structures of 1, 2 and 3, both metallosalen moieties and copper(I) clusters are incorporated in a defined network. Moreover, the connection of metallosalens in 1 and 2 features in a single linear 2-coordinate copper(I) atom and two CuII-CuI interaction of the [Cu2CN] network, while the NiII(salen) in 3 was bridged by CuII3I2 clusters. The stability of 1 and 2 are examined by thermogravimetric analysis, showing a thermal stability of ~250 °C and ~300 °C respectively (Figures S12–S13, ESI†). The framework of 3 is also stable up to ~300 °C (Figure S14, ESI†).

It is highly desirable to develop a green and atom economic catalytic system for selective aerobic oxidation using environment-friendly oxidant (O2, TBHP, H2O2 etc.). Catalytic oxidation of aromatic alcohols to the corresponding aldehydes or ketones was chosen as a model reaction to investigate the catalytic property of copper(I)-metallosalen CPs. We conducted the oxidation of aromatic alcohols using 1.5 mol% of the CP (1, 2 or 3) as catalyst and 1.5 equiv TBHP as the oxidant with acetone as the solvent at 20 °C under atmospheric pressure. Table 1 lists the substrate (aromatic alcohols) conversion, the product selectivity (aldehydes/ketones per mole of total products) and turnover frequency (TOF, moles of products per mole of catalysts per hour) of CPs 1-3. For the oxidation of 1-

Table 1. Catalytic oxidation of aromatic alcohols with copper(I)-metallosalen CP 1, 2 and 3

<table>
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<th>Entry</th>
<th>Substrate</th>
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<th>Conv. [%]</th>
<th>Select. [%]</th>
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</table>

† Reaction condition: aromatic alcohol (0.65 mmol), catalyst (1.5 mmol%), TBHP (0.975 mmol), acetonitrile (5 ml), 293 K. Reaction time, hour. Conversion % and Selectivity % were determined by HPLC analysis. TOF = turnover frequency calculated as mol(product)/[mol(catalyst) × (reaction time)], h−1. Without catalyst, not measured. TBHP (2.925 mmol), 323 K.

In order to further examine the photocatalytic efficiency of the copper(I)-based CPs 1-3, we performed the degradation of the organic dye methylene blue (MB). The optical response of CPs 1-3 was investigated by diffuse-reflectance UV–Vis spectroscopy (Figure 3). From the reflection spectra, it is obvious that all of the copper(I)-based CPs show a clear absorption in the visible light region. They can absorb photons with energy equal or higher than their HOMO–LUMO gaps (Table S4, ESI†). The catalytic behavior and degradation rates of the CPs on MB aqueous solution (12 mg/L) using 30% H2O2 as the oxidant was examined by means of UV-Vis spectrophotometry in the presence or absence of visible light illumination (Figure 4). In the absence of light, degradation rate of 92% (1, 2) and 25% (3) were observed with time increasing from 0 to 22 min (Figure S16-S19, ESI†). In the presence of visible light illumination with different wavelength range, higher degradation rate was observed for 1, 2 (99%, 300-400 nm; 97%, λ > 560 nm) and 3 (57%) within 22 min (Figure S16, S20-S22, ESI†). This improved degradation efficiency with light illumination indicates that CPs 1-3 are photo-catalytically active in MB degradation.

In order to further figure out the catalytic degradation property of NiII/CuI(salen) and copper(I) units in 1-3, CP 4 with only...
CuI2 clusters (Figure S23-S26, Table S1, ESI†) was synthesized as a reference compound. The thermal stability and optical response of CP4 were also investigated (Figure S27 and S3, Table S4, ESI†). In the MB degradation experiment (Figure 4a), no activity can be found for 4 in the absence of light illumination, while good photocatalytic efficiency (55%) was achieved by 4 in the presence of visible-light illumination (Figure 4 and Figure S28). This result indicates that copper(I) clusters of CPs 1-3 are photo-catalytically active centers, but the metallosalen unit is responsible for better degradation efficiency than 4 in term of degradation rate.

Proposed catalytic mechanism of the dual catalytic system of 1 and 2 was illustrated in Figure 5. In the presence of visible light, copper(I) units of all four complexes can absorb photons and promote the chemical transformation.16,19,22 In contrast to 4, the immobilization of accessible NiII/CuII(salen) catalytic centers on the solid surfaces12e, f, 25 render them highly efficient transition metal catalytic activity towards MB degradation and the aromatic alcohol oxidation. Compared with the CuI2 clusters in 3, CuI···CuI interaction of [CuCN]n chains in 1 and 2 may be changeable, which can lead to structural dynamics of MOFs/CPs,24 resulting in higher activity than 3.

In the control experiment of alcohol oxidation, low activity (conversion of 20% to 28%, Table S5, Entries 1-4, ESI†) was observed with a physical mixture of metallosalen ligands (NiL2 or CuL2) and CuCN. We further carried out the recovery experiment. During three cycles of the oxidation of benzyl alcohol and 1-phenylethyl alcohol, conversion of 29% and 90% (Table S5, Entries 5-8, ESI†) was observed with 1, respectively. Furthermore, the photocatalytic stability of 1 and 2 were examined by three cycles of repeated reactions maintaining at degradation of >90% (Figure S29 and S30, ESI†). To confirm the heterogeneous nature of the reaction, quantitative analysis using atomic absorption spectroscopy (AAS)25 was employed to determine the amount of metal in the final leached solution. The AAS analysis indicates that less than 0.6% (the alcohol oxidation) and 0.1% (the MB degradation) of the copper ions in 1 or 2 are leached out into the reaction solution. The powder X-ray diffraction (PXRD) analysis of the solid residues recovered by centrifugation after each cycle illustrates a similar pattern as that
of pristine solids of 1 and 2 (Figure 6, Figure S31 and S32, ESI†). Some deviation could be the result of the change of the weak Cu(I)···Cu interaction in [Cu(CN)₄] chains. The above results indicate that 1 and 2 are heterogeneous catalytic materials, which can be reused in mild reaction condition (e.g., room temperature, few hours and moderate oxidant).

In summary, we developed a readily applicable metalloigand way to prepare copper(I)-metallasalen CP materials with dual catalytic activity by the direct combination of two metal catalytic species in one single framework. The immobilization of Cu(I)/Ni(II) (salen) in these CPs accounts for the catalytic efficiency of aromatic alcohol oxidation and enhanced visible-light-induced photocatalytic performances on organic dye methylene blue (MB). The preparation, application and structure-property investigation of mixed-valence and mixed-metal 1D and 2D coordination polymers pave the way for the potential of efficient bi/multimetallic multifunctional catalytic materials.

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Notes and references

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