This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Chemical Science

EDGED ARTICLE

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

Yun-Long Hou,[a] **Sheng-Xia Li,**[a] **Raymond Wai-Yin Sun,**[a] **Xin-Yuan Liu,**[b] **Seik Weng Ng**[c, d] **and Dan Li***[a]

Three copper(I)-metallosalen coordination polymers (CPs), $\{[Ni^{II}(SalImCy)]_2(Cu^ICN)_9\}_n$ (**1**), $\{[Cu^{II}(SalImCy)]_2(Cu^ICN)_9\}_n$ (**2**) and $\{[Ni^{II}(SalImCy)](Cu^II)_2·DMF\}_n$ (**3**) were prepared by direct combination of Ni^{II}/Cu^{II}(salen) motifs with $[Cu^ICN]_n$ chains and Cu_2I_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 10 demonstrates the effective integration of tradition metal catalytic Ni^{II}/Cu^{II}(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 15 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 20 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 25 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 30 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, 12] Hupp and other groups reported some examples of Mn^{II}/Cu^{II}(salen) MOFs on asymmetric catalysis[12a-c] and

35 separation of chiral and achiral small molecules[12d]. Mn^{II}/Ni^{II}(salen) 1D CPs have also been reported to exhibit great heterogeneous catalytic activity in olefin epoxidation.[12e, f] More recently we have reported the successful preparation of a Cu^II-Cu^{II}(salen)-based 1D CP showing promising bimetallic catalytic 40 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 45 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 50 framework of CPs *via* the metalloligand 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 55 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 60 other hand, Ni^{II}(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,[12e, f] the oxidation of CO[18] and photocatalytic degradation of organic dyes.[19, 3] However, very 65 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) 70 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

a Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Guangdong 515063, P. R. China. E-mail: dli@stu.edu.cn
b Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, P. R. China
c Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia.
*d Chemistry Department, Faculty of Science, King Abdulaziz University, PO Box 80203 Jeddah, Saudi Arabia.*

visible-light-induced degradation of dye pollutant methylene blue (MB) using *t*-butyl hydroperoxide (TBHP) or hydrogen peroxide (H_2O_2) as a sacraficial oxidant.

Results and discussion

Three copper(I)-metallosalen CPs, $\{[Ni^{II}(SalImCy)]_2$ $(Cu^ICN)_9\}_n$ (**1**, wherein SalImCy = *N,N'*-bis-[(imidazol-4-yl)methylene]cyclohexane-1,2-diamine), $\{[Cu^{II}$ $(SalImCy)]_2$ $(Cu^ICN)_9\}_n$ (**2**) and $\{[Ni^{II}(SalImCy)](Cu^II)_2 \cdot DMF\}_n$ (**3**), were prepared by the solvothermal synthesis of the metallosalen precursors and copper(I) halides and pseudohalides. **1** and **2** were prepared by Ni^{II}/Cu^{II}(salen) and CuCN in a molar ratio of 1:5 in a DMF/CH_3CN mixture (**1**, v/v, 2:1; **2**, v/v, 1:1) at 120 °C for 72 h, **3** was prepared by Ni^{II}(salen) and CuI in a molar ratio of 1 : 2 in a DMF/C_2H_5OH 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($Cu^II)_2]_n$ (**4**), which contains copper(I) iodine clusters, was also prepared by 4,4′-bis[(4-cyanophenyl)methyl]-3,5-dimethylpyrazole and CuI in a molar ratio of 1:2 in CH_3OH 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), C_2H_5OH and CH_3CN at room temperature. CP **4** is insoluble in water and C_2H_5OH but is soluble in DMF and CH_3CN.

The metallosalen precursors, $[Ni^{II}(SalHImCy)](NO_3)_2$ (NiL-H_2), $[Cu^{II}(SalHImCy)](NO_3)_2$ (CuL-H_2) and $[Cu^{II}(SalMImCy)]$ $(NO_3)_2 \cdot H_2O$ (CuL-Me$_2$), were *in situ*-prepared from 4-1H-imidazole-4-carbaldehyde, 1*S*, 2*S* (+)-1, 2-cyclohexanediamine and metal salts. X-ray crystal analysis of CuL-Me$_2$ reveals that the Cu^{II} 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.[20] In addition to CuL-Me$_2$, NiL-H_2 and CuL-H_2 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 Ni^{II}(salen) ligand, five Cu^I atoms and four and a half CN^- molecules. The Ni^{II} ion adopts a square-planar chelating coordination geometry (Figure 1a). The two deprotonated imidazol N atoms of the Ni^{II}(salen) are coordinated to two separate Cu^I atoms (Cu1 and Cu5) from $[Cu^ICN]_n$ clusters. The Cu^I5 atom (Cu5) adopts a linear coordination geometry to bridge two Ni^{II}(salen) [Cu5-$N_{imidazol}$, 1.864(0) Å]. The Cu^{I}1 atom with a 3-coordinated triangular geometry [Cu1-$N_{imidazol}$, 2.047(10) Å] is bound with two CN^- ligands of $[Cu^ICN]_n$ chains to form 1D zigzag chains along the *a*-axis (Figure 1b), which are further
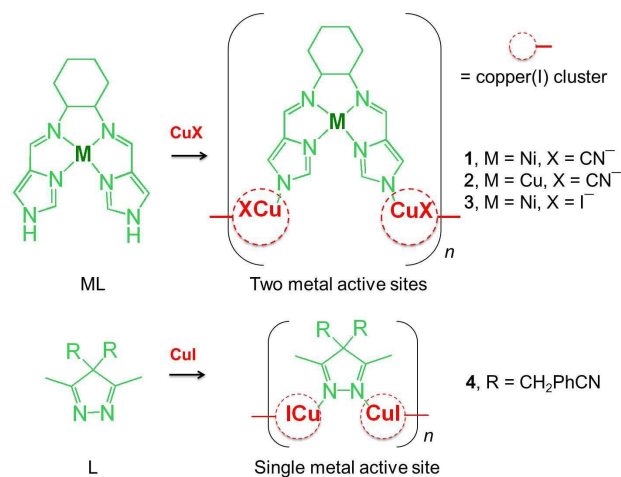
Scheme 1. Synthesis of **1**, **2**, **3**, **4** and their precursors.
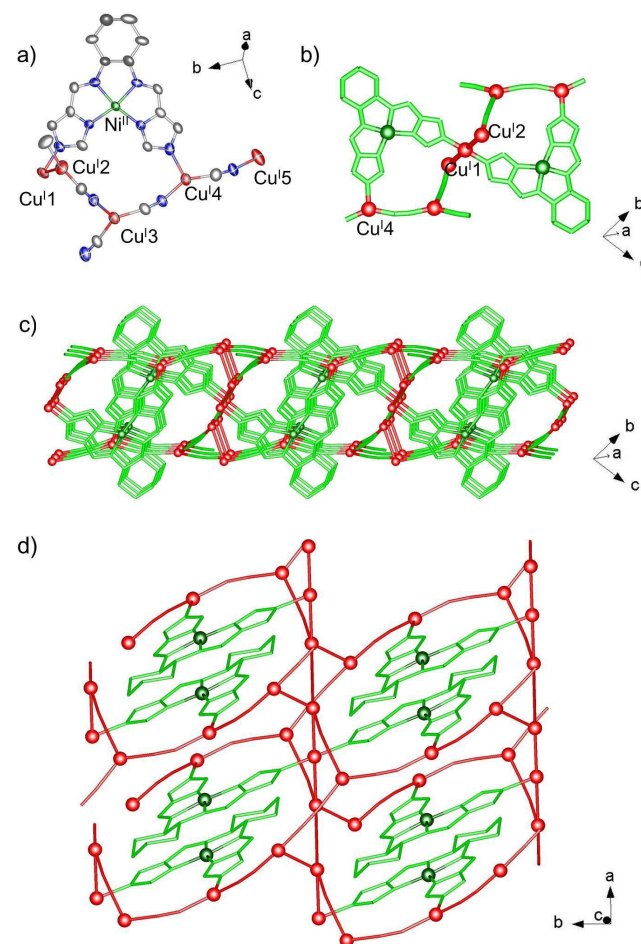

Fig. 1 (a) Asymmetric unit of **1** with labeled atoms. (b) A representative zigzag chain of **1** viewed along *a*-axis. (c) The 2D layer of **1** viewed along *a*-axis. (d) The 2D layer of **1** viewed along *c*-axis. In a, b, c and d, all hydrogen atoms are omitted for clarity, Cu, red; Ni, dark green.

extend by $[Cu^ICN]_n$ chains to furnish a 2D layer (Figure 1c and 1d, Figure S6, ESI†). There exists two different $Cu^I \cdots Cu^I$ interaction in the layer with a distance of 2.778(3) (Cu3$\cdots$Cu4) and 2.901(2) Å (Cu4$\cdots$Cu5) in the two adjacent 2-coordinated
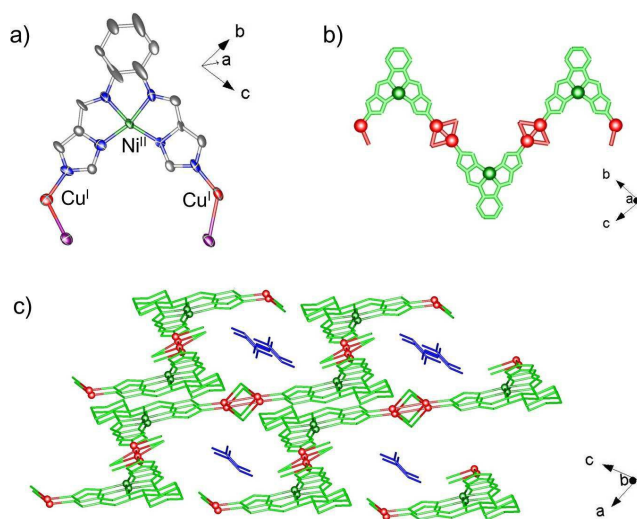
Fig. 2 (a) Asymmetric unit of **3** with labeled atoms. (b) A representative zigzag chain of **3** viewed along *a*-axis. (c) The 3D stacking of **3** viewed along *b*-axis (DMF, blue). In a, b and c, all hydrogen atoms are omitted for clarity, Cu, red; Ni, dark green.

Cu^I atoms. The layers stack into a three-dimensional structure (Figure S7, ESI†). The Cu^{II}(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 Ni^{II} ion of the Ni^{II}(salen) (Figure 2a) and a triangular 3-coordinate Cu^I ion of the rhomboid Cu$^I_2$I$_2$ cluster (Figure 2b). The Ni^{II}(salen) linker, with a bite angle of 112.3(2)° between two N-imidazol atoms, is bridged by two Cu$^I_2$I$_2$ 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 Cu^I···Cu^I interaction of the [Cu^{I}CN]$_n$ network, while the Ni^{II}(salen) in **3** was bridged by Cu$_2$I$_2$ 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 (O$_2$, TBHP, H$_2$O$_2$ etc.).[21] 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 acetonitrile as the solvent at 20 °C under atmospheric pressure. Table 1 lists the substrate (aromatic alcohols) conversion, the product selectivity(moles of 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**^{a}

Entry	Substrate	Catalyst	Time^b [h]	Conv.^{c} [mol%]	Select.^{c} [mol%]	TOF^d
1^e	Me	blank	8	7	f	f
2^g	Me	**1**	8	96	>99	7.9
3^g	Me	**2**	8	95	>99	7.8
4^g	Me	**3**	8	44	89	3.2
5^e	H	blank	2	<1	f	f
6	H	**1**	2	34	90	10.2
7	H	**2**	2	33	92	10.1
8	H	**3**	4	13	94	2.0
9^h	H	**1**	1	35	83	20.5

^{a} Reaction condition: aromatic alcohol (0.65mmol), catalyst (1.5mmol%), TBHP (0.975mmol), acetonitrile (5ml), 293K. ^{b} Reaction time, hour. ^{c} Conversion % and Selectivity % were determined by HPLC analysis. ^{d} TOF = turnover frequency calculated as mol(product)/[mol(catalyst) × (reaction time)], h^{-1}. ^{e} without catalyst. ^{f} not measured. ^{g} TBHP (2.925 mmol). ^{h} 323K.

phenylethyl alcohol and benzyl alcohol, only 7% and <1% conversion was observed in blank experiment respectively (Table 1, Entry 1 and 5), while **1**, **2** and **3** exhibit moderate to good catalytic efficiency (conversion of 96%, 95% and 44%, Table 1, Entries 2-4) in 1-phenylethyl alcohol oxidation. **1**, **2** and **3** was also found to have conversion of 34%, 33% and 13%, and selectivity of >90% in benzyl alcohol oxidation (Table 1, Entries 6-8). The effect of reaction time was also examined by **1**-catalyzed oxidation of benzyl alcohol at 50 °C (Table 1, Entry 9 and Figure S15, ESI†). Above results reveal that CPs **1-3** are effective transitional metal catalysts with good performance in the aromatic alcohol oxidation.

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 copper(I)-based solids show a clear optical response 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% H$_2$O$_2$ 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%, λ > 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 Ni^{II}/Cu^{II}(salen) and copper(I) units in **1-3**, CP **4** with only
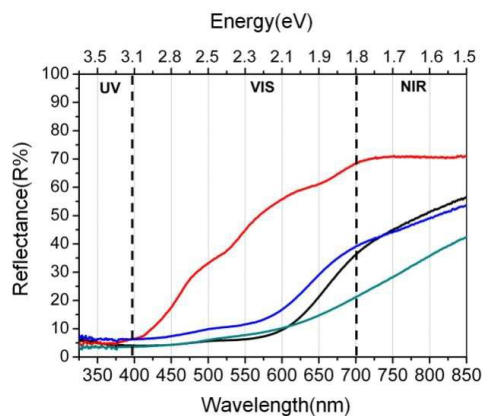
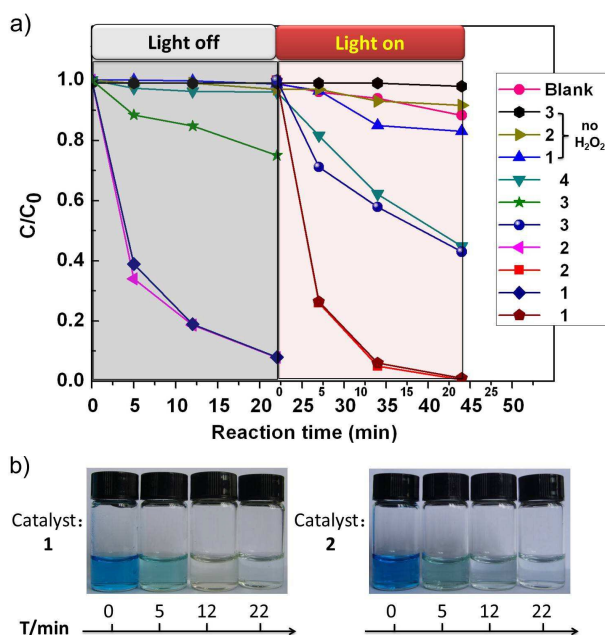**Fig. 3** UV-Vis diffuse reflectance spectra of **1**(blue), **2**(dark), **3**(green) and **4**(red).

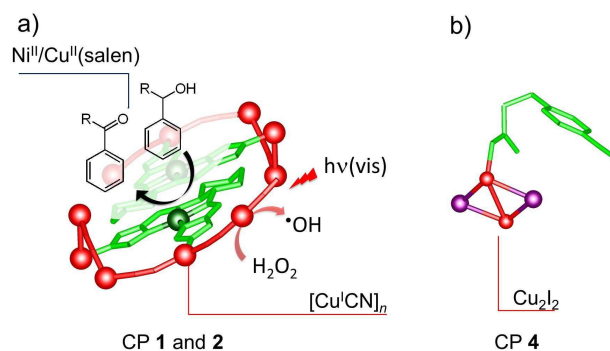**Fig. 5** (a) The diagram of the dual catalytic mechanism of CP **1** and **2**: metallosalen-based transition metal catalysis (black) and $[Cu^ICN]_n$-based photocatalysis(red). (b) Cu_2I_2-based photoactive unit in CP **4**.

Fig. 4 (a) Photocatalytic degradation rates of MB catalyzed by upon visible-light illumination ($\lambda > 400nm$). (b) Photographs of MB solutions catalyzed by **1** and **2** at different time intervals.
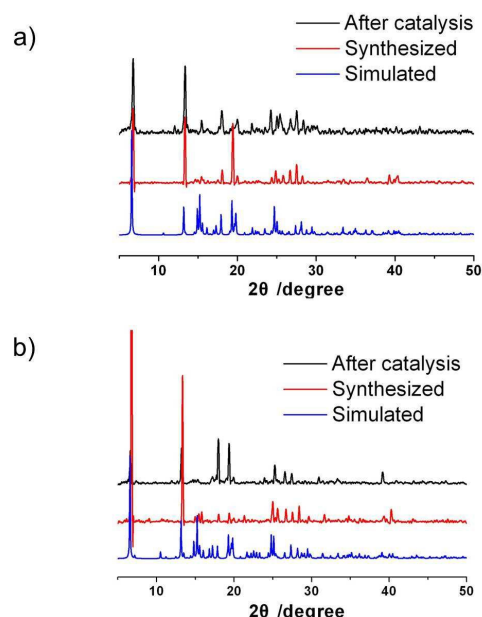
Fig. 6 The PXRD patterns of **1**(a) and **2**(b) for catalytic oxidation of aromatic alcohols.

$Cu^I_2I_2$ clusters (Figure S23-S26, Table S1, ESI†) was synthesized as a reference compound. The thermal stability and optical response of CP **4** were also investigated (Figure S27 and 3, Table S4, ESI†). In the MB degradation experiment (Figure 4a), no
[5] 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
[10] 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
[15] promote the chemical transformation.[16,19,22] In contrast to **4**, the immobilization of accessible Ni^{II}/Cu^{II}(salen) catalytic centers on the solid surfaces[12e, f, 23] render them highly efficient transition metal catalytic activity towards MB degradation and the aromatic alcohol oxidation. Compared with the $Cu^I_2I_2$ clusters in **3**,

$Cu^I \cdots Cu^I$ interaction of $[Cu^ICN]_n$ chains in **1** and **2** may be
[20] 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
[25] observed with a physical mixture of metallosalen ligands ($NiL-H_2$ or $CuL-H_2$) 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.
[30] 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
[35] 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
[40] 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 $Cu^I \cdots Cu^I$ interaction in $[Cu^I CN]_n$ 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 metalloligand way to prepare copper(I)−metallosalen CP materials with dual catalytic activity by the direct combination of two metal catalytic species in one single framework. The immobilization of Cu^{II}/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.

Acknowledgements

Notes and references

1   a) M. J. Maroney and S. Ciurli, *Chem. Rev.*, **2014**, 114, 4206; b) E. I. Solomon, U. M. Sundaram and T. E. Machonkin, *Chem. Rev.*, **1996**, 96, 2563; c) M. Rolff, J. Schottenheim, H. Decker and F. Tuczek, *Chem. Soc. Rev.*, **2011**, 40, 4077.

2   L. Que Jr and W. B. Tolman, *Nature*, **2008**, 455, 333.

3   a) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, **2009**, 38, 1450; b) A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, **2010**, 110, 4606; c) T. Zhang and W. Lin, *Chem. Soc. Rev.*, **2014**, 43, 5982; d) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, **2014**, 43, 6011.

4   a) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, **2004**, 43, 2334; b) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, **2005**, 44, 4670.

5   a) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, **2012**, 112, 1196; b) Y. Liu , W. Xuan and Y. Cui, *Adv. Mater.*, **2010**, 22, 4112; c) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, **2009**, 38, 1248.

6   a) J.-L. Wang, C. Wang and W. Lin, *ACS Catal.*, **2012**, 2, 2630; b) S. Pullen, H. Fei, A. Orthaber, S. M. Cohen and S. Ott, *J. Am. Chem. Soc.,* **2013**, 135, 16997; c) P. Wu, C. He, J. Wang, X. Peng, X. Li, Y. An and C. Duan, *J. Am. Chem. Soc.*, **2012**, 134, 14991; d) A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent, and M. J. Rosseinsky, *Angew. Chem. Int. Ed.*, **2012**, 51, 7440; e) K. G. M. Laurier, F. Vermoortele, R. Ameloot, D. E. De Vos, J. Hofkens and M. B. J. Roeffaers, *J. Am. Chem. Soc.*, **2013**, 135, 14488.

7   a) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science*, **2013**, 341, 974; b) T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, **2013**, 113, 734.

8   (*a*) F. Vermoortele, R. Ameloot, A. Vimont, C. Serrec and D. D. Vos, *Chem. Commun.*, **2011**, 47, 1521; (*b*) B. Li, Y. Zhang, D. Ma, L. Li, G. Li, G. Li, Z. Shi and S. Feng, *Chem. Commun.*, **2012**, 48, 6151; (*c*) J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. Yakovenko, Z. U Wang, L.-B. Sun, P. B. Balbuena and H.-C. Zhou, *Chem. Commun.*, **2012**, 48, 9995; (*d*) R. Srirambalaji, S. Hong, R. Natarajan, M.

9   A. Arnanz, M. Pintado-Sierra, A. Corma, M. Iglesias and F. Sánchez, *Adv. Synth. Catal.*, **2012**, 354, 1347.

10   S. M. Cohen, *Chem. Rev.*, **2012**, 112, 970.

11   a) S. Kitagawa, S.-i. Noro and T. Nakamura, *Chem. Commun.*, **2006**, 42, 701; b) G. Kumar and R. Gupta, *Chem. Soc. Rev.,* **2013**, 42, 9403; c) B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, **2010**, 43, 1115; d) M. C. Das, S. Xiang, Z. Zhang and B. Chen, *Angew. Chem. Int. Ed.*, **2011**, 50, 10510; e) Z.-Y. Gu, J. Park, A. Raiff, Z. Wei, and H.-C. Zhou, *ChemCatChem*, **2014**, 6, 67.

12   a) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chem. Commun.*, **2006**, 42, 2563; b) F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, *J. Am. Chem. Soc.,* **2010**, 132, 15390; c) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, **2009**, 38, 1450; d) M. C. Das, Q. Guo, Y. He, J. Kim, C.-G. Zhao, K. Hong, S. Xiang, Z. Zhang, K. M. Thomas, R. Krishna and B. Chen, *J. Am. Chem. Soc.*, **2012**, 134, 8703; e) Y. Huang, T. Liu, J. Lin, J. Lü, Z. Lin and R. Cao, *Inorg. Chem.,* **2011**, 50, 2191; f) A. Bhunia, M. A. Gotthardt, M. Yadav, M. T. Gamer, A. Eichöfer, W. Kleist and P. W. Roesky, *Chem.–Eur. J.*, **2013**, 19, 1986.

13   Y.-L. Hou, R. W.-Y. Sun, X.-P. Zhou, J.-H. Wang and D. Li, *Chem. Commun.*, **2014**, 50, 2295.

14   a) P. Vanelderen, J. Vancauwenbergh, B. F. Sels and R. A. Schoonheydt, *Coord. Chem. Rev.*, **2013**, 257, 483; b) R. Peng, M. Li and D. Li, *Coord. Chem. Rev.*, **2010**, 254, 1.

15   a) D. R. McMillin and K. M. McNett, *Chem. Rev.*, **1998**, 98, 1201; b) S. B. Harkins and J. C. Peters, *J. Am. Chem. Soc.*, **2005**, 127, 2030; c) M. Hashimoto, S. Igawa, M. Yashima, I. Kawata, M. Hoshino and M. Osawa, *J. Am. Chem. Soc.*, **2011**, 133, 10348.

16   a) S. E. Creutz, K. J. Lotito, G. C. Fu and J. C. Peters, *Science*, **2012**, 338, 647; b) A. C. Hernandez-Perez, A. Vlassova and S. K. Collins, *Org. Lett.*, **2012**, 14, 2988; c) T. Wen, D.-X. Zhang, J. Liu, R. Lin and J. Zhang, *Chem. Commun.*, **2013**, 49, 5660.

17   (a) X.-P. Zhou, D. Li, T. Wu and X. Zhang, *Dalton Trans.,* **2006**, 2435; (b) S.-H. Lin, X.-P. Zhou, D. Li and S. W. Ng, *Cryst. Growth Des.*, **2008**, 8, 3879; (c) X.-P. Zhou, W.-X. Ni, S.-Z. Zhan, J. Ni, D. Li and Y.-G. Yin, *Inorg. Chem.,* **2007**, 46, 2345; (d) J.-Z. Hou, M. Li, Z. Li, S.-Z. Zhan, X.-C. Huang and D. Li, *Angew. Chem., Int. Ed.*, **2008**, 47, 1711; e) W.-X. Ni, M. Li, X.-P. Zhou, Z. Li, X.-C. Huang and D. Li, *Chem. Commun.*, **2007**, 43, 3479; f) M. Li, Z. Li and D. Li, *Chem. Commun.*, **2008**, 44, 3390.

18   R. Q. Zou, H. Sakurai and Q. Xu, *Angew. Chem., Int. Ed.,* **2006**, 45, 2542.

19   a) P. Mahata, G. Madras and S. Natarajan, *J. Phys. Chem. B,* **2006**, 110, 13759; b) J. Han, Z. Yu, X. He, P. Li, Y. Wang and C.-Y. Quan, *Inorg. Chim. Acta*, **2012**, 388, 98.

20   a) H. Abourahma, B. Moulton, V. Kravtsov and M. J. Zaworotko, *J. Am. Chem. Soc.*, **2002**, 124, 9990; b) X.-C. Huang, J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, **2004**, 126, 13218; c) T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, **2013**, 113, 734.

21   Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang and Y. Yang, *Chem. Soc. Rev.*, **2014**, 43, 3480.

22   a) Z. Xiong, L. L. Zhang and X. S. Zhao, *Chem. Eur. J.*, **2011**, 17, 2428; b) H. Yang, X.-W. He, F. Wang, Y. Kang and J. Zhang, *J. Mater. Chem.*, **2012**, 22, 21849; c) S. L. Castro, S. G. Bailey, R. P. Raffaelle, K. K. Banger and A. F. Hepp, *Chem. Mater.*, **2003**, 15, 3142; d) N. Zhang, S. Liu and Y.-J. Xu, *Nanoscale*, **2012**, 4, 2227; e) A. A. Ismail, D. W. Bahnemann, L. Robben, V. Yarovyi and M. Wark, *Chem. Mater.*, **2010**, 22, 108.

23   H. Fei, J. Shin, Y. S. Meng, M. Adelhardt, J. Sutter, K. Meyer and S. M. Cohen, *J. Am. Chem. Soc.*, **2014**, 136, 4965.

24   J.-H. Wang, M. Li and D. Li, *Chem. Sci.*, **2013**, 4, 1793.

25   M. Tonigold, Y. Lu, B. Bredenkötter, B. Rieger, S. Bahnmüller, J. Hitzbleck, G. Langstein and D. Volkmer, *Angew. Chem. Int. Ed.*, **2009**, 48, 7546.

For TOC