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COMMUNICATION

Oxygen and methanol mediated irreversible coordination polymer structural transformation from a 3D Cu(I)-framework to a 1D Cu(II)-chain

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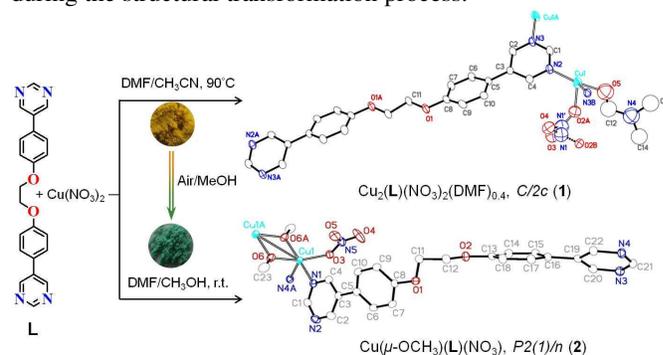
An interesting naked-eye irreversible structural transformation occurs when a 3D Cu(I)-polymeric complex $\text{Cu}_2\text{L}(\text{NO}_3)_2(\text{DMF})_{0.4}$ (**1**) is suspended in CH_3OH in air to produce a 1D-Cu(II) polymeric complex $\text{Cu}(\mu\text{-OCH}_3)(\text{L})(\text{NO}_3)$ (**2**) ($\text{L} = 1,2\text{-bis[4-(pyrimidin-4-yl)phenoxy]ethane}$). The transformation mechanism from **1** to **2** was also investigated.

In coordination polymers,¹ structural transformation² which is caused by some external stimuli such as solvent, ionic templates and ligand exchange,³ light,⁴ temperature variation⁵ and sometimes mechanochemical forces⁶ often occurs. In some cases, structural transformations based on the coordination polymers are accompanied with the dimensionality and color changes resulted from the variation of the central metal valence and metal coordination mode. Such stimuli-responsive dynamic structural transformation is important, which is very useful for preparing of new switching or sensing materials.

Among various metal-complexes structural transformation, the transformation of copper species is more interesting and valuable. As we know, copper proteins in biological systems can provide various functions including dioxygen transport by hemocyanin, oxygenation and dehydrogenation of substrates combined with the transformation of O_2 to either H_2O_2 or water.⁷ With the hope of understanding and mimicking such biological oxygenation behaviors, the synthesis of new Cu(I)-coordinating systems and the investigation of their spontaneous oxygenation are necessary. Such effort will generate a sufficiently large database from which the specific artificial bionic enzymes could be sieved out.

Our previous studies showed that the coordination polymers generated from open-chain polyether-bridged organic linkers are flexible. For example, the polymeric coordination patterns could be tuned by the temperature based on the ligand conformation variation.⁸ Motivated by our interest in temperature-dependent synthesis of coordination polymers, in

this contribution, we report two new coordination polymers $\text{Cu}_2(\text{L})(\text{NO}_3)_2(\text{DMF})_{0.4}$ (**1**, orange) and $\text{Cu}(\mu\text{-OCH}_3)(\text{L})(\text{NO}_3)$ (**2**, green-blue) based on a new open-chain polyether-bridged organic spacer **L** at different temperatures (Scheme 1, ESI[†]). The flexible ligand **L** respectively adopts *trans*- and *cis*-conformations at high (90°C) and low (r.t.) temperatures, which is in good agreement with our previous observation.⁸ Notably, **1** undergoes an oxygen and methanol triggered naked-eye structural transformation to **2**, and the structural feature changed from 3D porous framework (**1**) to a 1D double chain motif (**2**), and the valence of the copper ion changed from univalent to bivalent correspondingly. The dioxygen was supposedly transformed to H_2O_2 via superoxide radical anion during the structural transformation process.



Scheme 1. Representation of the synthesis of **1-2** and the structural transformation from **1** to **2**. Crystals of **1**, on being kept in MeOH in the air at the ambient temperature for about 36 h, undergo a visual irreversible structural transformation to yield a green-blue product **2** (the color change is shown in the figure with powdered samples of **1** and **2**).

As shown in Scheme 1, compound **1** was isolated as orange crystalline solids by the combination of **L** (molar ratio $\text{L} : \text{Cu(II)} = 1 : 2$) in a mixed-solvent system (DMF/MeCN) at 90°C in good yield (65 %). Single-crystal analysis (ESI[†]) revealed

that compound **1** crystallizes in the monoclinic $C2/c$ space group.

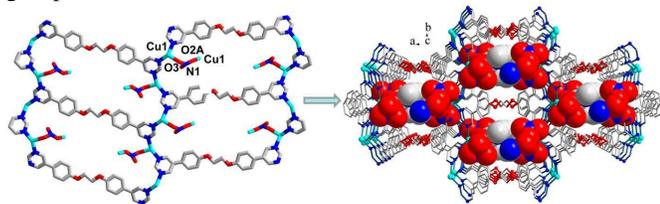


Fig. 1 The Cu(I) nodes in **1** are connected to each other by the tetradentate **L** into a 2D net. These 2D nets are further interlocked together through $\mu\text{-NO}_3^-$ ($\text{Cu(1)-O(3)-N(1)-O(2)-Cu(1)}$) linkage, basically perpendicular to the net plane) into a 3D framework containing square-like channels, in which the disordered DMF and NO_3^- are located. The disordered DMF molecules are omitted for clarity in left figure, and the DMF and NO_3^- in right figure are shown in space-filling model.

As shown in Fig. 1, each Cu(I) center in **1** lies in a tetrahedral $\{\text{CuN}_2\text{O}_2\}$ coordination sphere. The two N-donors come from two terminal pyrimidyl groups and two O-donors come from a coordinated NO_3^- anion and a coordinated DMF solvent molecule, respectively. In the solid state, Cu(I) nodes are linked together by the *trans*-tetradentate **L** linkers into a 2D net extended in the crystallographic ab plane (Fig. 1). These 2D nets are further interlocked together by the $\mu\text{-NO}_3^-$ to form a 3D framework containing square-like open channels (dimensions $\sim 10 \times 10 \text{ \AA}$) running along the crystallographic c axis. The shortest interlayer Cu(I)–Cu(I) distance is 5.440 \AA . The disordered NO_3^- anions and DMF molecules are located in the channels (Fig. 1). XRPD patterns indicated that the obtained sample is pure, and the X-ray photoelectron spectroscopy (XPS) measurement indicates that the copper center in **1** is univalent (Fig. 2),⁹ which is in well agreement with the single-crystal X-ray diffraction analysis (ESI†).

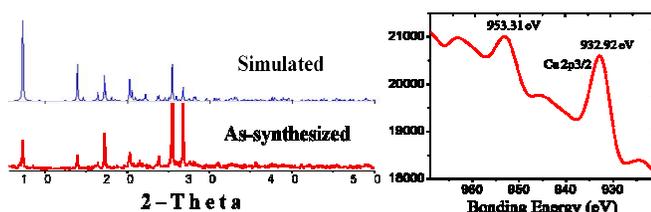


Fig. 2 XRPD pattern (left) and XPS spectrum (right) of **1**.

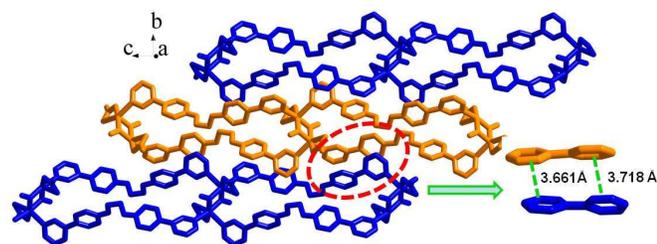


Fig. 3 1D chain of **2** composed of $\{\text{Cu}_2(\mu\text{-OCH}_3)_2\}$ cluster cores and **L** in the solid state. The interchain $\pi\text{-}\pi$ interactions exist in **2**.

Compound **2** was obtained as green-blue crystalline solids in DMF/MeOH mixed-solvent system at room temperature. It is different from **1**, the ligand **L** in **2** adopts *cis*-conformation, and as a bidentate linker to bind copper nodes. Single-crystal X-ray

diffraction studies (ESI†) revealed that **2** crystallizes in the monoclinic space group $P2(1)/n$. Each Cu(II) node locates in a square pyramidal coordination sphere $\{\text{CuN}_2\text{O}_3\}$ which is composed of two pyrimidyl N-donors ($d_{\text{Cu-N}}$ bond lengths are $2.024(3)$ and $2.333(3) \text{ \AA}$, respectively), three O atoms from one monodentate nitrate ($d_{\text{Cu-O}} = 2.160(11) \text{ \AA}$) and two bridging methoxide groups (Cu-O bond lengths range from $1.934(2)$ to $2.030(2) \text{ \AA}$) (Scheme 1). The methoxide groups are co-bridging two Cu(II) nodes to form a $\{\text{Cu}_2(\mu\text{-OCH}_3)_2\}$ cluster core. The $d_{\text{Cu-Cu}}$ in $\{\text{Cu}_2(\mu\text{-OCH}_3)_2\}$ unit is $3.0359(10) \text{ \AA}$, while the $\langle \text{Cu-O-Cu} \rangle$ angles vary from $76.73(8)$ to $103.26(2)^\circ$. These geometric details are comparable with other reported methoxide-bridged dinuclear Cu(II) compounds.¹⁰ These $\{\text{Cu}_2(\mu\text{-OCH}_3)_2\}$ cluster cores are bridged by the *cis*-bidentate ligand **L** into an infinite 1D double chain along crystallographic c axis (Fig. 3). The interchain $\pi\text{-}\pi$ interactions drive the 1D chains into a 2D net in the crystallographic bc plane. Again, the XRPD pattern indicates that the as-synthesized compound **2** is pure (Fig. 4). It is different from **1**, XPS (Fig. 4) and electron paramagnetic resonance (EPR) measurements (Fig. S3, ESI†) of **2** demonstrate that the copper cation is bivalent.⁹

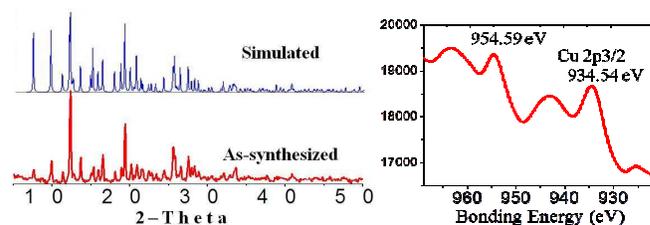


Fig. 4 XRPD pattern (left) and XPS spectrum (right) of **2**.

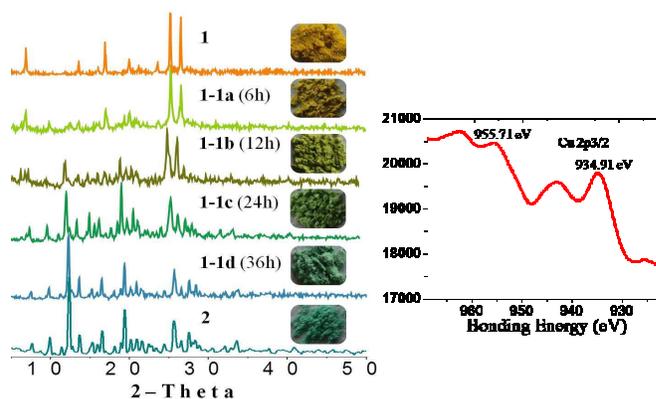


Fig. 5 Left: XRPD patterns of **1**, **1-1a** (in CH_3OH 6h), **1-1b** (in CH_3OH 12h), **1-1c** (in CH_3OH 24 h), **1-1d** (in CH_3OH 36 h) and **2**. Photographs showing the color change of the samples of **1** in CH_3OH in air at different time. Right: XPS spectrum of **1-1d**.

The spontaneous structural transformation from **1** to **2** was accidentally found when we explored the solvent-exchange (DMF by MeOH) based on **1** under ambient conditions. The transformation started once compound **1** was suspended in MeOH in air along with a visual color change. As shown in Fig. 5, the color of **1** changed gradually from orange to green-blue (**2**) during the transformation process. Besides the naked-eye color change, the structural transformation process was monitored by X-ray powder diffraction. As shown in Fig. 5,

XRPD patterns show that the peaks corresponding to **2** gradually appeared while the characteristic peaks of **1** disappeared by degrees as time goes on. In 36 h, the XRPD pattern of **1-1d** is fully coincident with that of **2**, indicating the structural transformation was finished (from $C2/c$ to $P2(1/n)$). In addition, the IR spectrum performed on **1-1d** shows that the band associated with $>C=O$ at 1655 cm^{-1} is disappeared, indicating the coordinated DMF molecules are out of the copper coordination sphere (Fig. S4, ESI†).

Besides XRPD patterns, the observation of Cu 2p_{3/2} peak at 934.91 eV in XPS (Fig. 5) of **1-1d** also demonstrated the oxidation from Cu(I) in **1** to Cu(II) in **2**. The binding energy peak shift of 1.99 eV is consistent with the reported difference of binding energy peak between Cu(I) to Cu(II).^{9a} Accordingly, the EPR spectrum of **1-1d** is the same as that of **2** (Fig. S3, ESI†). Furthermore, ICP (Inductively Coupled Plasma) measurement (Fig. S5, ESI†) indicates that the amount of copper in **1-1d** increases from 18.1% (calcd. 18.2% in **1**) to 12.1%, which is identical to that of **2** (calcd. 12.1%). The elemental analysis also indicated that composition of **1-1d** is the same as that of **2** (Table S1, ESI†). In addition, the process of structural transformation can be accelerated with the increase of the reaction temperature (Table S2, ESI†). For example, the transformation from **1** to **2** at 60°C (26 h) is much faster than that of at room temperature (36 h), indicating that this structural transformation is a dynamic controlled process. Unfortunately, the crystals of **1** did not diffract the X-ray beams due to the loss of the single crystallinity during the transformation process.

We assume herein that the oxygen from air acts as the oxidant in the process of structural transformation. To confirm such an assumption, several parallel experiments were carried out. When compound **1** was suspended in CH₃OH under N₂ atmosphere at room temperature, the corresponding XRPD pattern indicated that no structural transformation occurred and the framework of **1** remains intact (Fig. S6, ESI†). Secondly, the structural transformation in MeOH is much faster under pure oxygen atmosphere (22 h) than that of in air (36 h) (Fig. S6, ESI†). Besides oxygen, the MeOH medium is also essential to this transformation. As mentioned above, the coordinated DMF molecules in **1** are replaced by the MeOH in **2**. When **1** was immersed in other kinds of ROH solvents such as EtOH or *i*-PrOH, no structural transformation was observed based on the XRPD patterns (Fig. S7, ESI†), the coordinated DMF molecules in **1**, however, are partly exchanged by the corresponding ROH solvent molecules. It is different ROH solvents, the water template drives compound **1** to an unknown structural motif based on the X-ray powder diffraction (Fig. S8, ESI†). So, CH₃OH might be a unique co-ligand to facilitate the formation of {Cu₂O₂} cluster node during this transformation process, whereas EtOH, *i*-PrOH and H₂O cannot trigger the transformation of **1** to **2**. It is noteworthy that no ligand was detected in mother liquor based on ¹H NMR spectrum (Fig. S9, ESI†), indicating that it might be a solid-state structural transformation.

The isolation of similar bivalent Cu₂(OMe)₂ species from the reaction of Cu(I) precursor bearing cyclic and noncyclic

ligands with dioxygen has been reported by some other groups,¹¹ but the formation process is still not understood. The earlier studies suggest that oxygenations of Cu(I) complexes proceed via formation of a Cu(II)-superoxo species generated from the superoxide radical anions.¹² So the ESR spin-trap technique (with 5, 5-dimethyl-1-pyrroline N-oxide, DMPO) was used to detect the O₂^{•-} radical species. When DMPO was added to the MeOH solution of **1**, the ESR spectra clearly indicate that the O₂^{•-} was trapped by DMPO based on the observed six characteristic peaks of the DMPO-O₂^{•-} adducts (Fig. 6).¹³ Reasonably, no color change was observed once the O₂^{•-} radicals were trapped by DMPO, indicating that structural transformation from **1** to **2** did not occur. When superoxide dismutase SOD (2000 U mL⁻¹) was added to the above solution, the signal intensities of the O₂^{•-} radical species were significantly weakened as time goes on, which further confirmed the formation of O₂^{•-} radical species during the process. According to the above observation, a possible mechanism for this structural transformation was suggested. As shown in Fig. 6, Cu(I) ion in **1** was oxidized to Cu(II) ion in **2** by O₂ to generate a Cu(II)-(O₂^{•-}) superoxo species which further linked one more Cu(I) ion to produce a Cu₂O₂ peroxo species.¹⁴ The peroxo intermediate was anticipated to react with two MeOH to generate a binuclear di- μ -methoxocopper(II) complex and released the H₂O₂.^{11e,15}

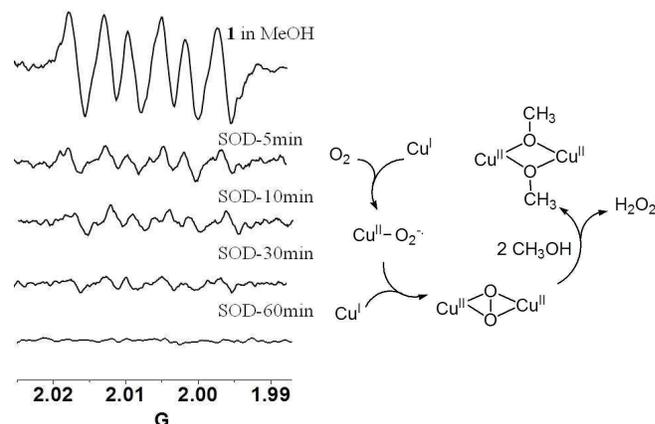


Fig. 6 Left: ESR spectrum of **1** in MeOH with DMPO. The observed six characteristic peaks confirms the formation of the DMPO-O₂^{•-} adducts, and the signal intensity change of ESR spectra after addition of SOD to it. Right: the suggested transformation mechanism.

In summary, we have synthesized two coordination polymers generated from a new ethylene glycol ether-bridged dipyrimidyl ligand. The different reaction conditions resulted in different metal valence and ligand conformation, consequently, the different coordination patterns. In addition, an interesting irreversible naked-eye detectable structural transformation from a 3D Cu(I) complex (orange) to a 1D Cu(II) chain (green-blue) was observed. The O₂ and CH₃OH medium are the indispensable factors to induce this transformation. The formed O₂^{•-} radical anion, an essential active species for the structural transformation, was trapped by DMPO and SOD, which provided solid evidence for the Cu(I) spontaneous oxygenation

in air, furthermore, an useful O₂ transformation mode based on Cu(I) coordination species.

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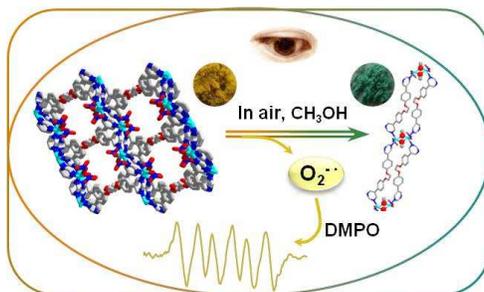
Notes and references

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† Electronic supplementary information (ESI) available: Synthesis and characterization data for all compounds, including figures for ORTEP, XPS, XRPD, ¹H NMR, IR, CIF files and crystal data. See DOI: 10.1039/b000000x/

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For Table Content



An irreversible naked-eye structural transformation from a 3D Cu(I)-framework to a 1D Cu(II)-chain mediated by oxygen and methanol is reported.