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Red luminescent polymeric cuprous organosulfide generated by solvothermal redox reaction

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A new polymeric metal organosulfide $[\mathrm{Cu^I}_3(\mathrm{pymt})_3]_n$ (pymt = pyrimidine-2-thiolate) with strong red photoluminescence was synthesized through solvothermal redox reaction, and crystallographically characterized to be a one-dimensional chiral structure containing metal–metal interactions.

Considerable effort is currently devoted to the synthesis and investigation of new functional coordination polymers involving interplay and synergy between multiple physical properties.[1,2] One of the most effective and attractive approaches for the assembly of polymeric frameworks is the incorporation of appropriate metal ions (connectors) and multifunctional bridging ligands (linkers) under hydrothermal conditions,[3] together with many interesting phenomena[4,5] such as a redox process of copper, ligand oxidative coupling, hydrolysis and substitution, but the predication of results is still a challenging subject. In contrast to the great deal of work on hydrothermal synthesis with oxygen or nitrogen donor ligands, there have been few reports of studies on organosulfur ligands.[6,7] Moreover, the existence of *in situ* redox process with organosulfur as reducing agents under solvothermal conditions has also rarely been explored. However, the incorporation of thiolate-S as a bridge between adjacent transition metal sites in coordination polymer is highly desirable in terms of magnetic, conductive and luminescent behavior, since the orbital energies are better matched for S and there will be greater delocalization of spin density towards the bridging atom. On the other hand, the versatile binding modes of sulfide moieties can induce the formation of aesthetic structural motifs.

Particularly, functional materials of coinage metal ions with d^{10} closed-shell electronic configuration have attracted much attention regarding the nature of the low energy luminescent excited states and the presence of metal–metal interactions.[8] In this respect, we have focused on exploring the functional solids based on coinage metals and organosulfur ligands.[7] Here we wish to report a novel cuprous organosulfide coordination polymer, $[\mathrm{Cu^I}_3(\mathrm{pymt})_3]_n$ **1** (pymt = pyrimidine-2-thiolate), which was generated by solvothermal reaction along with the reduction of $\mathrm{Cu^{II}}$ to $\mathrm{Cu^I}$. It is noteworthy that the direct assembly using $\mathrm{Cu^I}$ salt as precursor is hard to control and obtain single crystals suitable for X-diffraction analysis, although the reaction of thiols with $\mathrm{Ag^I}$ ions has led to polymeric species under appropriate conditions in our group.[7,9] Interestingly, **1** exhibits strong red photoluminescence and thermal stability.

The solvothermal reaction of $\mathrm{Cu^{II}}$ salt with Hpymt in mixed DMF/MeOH solution at 90 °C for 30 h followed by cooling to room temperature produces very fine yellow prismatic crystals of **1** in 70% yield. Elemental analysis† showed the formula of product was $[\mathrm{Cu^I}(\mathrm{pymt})]$. Obviously, this reaction resulted in an *in situ* redox process of copper. In order to understand the possible mechanism, dropwise addition of $\mathrm{Ba^{2+}}$ buffer solution into the reaction filtrate, which is acidic, resulted in a small quantity of white precipitates. This indicates the creation of $\mathrm{SO_4}^{2-}$ during the reaction. Thus, we speculate that some of the pymt may act as a reducing reagent through desulfurization followed by an oxidation process.[10] To our knowledge, this is the first example of a structurally characteristic $\mathrm{Cu^I}$–thiolate coordination polymer generated by the redox reaction of $\mathrm{Cu^{II}}$ with single a thiol ligand under solvothermal conditions, whereas previous reports have revealed that some organocyanogen[5] species had intriguing reactivity as reducing agents that could reduce $\mathrm{Cu^{II}}$ to $\mathrm{Cu^I}$ under hydrothermal conditions.

Single-crystal X-ray analysis‡ has revealed that there are three crystallographically independent metal centres bridged by organic ligands. As shown in Fig. 1, three $\mathrm{Cu^I}$ atoms locate at a similar trigonal coordination environment with a nitrogen atom and two sulfur atoms from three different pymt ligands. The average Cu–N and Cu–S bond distances are 2.020 and 2.241 Å, respectively, similar to those found in other $\mathrm{Cu^I}$ complexes containing Cu–N and Cu–S bonds.[8] Three Cu atoms form a slightly distorted isosceles triangle *via* two Cu–Cu interactions. The distances of Cu1–Cu2 and Cu2–Cu3 are 2.789(3) and 2.970(3) Å, respectively, which are close to the sum of the van der Waals radii (2.80 Å) of $\mathrm{Cu^I}$ centers,[11] implying the existence of Cu–Cu interactions. The Cu1–Cu3 separation (3.303 Å) is longer. The internal angles of the triangle are 69.90° for Cu1–Cu2–Cu3, 57.62° for Cu2–Cu1–Cu3 and 52.48° for Cu1–Cu3–Cu2, respectively. Each pymt ligand acts as a μ_3-bridge to link three copper atoms through S and N donors. The repeating trinuclear units extend into an infinite one-dimensional chain polymer *via* the S and N atoms of pymt ligands bridging Cu atoms of the adjacent unit along the crystallographic *b* axis (Fig. 2), which is different from the hexanuclear $\mathrm{Cu^I}$ complex[12] containing a derivative of pymt ligand because of steric hindrance in the latter. The arranged fashion of copper atoms in the chain is also different from that two $\mathrm{Ag_4}$ tetrahedral sharing one apex Ag atom found in analogue $[\mathrm{Ag_6(pymt)_6}]_n$.[9] In fact, the striking feature of this chain is a distorted helix generated around crystallographic 2_1 screw axis that crystallizes in the chiral space group $P2_12_12_1$. Although the bulk product is racemic because the complex was derived from spontaneous resolution from achiral components without any chiral sources, each crystal, however, has chirality. So we have performed *quasi* Kurtz[13] powder second harmonic generation measurements (λ = 1064 nm) on the complex in order to confirm its acentricity as well as to evaluate its potential as

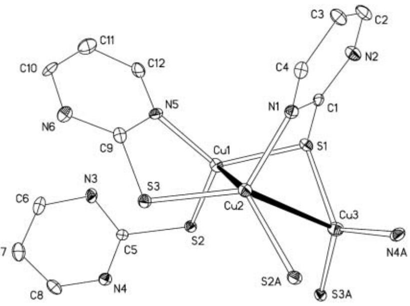

Fig. 1 View of the coordination arrangement of the copper atoms in **1**. Thermal ellipsoids for the nonhydrogen atoms were drawn at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–N5 2.027(6), Cu1–S1 2.233(4), Cu1–S2 2.246(3), Cu1–Cu2 2.789(3), Cu2–N1 2.010(7), Cu2–S3 2.245(4), Cu2–S2A 2.252(5), Cu2–Cu3 2.970(3), Cu3–N4A 2.023(7), Cu3–S3A 2.227(3), Cu3–S1 2.245(4); Cu1–Cu2–Cu3 69.90(13).

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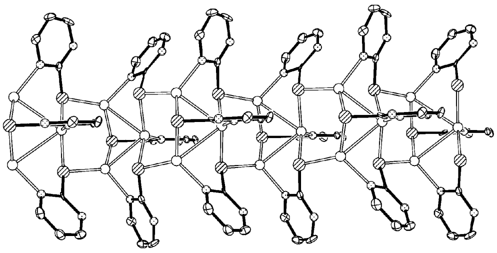

Fig. 2 View down the crystallographic *b* axis showing the one-dimensional chain structure of **1**.

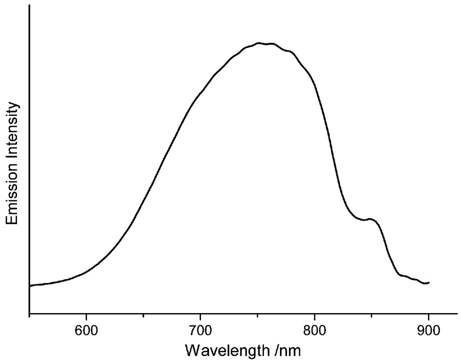

Fig. 3 Solid-state emission spectrum of **1** at room temperature.

second-order nonlinear optical candidate compound. Preliminary experimental results show that the complex displays much weaker powder SHG efficiency than that of technologically useful potassium dihydrogen phosphate (KDP), which precludes its use as an NLO material.

However, the fascinating characteristic of this coordination polymer is its rich red photoluminescent property. At ambient temperature, excitation of solid samples at $\lambda = 462$ nm produces an intense red emission with peak maximum at 752 nm (Fig. 3). The low energy emission of **1** was determined to be phosphorescence based on its microsecond-order decay lifetime (4.06 μs). Time-resolved emission measurements revealed that the red emission follows a single-exponential decay. According to the photoluminescent properties of the pymt ligand ($\lambda_{\max} = 488$ nm) and other Cu$^{\mathrm{I}}$–thiolate clusters,[8] the emission is tentatively assigned as originating from the triplet states of ligand-to-metal charge-tranfer (LMCT) and/or metal-to-ligand charge-transfer (MLCT) characters, mixed with metal-centered (ds/dp) states modified by Cu–Cu interactions with Cu$_3$ clusters. More detailed theoretical and spectroscopic studies are being pursued. It is noteworthy that this low energy luminescence is unusual, which is quite different from large numbers of blue emission coordination polymers[2] and represents the lowest energy emission or the longest emission wavelength, to our knowledge, in the luminescent d^{10} transition metal coordination polymers reported to date.[2,14] Furthermore, **1** also exhibits remarkable thermal stability. TGA analyses show that it has an onset temperature for decomposition at 290 °C. The stability of the complex makes it a potential candidate for practical application as a red optical device.

In summary, a luminescent coordination polymer **1** was synthesized through the redox reaction of Cu$^{\mathrm{II}}$ with single thiol ligand under solvothermal conditions. These results are important not only for developing a new possible strategy for the construction of diversely polymeric copper thiolates *via in-situ* solvothermal redox reaction but also for exploring a new method to prepare stably low energy photoluminescent materials. We are actively moving this synthesis strategy towards other related organosulfur derivatives and expect to obtain high dimensional molecule-based functional solids.

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Notes and references

† *Preparation* of [Cu$^{\mathrm{I}}_3$(pymt)$_3$]$_n$ **1**: A solution of CuCl$_2$·2H$_2$O (34 mg, 0.2 mmol) in MeOH (8 ml) was added to a solution of Hpymt (45 mg, 0.4 mmol) in DMF (5 ml) and the mixture was stirred for a few min in air, then transferred and sealed in a 23 ml Teflon reactor, which was heated in an oven to 90 °C for 30 h. The oven was cooled to room temperature at a rate of 5 °C h^{-1}. The resulting very fine yellow prismatic crystals of **1** were obtained in 70% yield (based on Cu). Anal: Calc. for **1**: C, 27.50; H, 1.73; N, 16.04. Found: C, 27.30; H, 1.95; N, 15.92%; IR (KBr, cm^{-1}): 3058 (w), 2918 (w), 1560 (vs), 1540 (vs), 1373 (vs), 1171 (vs), 1000 (w), 801 (w), 766 (m), 742 (s), 641 (m).

‡ *Crystal data* for **1**: C$_{12}$H$_9$N$_6$S$_3$Cu$_3$, $M = 524.05$, orthorhombic, space group $P2_12_12_1$, $a = 11.84(3)$, $b = 7.874(7)$, $c = 17.51(4)$ Å, $V = 1632(6)$ Å^3, $Z = 4$, μ(Mo–Kα) = 4.263 mm^{-1}, $D_c = 2.132$ g cm^{-3}. The structure, refined on F^2, converged for 3734 unique observed reflections with $I = 2\sigma(I)$ to give $R1 = 0.0579$ and $wR2 = 0.1044$ and $S = 1.061$. Flack parameter 0.21(2). CCDC 241012. See http://www.rsc.org/suppdata/cc/b4/b409000d/ for crystallographic data in .cif or other electronic format.

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