# Synthesis, Crystal Structure, and Optical Limiting Effect of a Cu(I) Coordination Polymeric Cluster Bridged by Chiral-carbon Skeleton Bipyridyl Ligand

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Solution reaction of Cu(I) iodide with chiral-carbon skeleton ligand 2,3-di(4-pyridyl)-2,3-butanediol (*meso*-dpb) in DMSO generated a novel 2D coordination polymeric cluster $[(CuI)_4(dpb)_4(DMSO)_4(CH_3OH)_4(H_2O)]_n$ (**1**), in which the dpb exhibits a *TT* conformation and the adaptable $Cu_2I_2$ rhomboid cluster unit facilitates the formation of a final noninterpenetrating motif. The nonlinear optical limiting property of **1** was also studied at 532 nm. The limiting threshold was determined to be $0.42\,J\,cm^{-2}$ and this value is three times better than $1.6\,J\,cm^{-2}$ of $C_{60}$.

The construction of supramolecular polymeric networks is of great interest in recent years, not only for their intriguing architectures and topologies[1] but also for their potential properties as functional solids.[2] Nonlinear optical (NLO) materials have arisen much interest in optical signal switching, frequency generation, optical data storage, optical communication, and image processing.[3] As an important aspect of NLO properties,[4] optical limiting is a phenomenon where the light transmission through a material tends to saturate as the incident intensity increases. It is, therefore, attracting significant current attention as a means of optical device and eye protection, with both military and laboratory applications.[5] For the moment, materials employed for optical limiting are mainly focused on small molecules,[3] hyperbranched polyarylenes,[6] metalloporphyrin,[7] diacetylenes,[8] and some other organometallic compounds.[9] Because inorganic complexes possess a large transparency range available as large single crystals and suffer very low optical losses,[10] the optical-limiting merit of transition-metal complexes and clusters has also been explored enough.[11] However, there is relatively little report on optical limiting of transition-metal coordination polymers.[12] Herein, we first select the chiral-carbon skeleton bipyridyl ligand 2,3-di(4-pyridyl)-2,3-butanediol (dpb)[13] as bridging ligands to study the synthesis, structure, and optical limiting capability of its adduct with CuI: $[(CuI)_4(dpb)_4(DMSO)_4(CH_3OH)_4(H_2O)]_n$ (**1**). The complex is a coordination polymer, also a polymeric cluster with $CuI_2Cu$ rhomboid unit. Its good optical limiting effect shows the rationality from combination of hybrid polymer and inorganic cluster.

Single crystals of complex **1** were easily synthesized by the stoichiometric reaction of organic ligands *meso*-dpb with CuI in DMSO at ambient temperature.[14] X-ray determination[15] shows complex **1** consists of basic $Cu_2I_2$ units and ditopic dpb linkers in a *TT* conformation. The asymmetric unit consists of a CuI molecule, a half of dpb ligand binding to Cu with pyridyl group, and a DMSO molecule (Figure 1). The Cu–I, Cu–N, and Cu–Cu distances are 2.6743(5), 2.055(3), and 2.795(2) Å, respectively. The Cu–I–Cu and I–Cu–I angles are 63.01(3) and 116.99(3)°. In **1** the torsion angle of C(1)–C(6)–C(6D)–C(1D) (180°) and other bond parameters are the same as those in its free state.[13b] Each $Cu_2I_2$ rhomboid cluster unit is nodally corner-connected with four adjacent units via four dpb ligands: such connectivity generates 2D grids. The grids are identical and extend to an infinite noninterpenetrating (4, 4) layered net (Figure 2). In the layer, four neighboring $Cu_2I_2$ units and dpb ligands show a rhomboidal distribution with a nearest Cu···Cu side length of 13.50 Å, and the length of the furthest diagonal Cu···Cu distance is 23.88 Å. The interlayer separation is 7.25 Å. The disordered DMSO molecules are located between the layers and have O···H–O and S···H–N hydrogen-bonding interaction with dpb ligands to reinforce the crystal packing.

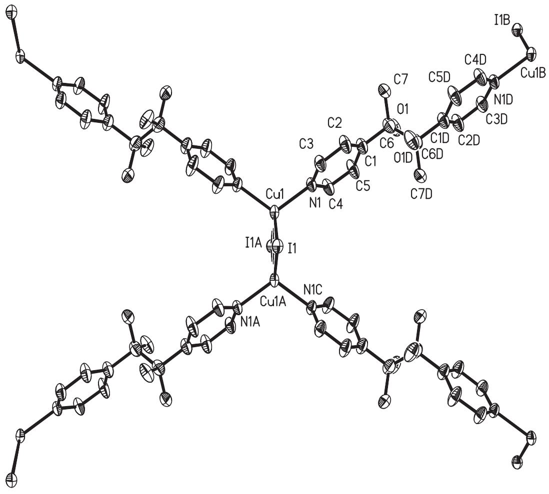

**Figure 1.** The nodally connectivity between the $Cu_2I_2$ cluster units in $[(CuI)_4(dpb)_4(DMSO)_4(CH_3OH)_4(H_2O)]_n$ (**1**).

The optical limiting effect of the compound is depicted in Figure 3. The peak fluence for *Z*-scan is about $1\,J\,cm^{-2}$ in ns *Z*-scan. The transmittance is normalized to its linear transmittance at low incident fluence. The present adduct, which has polymeric cluster skeleton, shows the result that its optical limiting capacity is obviously better than that of many clusters. At very low fluence it responds linearly to the incident light fluence obeying Beer's law. Under a closed-aperture configuration the light transmittance starts to deviate from Beer's law of the linear response when the input light fluence rises to $0.1\,J\,cm^{-2}$. The transmitted light becomes increasingly divergent as the incident irradiance rises. When the incident irradiance is greater than $0.12\,mJ\,cm^{-2}$, the observed NLO process is no longer pure third-order in nature, and additional excited-state absorption be-

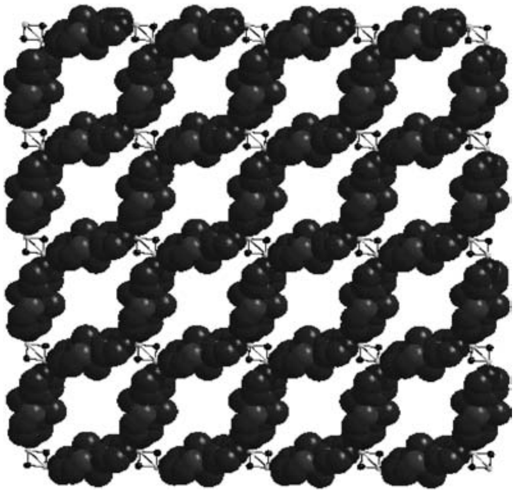

**Figure 2.** Schematic presentation showing the 2D "open" nets based on $Cu_2I_2$ building block in **1**.

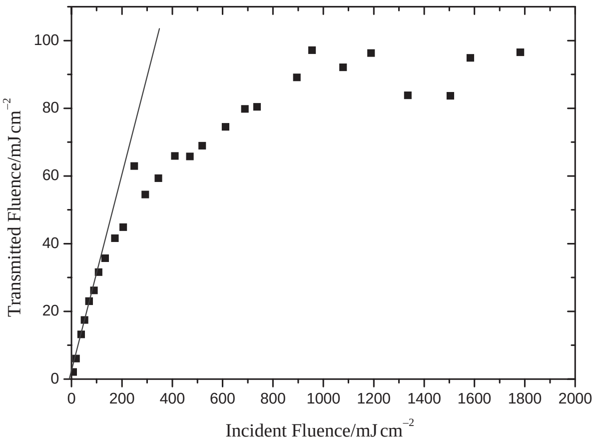

**Figure 3.** The optical limiting experiment of **1** in DMF solution.

comes increasingly important. The presence of additional excited-state absorption at high irradiance enhances the optical limiting performance. The combination of the two NLO processes makes this new material more attractive for optical limiting application than other materials in which the excited-state absorption or the third-order refractive nonlinearity is the only NLO mechanism. The value of the limiting threshold was measured as $0.42\,\mathrm{J\,cm^{-2}}$ for title adduct from the optical limiting experimental data. It is clear that the limiting performance of **1** in the DMF solution is three times better than that displayed in $C_{60}$.[16] Lower limiting threshold and saturation level provide greater safety margin for device protection. From the perspective of the OL application, the present cluster with polymeric 2D "open" structure is comparable to (or slightly better than) the known good optical limiting materials, such as the one-dimensional coordination polymeric cluster $\{[\mathrm{AgI(inh)}]_6(\mathrm{KI})\}_n$[17] and the two-dimensional microporous polymer cluster $\{[\mathrm{NEt_4}][\mathrm{Mo_2O_2S_6Cu_6I_3(4,4'\text{-}bipy)_5}]\cdot\mathrm{MeOH}\cdot\mathrm{H_2O}\}_n$.[18] The good optical limiting data for **1** implies an overall balance effect on NLO from skeletal structure. Previous study showed that complexes with heavy atoms are expected to have favorable NLO properties.[11a] So, as far as the title polymer is concerned, we deduced that the transition-metal $Cu_2I_2$ cluster, the chiral-carbon ligand skeleton[2c] and the final polymeric aggregation[18] play important role in determining its NLO properties.

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14 A mixture of *meso*-dpb (0.198 g, 1.0 mmol) and DMSO (5 mL) was heated and stirred for 10 min in air till it dissolved totally, The solution was then cooled to room temperature and a colorless solution of CuI (0.190 g, 1.0 mmol) + KI in DMSO was added, after 3 days a light-yellow product in 42% was yield. Found: C, 37.26; H, 4.44; N, 5.54%. Calcd. for $C_{68}H_{106}Cu_4I_4N_8O_{17}S_4$: C, 37.16; H, 4.86; N, 5.18%; IR data (KBr pellet, cm$^{-1}$): $\nu$(O–H), 3292b, and 2990w, 1656s, 1601s, 1549w, 1489w, 1411s, 1218m, 1134m, 1016s, 949m, 839m, 775m, 624m, 545w.

15 Crystal data for complex $C_{68}H_{106}Cu_4I_4N_8O_{17}S_4$, MW 2197.61, monoclinic, space group $C2/m$, $a = 19.122(2)$, $b = 18.499(2)$, $c = 7.2538(8)$ Å, $V = 2565.1(5)$ Å$^3$, $Z = 1$, $D_{\mathrm{calcd}} = 1.423$ g/cm$^3$, $F(000) = 1098$, $\mu = 2.157\,\mathrm{mm^{-1}}$. $R = 0.0401$, $wR = 0.1275$. All measurements were on a Bruker APEX-II area-detector diffractometer by using an $\omega$-scan technique at 291(2) K. Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å. CCDC-295021.

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