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Synthesis of a 2D polymeric cluster $\{[NEt_4][Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot MeOH\cdot H_2O\}_n$ with a significant improvement of optical limiting effect†

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The self-assembly reaction of the monomeric nest-shaped cluster $[NEt_4]_2[MoOS_3Cu_3I_3]$ 1 or twin nest-shaped cluster $[NEt_4]_4[Mo_2O_2S_6Cu_6I_6]$ 2 with the bridging ligand 4,4′-bipyridine (4,4′-bipy) gave a 2D polymeric cluster $\{[NEt_4][Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot MeOH\cdot H_2O\}_n$ 3, which exhibits a significant improvement of optical limiting effect in its nonlinear optical properties relative to 1 or 2.

Thiometallic clusters continue to attract great interest not only because of their unusual catalytic activities in biological and industrial processes[1] but also their intriguing optical and electrical properties.[2] Among these physical properties, there is an interest in their optical limiting effect for potential application in protecting optical sensors from laser beams of high intensity. The design and synthesis of new materials with large optical limiting capability represents an active field in modern chemistry, physics, and material science.[3] Results from previous studies suggest that structural, geometrical and constitutional alternations of these clusters can give rise to variations in nonlinear optical properties (NLO).[4] Thus, the relative contributions of different NLO mechanisms change with the types of clusters, which is expected to explore a switching for NLO properties of inorganic clusters. In particular, polymeric aggregation of thiometallic clusters could result in enhancement of the optical limiting effect (OL).[5] However, it is suspected that the polymeric structures in the solid state could dissociate in solution due to the weak bridging interaction of labile anions. We herein report a significant improvement in OL effect by converting a monomeric thiometallic cluster to an inorganic–organic polymeric hybrid material, which shows a low tendency to dissociate in solution using 4,4′-bipyridine (4,4′-bipy), a versatile linker, for the synthesis of open chain polymers and supramolecular cyclophanes.

It was reported that when $[NEt_4]_2[MoOS_3Cu_3I_3]$ **1** was treated with an excess of NEt_4I in CH_2Cl_2, dimerisation occurred affording a twin nest-shaped cluster $[NEt_4]_4[Mo_2O_2S_6Cu_6I_6]$ **2**.[6] The iodide anion in clusters **1** and **2** can be substituted by pyridine (py) to give a neutral cluster $[MoOS_3Cu_3I(py)_5]$.[6,7] Based on this finding, reaction of **1** or **2** with an excess of 4,4′-bipy in DMF–MeCN resulted in the formation of an air-stable, two-dimensional (2D) polymeric cluster with two different nest-shaped cluster subunits, $\{[NEt_4][Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot MeOH\cdot H_2O\}_n$ **3**.‡ Polymeric cluster **3** shows good stability in the solid state as well as in solution.

A single-crystal X-ray diffraction study of **3** reveals an infinite 2D coordination network that crystallizes in a triclinic system with space group *P*1.§ The polymeric cluster has no center of symmetry. This feature has an important influence on the optical properties of cluster compounds. The structure of **3** consists of an open 2D anionic network with distorted hexagonal chair cavities, $[NEt_4]^+$ counter ions and lattice solvent molecules. As shown in Fig. 1, some of the iodine atoms in clusters **1** and **2** were substituted by 4,4′-bipy ligands, with the remaining iodine atoms terminally coordinating to copper atoms. Apart from one non-bridged 4,4′-bipy ligand, the other 4,4′-bipy ligands form nearly linear bridges between Cu atoms of neighboring nest-shaped $[MoOS_3Cu_3]$ cores. Interestingly, the configuration of polymeric anions can be viewed as two zigzag chains, which are propagated by cell translations along the *a* and *b* axes (Fig. 2). The edges of one chain formed by $[Cu_2(\mu\text{-S})(\mu\text{-4,4'-bipy})]_2$ double bridges and a $[Cu_2(\mu\text{-4,4'-}$

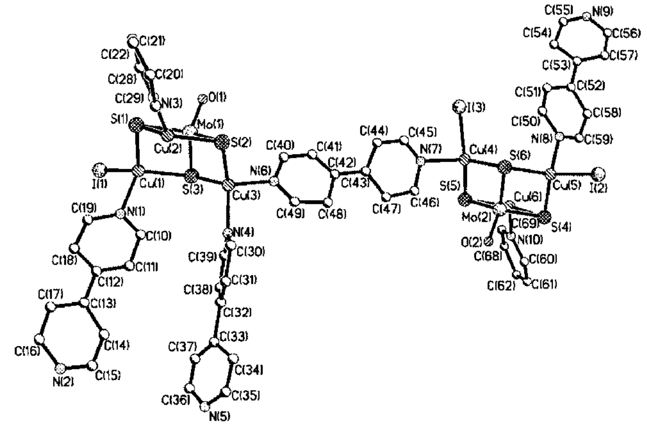

Fig. 1 Structure of the anion in **3** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

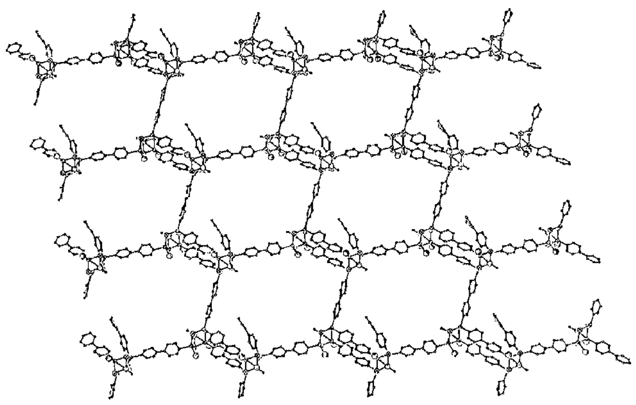

Fig. 2 Perspective view along the *c* axis of the 2D network in $[Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]^-{}_\infty$, showing the cavities.

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† Electronic supplementary information (ESI) available: preparation, crystal structure details and nonlinear optical measurements for **3**. See http://www.rsc.org/suppdata/cc/b1/b101929p/

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bipy)] single bridge are alternately perpendicular to each other by turning points of 4,4′-bipy shared copper atoms, while another chain is extended *via* [Cu(μ-S)Cu] moieties. Two zigzag chains share the same [Cu_2(μ-S)(μ-4,4′-bipy)]$_2$ double bridges, the intersections of which are nest-shaped [$MoOS_3Cu_3$] cluster cores. Another important structural feature of the cluster anion is the cross extending of two zigzag chains that creates very large chair-shaped inner cavities (*ca.* 21.67 × 21.74 Å). These dimensions are much larger than those in other reported 2D network complexes with 4,4′-bipy bridges.[8] The average distance between adjacent Mo atoms is 14.84 Å in the inner cavity. The coordination at the Mo centers remains nearly tetrahedral: the angles range from 107.77(19) to 113.5(6)°. The angles around Cu atoms range from 95.9(6) to 122.0(5)°, suggesting that the coordination geometry of the Cu atoms is highly distorted tetrahedral. This, together with the observation of 4,4′-bipy with non-planar pyridine rings bridging many Cu centers with elongation of the Mo–Cu bond lengths relative to **1** and **2**, is necessary for building up a 2D network polymeric cluster **3** with very large cavities. To our best knowledge, polymer **3** features the first example of a heterometallic cluster polymer with thiometalates and 4,4′-bipy bridges.

The NLO properties of polymeric cluster **3** were investigated. The nonlinear refractive negative n_2-values of nest-shaped Mo/Cu/S clusters indicate strong self-defocusing performances.[6,7,9] Our motivation to study clusters of this structural mode originates from the fact that the combination of the self-defocusing and nonlinear absorption makes the cluster a competent candidate for optical limiting application.[10] Furthermore, an obvious improvement of optical limiting capability is found when the monomeric nest-shaped clusters are assembled to lead to twin nest-shaped clusters, probably due to skeletal extension of the metal nuclei.[4] Accordingly, it is speculated that the clusters **1** and **2** in polymeric forms such as **3** may also possess large optical limiting effects.

With reference to the similar measurement conditions for clusters **1** and **2**, *z*-scan theory was employed to obtain the NLO parameters for **3**.[11] The peak fluence for a *z* scan is *ca.* 1 J cm^{-2} for a *z* scan over 1 ns. The α_2 and n_2 values extracted from 7 ns experimental data are 2.6×10^{-5} m W^{-1} M^{-1} and -4.2×10^{-12} m^2 W^{-1} M^{-1}, respectively. The nonlinear absorptivity is comparable to those of [$W_2S_8Ag_4(AsPh_3)_4$][12] and [$MoS_4Cu_6I_4(py)_4$]$_n$,[5] but, is obviously superior to those of **1**[9] and **2**.[6] The nonlinear refractive self-defocusing behavior is also stronger in **3** than in **1**[9] and **2**.[6] Of note is the optical limiting results for **3** at a relatively low concentration of 1.2×10^{-4} mol L^{-1} in DMF solution (Fig. 3). The transmittance is normalized to its linear transmittance at low incident fluence. The thresholds (fluence at which transmittance drops to half its linear value) of the sample are 0.4 and 0.7 J cm^{-2}, respectively, when irradiated by 0.5 and 10 Hz repetition-rate laser pulses. These values are much lower than those of 10 and 2 J cm^{-2} for **1**[9] and **2**,[6] respectively, indicating that the optical limiting performance for polymeric cluster **3** was efficiently improved compared with that of the monomer and twin nest-shaped clusters **1** and **2**. Also, polymeric cluster **3** shows good photostability during the optical determinations. Important evidence for this is that the sample still retained good optical limiting behaviour while the fluence of the 10 Hz laser pulses is passed through the solution sample.[13] Further support arises from the fact that the sample remained effective three months after its preparation.

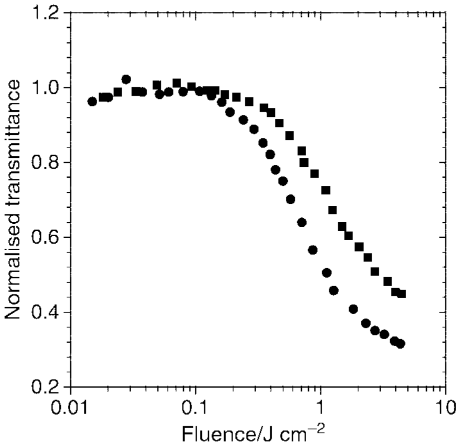

Fig. 3 Optical limiting response of **3** obtained for 7 ns, 532 nm laser pulses with various pulse intervals: 0.5 Hz (●) and 10 Hz (■). The solution was loaded in a 1 mm cell with a linear transmittance of 72%.

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Notes and references

‡ *Characterization* of **3**: FTIR (KBr, cm^{-1}): ν(O–H) 3438br, ν(Mo–O) 951s, ν(Mo–μ-S) 459m, ν(Mo–μ$_3$-S) 434m. ^{1}H NMR (DMSO-d_6): δ 1.10 (CH_3 in NEt_4), 2.92 (CH_2 in NEt_4), 7.64 (d, H in py), 8.72 (d, H in py). ^{95}Mo NMR (DMSO-d_6): δ 663, 687. Found: C, 32.84; H, 2.92; N, 7.26. Calc. for $C_{58}H_{60}N_{11}O_2I_3S_6Cu_6Mo_2 \cdot CH_3OH \cdot H_2O$: C, 33.12; H, 3.11; N, 7.20%.

§ *Crystallographic data* for **3**: $C_{59}H_{66}N_{11}O_4I_3S_6Cu_6Mo_2$, M = 2139.41, triclinic, space group $P1$, a = 11.03290(10), b = 11.8242(2), c = 15.3874(2) Å, α = 72.2980(10), β = 81.4440(10), γ = 84.8620(10)°, V = 1888.94(4) Å^3, Z = 1, T = 293(2) K, D_c = 1.881 g cm^{-3}, μ(Mo-Kα) = 3.416 mm^{-1}, 13 699 reflections measured, 10 605 unique (R_{int} = 0.0598) which were used in the calculations. The final $R1$ = 0.0646 and $wR2$ = 0.1531 for 6228 reflections with $I > 2.0\sigma(I)$ and 795 variable parameters.

CCDC 158546. See http://www.rsc.org/suppdata/cc/b1/b101929p/ for crystallographic data in CIF or other electronic format.

1 D. Coucouvanis, *Acc. Chem. Res.*, 1991, **24**, 1; R. H. Holm, *Adv. Inorg. Chem.*, 1992, **38**, 1; J. B. Howard and D. J. Low, *Chem. Rev.*, 1996, **96**, 2965.

2 S. Shi, W. Ji., S. H. Tang, J. P. Lang and X. Q. Xin, *J. Am. Chem. Soc.*, 1994, **116**, 3615; T. Xia, A. D. K. Mansour, D. J. Hagan, A. A. Said, E. W. Van Stryland and S. Shi, *J. Opt. Soc. Am. B*, 1998, **15**, 1497.

3 T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, 1924; J. W. Perry, K. Mandour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Marder, P. Miles, T. Wada, M. Tian and H. Sasabe, *Science*, 1996, **273**, 1533.

4 Z. R. Chen, H. W. Hou, X. Q. Xin, K. B. Yu and S. Shi, *J. Phys. Chem.*, 1995, **99**, 8717; S. Shi, Z. Lin, Y. Mo and X. Q. Xin, *J. Phys. Chem.*, 1996, **100**, 10 695.

5 J. P. Lang, K. Tatsumi, K. Kawaguchi, J. M. Lu, P. Ge, W. Ji and S. Shi, *Inorg. Chem.*, 1996, **35**, 7924; H. W. Hou, Y. T. Fan, C. X. Du, Y. Zhu, W. L. Wang, X. Q. Xin, M. K. M. Low, W. Ji and H. G. Ang, *Chem. Commun.*, 1999, 647; C. Zhang, Y. L. Song, Y. Xu, H.-K. Fun, G. Y. Fang, Y. X. Wang and X. Q. Xin, *J. Chem. Soc., Dalton Trans.*, 2000, 2823.

6 H. W. Hou, D. L. Long, X. Q. Xin, X. Y. Huang, B. S. Kang, P. Ge, W. Ji and S. Shi, *Inorg. Chem.*, 1996, **35**, 5363.

7 P. Ge, S. H. Tang, W. Ji, S. Shi, H. W. Hou, D. L. Long, X. Q. Xin, S. F. Lu and Q. J. Wu, *J. Phys. Chem. B*, 1997, **101**, 27.

8 Recent examples: Q. M. Wang, X. T. Wu, W. J. Zhang, T. L. Sheng, P. Lin and J. M. Li, *Inorg. Chem.*, 1999, **38**, 2223; H. Gudbjartson, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599; Z. Shi, S. H. Feng, S. Gao, L. R. Zhang, G. Y. Yang and J. Hua, *Angew. Chem., Int. Ed.*, 2000, **39**, 2325; S. M. F. Lo, S. S. Y. Chui, L. Y. Shek, Z. Lin, X. X. Zhang, G. H. Wen and I. D. Williams, *J. Am. Chem. Soc.*, 2000, **122**, 6293.

9 H. W. Hou, Y. R. Ye, X. Q. Xin, J. Liu, M. Q. Chen and S. Shi, *Chem. Mater.*, 1995, **7**, 472; S. Shi, W. Ji, W. Xie, T. C. Chong, H. C. Zeng, J. P. Lang and X. Q. Xin, *Mater. Chem. Phys.*, 1995, **39**, 298.

10 See, for example: M. J. Soileau, ed., *Proc. Soc. Photo-Opt. Instrum. Eng.*, 1989, 1105; S. Link and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 8410.

11 M. Sheik-Bahae, A. A. Said, T. M. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760.

12 G. Sakane, T. Shibahara, H. W. Hou, X. Q. Xin and S. Shi, *Inorg. Chem.*, 1995, **34**, 5363.

13 I. C. Khoo, M. V. Wood, B. D. Guenther, M. Shih and P. H. Chen, *J. Opt. Soc. Am. B*, 1998, **15**, 1533.