Strong optical limiting (OL) capability of the two-dimensional network cluster polymer $[MoS_4Cu_6I_4(py)_4]_n$

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The two-dimensional network compound $[MoS_4Cu_6I_4(py)_4]_n$ is the first example of a cluster polymer showing very large optical limiting effects; its nonlinear absorptive index α_2 and nonlinear refractive value n_2 are 1.5×10^{-9} m W^{-1} and -2.5×10^{-17} m^2 W^{-1}, respectively, in 6.5×10^{-5} mol dm^{-3} DMSO solution; the optical limiting threshold was determined to be 0.6 J cm^{-2}, which is about three times better than that of C_{60}.

Research into optical limiting (OL) materials has become increasingly intensive because of their potential applications in the protection of optical sensors from high-intensity laser beams. Thus the design and synthesis of new materials with large optical limiting capability represents an active field in modern chemistry, physics, and materials science.[1,2] Our research interest focuses on cluster compounds. Although many clusters show strong nonlinear optical (NLO) absorptive and NLO refractive properties, only the clusters $[NBu_4]_2[MoOS_3Cu_3BrCl_2]$, $[NBu_4]_2[MoOS_3(CuSCN)_3]$, $[NBu_4]_3[MS_4M'_3BrX_3]$ (M = Mo, W; M′ = Cu, Ag; X = Cl, Br, I), $[NBu_4]_3[MoOS_3Cu_3BrI_3]$, $[WS_4Cu_4(SCN)_2(py)_6]$, $[Mo_2Ag_4S_8(PPh_3)_4]$ and $[NEt_4]_4[Mo_2O_2S_6Cu_6Br_2I_4]$ exhibit large optical limiting effects.[3–10] The limiting thresholds of $[NBu_4]_3[MS_4M'_3BrX_3]$, $[WS_4Cu_4(SCN)_2(py)_6]$ and $[Mo_2Ag_4S_8(PPh_3)_4]$ were measured to be 0.6, 0.3 and 0.1 J cm^{-2}, respectively. These data are comparable to those of phthalocyanine derivations and better than that observed in C_{60}.[1,11]

The complex $[MoS_4Cu_6I_4(py)_4]_n$ is one of *ca.* 20 cluster polymers. While $[NBu_4N][MS_4Tl]$ (M = Mo, W) have strong NLO absorptive and NLO refractive properties,[12,13] they do not exhibit optical limiting effects. $[MoS_4Cu_6I_4(Py)_4]_n$ is the first cluster polymer to show strong optical limiting effects.

The polymer $[MoS_4Cu_6I_4(py)_4]_n$ was prepared by the reaction of $(NEt_4)_2MoS_4$, CuI and cyanopyridine with pyridine in MeCN solution. The crystal structure of $[MoS_4Cu_6I_4(py)_4]_n$, together with some bond parameters, is shown in Fig. 1.†

The basic structural unit of the polymer $[MoS_4Cu_6I_4(py)_4]_n$ may be regarded as an octahedron, in which MoS_4 is enveloped by six copper atoms. The same Mo–S bond lengths [2.268(3) Å] and similar S–Mo–S bond angles [108.6(1)–109.92(6)°] reveal that the structure of the central MoS_4 core is close to that of the $[MoS_4]^{2-}$ tetrahedron. Each S atom acts as a tetradentate ligand binding with three Cu atoms and one Mo atom. There are two types of copper atoms in the Cu_6 octahedron, two axial Cu(2) atoms and four equatorial Cu(1) atoms. The distance Cu(2)–Mo is not equal to Cu(1)–Mo, while several Cu–Mo–Cu bond angles are inequivalent. Thus, six Cu atoms form a distorted octahedron. Cu(2) atoms each coordinate with two S atoms and one terminal I(2) atom, and exhibit triangular planar geometry. Cu(1) atoms bind with two S atoms, one μ-I(1) atom and one N from py, and adopts a distorted tetrahedral geometry. Each $[MoS_4Cu_6I_4(py)_4]$ unit forms four Cu(1)–I(1)–Cu(1) bridges with four $[MoS_4Cu_6I_4(py)_4]$ units leading to the two-dimensional network structure.

Two shoulder peaks at 300 and 410 nm are observed in the electronic spectrum of $[MoS_4Cu_6I_4(py)_4]_n$. The polymer has a relatively low linear absorption in the visible and near IR region. Z-scan data indicate that the polymer exhibits both strong NLO absorption and NLO refraction (self-defocusing effects), which were measured as described in ref. 13.

It should be pointed out that both excited state population (and absorption) and two-photon absorption can be responsible for the measured NLO effect.[14] Fig. 2 shows typical Z-scan measurements of the polymer in DMSO solution without the aperture. The open circles are the experimental data, and the solid curves are the theoretical fit by using Z-scan theory described in ref. 13. It is obvious that the theoretical curves qualitatively reproduce well the general pattern of the observed experimental data. This fact suggests an effectively third-order characteristic for the experimentally detected NLO effects. The

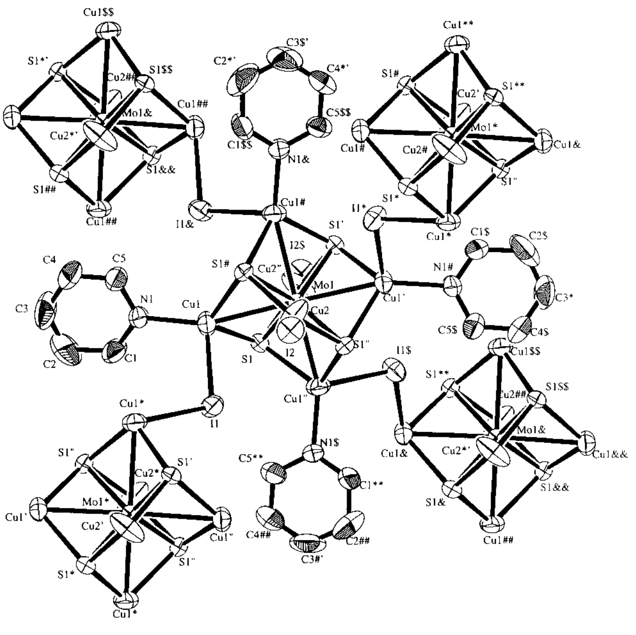

Fig. 1 The crystal structure of $[MoS_4Cu_6I_4(py)_4]_n$. Selected bond lengths (Å) and angles (°): Mo(1)–S(1) 2.268(3), Mo(1)–Cu(1) 2.684(2), Mo(1)–Cu(2) 2.653(2), I(1)–Cu(1) 2.784(2), I(2)–Cu(2) 2.455(2), Cu(1)–N(1) 1.995(10); S(1)–Mo(1)–S(1)′ 108.6(1), S(1)′–Mo(1)–S(1)″ 109.92(6), Cu(1)–Mo(1)–Cu(1)′ 168.80(7), Cu(1)–Mo(1)–Cu(2) 84.40(4), Cu(1)–Mo(1)–Cu(1)# 90.55(1), Cu(1)–Mo(1)–Cu(2)″ 95.60(4), Cu(1)–Mo(1)–S(1) 55.49(9), Cu(1)–Mo(1)–S(1)′ 117.19(9), Cu(2)–Mo(1)–S(1)′ 125.72(6), Cu(2)–Mo(1)–S(1)″ 54.28(6), I(1)–Cu(1)–S(1) 94.87(9), I(2)–Cu(2)–S(1)″ 125.82(7), I(2)–Cu(2)–Mo(1) 180.0, Mo(1)–S(1)–Cu(1) 71.33(9).

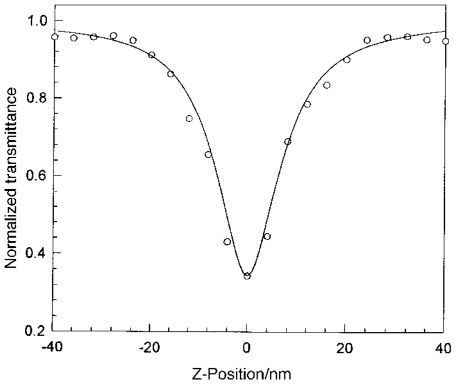

Fig. 2 Z-scan data showing NLO absorption of $[MoS_4Cu_6I_4(py)_4]_n$.

effective nonlinear absorptive index α_2 is 1.5×10^{-9} m W^{-1} in 6.5×10^{-5} mol dm^{-3} DMSO solution. The data is comparable to those of $[Mo_2Ag_4S_8(PPh_3)_4]$ and $[W_2Ag_4S_8(AsPh_3)_4]$ which have the largest α_2 values known, and superior to those of other inorganic clusters.

The Z-scan data measured with the aperture are depicted in Fig. 3. The data show that the polymer $[MoS_4Cu_6I_4(py)_4]_n$ has a negative sign for the refractive nonlinearity, which gives rise to self-defocusing behavior. A reasonably good fit between the experimental data and the theoretical curves described in ref. 13 was obtained. The effective third-order NLO absorptive index n_2 is -2.5×10^{-17} m^2 W^{-1}. The polymer is composed of octahedral structural units $[MoS_4Cu_6I_4(py)_4]$ and its NLO refractive behavior differs from that of cluster polymers $\{[NBu_4][MS_4Tl]\}_n$ (M = Mo, W), which consist of dinuclear structural units $[MS_4Tl]$ and exhibit strong self-focusing effects. However, twin nest-shaped clusters consisting of two nest-shaped structural units have the same NLO refractive properties as $[MoS_4Cu_6I_4(py)_4]_n$, with strong self-defocusing behavior.

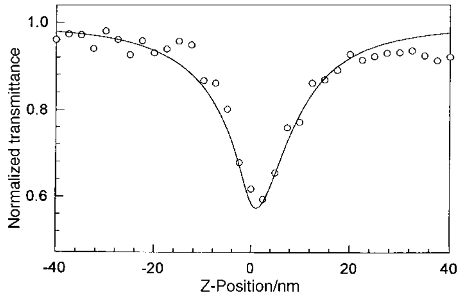

Fig. 3 Z-scan data showing NLO refraction of $[MoS_4Cu_6I_4(py)_4]_n$.

We also observed that the polymer possesses large optical limiting (OL) effects because of its very strong NLO absorption (α_2 value is the largest for any known inorganic cluster). The measurement of the transmitted pulse energy was conducted with a full collection of the transmitted pulse, and no aperture was used. The OL capability utilizing only the NLO absorption is demonstrated in Fig. 4 (open circles). The solid curves in Fig. 4 are from the theoretical model described in ref. 14. It is manifest that the observed OL effect arises as a direct consequence of the ionization recombination process. The light energy transmitted starts to deviate from Beer's law as the input light fluence reaches *ca.* 0.3 J cm^{-2}, and the solution become increasely less transparent as the incident fluence rises. The limiting threshold, which is defined as the incident fluence at which the actual transmittance falls to 50% of the corresponding linear transmittance, is 0.6 J cm^{-2} in DMSO solution. This value is three times better than that of C_{60}. These results clearly indicate that the cluster polymer exhibits strong NLO properties and *also* a large OL capability. The properties should make the polymer a very promising candidate for broad-band OL application.

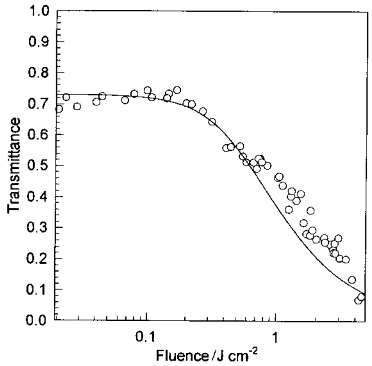

Fig. 4 Dependence of the transmitted energy at 532 nm of a DMSO solution of $[MoS_4Cu_6I_4(py)_4]_n$ on the incident light fluence. Beating rate: single shot (5 s interval).

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Notes and references

† *Crystal data*: $C_{20}H_{20}N_4S_4I_4Cu_6Mo$, M = 1429.48, tetragonal, space group $I\bar{4}2d$ (no. 122), a = 14.814(3), c = 15.712(5) Å, V = 3447.75 Å^3, Z = 4, D_c = 2.75 g cm^{-1}, $F(000)$ = 2640.00, μ (Mo-Kα) = 78.3 cm^{-1}, $2\theta_{max}$ = 55.0°. All measurements were made on a Rigaku RAXIS-IV image plate area detector. A total of 1012 reflections were collected. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least-squares refinement was based on 853 observed reflections $[(I > 2.00\sigma(I)]$ and 91 variable parameters and converged with R = 0.043 and R_w = 0.042. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985 and 1992). CCDC 182/1183. See http://www.rsc.org/suppdata/cc/1999/647/ for crystallographic files in .cif format.

1 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.
2 R. Signorini, M. Zerbetto, M. Meneghetti, R. Bozio, M. Maggini, C. D. Faveri, M. Prato and G. Scorrano, *Chem. Commun.*, 1996, 1891.
3 H. W. Hou, X. R. Ye, X. Q. Xin. J. Liu, M. Q. Chen and S. Shi, *Chem. Mater.*, 1995, **7**, 472.
4 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.
5 S. Shi, W. Ji, S. H. Tang, J. P. Lang and X. Q. Xin, *J. Am. Chem. Soc.*, 1994, **116**, 3615.
6 S. Shi, W. Ji, J. P. Lang and X. Q. Xin, *J. Phys. Chem.*, 1994, **98**, 3570.
7 P. E. Hoggard, H. W. Hou, X. Q. Xin and S. Shi, *Chem. Mater.*, 1996, **8**, 2218.
8 M. K. M. Low, H. W. Hou, H. G. Zheng, W. T. Wong, G. X. Jin, X. Q. Xin and W. Ji, *Chem. Commun.*, 1998, 505.
9 W. Ji, S. Shi, H. J. Du, P. Ge, S. H. Tang and X. Q. Xin, *J. Phys. Chem.*, 1995, **99**, 17 297.
10 H. W. Hou, X. Q. Xin. J. Liu, M. Q. Chen and S. Shi, *J. Chem. Soc., Dalton Trans.*, 1994, 3211.
11 L. W. Tutt and A. Kost, *Nature*, 1992, **356**, 224.
12 J. P. Lang, K. Tatsumi, H. Kawaguchi, J. M. Lu, P. Ge, W. Ji and S. Shi, *Inorg. Chem.*, 1996, **35**, 7924.
13 B. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron*, 1990, **26**, 760.
14 W. Ji, H. J. Du and S. Shi, *J. Opt. Soc. Am.*, 1995, **12**, 876.

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