Nanosecond and Picosecond Optical Limiting Properties of a Square-planar Complex $C_{30}H_{24}N_6O_4S_4Cu$, CuL_2 [HL = *p*-nitrobenzaldehyde S-benzyl dithiocarbazate]

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(Received July 26, 1999; CL-990656)

Optical limiting properties of a square-planar complex $C_{30}H_{24}N_6O_4S_4Cu$, CuL_2 [HL = *p*-nitrobenzaldehyde S-benzyl dithiocarbazate] were investigated with laser pulses of 7-ns and 35-ps duration. The measured nanosecond and picosecond limiting thresholds for CuL_2 are *ca.* 1 and 1.4 J cm^{-2} at 532 nm, respectively. The nanosecond limiting threshold is comparable to that of C_{60}.

Optical limiting (OL) materials have been under intensive investigations because of their potential application in the protection of optical sensors and human eyes from undesired intense laser beams.[1] An ideal optical limiters should have the capability of being transparent for low-energy light beam and opaque under high-energy laser radiation. The most frequently reported OL materials are fullerenes (C_{60})[2,3] and metallo-phthalocyanine complexes,[4-6] which are considered as the best compounds for the protection application. Recently, inorganic clusters have also been investigated as promising OL materials.[7,8] In our continuing study of nonlinear optical materials [9,10] and their potential application to OL, we report herein the nanosecond and picosecond optical limiting properties of square-planar complex $C_{30}H_{24}N_6O_4S_4Cu$, CuL_2 [HL = a bidentate Schiff-base ligand, *p*-nitrobenzaldehyde S-benzyl dithiocarbazate]. With an aperture placed in front of the transmission detector, the nanosecond limiting threshold for CuL_2 is *ca.*1 J cm^{-2} at 532 nm, which is comparable to that of C_{60}.

The preparation of complex $C_{30}H_{24}N_6O_4S_4Cu$, CuL_2 was described previously by refluxing $Cu(OAc)_2{\cdot}H_2O$ and the Schiff-base *p*-nitrobenzaldehyde S-benzyl dithiocarbazate, HL in ethanol in a 1:2 molar ratio and the geometry about Cu(II) are square-planar with two deprotonated bidentate ligands L^- arranged in a *trans* fashion.[11] The electronic spectrum in Figure 1 shows that there is a relatively low linear absorption in the visible and near-IR region. A broad transparent range is an important criterion in the assessment of OL materials.

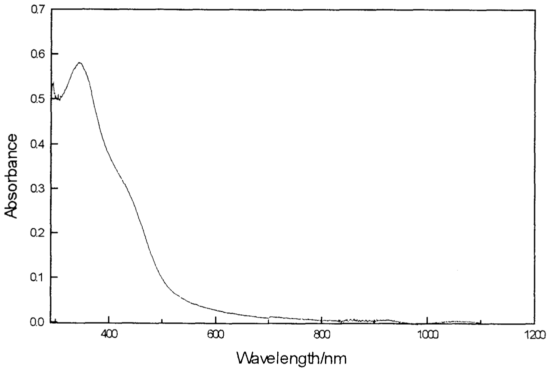

Figure 1. Electronic spectrum of CuL_2 in CH_2Cl_2 solution. The concentration: 2.35 x 10^{-5} M; and the optical path: 1cm.

A dichloromethane (CH_2Cl_2) solution of the complex was contained in quartz cell. The sample were irradiated by a Q-switched Nd:YAG laser, which produced linearly polarized 7-ns (FWHM) light pulses at 1064 nm and 532 nm (by a second-harmonic crystal) for the nanosecond measurements. The laser was operated at a repetition rate of 10 Hz. The spatial profiles of the pulses were nearly Gaussian after passing through a spatial filter. The pulses were split into two parts: the reflected was used as reference, and the transmitted was focused onto the sample by using a focusing mirror of 25-cm focal length. The sample was placed at the focus where the spot radius of the pulses was 30 ± 5 and 72 ± 6 μm for the 532-nm and 1064-nm pulses, respectively. Both the incident and transmitted laser pulses were monitored simultaneously by using two energy detectors (Rjp-735 energy probes, Laser Precision).

The picosecond limiting effect was observed under experimental conditions that were similar to the nanosecond measurements except that the 35-ps (FWHM) laser pulses were produced by a frequency-doubled, mode-locked, Q-switched, Nd:YAG laser, and that the spot radius was 24 ± 5 μm.

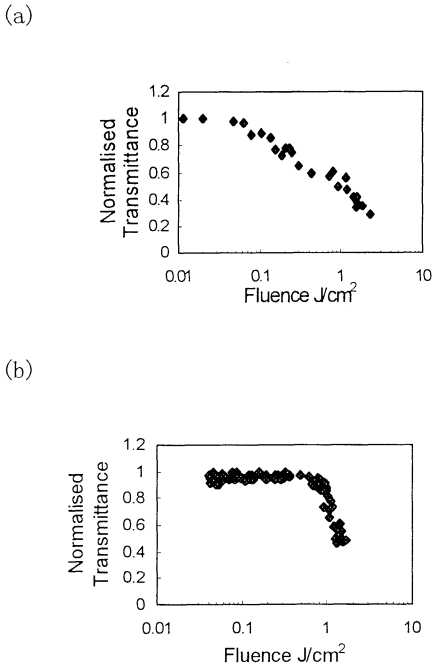

Figure 2. Energy-dependent transmittance of CuL_2 (4.4 x 10^{-4} M) in CH_2Cl_2 solution. Optical path: 1 mm; laser wavelength: 532 nm; repetition rate: 10 Hz; and pulse duration: (a) 7 ns, and (b) 35 ps.

The limiting phenomenon was observed by measuring the nonlinear (energy-dependent) transmission. An aperture was placed in front of the transmission detector when the measurements were performed. Figure 2(a) displays measurements of the limiting effect of CuL_2 in CH_2Cl_2 solution with the nanosecond pulses at 532 nm. The solution transmittance is independent of the incident fluence at < 0.1 J cm^{-2}, obeying Beer's law. (The linear transmittance is about 75%.) When the incident fluence exceeds 0.1 J cm^{-2} the solution transmittance decreases as the incident fluence increases, thus exhibiting a typical limiting effect. The limiting threshold is defined as the incident fluence at which the solution transmittance falls to 50% of the linear transmittance. From Figure 2(a), we determined the nanosecond limiting threshold of CuL_2 in CH_2Cl_2 solution to be *ca.* 1 J cm^{-2}.

Figure 2(b) displays limiting performance of CuL_2 at 532 nm with the 35-ps pulses. The solution transmittance starts to decrease rapidly when the incident fluence reaches about 0.7 J cm^{-2} and the limiting threshold obtained is *ca.* 1.4 J cm^{-2}.

The nanosecond limiting threshold of 1 J cm^{-2} for CuL_2 is comparable to that of C_{60} in toluene solution, while the picosecond limiting threshold is about 0.6 J cm^{-2} larger.[3] The CuL_2 solution was very stable and no photodegradation was observed when the pulse repetition rate reaches 10 Hz.

Under the nanosecond laser pulses, the limiting effect in the CuL_2 solution was also observed at 1064 nm, with a limiting threshold of > 4 J cm^{-2}. This result shows that CuL_2 possesses a broadband limiting response.

It should be pointed out that our results were obtained with the aperture placed in front of the transmission detector. It is known that such an aperture can enhance the limiting effect by blocking a part of the transmitted beam, which is expanded due to self-lensing effect in the high-power regime.[12] The limiting effects were observed to deteriorate without the aperture, indicating that a self-lensing effect occurs in the CuL_2 solution. This is clearly demonstrated that the observed limiting effect can be attributed to both nonlinear absorption and nonlinear refraction processes. It should be emphasized that the nature of the nonlinear absorption and refraction is not clear by the limiting measurement. Our Z-scans[13] revealed a positive sign for the change in the refractive index. This rules out thermal lensing effects. The observed nonlinear refraction can be caused by excited-state refraction, electronic instantaneous Kerr nonlinearity or other electronic processes. More experiments such as time-resolved pump-probe measurements[14] are needed to determine such a nature.

It is also interesting to compare ML_2 with a closely related compound, CuL^a_2 [HL^a = a similar bidentate Schiff-base ligand, *p*-dimethylaminobenzaldehyde S-benzyl dithiocarbazate, unpublished results][15]; the picosecond limiting threshold measured under the same conditions is about 3 J cm^{-2} while the nanosecond liming effect is poor and the solution transmittance cannot drop to 50% of the linear transmittance. Therefore it could be concluded that the strong electron-withdrawing nitro [NO_2] substituent is more effective to enhance the nonlinear refraction than the strong electron-donating group [$N(CH_3)_2$], thus improving the optical limiting performance, which may be associated with the work by Leite,[12] who used thermal lensing in a thick cell of nitrobenzene in combination with spatial filtering to achieve optical limiting. Further work to understand the mechanism is in progress.

This research was funded by State Key Project of Fundamental Research and the National Natural Science Foundation of China and the National University of Singapore.

References and notes

1 J. P. Perry, in "Nonlinear Optics of Organic Molecules and Polymers," ed by H. S. Nalwa and S. Miyata, CRC Press, Boca Ratón, FL (1997), Chap. 12, P. 813

2 L. W. Tutt and A. Kost, *Nature,* **356**, 225 (1992).

3 D. G. Mclean, R. L. Sutherland, M. L. Brant, D. M. Brandelik, and T. Pottenger, *Opt. Lett.*, **18**, 858 (1993).

4 J. M. Perry, K. Mansour, 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*, **273**, 1533 (1996).

5 G. de. la Torre, P.Vázquez, F. Agulló-López, and T. Torres, *J. Mater. Chem.*, **8**, 1671 (1998) and references cited therein.

6 S. Hughes, G. Spruce, B. S. Wherrett, and T. Obayashial, *J. Appl. Phys.* **81,** 5905 (1997).

7 M. K. M. Low, H. W. Hou, H. G. Zheng, W. Wong, G. X. Jin, X. Q. Xin, and W. Ji, *Chem. Commun.*, **1998**, 505 and references cited therein.

8 S. Shi, W. Ji, S. H. Tang, J. P. Lang, and X. Q. Xin, *J. Am. Chem. Soc.*, **116**, 3615 (1994).

9 T. P. Tian, C. Y. Duan, Z. L. Lu, X. Z. You, T. C. W. Mak, and Z. Y. Zhang, *Inorg. Chem.*, **36**, 1247 (1997).

10 X. M. Zhang, B. Z. Shan, C. Y. Duan, and X. Z. You, *Chem. Commun.*, **1997**, 1131.

11 Y. P. Tian, C. Y. Duan, Z. L. Lu, and X. Z. You, *Trans. Met. Chem.*, **21**, 254 (1996).

12 R. C. C. Leite, S. P. S. Porto, and T. C. Damen, *Appl. Phys. Lett.*, **10**, 100 (1967).

13 M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, *IEEE J. Quant. Electron.*, **26**, 760 (1990).

14 T. Xia, A. Dogariu, K. Mansour, D. J. Hagan, A. A. Said, S. Shi and E. W. Van Stryland, *J. Opt. Soc. Am. B*, **15**, 1497 (1998).

15 Y. P. Tian, C. Y. Duan, Z. L. Lu, and X. Z. You, *Polyhedron*, **15**, 2263 (1996).