New Nonlinear Optical Chromophore: Synthesis, Structures, and Optical Limiting Effect of Transition-Metal Clusters (n-Bu4N)3[WM3Br4S4] (M = Cu and Ag)

S. Shi*,†and W. Ji‡

Optical Crystal Laboratory and Department of Chemical Engineering and Department of Physics, National University of Singapore, Kent Ridge, Singapore

J. P. Lang and X. Q. Xin

Department of Chemistry, Nanjing University, Nanjing, PRC

Received: December 23, 1993; In Final Form: February 15, 1994

Cubane-like heteronuclear transition-metal clusters (n-Bu4N)3[WCu3Br4S4] (I) and (n-Bu4N)3[WAg3Br4S4] (II) were synthesized by solid-state reactions. These molecules respond nonlinearly to the incident light and exhibit a strong optical limiting effect with threshold and transmitted saturation levels of 1.6 and 0.7 J/cm² for compound I and 0.8 and 0.5 J/cm² for compound II, as examined in a 1-mm cell with 7-ns laser pulses at 532 nm. The optical limiting power of compound I is comparable to that of C_{60} while the optical limiting power of compound II is about 2 times stronger than that of C_{60}, one of the best molecules reported for optical limiting.

Introduction

Nonlinear optics is one of a few research frontiers where tremendous interest arises not only from the quest for understanding of new physical phenomena but also from the potential technological applications.[1] The current development of optical signal detection techniques (such as signal acquisition, remote sensing, and night vision) is often frustration by the intrinsic incompetence in self-protection of highly sensitive optical detectors. Every detector has a finite power window. It is often the case that the more sensitive a detector is toward a weak signal, the more fragile it is toward an undesired strong signal. This paradox situation calls for research on optical limiting (OL) materials that are transparent to weak and opaque to strong signals. The idea is to use such a material (in the form of a film or a slab) as an optical limiter to protect the sensitive devices by letting only the weak signals pass and blocking the strong ones.

Unfortunately, most of the materials do not have such a desired optical property. On the contrary, they often become more transparent under high fluences of light because of the depletion of the electronic ground state. Two-photon absorption was discovered to be able to produce an optical limiting effect, but only in the range of very high light intensity.[2,3] Recently, fullerene C_{60} was found to possess such an unusual optical limiting capability by one-photon mechanisms and hence received tremendous attention.[4–6] Inorganic clusters with their cage structures analogous to that of C_{60} and large optical nonlinearity have also started to receive attention in this respect.[7,8] We report here the optical limiting effect of two transition-metal clusters, (n-Bu4N)3[WCu3Br4S4] (I) and (n-Bu4N)3[WAg3Br4S4] (II).

Experimental Section

Compound I was synthesized by a solid-state reaction. A well-ground mixture of 1.0 mmol of ammonium tetrathiotungstate ((NH4)2WS4), 4.0 mmol of copper(I) bromide (CuBr), and 3.0 mmol of tetrabutylammonium bromide (n-Bu4NBr) was sealed in a reaction tube under argon. A dark solid was obtained by heating the mixture to 100 °C for 15 h. After extracting the dark solid product with 40 mL of dichloromethane (CH2Cl2) and filtering the extract, we obtained brick red crystals of (n-Bu4N)3[WCu3Br4S4] by slow evaporation of the solvent. Com-

pound II was synthesized according to the same procedure but with copper(I) bromide replaced by silver(I) bromide. Results of elemental analysis agree well with the molecular formulas. Anal. (Calcd) for compound I, C48H108Cu3WBr4N3S4: W, 11.56 (11.88); Cu, 12.09 (12.32); Br, 21.01 (20.65); S, 8.11 (8.27); N, 2.56 (2.71); C, 37.01 (37.24); H, 6.99 (7.03). Anal. (Calcd) for compound II, C48H108Ag3WBr4N3S4: W, 10.61 (10.94); Ag, 18.97 (19.24); Br, 19.33 (19.01); S, 7.14 (7.61); N, 2.51 (2.50); C, 34.12 (34.26); H, 6.45 (6.48).

X-ray data were collected on a Siemens R3m/V diffractometer with Mo Kα radiation (λ = 0.710 73 Å). Crystal structures were determined by use of Siemens SHELXTL PLUS software. Compound II: fw = 1681; cubic, $a = b = c$ = 24.221(4) Å, V = 14208.7 Å³; R = 0.071, R_w = 0.068. Compound I: fw = 1548; trigonal, $a = b$ = 17.410(7), c = 39.102(5) Å, V = 10265.2 Å³; isostructural to compound II.

The acetonitrile solutions of I and II were placed in a 1-mm quartz cuvette for optical measurements. Their optical responses were measured with linearly polarized, 7-ns pulses from a Q-switched frequency-doubled Nd:YAG laser. The spatial profiles of the optical pulses (λ = 532 nm) were nearly Gaussian, and the light was focused onto the sample with 25-cm-focal length focusing mirror. The spot radius of the laser beam was measured to be 35 μm (half-width at $1/e^2$ maximum). The interval between the laser pulses was set at 20 s so that every pulse of light was assured to meet fresh molecules in the sample to eliminate influence of any photodegradation. The incident and transmitted pulse energies were measured simultaneously by two laser precision detectors (RjP-735 energy probes) which were linked to a computer by an IEEE interface.

Results and Discussion

In the solid state, the cluster anions of the compounds assume cubane-like structures.
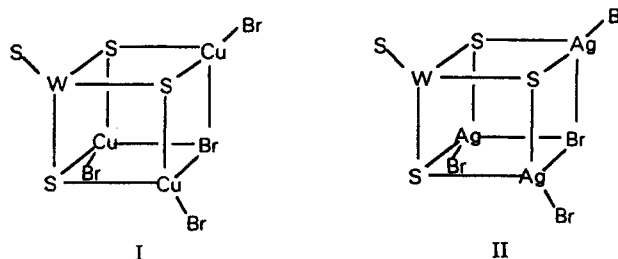
I   II
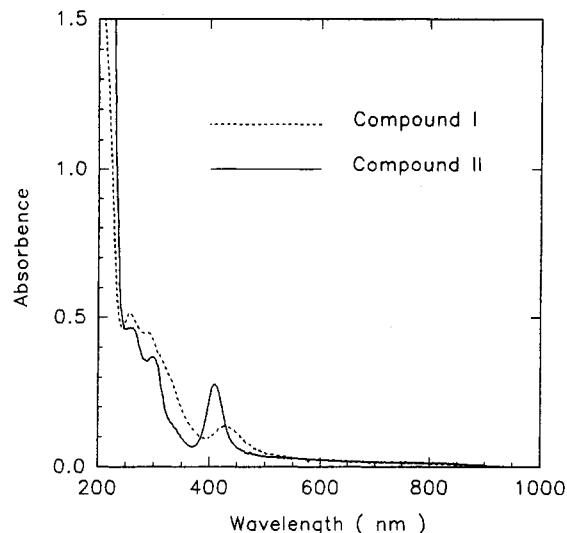
Figure 1. Absorption spectra of compounds I and II in acetonitrile solution with 1-mm optical length, with compound I at 3.9×10^{-4} M and compound II at 1.3×10^{-4} M.
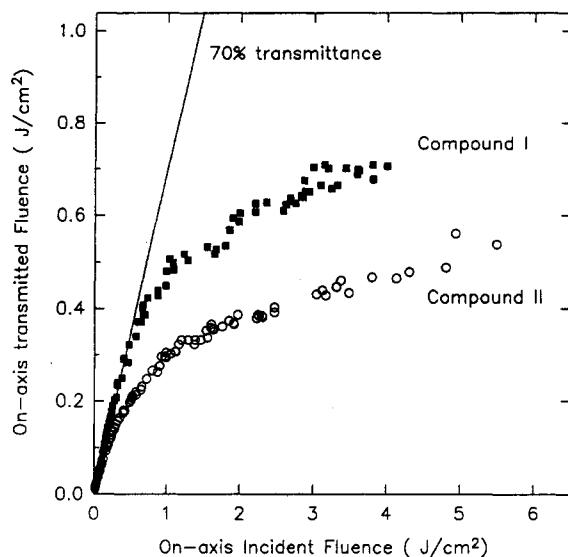

Figure 2. Optical limiting response to 7-ns, 532-nm laser pulses, with compounds I and II in acetonitrile with 1-mm optical length: filled squares, compound I; open circles, compound II. The solid straight line showing a linear transmittance of 70% is a guide for the eye. Solutions with 70% transmittance at 532 nm correspond to 5.7×10^{-3} M of I or 1.9×10^{-3} M of II.

Their UV–vis spectra in acetonitrile are shown in Figure 1. It is noticed that both compounds I and II have relatively low linear absorptivity at 532 nm.[9] This result is important since an ideal optical limiter should be transparent at low fluences.

The optical limiting effects of the compounds are depicted in Figure 2. At very low fluences they respond linearly to the incident light obeying Beer's law. Deviation from the linear response takes place when the incident fluence reaches about 0.4 J/cm². The materials become increasingly less transparent as the light fluence rises. Control experiments with the compounds in acetonitrile/acetone solutions (with the volume-to-volume ratio of the two solvents varying from 95:5 to 5:95) produced identical results. Experiments with solvents alone afforded no detectable OL effect. All these indicate that solvent contributions are negligible. The limiting threshold[10] was measured as 1.6 J/cm² for compound I and 0.8 J/cm² for compound II with the saturation fluences of 0.7 J/cm² for the former and 0.5 J/cm² for the latter, respectively (Figure 2). The threshold and saturation values of compound I are comparable to those of C_{60},[11] one of the best molecules reported for optical limiting,[6] while both the limiting
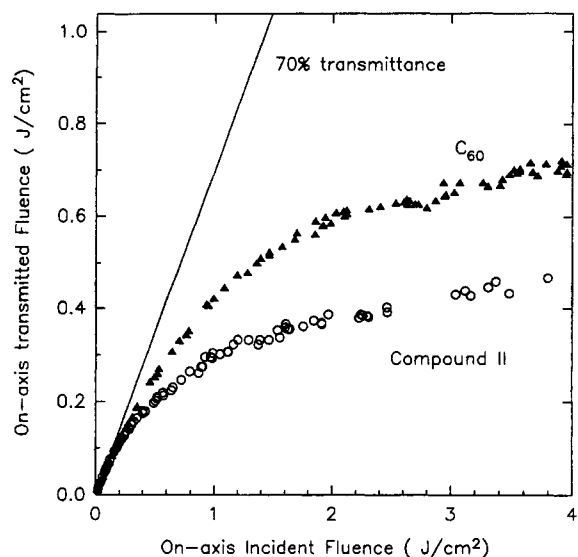

Figure 3. Comparison of optical limiting capability between compound II in acetonitrile and C_{60} in toluene: open circles, compound II; triangles, C_{60} (wavelength 532 nm, optical path 1 mm; pulse width 7 ns). The C_{60} solution of 70% transmittance corresponds to a concentration of 1.9×10^{-3} M.

threshold and the saturation fluence of compound II are only about half of those of C_{60} measured under identical conditions.[12] Lower limiting threshold and saturation levels provide a greater safety margin for device protection. Figure 3 shows a comparison between C_{60} in toluene and compound II in acetonitrile, both at 70% linear transmittance. An independent Z-scan[13,14] experiment (sensitivity $\lambda/25$) shows that the nonlinear refraction index change of the compounds is negligible within the light fluence range of this study. Clearly, the observed optical limiting power of the clusters stems nearly solely from a nonlinear absorptive process.

It is interesting to note that both C_{60} and (n-Bu$_4$N)$_3$[WM$_3$Br$_4$S$_4$] (M = Cu and Ag) have cage structures, yet the presence of heavy elements in the latter compounds makes it possible for them to possess strong optical limiting power with fewer skeleton atoms. C_{60} has 60 skeleton atoms whereas (n-Bu$_4$N)$_3$[WM$_3$Br$_4$S$_4$] has only eight. A significant improvement of optical limiting capability is seen when skeleton Cu atoms are replaced by Ag atoms (Figure 2). There seems to be a heavy atom effect, arising from the fact Ag atoms can facilitate intersystem crossing more effectively via spin–orbit coupling than Cu atoms. The importance of the heavy atom effect to the efficiency of nonlinear absorptions has already been noticed in the cases of metallophthalocyanine systems.[15]

The direct implementation of the acetonitrile solutions of the two compounds as optical limiters is frustrated by their low optical damage thresholds. Photodegradation was observed when the incident light energy exceeds 3 J/cm². The optical limiting capability starts to decrease and data become scattered if both high fluence of incident light and the short pulse interval (e.g., <0.5 s) are employed. In view of the fact that the skeletons of the cubane-like clusters are kept by four strong μ_3-S bridges, it seems likely that the photodegradation in acetonitrile reflects light-induced terminal ligand substitution by solvent. It is possible to eliminate such ligand substitution by incorporating the clusters into polymers where solvent molecules no longer exist. Further work is under way to verify this hypothesis. A possible drawback of solid samples is that they lack healing capability after photodamage.

Transition-metal chalcogenide clusters, as represented by (n-Bu$_4$N)$_3$[WM$_3$Br$_4$S$_4$] (M = Cu and Ag), possess several unique properties which define themselves as a promising group of nonlinear optical materials. First, unlike C_{60} and organic nonlinear optical materials, the constituent elements of these

clusters can be made heavy to facilitate intersystem crossing (heavy atom effect). Second, they are often stable at more than one oxidation state. Both their sizes and total charges can be changed to adjust the energies of relevant electronic states, which in conjunction with the possible substitutions at both terminal and skeleton positions can be used to introduce or remove the resonance enhancement of OL capability and other nonlinear optical properties. The great advantage of combining nonlinear optical research with transition-metal cluster chemistry also rests on the wealth of existing knowledge on clusters. It opens up broad prospects of producing nonlinear optical materials through inorganic synthesis.

References and Notes

(1) (a) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds. *Materials for Nonlinear Optics, Chemical Perspectives*; American Chemical Society: Washington, DC, 1991. (b) *Conference on Lasers and Electro-Optics*, Vol. 11, OSA technical digest series; Optical Society of America: Washington, DC, 1993; pp 614–621. (c) Coulter, D. R.; Miskowski, V. M.; Perry, J. W.; Wei, T. H.; Van Stryland, E. W.; Hagan, D. J. *Proc. Soc. Photo-Opt. Instrum. Eng.* **1989**, *1105*, 42.

(2) Ralston, J. M.; Chang, K. R. *Appl. Phys. Lett.* **1969**, *15*, 164.
(3) Van Stryland, E. W.; Wu, Y. Y.; Hagan, D. J.; Soileau, M. J.; Mansour, K. *J. Opt. Soc. Am. B* **1988**, *5*, 1980.
(4) Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225.
(5) Henari, F.; Callaghan, J.; Stiel, H.; Blau, W.; Cardin, D. J. *Chem. Phys. Lett.* **1992**, *199*, 144.
(6) McLean, D. G.; Sutherland, R. L.; Brant, M. C.; Brandelik, D. M.; Fleitz, P. A.; Pottenger, T. *Opt. Lett.* **1993**, *18*, 858.
(7) Tutt, L. W. and McCahon, S. W. *Opt. Lett.* **1990**, *15*, 700.
(8) Allan, G. R., Labergerie, D. R.; Rychnovsky, S. J.; Boggess, T. F.; Smirl, A. L. *J. Phys. Chem.* **1992**, *96*, 6313.
(9) Molecular extinction coefficient at 532 nm is 2.63×10^2 dm^3 mol^{-1} cm^{-1} for compound I and 8.68×10^2 dm^3 mol^{-1} for compound II.
(10) We define the limiting threshold as the incident fluence at which the actual transmittance falls to 50% of the corresponding linear transmittance.
(11) By following the standard procedures,[16] C_{60} was separated and purified from the carbon soot which was purchased from Texas Fullerenes Corp. The absorption spectrum of C_{60}–toluene solution shows excellent agreement with the published results.[16]
(12) The limiting threshold we measured for C_{60}–toluene solution at 70% linear transmittance (λ = 532 nm) is 1.5 J/cm^2, which compares well with the reported value of 1.6 J/cm^2.[6]
(13) Sheik-bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quant. Electron.* **1990**, *26*, 760.
(14) Sheik-bahae, M.; Said, A. A.; Van Stryland, E. W. *Opt. Lett.* **1989**, *14*, 955.
(15) Wei, T. H.; Hagan, D. J.; Sence, M. J.; Van Stryland, E. W.; Perryand, J. W.; Coulter, D. R. *Appl. Phys. B* **1992**, *54*, 46.
(16) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Wetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.