

**Synthesis and Optical Limiting Capability of
Cubane-like Mixed Metal Clusters
(*n*-Bu₄N)₃[MoAg₃BrX₃S₄] (X = Cl and I)**

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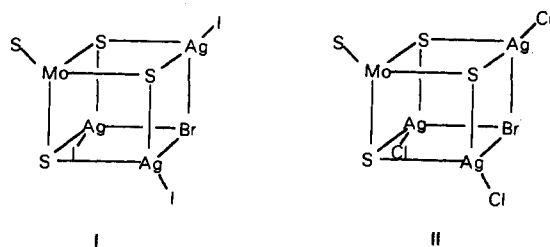
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In recent years, materials exhibiting strong nonlinear optical effects have been under intensive research. In particular, optical limiting materials have received considerable attention as a result of a growing need for optical sensor protection.¹ The current advance of optical detection systems for applications such as signal acquisition and night vision demands the development of protective devices, such as passive optical limiters, so that highly sensitive detectors can survive undesired high-intensity signals. An ideal optical limiter should acquire the capability of being transparent at low fluences of incident light, opaque at high fluences, and capable of switching back and forth between these two states in quick response to external optical signals. It has been demonstrated that such an optical limiting (OL) function can be realized by exploiting the nonlinear absorption and/or nonlinear refraction of materials.²

However, most of materials do not possess such an unusual optical property. On the contrary, they often become more transparent under a strong optical field owing to the depletion of the electronic ground state. Fullerene³ C₆₀ and metallo-phthalocyanine complexes⁴ received tremendous attention recently because of their optical limiting capability. As part of our search for optical limiting materials, we have surveyed the nonlinear transmission of a number of inorganic clusters. Here we present experimental data using 7-ns, 532-nm laser pulses on two such clusters, (*n*-Bu₄N)₃[MoAg₃BrI₃S₄] (I) and (*n*-Bu₄N)₃[MoAg₃BrCl₃S₄] (II).



Compound I was synthesized according to literature methods.⁵ Results of elemental analysis and IR spectra agree well with the data reported.⁶ New compound II was synthesized by heating

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(1) See, for example: *Conference on Lasers and Electro-Optics, 1993*; OSA Technical Digest Series, Vol. 11; Optical Society of America: Washington, DC, 1993; pp 614–621.

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a well-ground solid mixture of (NH₄)₂MoS₄ (1.0 mmol), AgCl (4.0 mmol), and (*n*-Bu₄N)₃Br (3.0 mmol) in a reaction tube at 100 °C under argon for 15 h. After extraction of the reaction mixture with 50 mL of DMF and slow evaporation of the solvent, dark brown crystals were collected from the filtrate. The results of the elemental analysis agree well with the formula of the compound.

In the solid state, the cluster anion of compound I is reported to assume a cubane-like structure, with the four metal atoms and the four nonmetal atoms in statistical distributions, respectively.⁵ A similar structure is established for compound II on the basis of the single-crystal X-ray diffraction data collected in this study. Their electronic spectra in CH₃CN solutions were shown in Figure 1.

The CH₃CN solutions of I and II were placed in a 1-mm-thick quartz cell for optical measurements. The samples were irradiated⁷ by linearly polarized, 7-ns pulses from a Q-switched and frequency-doubled Nd:YAG laser (λ = 532 nm). 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 the influence of any photodegradation.

The optical limiting effects of the compounds are depicted in Figure 2. The light energy transmitted starts to deviate from normal linear behavior as soon as the input light fluence reaches about 0.3 J/cm², and the materials become increasingly less transparent as the light fluence rises. Control experiments conducted with the compounds in CH₃CN/CH₃COCH₃ mixed solvents (with composition varied from 95:5 to 5:95 v/v) give almost identical results. Clearly, the solvent effects are small. The limiting threshold⁸ was measured as 0.5 J/cm² for compound I and 0.6 J/cm² for compound II, both with a saturation fluence transmitted to 0.3 J/cm². These threshold values are only about only 1/3 of that of C₆₀ measured under identical conditions, and their saturation energies are about 1/2 of that of C₆₀. In other words, these parameters of the clusters are 3 and 2 times better than that of C₆₀, the best molecular optical limiting material reported. It is interesting to note that both C₆₀ and (*n*-Bu₄N)₃[MoAg₃BrX₃S₄] (X = Cl and I) have cage structures, yet the presence of heavy elements in the latter compounds makes it possible for them to possess stronger optical limiting power with fewer skeleton atoms. C₆₀ has 60 skeleton atoms whereas (*n*-Bu₄N)₃[MoAg₃BrX₃S₄] has only eight.

A Z-scan⁹ experiment (with a sensitivity of λ/25) was performed with the same laser to reveal the electronic-structural origin of the observed optical limiting effect. Within experimental error, no difference was found between data of open-aperture and closed-aperture Z-scans. These data eliminate possible nonlinear refractive contributions to the observed OL effect. On the basis of the data fitting to the results of the Z-scan experiment, we conclude that the optical limiting capability of the clusters stems from a nonlinear absorptive process.

To verify this conclusion further, we conducted an excite-probe experiment where the same frequency-doubled Nd:YAG laser was employed to provide an excitation pulse, and a continuous-wave light beam from either an argon ion laser (515 nm) or a He-Ne laser (633 nm) was used to probe changes of light absorption of the sample as a function of excitation fluence. Results of the excite-probe measurements confirm that the clusters respond to the excitation pulse with sudden increases of absorption

(6) Anal. (calcd) for compound I (C₄₈H₁₀₈Ag₃BrI₃MoN₃S₄): Mo, 5.41 (5.53); Ag, 18.60 (18.67); I, 21.89 (21.95); Br, 4.59 (4.61); S, 7.47 (7.41); N, 2.47 (2.42); C, 33.10 (33.18); H, 6.19 (6.22).

(7) The laser beam was focused onto the sample with a 25 cm focal length focusing mirror which provided a near-Gaussian spatial intensity profile with a spot radius of 35 μm (half-width at 1/e² maximum).

(8) We define the limiting threshold as the incident fluence at which the actual transmittance falls to 50% of the corresponding linear transmittance.

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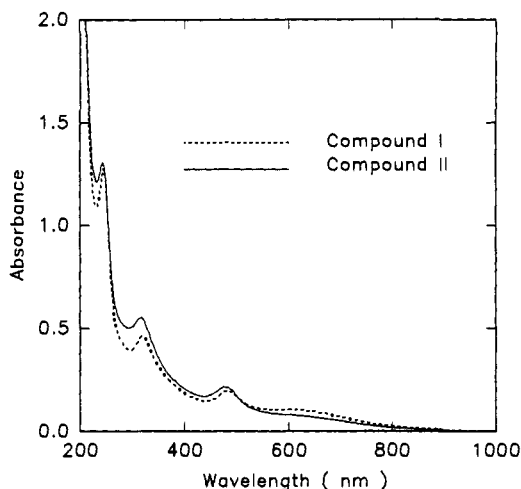


Figure 1. Absorption spectra of compounds I and II in acetonitrile solution with a 1-mm optical length: compound I at 1.0×10^{-4} M; compound II at 4.4×10^{-4} M.

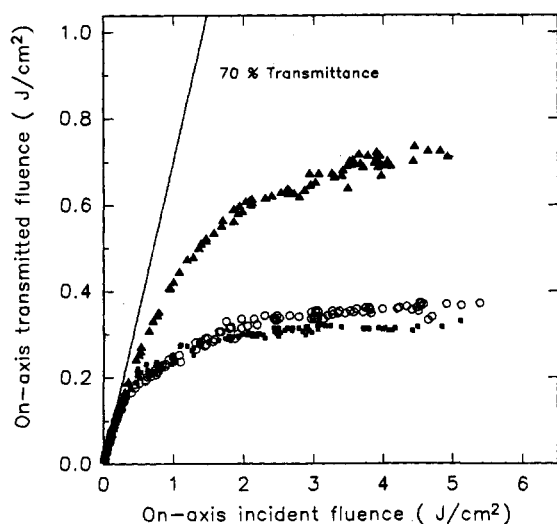


Figure 2. Optical limiting responses to 7-ns, 532-nm laser pulses, of compounds I and II in acetonitrile and C_{60} in toluene: ■, I; ○, II; ▲, C_{60} . Solutions with 70% transmittance at 532 nm correspond to 1.4×10^{-4} M I, 5.6×10^{-4} M II, or 1.9×10^{-3} M C_{60} , respectively.

at 515 and 633 nm (a process that turns on within nanoseconds¹⁰ and off with $\tau \sim 1$ ms), a typical behavior of excited-state absorption. When the intense excitation pulse arrives, a large portion of the clusters are lifted to their initial electronic excited state. The clusters in the initial excited states compete with those in the ground state for photons to transit to higher excited states. Results of both the optical limiting and the excite-probe experiments show that the clusters $(n\text{-Bu}_4\text{N})_3[\text{MoAg}_3\text{BrX}_3\text{S}_4]$ exhibit the rare optical property that the light absorption cross sections of their initial excited states (σ_{ee} , initial excited state \rightarrow higher excited states) are larger than the corresponding absorption cross sections of their ground states (σ_{ge} , ground state \rightarrow initial excited state), at least in the 515–633-nm region. This property is demonstrated as an instantaneous increase of absorption at 515 or 633 nm upon excitation at 532 nm in the excite-probe experiment. It is also manifested as an increase of absorptivity at 532 nm as the incident energy of the 532-nm pulses (532-nm-light self-induced increase of light absorption) in the optical limiting experiment.

So far as the OL effect is concerned, compounds I and II constitute an instructive comparison. Replacement of only the

(10) The fast increases (on a nanosecond scale) of the light absorption of the clusters were also confirmed by the temporal profile analysis of the transmitted laser pulses. The later portion of a 7-ns incident pulse is much less transmitted as compared to the early portion of the same pulse, consistent with the notion that the excited-state absorption is switched on within nanoseconds.

terminal chlorine ligands by iodine has an appreciable but limited effect on the saturated transmittance level (Figure 2). The comparison can be further extended to include the compounds $(n\text{-Bu}_4\text{N})_3[\text{WCu}_3\text{Br}_4\text{S}_4]$ (III) and $(n\text{-Bu}_4\text{N})_3[\text{WAg}_3\text{Br}_4\text{S}_4]$ (IV), also studied in our laboratory, where a significant improvement of optical limiting capability is seen when Cu skeleton atoms are replaced by heavier Ag atoms.¹¹ The general trend of enhancement of the OL effect is seen with the incorporation of more heavy atoms. Substitution at skeleton positions exhibits stronger influence on OL capability than substitution at terminal positions.

The idea behind our choice of exploring transition metal chalcogenide clusters, as represented by $(n\text{-Bu}_4\text{N})_3[\text{MoAg}_3\text{BrX}_3\text{S}_4]$ (X = Cl and I), for OL applications is based on a number of important properties that distinguish these clusters from C_{60} , organic molecules, and other nonlinear optical materials and make them very promising candidates for OL applications. (1) The constituent elements of these transition metal clusters are generally heavy. This is advantageous because incorporation of heavy atoms introduces many more sublevels into the energy hierarchy as compared to carbon-based molecules with the same number of skeleton atoms, which permits more spin-allowed excited state-excited state transitions to take place and hence larger σ_{ee} 's. (2) The heavy atoms in the clusters can also facilitate intersystem crossing via spin-orbital coupling. A large spin-orbital coupling constant can be very beneficial if the desired nonlinear absorptions (large σ_{ee} 's) are associated with the $T_1 \rightarrow T_n$ electron transitions as in the cases of C_{60} and phthalocyanine systems.^{3,4} (3) Both the skeleton and terminal elements can be altered to meet the requirements of orbital symmetry and energies to introduce or remove resonance enhancement and optimize the desired nonlinear optical properties. (4) Compared to those clusters held together by pure M–M bonds, the transition metal chalcogenide clusters also have the advantage that their constituent metals are all triply (μ_3) bridged by chalcogenides. The μ_3 -bridging mode provides the cage skeletons with great stability especially toward the light-induced fragmentation of the clusters caused by the electron transition between the skeleton bonding and antibonding orbitals.

The direct implementation of the solutions of the two compounds as optical limiters is frustrated by their low optical damage thresholds. Photodegradation becomes detectable when the incident light fluence exceeds 3 J/cm^2 and the pulse repetition rate exceeds 1 Hz. Transmittance increases and data become scattered if both a higher fluence of incident light and a shorter pulse interval are employed. It is clear that the observed OL effect is not attributable to the buildup of photodegradation products. This is because the photodegradation products have much weaker OL capabilities (if any) than their parent clusters. If short pulse intervals are used, the transmittance data points become closer to the 70% straight line in Figure 2. In view of the fact that the skeletons of the cubane-like clusters are relatively stable, it seems likely that the photodegradation reflects processes associated with terminal ligand substitution by solvent. It is possible to eliminate this weak point by incorporating the clusters into polymers where solvent molecules no longer exist. Further work is under way to verify this hypothesis.

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Supplementary Material Available: Elemental analysis of II, setups for optical limiting, z -scan, and excite-probe experiments, and time-resolved response of clusters to an excitation pulse (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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