Synthesis and Optical Limiting Capability of Cubane-like Mixed Metal Clusters (n-Bu4N)2[MoAg3Br1X3S4] (X = Cl and I)  

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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. 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 under a strong optical field owing to the depletion of the electronic states of the limiting materials. As part of our search for optical limiting capability of the clusters, we have surveyed the nonlinear optical property. 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. Fullerene C60 and metallophthalocyanine complexes received tremendous attention recently because of their optical limiting capability. As part of our search for optical limiters, 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)2[MoAg3Br1S4] (I) and (n-Bu4N)2[MoAg3Br1Cl3S4] (II).  

![Diagram of clusters I and II](image)

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

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6 Anal. (calcd) for compound I (C9H24Ag3Br1MoNS4): 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 1/2 maximum).  
8 We define the limiting threshold as the incident fluence at which twice of the corresponding linear transmittance falls to 50%.

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with the notion that the excited-state absorption is switched on within less transmitted laser pulses. The later portion of a 7-11s incident pulse is much the clusters were also confirmed with a 1-mm optical length compound I at 1.0 \times 10^{-4} M.

So far as the OL effect is concerned, compounds I and II constitute an instructive comparison. Replacement of only the 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-Bu4N)3[WCuBr3S4] (III) and (n-Bu4N)3[WAg3Br6S4] (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-Bu4N)3[MoAg3Br6S4] (X = Cl and I), for OL applications is based on a number of important properties that distinguish these clusters from C60, 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 \( \sigma_{el} \)‘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 \( \sigma_{el} \)’s) are associated with the \( T_1 \rightarrow T_n \) electron transitions as in the cases of C60 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 bridged by chalcogenides. The \( \mu_3 \)-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/cm² 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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(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.