Large Nanosecond and Picosecond Optical Limiting Response of Novel Transition-Metal Planar Chalcogen Cluster Complex $[WS_4Cu_4I_2(py)_6]$

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Large nanosecond and picosecond optical limiting responses of novel planar transition-metal chalcogen cluster complex $[WS_4Cu_4I_2(py)_6]$ were studied by using a double frequency nanosecond/picosecond Nd:YAG pulse laser system at wavelength of 532 nm. The experimental results demonstrated that the optical limiting behaviors of this metal cluster are better than fullerene-C_{60} under both nanosecond and picosecond laser pulse excitation.

Optical limiting (OL) is an active research area of nonlinear photonic techniques because of their potential applications in the protection of optical sensors from high-intensity laser pulses. Optical limiting based on nonlinear absorption had been reported in 1969.[1] Recently, the ns optical limiting characteristic of metal clusters has attracted much attention.[2–6] The large nanosecond optical limiting response was observed in various kind of structure of clusters. The ideal "optical limiters" should have rapid response (picosecond pulses for some applications). Picosecond-optical limiting properties of fullerene and its derivatives, King's complex, and square-planar complex have been reported.[7–10] Commonly, fullerene is the basic optical limiting material. Optical limiting properties of any other materials stronger than those of fullerene under both picosecond and nanosecond pulses excitation haven't been reported yet. For square-planar complex, only the nanosecond optical limiting threshold of square-planar complex is comparable to that of fullerene-C_{60}. In this paper, we report large optical limiting response of both nanosecond and picosecond pulses.

The novel complex $[WS_4Cu_4I_2(py)_6]$ (py=C_5H_5N) was synthesized through reacting $(NH_4)_2WS_4$, CuI with py. The electronic spectrum is shown in Figure 1. The linear absorption of compounds in DMF solution is weak in the visible and near-IR

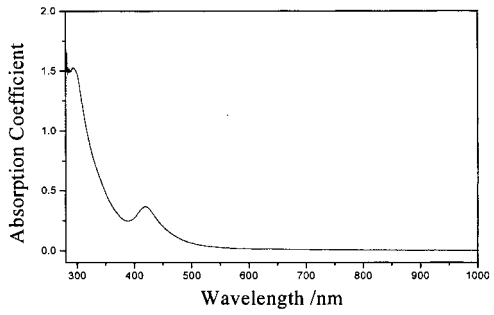

Figure 1. Ground state absorption spectra of metal cluster $[WS_4Cu_4I_2(py)_6]$ in DMF solution with a non-saturation concentrations of 10^{-4}M in a 1-cm-think glass cell.

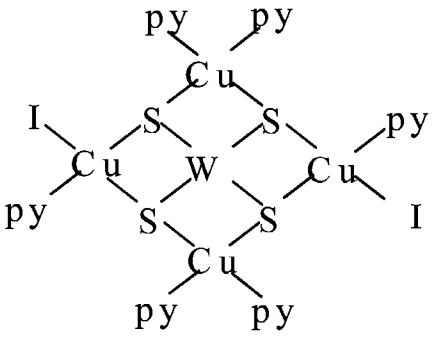

Figure 2. The molecular scheme of cluster $[WS_4Cu_4I_2(py)_6]$.

regions. Figure 2 shows the molecular scheme of metal cluster $[WS_4Cu_4I_2(py)_6]$ which has a pentanuclear 'open' planar structure. The metal cluster $[WS_4Cu_4I_2(py)_6]$ is dissolved in DMF and placed in a 0.5-cm-thick glass cell for optical limiting experiment. The laser pulse was from a Continuum Np70 ns/ps Nd:YAG laser system, whose frequency was doubled to 532 nm with a pulse width of 40 ps and 10 ns, respectively. The laser pulse was focused into a cell by a f = 30 cm lens. The laser beam was divided into two beams. One was used to monitor the incident laser energy; the other was focused into the sample cell. The input and the output energies of both beams were measured with an energy meter (Laser Precision Corporation Rjp-735), while the incident energies were varied with a Newport Com. attenuator. The fullerene has good optical limiting characteristic for both ns and ps laser pulse.[10] We measured the picosecond optical limiting behavior curve of the cluster and fullerene with the linear transmittances of 78% and 76%, respectively. With the same experimental setup nanosecond optical limiting performances of the cluster and fullerene solution were studied. The linear transmittances of the samples we used are 70% for both the cluster and fullerene solution. The nanosecond and picosecond optical limiting experimental results of the cluster $[WS_4Cu_4I_2(py)_6]$ are shown in Figure 3 and Figure 4 (where open square and triangle correspond to the fullerene and cluster, respectively.).

The results of the optical limiting experiment for planar transition-metal chalcogen cluster $[WS_4Cu_4I_2(py)_6]$ and fullerene clearly show that the metal cluster $[WS_4Cu_4I_2(py)_6]$ has a lower limiting clamped output than fullerene-C_{60} for both nanosecond and picosecond pulses. Nonlinearities of the metal cluster $[WS_4Cu_4I_2(py)_6]$ were studied by the following pump-probe technique.

A frequency-doubled Nd:YAG pulse laser with a 532 nm wavelength and 10 ns pulse width was used as a pump beam

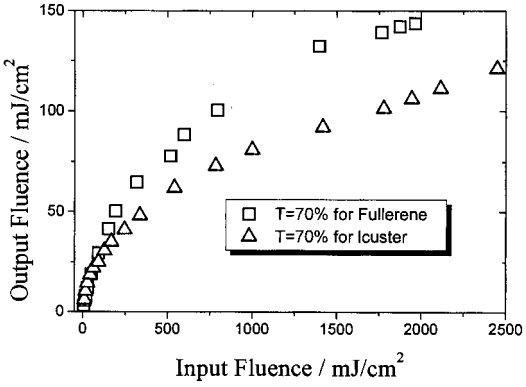

Figure 3. Optical limiting of fullerene-C_{60} and metal cluster $[WS_4Cu_4I_2(py)_6]$ for nanosecond pulse laser.

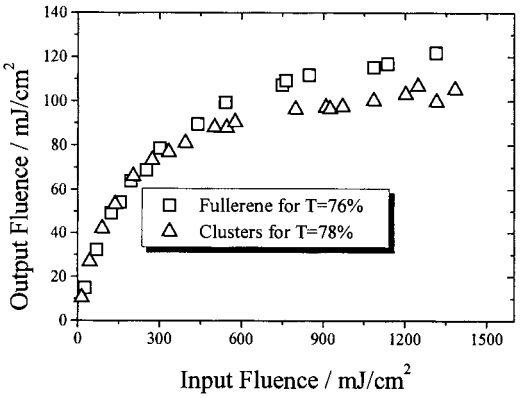

Figure 4. Optical limiting of fullerene-C_{60} and metal cluster $[WS_4Cu_4I_2(py)_6]$ for picosecond pulse laser.

(pulse energy of 300 μJ). A CW He–Ne laser with wavelength of 632.8 nm was used as a probe beam (optical power of 20 mW). Both collinearly passed through a sample in DMF solution with a thickness L = 0.5 cm. The beam passed through a stopping filter at 532 nm, and then went into a photometer. Only the probe beam (632.8 nm) passed through the photometer and went into detector. Probe intensity is measured as a function of time with rapid multiplier phototube connected to a BOXCAR. The change of the probe beam intensity versus the delay time was recorded after the pump beam. Experimental curve is shown in Figure 5. The optical nonlinearities of the cluster, fullerene-C_{60} were studied by using the same experiment setup, respectively. Fullerene-C_{60} exhibits an excited-state nonlinearity. Figure 5 shows a comparison of pump-probe results for the metal cluster $[WS_4Cu_4I_2(py)_6]$, and fullerene-C_{60}, respectively. Rapid decreasing of the transmittances of the cluster and fullerene-C_{60} indicates that the cluster $[WS_4Cu_4I_2(py)_6]$ has rapid optical response, which is similar to fullerene-C_{60}. We concluded that the origins of the nonlinearity of the cluster are similar to fullerene-C_{60}. Its nonlinearity mainly comes from excited state absorption. Both the cluster and the fullerene have high triplet excited-state absorption in nanosecond pulse laser. But in picosecond pulse laser, the optical limiting behavior is caused by singglet excited-state absorption, the absorption of triplet excited-state absorption can be

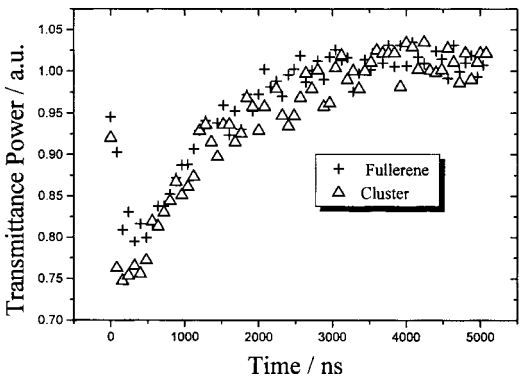

Figure 5. Pump-Probe experimental results, the cross and triangle are correspond to experimental results of the fullerener and cluster, respectively.

neglected.[11] Their picosecond optical limiting behavior is caused by singlet and excited-state absorption.

In summary, we report the large optical limiting properties of novel metal cluster $[WS_4Cu_4I_2(py)_6]$ by using both nanosecond and picosecond laser pulse. Under our experimental conditions, metal cluster $[WS_4Cu_4I_2(py)_6]$ has better optical limiting properties than fullerene-C_{60} for both nanosecond and picosecond laser pulse. The OL performance of the cluster has been demonstrated to be attributed to the excited-state absorption by the pump-probe technique.

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