Large optical limiting properties of the pentanuclear 'open' structural cluster compound $[WS_4Cu_4(SCN)_2(py)_6]$

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Optical limiting properties of a pentanuclear 'open' structural inorganic cluster have been studied with 7 ns laser pulses of 532 nm wavelength; the limiting threshold of the cluster $[WS_4Cu_4(SCN)_2(py)_6]$ is 0.3 J cm^{-2}, which is about five times better than that observed in C_{60}.

Optical limiting materials are substances whose transmission is high when they are illuminated by low-intensity light but low when exposed to intense laser radiation. Because of their potential applications in the protection of optical sensors from high-intensity laser beams, the search for better optical limiting materials has become increasingly intensive. The most frequently reported materials are fullerenes (C_{60})[1,2] and phthalocyanine complexes,[3,4] which are generally regarded as the best compounds for optical limiting. Recently, large non-linear optical effects have also been found in inorganic clusters.[5–22] The structures of these clusters vary widely, they include butterfly-shaped clusters,[6] trinuclear linear clusters,[7] nest-shaped clusters,[8–10] 'half-open' cubane-like clusters,[11,12] cubane-like clusters,[13–16] hexagonal prism-shaped clusters,[17,18] twin-nest-shaped clusters[19,20] and twenty-nuclear supracage-shaped cluster.[21]

A good optical-limiting material should possess strong limiting responses to ns laser pulses in the visible and near-IR spectral regions. This is because the most likely encountered powerful light sources are Q-switched Nd : YAG lasers. In this regard, the optical limiting properties of cubane-like clusters and hexagonal prism-shaped clusters have been found to be the best amongst all the clusters studied, with limiting threshold in the order of *ca.* 0.1 J cm^{-2}.[13–15,17] This is comparable to those of phthalocyanine derivatives and better than that of C_{60}.[2,3] However, such performances were achieved under the single-shot condition; and when the pulse repetition rate exceeded 1 Hz, photodegradation occurred.[13] To overcome this problem, we have investigated different structural types of inorganic clusters. Here, we report the observation of superior limiting behavior in a pentanuclear 'open' structural cluster $[WS_4Cu_4(SCN)_2(py)_6]$ with a pulse repetition rate of up to 10 Hz.

The preparation of the cluster $[WS_4Cu_4(SCN)_2(py)_6]$ was reported elsewhere.[23,24] We obtained the cluster $[WS_4Cu_4(SCN)_2(py)_6]$ by the reaction of $[NH_4]_2WS_4$, CuSCN and KSCN with py. The structure was identified from IR spectra, elemental analysis and unit cell parameters.† The cluster has an 'open' structure with five metal atoms (one W and four Cu atoms) in the same plane. Four S–S edges of the tetrahedral WS_4^{2-} core are coordinated by four Cu atoms, giving a WS_4Cu_4 aggregate of approximate D_{2h} symmetry, as shown in the inset of Fig. 1. Its electronic spectrum in Fig. 1 illustrates 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 optical limiting materials.

Fig. 2 displays measurements of optical limiting effects in a DMF solution of $[WS_4Cu_4(SCN)_2(py)_6]$‡ with 532 nm laser pulses of 7 ns duration. The transmittance defined here is the ratio of the transmitted pulse energy to the incident pulse energy at 532 nm. It is obvious that the solution transmittance is independent of the incident fluence at < 0.1 J cm^{-2}. (The linear transmittance is 63%, which includes the Fresnel reflection losses of the two surfaces of the cell. If the surface losses are excluded, the transmittance of the solution is 69%.) When the

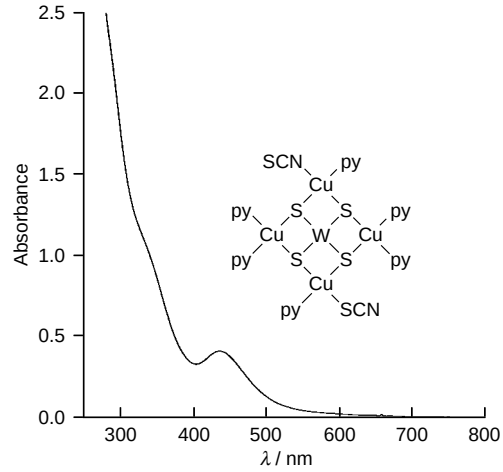

Fig. 1 Electronic spectrum of $[WS_4Cu_4(SCN)_2(py)_6]$ in DMF (1.3×10^{-3} M). Optical path: 1 mm. The inset shows the structure of $[WS_4Cu_4(SCN)_2(py)_6]$.

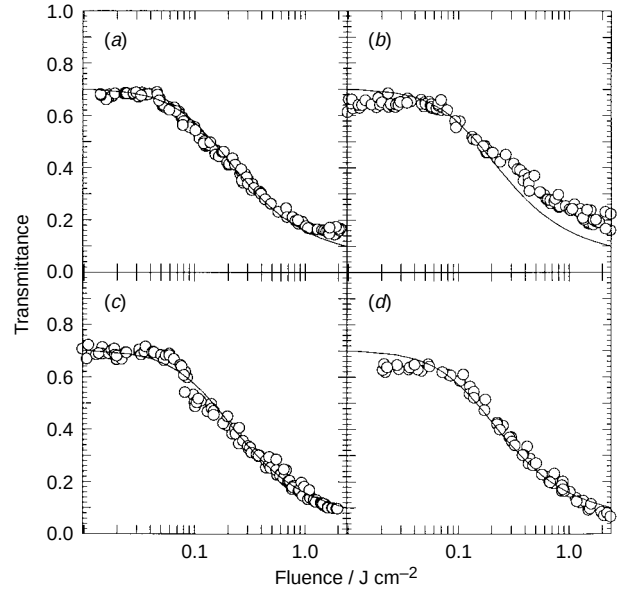

Fig. 2 Energy dependent transmittance of a $[WS_4Cu_4(SCN)_2(py)_6]$ DMF solution (1.1×10^{-3} M). Optical path: 1 mm; laser wavelength: 532 nm; pulse duration: 7 ns; and repetition rates: (*a*) 10, (*b*) 5, (*c*) 1 Hz and (*d*) single shots (30 s interval)

Table 1 The limiting thresholds of compounds measured at 532 nm with ns laser pulses

Compound	Solvent	Linear transmission (%)	Limiting threshold/ J cm^{-2}	Ref.
C_{60}	Toluene	62	1.6	2
$[NBu^n_4]_3[WCu_3Br_4S_4]$	MeCN	70	1.1	15
$[NBu^n_4]_3[WAg_3Br_4S_4]$	MeCN	70	0.6	15
$[NBu^n_4]_3[WAg_3BrI_3S_4]$	MeCN	70	0.5	15
$[NBu^n_4]_3[WAg_3BrCl_3S_4]$	MeCN	70	0.6	15
$[WS_4Cu_4(SCN)_2(py)_6]$	DMF	69	0.3	This work
Phthalocyanine derivatives	Toluene	85	≈0.1	3, 4
$[Mo_2Ag_4S_8(PPh_3)_4]$	MeCN	92	≈0.1	17

incident fluence exceeds 0.1 J cm^{-2}, the solution transmittance decreases as the incident fluence is increased, thus exhibiting a typical optical limiting effect. The limiting threshold is defined as the incident fluence at which the solution transmittance falls to 50% of the linear transmittance. From Fig. 2, we determine the limiting threshold of the $[WS_4Cu_4(SCN)_2(py)_6]$ DMF solution to be *ca.* 0.3 J cm^{-2}.

Fig. 2 also displays the optical limiting performance of the cluster measured with the pulse repetition rate ranging from single shots to 10 Hz. Within our experimental errors, no significant difference is found among these measurements, thereby indicating that the photostability of $[WS_4Cu_4(SCN)_2(py)_6]$ is considerably better compared to the cubane-like and hexagonal prism-shaped clusters.[13–15,17]

It is interesting to compare this new cluster with other well known optical limiting materials for 7 ns pulsed radiation of 532 nm wavelength. Table 1 shows the limiting thresholds of the cluster $[WS_4Cu_4(SCN)_2(py)_6]$, cubane-like clusters, hexagonal prism-shaped clusters, C_{60} and phthalocyanine derivatives. It is clear that the limiting performance in the $[WS_4Cu_4(SCN)_2(py)_6]$ DMF solution is five times better than that displayed in C_{60} and three times higher than that in phthalocyanine derivatives. It should be emphasized, however, that the Q absorption band in phthalocyanine derivatives makes them narrow-band limiters, while the spectrum of $[WS_4Cu_4(SCN)_2(py)_6]$ shown in Fig. 1 indicates that the new cluster should be a broad-band limiter.

It should be pointed out that our measurement of the transmitted pulse energy was conducted with a full collection of the transmitted pulse, and no aperture was used. Therefore, the observed optical limiting originates from a non-linear absorptive process. The limiting mechanism in cubane-like clusters has been studied in detail.[15] The initial linear absorption promotes electrons from the ground to an excited singlet state. These excited electrons are transferred to the lowest triplet state mainly by a process of ionization and germinate recombination. If the absorption cross-section of the triplet state is greater than that of the ground state, then reverse saturable absorption occurs, resulting in the optical limiting effect.

We have found that this non-linear process can be approximately expressed by[15]

$$T = \frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{1 + B[1-\exp(-\alpha L)]F_{in}^2}}$$

where T is the transmittance, R is the reflectance of the cell surface, L is the optical path, α is the linear absorption coefficient, F_{in} is the incident fluence, and B is a parameter determined by the product of the lifetime and ionization cross-section of the excited singlet state, the absorption cross-section of the excited triplet state, and the probability of the germinate recombination. The solid curves in Fig. 2 are calculated by this expression with $B = 4.3 \times 10^4$ cm^4 J^{-2}. Nearly perfect fits indicate that the optical limiting in the cluster is caused by the absorption of the excited triplet state whose population is generated mainly by the process of ionization and germinate recombination.

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Notes and References

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† IR spectra: ν(W–S_{br}), 435 cm^{-1}; ν(SCN), 2081 cm^{-1}; ν(py), 1595, 1441, 752, 695 cm^{-1}. Anal. Calc. for $C_{32}H_{30}Cu_4N_8S_6W$: C, 33,22; H, 2.61; Cu, 21.97; N, 9.68; W, 15.9. Found: C, 33.00; H, 2.40; Cu, 21.78; N, 9.80; W, 16.3%. The cluster is orthorhombic, space group *Pbcn* (no. 60) with a = 19.786(2), b = 13.629(2), c = 15.080(2) Å.

‡ The optical limiting effects were observed with 532 nm wavelength laser pulses of 7 nanosecond duration. The laser pulses were produced by a frequency-doubled, Q-switched Nd:YAG laser operated with multiple axial modes. The pulse energy was spatially filtered to be a nearly Gaussian profiles and then was split into two parts: one was used as a reference for the incident energy and the other was focused onto the sample. The sample was a solution of $[WS_4Cu_4(SCN)_2(py)_6]$ dissolved in DMF (1.1×10^{-3} M) and contained in a 1 mm thick quartz cell. Both incident and transmitted pulse energy were measured with two pyroelectric probes (RjP-735, Laser Precision), simultaneously. The measurements were conducted over *ca.* 8 h.

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