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A new approach to superior optical limiting materials—planar 'open' heterothiometallic clusters†

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A new approach to superior optical limiting materials, utilizing planar 'open' skeleton heterothiometallic clusters, is reported by incorporating heavy atoms and altering cluster skeletons and is found to decrease the limiting thresholds to as low as 0.07 J cm^{-2}, among the best for OL materials.

Rapid recent developments of both high-power frequency-tunable lasers and optical signal detection techniques have led to increasing demands for broadband nonlinear optical materials.[1] These materials have been designed either to protect sensitive optical sensors such as the human eye from intense optical radiation[2] or to be used in optical computers and broadband communications for data acquisition, storage, transmission, and processing.[1,3] Over the past decades, research in the optical limiting (OL) materials has been largely focused on inorganic semiconductors, conjugated polymers, organic molecules, and organometallic compounds.[1–6] The general relationships between molecular structures and OL performance in various existing OL materials are, however, yet to be well established, and this has presented a difficult task in the effort to improve the OL properties through molecular structure design.[5d]

We have recently developed Mo(W)/S/Cu(Ag) heterothiometallic clusters as a new class of OL materials.[7] These clusters combine the advantages of inorganic heavy atoms, organic ligands, and versatile cluster structures. Studies have been conducted on the relationship between the structures and OL properties of these clusters with various skeleton shapes such as butterfly, nest, half-open cubane, trinuclear linear, cubane, hexagonal-prismatic, twin-nest, twenty-nuclear supercage and cluster polymer.[7,8] Unlike some traditional OL materials, the skeletons and constituent elements in these clusters were found to have considerable influence on their OL performance. Changes in cluster compositions (skeletal or terminal elements), such as incorporation of heavy atoms, generally enhance the OL performance of these clusters. Moreover, cubane-shaped and hexagonal-prismatic clusters show large OL effects.[7a,c] The OL effect of these two kinds of clusters are comparable to those of fullerene C_{60} and phthalocyanine derivatives, respectively, which are generally regarded to be among the best OL materials.[1,5,6] The enhancement in the OL properties of the hexagonal-prismatic clusters over the cubane-shaped clusters suggested that modification of cluster structures may further enhance their OL properties.

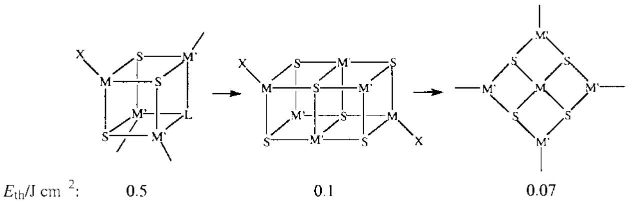
With these in mind, we have thus studied the OL properties of a series of planar clusters $[MS_4Cu_4X_2(py)_6]$ (X = I, M = W, **1**, Mo, **2**; X = Br, M = W, **3**, Mo, **4**; X = Cl, M = W, **5**, Mo, **6**) and $(Et_4N)_2[MS_4Cu_4(NCS)_4(2\text{-pic})_4]$ (M = W, **7**; Mo, **8**). The clusters **1–8** were all synthesized in our laboratories;[7b,8a] **1–6** were prepared from the reactions of $(NH_4)_2MS_4$, CuX and py† while **7** and **8** were obtained from the reactions of $(Et_4N)_2MS_4$ and CuSCN with 2-pic.[8a] The structures of **1**, **3** and **4** were determined by IR, elemental analyses and X-ray diffraction.‡

These clusters all have a pentanuclear planar 'open' structure with a $[MS_4Cu_4]$ aggregate of approximate D_{2d} symmetry (Scheme 2). Their electronic spectra show a relatively weak linear absorption in the VIS–NIR region.† The OL effects of clusters **1–8** in DMF solutions were measured with linear, polarized 8 ns duration laser pulses at 532 nm generated from a Q-switched frequency-doubled Nd:YAG laser.

The NLO process in these clusters can be approximately represented by eqn. (1)[6c]

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -\left[\alpha_0 + \left\{\left(1 + K_\alpha \frac{I}{I_s}\right)\sigma_g N \middle/ \left(1 + \frac{I}{I_s}\right)\right\}\right] I \tag{1}$$

where α_0 is the linear absorption coefficient of the solvent, σ_g is the absorption cross-section of the ground-state molecular solution, N is the concentration of the cluster sample solution, $I_s = h\gamma/\sigma_g\tau_{eg}$ is the saturable intensity, with τ_{eg} being the lifetime of the excited-state, and $K_\alpha = \sigma_e/\sigma_g$ is the ratio between the excited-state absorption cross-section and the ground-state absorption cross-section. The limiting thresholds of these clusters, which is defined here as the incident fluence at which the transmittance falls to 50% of the linear transmittance, were found to be 0.07, 0.08, 0.08, 0.10, 0.10 and 0.15 J cm^{-2}, respectively. Representative energy-dependent transmittance data for cluster **1**, shown in Fig. 1, shows a reduction in transmittance at high fluence. The limiting thresholds of **1–5** are comparable to those (*ca.* 0.1 J cm^{-2}) of phthalocyanine derivatives[6a,b] and hexagonal-prismatic $Mo_2Ag_4S_8(PPh_3)_4$,[7c] and, to our knowledge, among the lowest reported so far.[9] The limiting thresholds of **7** and **8** were found to be 0.3 and 0.5 J cm^{-2}, respectively, and higher than those of the neutral clusters $MS_4Cu_4X_2(py)_6$ (**1–6**) with halide and pyridine ligands.



Scheme 1

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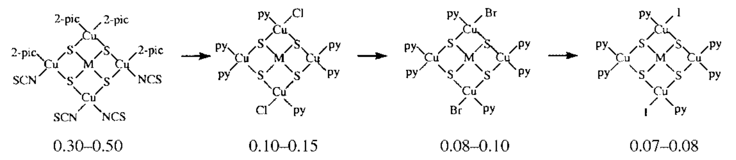
† Electronic supplementary information (ESI) available: 1, Preparation and characterization of the planar 'open' heterothiometallic clusters; 2, molecular structures of clusters; 3, pump–probe experiment setup and results; 4, ground-state absorption spectra of clusters; 5, figures for *Z*-scan experiments under open-aperture configuration of clusters; 6, figures of energy-dependent transmittance of clusters; 7, Table 1: limiting thresholds of compounds. See http://www.rsc.org/suppdata/cc/b1/b100395j/

DOI: 10.1039/b100395j



Scheme 2

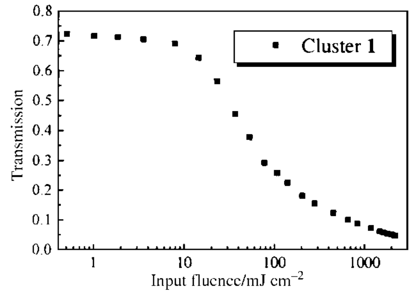


Fig. 1 The energy-dependent transmittance of **1**.

The alteration of the cluster skeleton (cubane-shaped → hexagonal-prismatic → pentanuclear planar) led to significant enhancements in OL properties of these clusters (Scheme 1). In addition, in the pentanuclear planar clusters, the substitution of light elements by heavy elements [Mo by W, and Cl or N (in SCN) by Br or I, respectively] further reduced the limiting thresholds (Scheme 2). The ESI gives a list of the limiting thresholds of these pentanuclear planar W(Mo)/S/Cu heterothiometallic clusters (**1–8**) and other OL materials reported earlier.†

Pump–probe measurements were conducted on clusters **1–8** to further investigate the physical origin of their optical nonlinearities.† A frequency-doubled Nd : YAG pulse laser with a 532 nm wavelength and 8 ns pulse width was used as a pump beam (pulse energy: 300 μJ). A CW He–Ne laser with 632.8 nm wavelength was used as a probe beam (optical power: 20 mW). The change of the probe beam intensity *vs.* the delay time was recorded after the pump beam by using BOXCAR. The optical nonlinearities of the clusters and fullerene C_{60} were studied using the same experimental setup. The pump–probe experimental results indicate that the optical nonlinearity responses of the clusters are similar to that of fullerene C_{60} which exhibits a typically excited-state nonlinearity.[5b] We can therefore reasonably conclude that the OL ability in clusters mainly arises from excited-state absorption processes. In the meantime, the results of *Z*-scan experiments[10] show that clusters **1–8** have remarkable and very strong nonlinear optical absorption effects.† The NLO absorptive experiment under an open-aperture configuration of **1** is depicted in Fig. 2. These NLO absorptive properties meet the essential requirements of ideal OL materials. We speculate that OL properties of **1–4** were enhanced in part by the planar skeleton and the heavy atoms in the clusters. The heavy atom effects of the planar 'open' structures in **1–4** may allow better spin–orbital couplings, and thus intersystem crossing at the excited states.[5d,7a] Large spin–orbital couplings might be beneficial if the nonlinear absorption of desired excited states are associated with the T_1–T_n electronic transitions as found for fullerene C_{60} and phthalocyanine systems.[5,6] In addition, the use of heavy atoms such as W and I may introduce more sublevels into the energy hierarchy, and provide more allowed electronic transitions for the initial excited state in **1–4**. The increased numbers of the allowed electronic transitions probably enhance the nonlinear absorption of the initial excited state to higher excited states. On the other hand, the planar clusters have higher symmetry than the cubane-shaped and hexagonal-prismatic clusters. The higher symmetry, as in the phthalocyanine systems,[5d] may decrease the probability of ground-state electronic transitions and give a smaller absorption cross-section σ_g and a larger σ_e/σ_g (K_α) ratio, which are obtained from the *Z*-scan measurements.

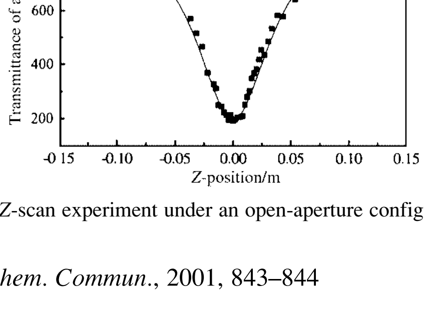


Fig. 2 The *Z*-scan experiment under an open-aperture configuration of **1**.

The current work showed that molecular engineering approaches such as incorporating heavy atoms and altering cluster skeletons are perhaps a promising research direction in search of better OL materials. Studies are under way to further probe the ultrafast OL mechanism of these planar 'open' heterothiometallic clusters **1–8** and to design and prepare better OL materials.

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Notes and references

‡ CCDC 156623–156625. See http://www.rsc.org/suppdata/cc/b1/b100395j/ for crystallographic data in .cif or other electronic format.

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