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Facile Syntheses and Tunable Non-Linear Optical Properties of Heterothiometallic Clusters with $[MS_4Ag_2]$ Units (M = Mo, W)

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Heterothiometallic clusters are of significant interest for their intriguing structures and topologies,[1–6] as well as their potential applications as non-linear optical (NLO) materials[7] and as the active sites of various metalloenzymes and catalytic reactions.[1] However, a dearth of facile preparative routes has proven a major impediment to the design and synthesis of these functionalised molecular materials.[3] The crystal engineering of M/S/Ag clusters[5,6] (M = Mo, W), in particular, has proven significantly more challenging for both control of complexity and diversity of structures than that of the Cu-containing counterparts.[2–4,7] Most of the known 1D polymeric M/S/Ag clusters have been synthesised by following a single protocol, namely, the reaction of $[NH_4]_2[MS_4]$ with $AgNO_3$ (or Ag_2S) and $Ln(NO_3)_3$.[6] This methodology is not broadly applicable because it has several clear disadvantages: 1) $AgNO_3$ reacts readily with $[MS_4]^{2-}$, resulting in a Ag_2S precipitate that is very difficult to react with further $[MS_4]^{2-}$ moieties; 2) only S atoms from $[MS_4]^{2-}$ moieties serve as the bridge to build M/S/Ag 1D chain clusters—no other linking atoms or units participate; 3) the solvent-coordinated rare-earth cations are trivalent and usually induce trivalent repeat units in the anionic chains, reducing the diversity and novelty of polymeric M/S/Ag clusters; 4) the known 1D M/S/Ag clusters synthesised by this method are formed in very low yields, which is a significant disadvantage with respect to applications as precursors for functional materials.[6] Herein, we report a new synthetic method for constructing M/S/Ag clusters in high yields, structural studies that reveal an unusual discrete octanuclear planar "open" square-like skeleton for $[Sr(DMAC)_6]_2[M_4S_{16}Ag_4]$ (M = Mo **1**, W **2**; DMAC = *N*,*N*′-dimethylacetylamide) and a novel 1D double-chain architecture for $\{[Sr(DMAC)_6][W_2S_8Ag_4I_2]\}_n$ (**3**), NLO studies that demonstrate strong third-order non-linear refraction, absorption and a large optical limiting (OL) capability, tuning of non-linearity by conceptual replacement of Mo by W, and time-dependent density functional theory (TD-DFT) studies that provide insight into the electronic transitions and spectral characterisation of these functionalised NLO molecular materials.

In our new procedure, Sr^{2+} cations and AgI take the roles of the directing cations and Ag^+ source, respectively, for synthesising M/S/Ag clusters. In comparison with Ag_2S and $AgNO_3$,[6] AgI can readily coordinate with $[MS_4]^{2-}$ moieties without producing the black Ag_2S precipitate, and thereby greatly increase the yields of the M/S/Ag clusters (75, 78 and 71% for **1**, **2** and **3**, respectively). At the same time, high-quality crystals of the M/S/Ag clusters can be obtained when the Ag_2S precipitate is absent during crystallisation. In addition, there is a strong affinity between the I^- and Ag^+ ions, and so I^- anions can act as other possible linking units, in addition to the S bridging ligands, resulting in a greater likelihood of skeletal novelty and diversity.

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Sr^{2+} is oxophilic; rather than combine with the cluster anions containing metallic M (Mo, W), Ag and non-metallic S atoms, it is coordinated by the oxygen atoms of the DMAC molecules (see Figure S2 in the Supporting Information). Nevertheless, the solvent-coordinated $Sr(DMAC)_6^{2+}$ ions certainly influence the assembly of the AgI and $[MS_4]^{2-}$ species in the reactions. When AgI and $[MS_4]^{2-}$ are added in a molar ratio of 1:1, $Sr(DMAC)_6^{2+}$ induces the formation of tetravalent discrete cluster anions with octanuclear planar "open" skeletons. This is in sharp contrast to solvent-coordinated rare-earth trivalent cations, which usually direct for the formation of trivalent 1D anionic single-chains from the same molar ratio of Ag^+ and $[MS_4]^{2-}$,[6a,b] and consistent with the proposition that cations with different valences and dimensions can control the formation of clusters with novel skeletons. Further, if the starting materials AgI and $[WS_4]^{2-}$ are added in a 2:1 molar ratio, the bivalent $Sr(DMAC)_6^{2+}$ tends to induce the formation of the 1D double-chain cluster **3**, in which both I^- and S^{2-} anions are acting as bridging units, and in which the highest Ag/W ratio thus far (2:1) for polymeric M/S/Ag clusters has been achieved.[2a,5a,6] This facile synthetic approach should be broadly applicable for the construction of new M/S/Ag clusters with unique structures and in high yields.

The structures of **1** and **2** are isomorphous (Figure 1 and Figure S1 in the Supporting Information); they are the first two discrete, heterothiometallic M/S/M′ (M = Mo, W; M′ = Cu, Ag, Au) clusters with metallic cations (see Figure S2 in the Supporting Information), and are the first examples of discrete M/S/Ag clusters with S atoms from $[MS_4]^{2-}$ units as the sole bridging units.[2–6] The anionic cluster skeleton of **1** exhibits an unusual octanuclear $[Mo_4S_{16}Ag_4]^{4-}$ aggregate with C_2 symmetry; it can be regarded as four butterfly-shaped $[MoS_4Ag_2]$ species connected by sharing four Ag corners. The eight metal atoms are nearly coplanar; the angle between metallic plane 1 (Mo1, Mo2, Mo1a, Mo2a) and metallic plane 2 (Ag1, Ag2, Ag1a, Ag2a) is 4.907(1)°. The configuration of the eight metal atoms is approximately square; each side of the square containing one Ag atom and two neighbouring Mo atoms is nearly linear [168.83(3)–174.69(3)°], while the angles about the Mo atoms linking two Ag atoms vary from 83.22(4) to 95.99(3)°, affording a $[Mo_4S_{16}Ag_4]^{4-}$ aggregate with a novel octanuclear planar "open" square-like structure. In this approximately square structure, the four Mo atoms lie at the corners and each of them has the same tetrahedral coordination environment formed by one terminal S, two μ_2-S and one μ_3-S atoms; every Ag atom, lying in the midpoint of each edge, is coordinated by two μ_2-S and two μ_3-S atoms to give a distorted tetrahedral geometry. Interestingly, the four μ_3-S atoms and four Ag atoms form an eight-membered ring (Figure 1), in which the axial S3···S3a (4.0016(8) Å) and equatorial S5···S5a distances (5.592(1) Å) differ greatly.

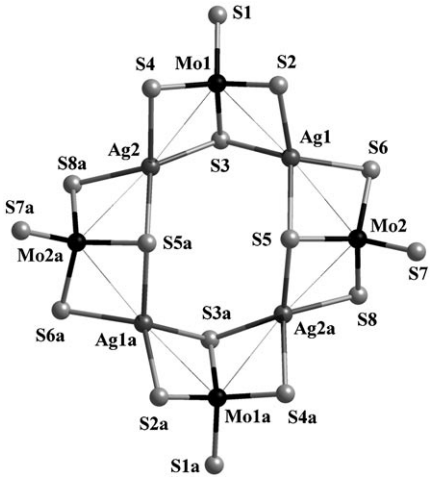

Figure 1. Ball and stick diagram of the anion of **1**.

Cluster **3** crystallizes in the triclinic space group $P\bar{1}$. As shown in Figure 2, the 1D polymeric anion is oriented along the crystallographic *a* axis; it can be viewed as a hexanuclear cyclic cluster fragment $[W_2(\mu_2\text{-}S)_6(\mu_4\text{-}S)_2Ag_4(\mu_2\text{-}I)_2]^{2-}$ (Figure S3 in the Supporting Information) linked by μ_2-S bridges to form a novel double-chain cluster configuration. Within the hexanuclear cluster building blocks, two metallic layers (Ag1···Ag2···W1a and Ag1a···Ag2a···W1) are sandwiched by three non-metallic layers (I1a···S1, S2a···S3a···S3···S2, I1···S1a). Each W atom has a tetrahedral coordination geometry formed by one μ_4-S and three μ_2-S atoms. Ag atoms all adopt four-coordinated modes, two of them being connected by one μ_2-S, one μ_2-I and two μ_4-S atoms, and another two being coordinated by one μ_4-S, one μ_2-I and two μ_2-S atoms. A remarkable feature of **3** is that there are three kinds of bridging units in its skeleton, namely, μ_2-S, μ_4-S and the unique μ_2-I in a molar ratio of 3:1:1; there are no μ_3-S atoms, although these are ubiquitous in M/S/Ag clusters.[2a,5,6] The μ_2-I bridge coordinates Ag atoms from two neighbouring $[WS_4Ag_2]$ species. The unique μ_2-I bridge has not, to the best of our knowledge, been seen previously in polymeric M/S/Ag clusters, which are bridged by S atoms only.[2a,5a,6] The 1D double-chain cluster skeleton can therefore be described as butterfly $[WS_4Ag_2]$ species connected in

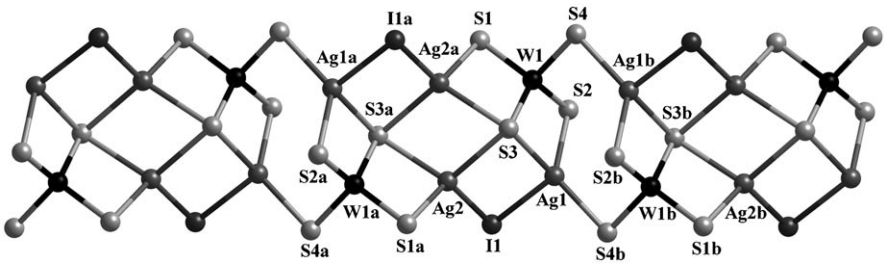

Figure 2. Ball and stick diagram of the anion of **3**.

a back-to-back mode by μ_2-I and μ_4-S bridges and in a face-to-face manner by μ_2-S bridges only. This linking mode for butterfly $[WS_4Ag_2]$ building units provides increased structural complexity for the double-chain skeleton of **3**, for which two serrate chains **A** $[Ag1a\text{-}I1a\text{-}Ag2a\text{-}S1\text{-}W1\text{-}S4]_n$ and **B** $[S4a\text{-}W1a\text{-}S1a\text{-}Ag2\text{-}I1\text{-}Ag1]_n$ are linked to each other by μ_4-S and μ_2-S bridges (Figure 2). The molar ratio of Ag and W atoms in **3** is 2:1, the highest known for polymeric M/S/Ag clusters.[2a,5a,6]

The experimental absorption spectra of **1**–**3** in acetonitrile are displayed in Figure S4 in the Supporting Information. The theoretical absorption spectra obtained from TD-DFT/PCM (polarized continuum model) calculations at the B3LYP/LanL2DZ level are in good agreement with the experimental observations, as displayed in Figure S4 in the Supporting Information. Figure 3 and Figures S5 and S6 in the Supporting Information show the orbitals that are involved in the most important transitions. For example, the absorption bands at 496 and 334 nm for cluster **1** are mainly attributed to transitions of HOMO-3→LUMO+7 and HOMO-13→LUMO, respectively. As shown in Figure 3, the HOMO-3 and HOMO-13 orbitals primarily consist of lone-pair orbitals, *n*, of S atoms, while the LUMO+7 and LUMO are π*-antibonding orbitals that are mainly composed of 4d orbitals of Mo atoms and lone-pair orbitals of S atoms. Similar transitions are found in clusters **2** and **3** (Figures S5 and S6 in the Supporting Information). It can therefore be concluded that the dipole-allowed vertical excitation energies of clusters **1**–**3** are mainly ascribed to transitions from lone-pair orbitals, *n*, of S or I atoms to π* orbitals dominated by the 4d orbital of Mo atoms (or 5d orbital of W atoms), respectively.

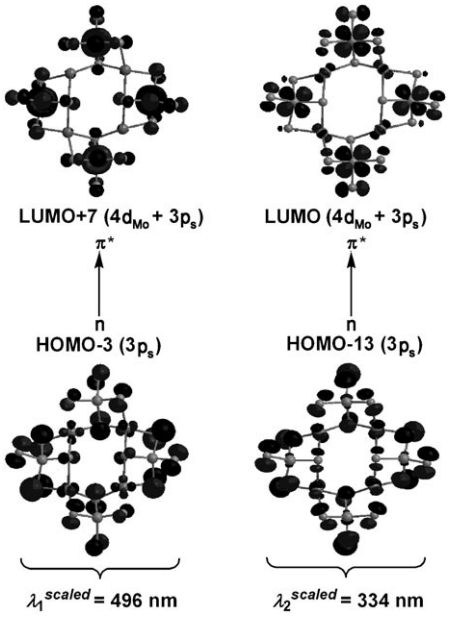

Figure 3. Assignment of the absorption signals for **1**. The orbitals are obtained by using the PCM method at the B3LYP/LanL2DZ level.

The third-order NLO properties of **1**–**3** in solutions of DMAC were investigated with linearly polarised 8 ns pulses at 532 nm generated from a *Q*-switched frequency-doubled Nd:YAG laser; typical results from the *Z*-scan experiments[8] are displayed in Figure 4 and Figures S7 and S8 in the Supporting Information. The NLO refractive indices (n_2) were calculated to be -1.01×10^{-10}, 1.69×10^{-11} and 7.30×10^{-12} esu for **1**–**3**, respectively. The two isomorphous clusters **1** and **2** exhibit diametrically opposed non-linear refractive properties, with **1** showing self-defocusing (SDF) performance and **2** demonstrating a self-focusing (SF) effect at this wavelength. Such a sign alteration of non-linear refraction on isomorphous clusters has been found only twice previously: in M/S/Cu heterobimetallic clusters with neutral pyridine-containing cubane-like or nest-shape skeletons.[9] This is the first time a sign switch from SDF to SF has been seen upon replacement of the central metal atoms (from Mo to W) in M/S/Ag heterobimetallic clusters, and therefore the first time this method of tuning the non-linear refractive performance has been demonstrated. It is significant that **1** is strongly absorbing at 532 nm, in contrast to **2**, which is essentially transparent at this wavelength; strong differences in linear optical absorption can be accompanied by significant differences in non-linear absorption and sizeable variation in the non-linear refraction. The key linear optical transition has been shown to have substantial Group 6 metal

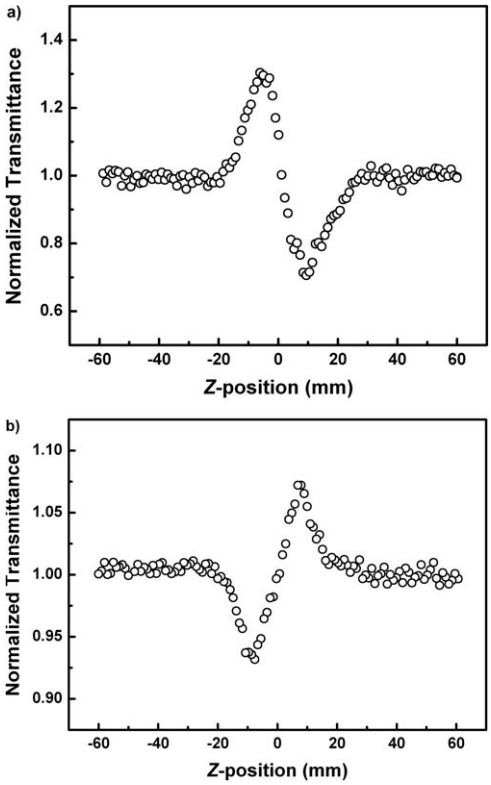

Figure 4. *Z*-scan data collected at 532 nm under the closed-aperture configuration for **1** (a) and **2** (b) in a 1.0×10^{-4} mol dm^{-3} solution of DMAC.

character, and so replacing this metal can suffice to switch non-linearity. It is not possible to probe this behaviour any further by computational means—the perturbation theory expression for the second hyperpolarisability contains 48 terms, all related to a product of four transition dipole moment matrix elements (in the numerators) and energy-level transition frequencies (in the denominators)[10]—but it is known that when the optical frequency is close to a single- or two-photon resonance, a few terms dominate the contribution to the second hyperpolarisability; in particular, a single-photon resonance generally gives rise to a negative n_2 value, since a single-photon resonance will cause a partial depletion of the ground state leading to a decrease in the molecular polarisability,[10] an effect we believe we are exploiting here through the metal-variation tuning of the optical absorption band.

The effective third-order susceptibilities $|\chi^{(3)}|$ are 8.10×10^{-12} (**1**), 4.30×10^{-13} (**2**), and 1.67×10^{-12} esu (**3**). The corresponding hyperpolarisabilities $|\gamma|$ (4.01×10^{-29} (**1**), 2.13×10^{-30} (**2**), and 1.64×10^{-30} esu (**3**)) were obtained from $\chi^{(3)}=\gamma NF^4$, in which N is the number density (concentration) of the cluster in the sample solution and $F^4=3.3$ is the local field correction factor. The γ value of **1** is clearly larger than those of many other heterothiometallic clusters with different cluster skeletons (Table S3 in the Supporting Information).[11]

The OL effect of **1** was also investigated with an 8 ns pulsed laser at 532 nm (Figure S9 in the Supporting Information). The limiting threshold, which is defined as the incident fluence at which the actual transmittance falls to 50% of the corresponding linear transmittance, was measured as 0.85 J cm^{-2} for **1**, which is approximately half that of the benchmark OL material C_{60} (1.6 J cm^{-2}).[12] This clearly indicates that cluster **1**, with an unusual octanuclear planar "open" distorted square framework, possesses strong third-order NLO properties and a large OL capability, and that it is a good candidate for optical materials applications.

In summary, a facile synthetic method has been successfully developed to construct two unusual discrete octanuclear planar "open" distorted-square M/S/Ag clusters and a unique 1D double-chain W/S/Ag cluster. In contrast to the previous synthetic protocol, this new approach can lead to the formation of M/S/Ag clusters with novel structures and remarkably enhanced yields. *Z*-scan experiments show that **1** exhibits strong third-order NLO properties and a large OL capability, whereas the isomorphous clusters **1** and **2** reveal differing non-linear refraction behaviour. The dipole-allowed excitations have been shown through TD-DFT/PCM calculations to be dominated by the transition from lone-pair n orbitals to π* orbitals, and with a significant Group 6 metal involvement in the low-energy transition, which is a key contributor to the tuning of the non-linear response. Further studies on the synthesis of new M/S/Ag clusters by this facile method are currently in progress.

Experimental Section

Details of the chemical synthesis, spectroscopic characterisation, structural, theoretical and non-linear optical studies are given in the Supporting Information.

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