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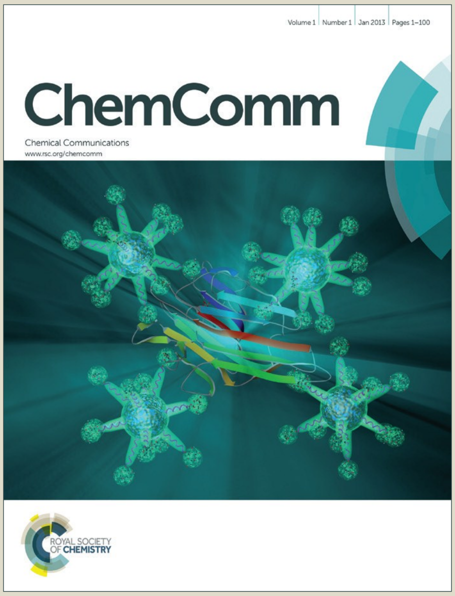

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ammonium-Crown Ether Supramolecular Cation-Templated Assembly of an Unprecedented Heterobicluster-Metal Coordination Polymer with Enhanced NLO Properties

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An ammonium-crown ether host-guest supramolecular cation-templated synthetic methodology has been developed to construct a structurally unprecedented heterobicluster-metal coordination polymer (HCM-CP 1) based on tetranuclear clusters $[WS_4Cu_3]^+$ with different connection environments, pentanuclear clusters $[WS_4Cu_4]^{2+}$, and Cu^+ building metal ions. HCM-CP 1 exhibits enhanced NLO properties, which may be ascribed to the incorporation of diverse building cluster components.

The design and synthesis of the solid-state crystalline compounds known as coordination polymers (CPs) are at the forefront of modern chemistry and materials science.[1,2] A contemporary challenge in this field is to construct multicomponent CPs, for their fascinating architectures as well as their superior functions.[3-5] Most extant multicomponent CPs are constructed from multiple organic linkers with diverse functional groups[3] and/or different kinds of metal ion building units.[4] Because metal clusters show a greater diversity of structures, a wider variety of electron configurations, and a richer array of coordination sites than simple metal ions, cluster-based CPs (C-CPs) have attracted significant recent attention.[6] However, CPs that simultaneously incorporate both cluster and metal building units (cluster-metal CPs)[5a,b] or two types of cluster building units (heterobicluster CPs)[5c,d] are little explored to date, and there are no reports of CPs incorporating two different clusters and metal building units into one framework (heterobicluster-metal CPs — HCM-CPs); to a large extent, this is due to the crystal engineering of heterobicluster-metal CPs facing significantly greater challenges with both phase separation and lack of order than the extant multicomponent CPs experience. With frameworks constructed from a greater variety of building units, HCM-CPs, in particular, should exhibit more diverse and complex architectures than the current multicomponent CPs, and accordingly multifunctional, enhanced, and/or completely novel physical properties can be anticipated for such materials. It is therefore critically important to carefully select appropriate building clusters and to develop effective methods for the construction of HCM-CPs.

Heterothiometallic clusters have been of long-standing interest for their manifold structures[7] and physical properties.[8] CPs fabricated by single heterothiometallic M/S/Cu (M = Mo, W) clusters have been shown to exhibit fascinating architectures and potential applications,[9,10] especially as nonlinear optical (NLO) materials.[10] However, in contrast to discrete M/S/Cu (M = Mo, W) clusters for which the range of possible structures and their corresponding NLO behaviour are well-known,[8a] the crucial structure-property correlations for M/S/Cu cluster-based CPs to ascertain their structural diversity and NLO function are yet to be undertaken. In this work, we report the ammonium-crown ether host-guest supramolecular cation-templated synthesis of an unprecedented anionic W/S/Cu HCM-CP; a structural study revealing a novel tetranodal (3,4,4,6)-connected network and a huge free volume for $^{3}_{\infty}\{\{[(NH_4)\subset(18\text{-crown-6})]_6\cdot 5DMF\cdot 5CH_3CN\cdot H_2O\}\subset\{[WS_4Cu_3(CN)_2]_2[WS_4Cu_3(CN)_2]_2[WS_4Cu_4(CN)_3][Cu(CN)_{1.5}]_2\}\}$ (**1**); and an NLO study that demonstrates a significantly enhanced NLO performance for **1** compared to those of CPs fabricated from single W/S/Cu building clusters.

1 was obtained by the templated assembly of $[NH_4]_2WS_4$ and CuCN in the presence of 18-crown-6 (Scheme 1). X-ray crystallographic analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/m$ and exhibits an unprecedented anionic 3-D heterobicluster-metal framework with a free volume and diverse channels that accommodate ammonium-crown ether host-guest supramolecular cations. A prominent structural feature of the anionic framework of **1** is the presence of tetranuclear clusters ($[WS_4Cu_3]^+$) with two kinds of connection environments, pentanuclear clusters ($[WS_4Cu_4]^{2+}$), and building metal ions (Cu^+), interconnected by ditopic

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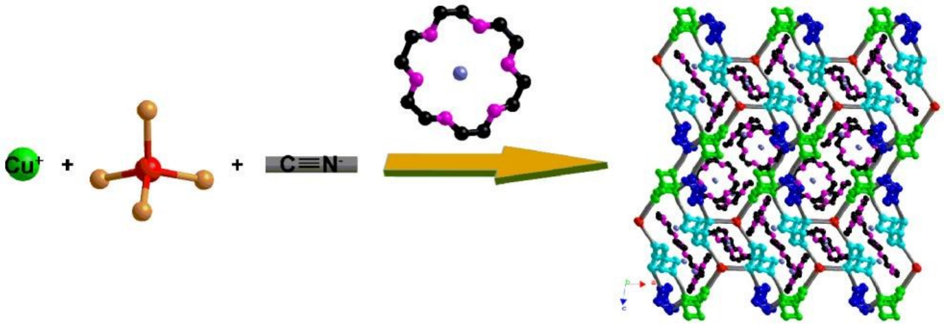
Electronic Supplementary Information (ESI) available: More experimental details; TGA, PXRD and density functional theory studies; Schemes S1-S4; Figures S1-S8; Tables S1-S3. CCDC 967653. See DOI: 10.1039/x0xx00000x

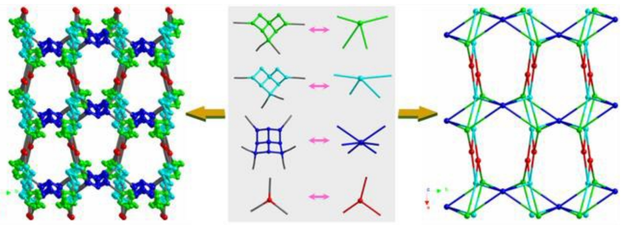


Scheme 1. Synthetic procedure for **1**. Left: the red and orange balls represent the W and S atoms in WS_4^{2-}, respectively; middle: the black, pink and purple balls represent the C and O atoms in 18-crown-6 and the N atom from $[NH_4]^+$, respectively, all H atoms being omitted for clarity; right: W1-containing tetranuclear clusters, W2-containing tetranuclear clusters, pentanuclear clusters, and Cu^+ ions are highlighted in green, cyanine, blue and red, respectively, while the grey sticks represent the CN^- bridge (viewed along the b-axis).

anionic bridges (CN^-) (Scheme 2, Figures S1-S2). The structural study shows that each C_2-symmetric pentanuclear cluster $[WS_4Cu_4]^{2+}$ is linked to four W1-containing tetranuclear clusters and two W2-containing tetranuclear clusters through single CN^- bridges, forming 1-D cluster chains along the *b*-axis; these chains are interlinked by $Cu(CN)_2^-$ bridges, affording 2-D nets that are supported by CN^- pillars to form the 3-D framework (Scheme S1). All tetranuclear clusters $[WS_4Cu_3]^+$ are in four-connected modes, but exhibit two kinds of connection environments; each W1-containing tetranuclear building cluster is linked to one W2-containing tetranuclear building cluster, two pentanuclear building clusters, and one Cu^+ building metal ion, through single cyanide bridges (Figure 1a), whereas each W2-containing tetranuclear building cluster is connected to one W1-containing tetranuclear building cluster, one pentanuclear building cluster and two Cu^+ building metal ions, again through single CN^- bridges (Figure 1b). The six-connected pentanuclear clusters are each linked to four W1-containing and two W2-containing tetranuclear clusters by single cyanide bridges (Figure 1c). The three-connected Cu^+ building metal ion is linked to one W1-containing and two W2-containing tetranuclear clusters, again through single cyanide bridges (Figure 1d). In **1**, there are therefore four kinds of building units: four-connected W1-containing and W2-containing tetranuclear building clusters, six-connected pentanuclear building clusters, and three-connected Cu^+ building metal ions (Scheme 2). **1** simultaneously exhibits both cluster-metal and cluster-cluster connectivity in the one framework (Scheme 2, Figures S1-S2), and is thereby considerably more complex than all previously reported frameworks with single metal-metal, cluster-cluster or cluster-metal connectivity.[2-6,9,10]

From a topological perspective, the four-connected tetranuclear building clusters, six-connected pentanuclear building clusters and three-connected Cu^+ building metal ions can be regarded as 4-, 6- and 3-connected nodes, respectively (Scheme 2). The 4-connected nodes have two kinds of Schläfli symbols: $(3{\cdot}4{\cdot}5{\cdot}6{\cdot}7{\cdot}8)$ for the W1-containing nodes and $(3{\cdot}4{\cdot}6{\cdot}7{\cdot}8^2)$ for the W2-containing nodes. The Schläfli symbols of the 6- and 3-connected nodes are $(3^2{\cdot}4^2{\cdot}5^2{\cdot}8^3{\cdot}9^6)$ and $(4{\cdot}6{\cdot}8)$, respectively. **1** therefore possesses an unprecedented tetranodal (3,4,4,6)-connected network with the Schläfli symbol $(4{\cdot}6{\cdot}8)_2(3{\cdot}4{\cdot}5{\cdot}6{\cdot}7{\cdot}8)_2(3{\cdot}4{\cdot}6{\cdot}7{\cdot}8^2)_2(3^2{\cdot}4^2{\cdot}5^2{\cdot}8^3{\cdot}9^6)$ (Scheme 2).

The non-interpenetrating anionic 3-D framework of **1** is supported solely by single cyanide bridges, resulting in a huge free volume.[10f] PLATON analysis[11] shows that the effective free volume in this 3-D anionic framework is 76.8% of its crystal volume (7635.7 Å^3 of the 9936(3) Å^3 unit cell volume in **1**), a larger free volume than most open zeolites and the highly porous Pt_3O_4 net (67%).[12] Consequently, each unit cell of the 3-D anionic framework can accommodate twelve ammonium-crown ether supramolecular cations $[(NH_4)\subset(18\text{-crown-}6)]^+$ as well as ten DMF, ten CH_3CN and two H_2O solvent molecules. When viewed along the *b*-axis, the packing diagram of **1** reveals channels generated by four-, six- and eight-membered rings with dimensions of 6.591 Å × 8.300 Å, 7.057 Å × 16.388 Å and 11.641 Å × 20.193 Å, respectively, that are occupied by the supramolecular cations (Schemes 1, S2-S4). The four-membered rings are constructed from two W2-containing tetranuclear clusters and two Cu^+ building metal ions, which are in turn linked via bridging pentanuclear clusters (Scheme S2). The six-membered rings are formed from two W1-containing and two W2-containing tetranuclear clusters and two Cu^+ building metal ions, and are connected in the same manner as the four-membered rings, namely, through the bridging pentanuclear clusters (Scheme S3). Interestingly, the eight-membered rings, which are constructed from two penta-



Scheme 2. Formation of the anionic W/S/Cu-containing **1**. Left: 3-D ball-and-stick packing diagram of the anionic heterobicluster-metal CP **1** viewed approximately along the c-axis (the W1-containing tetranuclear clusters, W2-containing tetranuclear clusters, pentanuclear clusters, and Cu^+ ions are highlighted in green, cyanine, blue, and red, respectively; the grey sticks represent the CN^- bridges); middle: building units of the anionic heterobicluster-metal CP **1** and their corresponding topological nodes; right: a topological view of the anionic heterobicluster-metal CP **1**.

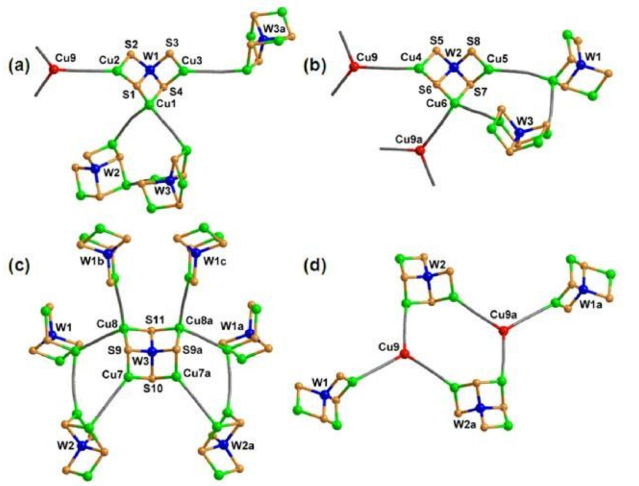


Fig. 1. Connectivity of (a) the W1-containing tetranuclear building cluster, (b) the W2-containing tetranuclear building cluster, (c) the pentanuclear building cluster, and (d) the Cu^+ building metal ion (ball-and-stick representation; the gray sticks represent CN^- bridges, with W blue, S orange, and Cu in the cluster green, and the Cu^+ building metal ions red).

nuclear clusters, two W1-containing tetranuclear clusters, two W2-containing tetranuclear clusters, and two Cu^+ building metal ions, are connected via shared pentanuclear clusters (Scheme S4).

Several methods[13] (solid-state syntheses under mild thermolysis, solvothermal syntheses, preformed cluster syntheses) have been shown to be effective in the construction of Mo(W)/S/Cu cluster-based CPs. However, the reported Mo(W)/S/Cu cluster-based CPs are all fabricated from single Mo(W)/S/Cu cluster building units.[9,10,13] Herein, an ammonium-crown ether supramolecular cation-templated synthesis has been utilized for the first time to construct Mo(W)/S/Cu heterobicluster-based CPs. In the self-assembly reaction of **1**, each NH_4^+ is encapsulated by a 18-crown-6 molecule to form a univalent host-guest supramolecular cation $[(NH_4)\subset(18\text{-crown-}6)]^+$. These crown ether-derived cations direct the assembly of the $[WS_4]^{2-}$ and CuCN moieties, affording an unprecedented 3-D anionic W/S/Cu heterobicluster-metal CP with diverse connectivities and a huge free volume (Scheme 1). We believe the ammonium-crown ether supramolecular cations play a key role in the formation of this heterobicluster-metal CP.

The UV-vis spectrum of **1** shows relatively low linear absorption in the visible and near-IR region (Figure S6); **1** is therefore a candidate for certain NLO applications. To assess this possibility, Z-scan experiments employing linearly polarized 5 ns laser pulses at 532 nm were performed on **1** in an aniline solution.[14] As shown in Figure 2, the absorption increases with increasing intensity of the incident laser, with the light transmittance (T) dropping to 30% at the focal point; the valley/peak pattern of the corrected transmittance curve displays self-focusing behaviour of the propagating light in the cluster sample of **1**. A reasonably good fit between the experimental data and the theoretical curves was achieved, which suggests that the experimentally observed NLO effects have an effective third-order character. The effective nonlinear absorption coefficient α_2 and refractive index n_2 were calculated to be $(98 \pm 8) \times 10^{-11}$ m W^{-1} and $(46 \pm 4) \times 10^{-18}$ m^2 W^{-1}, respectively. From these nonlinear absorptive and refractive values, the concentration-independent hyperpolarizability γ, which reflects integrated third-order NLO effects, was deduced to be $(73 \pm 7) \times 10^{-30}$ esu for **1**, which is larger than those of previously reported CPs at this benchmark wavelength (Table S3). In addition, there was no obvious third-order NLO signal found for either aniline, or 18-crown-6 or $[(NH_4)\subset(18\text{-crown-}6)]NO_3$ aniline solutions (Figures S7-S9) under the same Z-scan experiment conditions as those for **1**, which implies that the hyperpolarizability of **1** stems primarily from its complex anionic architecture. The cyanide-bridged HCM-CP **1** incorporates both pentanuclear clusters $[WS_4Cu_4]^{2+}$ and tetranuclear clusters $[WS_4Cu_3]^+$; we previously reported 3D cyanide-bridged W/S/Cu cluster-based CPs $\{[Et_4N]_2[WS_4Cu_4(CN)_4]\}_n$ (C-CP **2**) and $\{[n\text{-}Bu_4N][WS_4Cu_3(CN)_2]\}_n$ (C-CP **3**), but these were constructed from pentanuclear clusters $[WS_4Cu_4]^{2+}$ (**2**) or tetranuclear clusters $[WS_4Cu_3]^+$ (**3**) only. It is noteworthy that the γ value of **1** is 5.8 and 21.5 times greater than those of **2** and **3** at the benchmark wavelength (Table S3).[10d,e] This result suggests that the NLO performance of HCM-CPs can be significantly enhanced by incorporating diverse building clusters into a framework.

Time-dependent density functional theory (TD-DFT) calculations[15] were performed to provide information about the influence of the planar 'open' cluster/T-shaped cluster/Cu^+ metal ion building units on the electronic structure of the composite **1**. A C_1-symmetry model was used to rationalize the linear optical spectrum of **1**. Figure S6a shows the scaled calculated absorption spectrum of **1** (depicted by employing a Lorentzian function)[16] together with the experimental spectrum. The dipole-allowed vertical excitation energies of **1** are mainly assigned as $n \rightarrow \pi^*$ transitions. As schematically illustrated in Figure S6b, the lone pair orbitals, *n*, are primarily contributed from the S atoms, the π^* orbitals are dominated by the 5*d* orbitals of the W atoms and the *p* orbitals of the S atoms. While the TD-DFT calculations suggest that all low-energy transitions are formally $3p_S \rightarrow 5d_W + 3p_S$ in nature, the specific location of the orbitals differs - inter-cluster transitions between the different kinds of clusters (tetranuclear cluster $[WS_4Cu_3]^+$ and pentanuclear cluster $[WS_4Cu_4]^{2+}$) are found in HCM-CP **1** (Figure S6b). The contributions to the frontier orbitals from the atomic orbitals of the crucial tetranuclear clu-

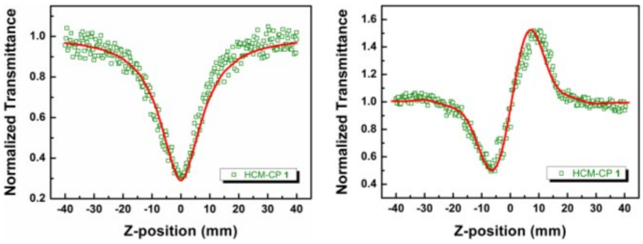


Fig. 2. Normalized open-aperture (left) and closed-aperture (right) Z-scan curves showing NLO absorption and refraction of HCM-CP **1**, respectively, at 532 nm with 5 ns pulse durations; the solid curves are theoretical fits based on Z-scan theory.

ster $[WS_4Cu_3]^+$/pentanuclear cluster $[WS_4Cu_4]^{2+}$ suggest that these clusters play a key role in controlling linear optical properties. The significant changes in the electron density distributions between ground and excited states correlate with the enhancement in cubic nonlinearity observed in HCM-CP **1**, and accordingly may be responsible for its enhanced NLO responses.

In summary, an ammonium-crown ether host-guest supramolecular cation-templated assembly protocol has been developed for the construction of a structurally unprecedented 3D anionic heterobicluster-metal CP, composed of tetranuclear clusters with two kinds of connection environments, pentanuclear clusters and Cu^+ building metal ions. This heterobicluster-metal CP exhibits a novel tetranodal (3,4,4,6)-connected topology and a huge free volume. Z-scan experiments on this anionic heterobicluster-metal CP reveal enhanced NLO properties by the incorporation of diverse building cluster components. Further studies on the synthesis of new heterobicluster-metal CPs based on heterothiometallic clusters are currently in progress.

This research was financially supported by the National Natural Science Foundation of China (50925207, 51172100, 51432006), the Ministry of Science and Technology of China (2011DFG52970), the Ministry of Education of China for the Changjiang Innovation Research Team (IRT1064), the Ministry of Education and the State Administration of Foreign Experts Affairs for the 111 Project (B13025), and Jiangsu Innovation Research Team. MGH and MPC thank the Australian Research Council for support.

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