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A highly efficient ''metalloligand'' strategy for the synthesis of ternary Ln–Ru–W hybrids†

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A series of novel ternary Ln–Ru–W hybrids constructed by metalloligands ($[Ru^{II}(bpy)_2(4,4'\text{-dcbpy})](PF_6)_2$, *m*-$H_2L_{Ru}$) and high-nuclear lanthanide clusters have been successfully synthesized using an efficient ''metalloligand'' strategy for the first time. Slow magnetic relaxation has been observed within the Dy-based hybrid.

Introduction of functional sites into porous coordination polymers or metal–organic frameworks (MOFs) has become one of the most emerging tendencies due to their significant applications in selective recognition of small molecules, gas storage and separation, catalysis and biomedical imaging.[1] One efficient strategy to introduce functional sites into coordination polymers is to make use of so-called 'metalloligands' with the potential coordination donor groups,[2] such as salen,[3] dipyrrinato,[4] porphyrin[5] and 2,2′-bipyridine (bpy) functions, available for binding a second metal ion. Bpy-based metalloligands, especially those photoactive M-$(bpy)_{3-x}(L)_x$ (M = Ru, Ir, Re and Os, L = other non-bpy ligands) species, have been successfully introduced into coordination polymers or MOFs with desired properties.[6] On the other hand, polyoxometalates (POMs), as a unique family of molecular scale anionic oxide clusters containing early transition metal elements (V, W, Mo and Nb), exhibit diverse structures, remarkable electronic features and great potential applications. These clusters with controllable shape, size and high negative charges have been widely used as the multidentate ligands, anion templates and charge compensators for the preparation of organic–inorganic hybrid materials with advanced functions.[7]

It is anticipated that the introduction of both POMs and metalloligands into hybrid materials will not only retain their individual virtues but also bring some new properties. However, the distinct nature of these components makes the preparation of POM–metalloligand-based hybrids remain a challenging task. To date, almost all of the reported POM–metalloligand hybrid solids have been assembled by electrostatic interactions or anchored on the surface of POMs by covalent bonds.[8] To the best of our knowledge, only two hybrid frameworks containing POMs and metalloligands have been reported.[9] Using a 'one pot' hydrothermal process, Zubieta *et al.* synthesized a novel three-dimensional (3-D) hybrid framework, $[\{Fe(TPyP)\}_3Fe(Mo_6O_{19})_2]\cdot xH_2O$ (TPyP: tetrapyridylporphyrin), which contains a 3-D $[\{Fe(tpypor)\}_3Fe]^{4n+}{}_n$ framework and isolated $\{Mo_6O_{19}\}^{2-}$ anions.[9a] Very recently, Wu and coworkers reported a two-dimensional (2-D) metalloporphyrin–POM-based hybrid framework, $\{[Cd(DMF)_2Mn^{III}(DMF)_2TPyP](PW_{12}O_{40})\}\cdot 2DMF\cdot 5H_2O$, which demonstrates excellent capability of scavenging dyes and of highly selective oxidation of alkylbenzenes.[9b]

We aim to develop a simple and effective method to construct new POM–metalloligand-based hybrids. After full consideration of the nature of these two components, we choose lanthanide ions as metal nodes due to their diverse coordination modes and strong coordination ability. Moreover, because lanthanide-based coordination polymers or MOFs tend to obtain the cation skeleton, the POMs with high negative charge and regular geometry shape can be easily introduced into the hybrid frameworks *via* charge balance. Following this approach, a series of novel ternary Ln–Ru–W hybrids with complex structures, $[\{Gd(OAc)(H_2O)\}\{Gd_4(\mu_2\text{-}OH)(\mu_3\text{-}OH)_4(H_2O)_{11}\}\{(\textbf{\textit{m}}\text{-}L_{Ru})_4(HCOO)\}]\{SiW_{12}O_{40}\}_2\cdot x DMF\cdot yH_2O$ (**Gd-1**, ***m*-L_{Ru}** = $[Ru^{II}(bpy)_2(4,4'\text{-dcbpy})]$, 4,4′-dcpy = 2,2′-bipyridyl-4,4′-dicarboxylic acid) and $[\{Ln\}\{Ln_4(\mu_3\text{-}OH)_4(H_2O)_{10}\}\{(\textbf{\textit{m}}\text{-}L_{Ru})_4(HCOO)_2\}]\{SiW_{12}O_{40}\}_2\cdot x DMF\cdot yH_2O$ (Ln = **Dy-2** and **Er-3**), have been successfully prepared.

Some of the most important factors are the negative charge and shape of POMs. When $H_4SiW_{12}O_{40}$ is replaced with other POMs, such as Keggin anions ($H_3PW_{12}O_{40}$ and $H_7PMo_{12}O_{40}$) or larger $Na_{10}\{Co_4(H_2O)_2(PW_9O_{34})_2\}$, **Gd-1**, **Dy-2** and **Er-3** could not be prepared. Hence, we proposed that the $\{SiW_{12}O_{40}\}$ anion with suitable size and charge could serve as a template in this system. Another effective parameter is the addition of HAc (>60 μL) in order to obtain the above products. The crystallization of the above compounds has a narrow volume rate of DMF–H_2O within 5 : 3 to 7 : 1. The above

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† Electronic supplementary information (ESI) available: Experimental details, asymmetry units for **Gd-1** and **Er-3**, structure determination of all compounds, tables providing the summary of crystal data and selected bonds and angles, TGA-DTA diagrams, simulated and measured PXRD patterns, UV-vis spectra, IR data, EDS spectra and magnetic analysis of **Gd-1** and **Er-3**. CCDC 936248 and 936249. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43277g

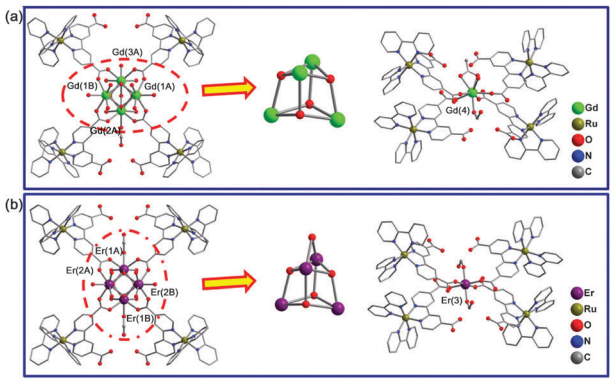

Fig. 1 (a) The coordination environments of Gd centers and the structural view of the $\{Gd_4(\mu_2\text{-}OH)(\mu_3\text{-}OH)_4\}$ core, symmetry code: (A) $0.5 + x, -0.5 + y, z$, (B) $0.5 - x, -0.5 + y, z$. (b) The coordination environments of Er centers and the structural view of the $\{Er_4(\mu_3\text{-}OH)_4\}$ core, symmetry code: (A) $0.5 - x, -0.5 + y, 0.5 - z$, (B) $-0.5 + x, -0.5 + y, z$.

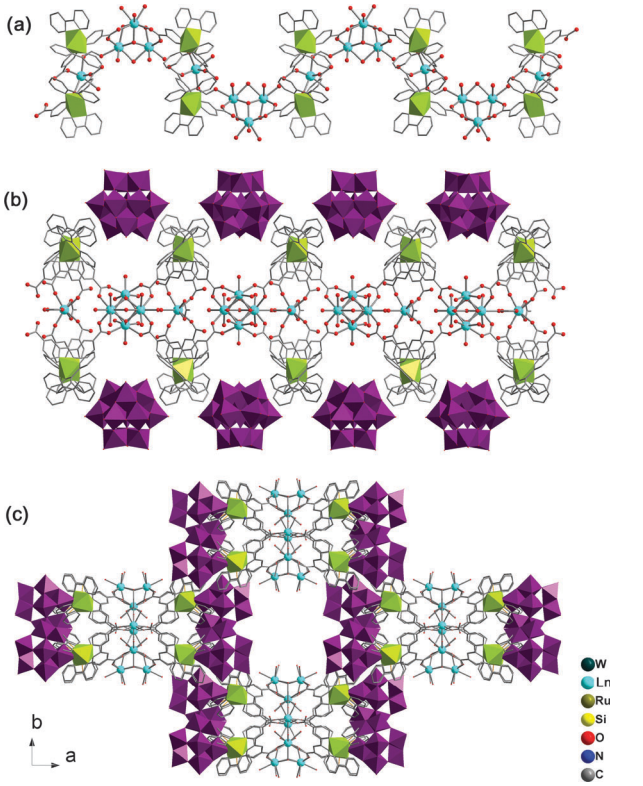

Fig. 2 (a) Structural view of the 1-D zigzag lanthanide-based coordination chain within compounds **Gd-1** and **Er-3**. (b) The structure of POMs and the 1-D lanthanide chain along the [010] direction. (c) The 3-D structure representations of **Gd-1** and **Er-3** views along the *c* axis. WO_6 and RuN_6 octahedrons are shown in kelly and purple colors respectively. The H atoms and solvent molecules are omitted for clarity.

compounds can also be prepared using $LnCl_3$. The X-ray single crystal diffraction analyses indicate that all compounds consist of the lanthanide-based coordination chain and noncoordinated Keggin $\{SiW_{12}O_{40}\}^{4-}$ anions with difference in the coordination environments and linkage modes of Ln centers. **Gd-1** crystallizes in an orthorhombic space group $Cmc2_1$ and contains four crystallographic independent Gd centers as shown in Fig. S1 (ESI†). Gd(1) is coordinated by two ***m*-L_{Ru}**, three water molecules and three OH groups in a distorted nine-coordinated mode. Gd(2) and Gd(3) adopt a similar nine-coordinated mode but with two water molecules and one $HCOO^-$ ion. Gd(1), Gd(2) and Gd(3) centers connect with each other by μ_2-OH and μ_3-OH bridges to form the distorted cubic tetranuclear $\{Gd_4(\mu_2\text{-}OH)(\mu_3\text{-}OH)_4(H_2O)_{11}\}$ unit (Fig. 1a). The separation distance of Gd···Gd ranges from 3.7 to 3.94 Å. The mononuclear Gd(4) center is in the eight-coordinated mode defined by four carboxylate oxygen atoms of the metalloligands, one OAc^- ion, one $HCOO^-$ ion and one water molecule. **Dy-2** and **Er-3** are isostructural but slightly different from **Gd-1**. Taking **Er-3** for example, it crystallizes in orthorhombic space group *Cmcm* and contains three crystallographic independent Er centers as shown in Fig. 1b and Fig. S2 (ESI†). Er(1) and Er(2) are eight-coordinated and bridged by four μ_3-OH species into a cubic tetranuclear $\{Er_4(\mu_3\text{-}OH)_4(H_2O)_{10}\}$ unit. The mononuclear Er(3) is coordinated by four ***m*-L_{Ru}** and two water molecules in a distorted octahedral geometry. More interestingly, a novel pentanuclear $\{Gd_5\}$ building unit can be further formed by the mononuclear Gd(4) and $\{Gd_4\}$ cluster bridged by the formate group (Fig. S3a, ESI†). The nearest separation distance of Gd(4) and $\{Gd_4\}$ units is about 5.83 Å. Otherwise, Er(3) and $\{Er_4\}$ units within **Er-3** connect with each other by the μ_2-HCOO bridge resulting in a 1-D $\{Er\text{-}\mu_2\text{-}(HCOO)\text{-}\{Er_4\}\}_\infty$ chain as shown in Fig. S3b (ESI†). The ***m*-L_{Ru}** ligand adopts a $\mu_3(\eta^1{:}\eta^1{:}\eta^1)$ coordination mode within these three compounds.

A remarkable structural feature of these compounds is the 1-D zigzag lanthanide-based coordination chains, $[\{Gd(OAc)(H_2O)\}\text{-}\{Gd_4(\mu_2\text{-}OH)(\mu_3\text{-}OH)_4(H_2O)_8\}\{(m\text{-}L_{Ru})_4(HCOO)\}]_\infty$ and $[\{Er\}\{Er_4(\mu_3\text{-}OH)_4\text{-}(H_2O)_{10}\}\{(m\text{-}L_{Ru})_4(HCOO)_2\}]_\infty$, which are built up by the mononuclear centers and tetranuclear units *via* alternate ***m*-L_{Ru}** ligands as shown in Fig. 2a. Three compounds possess similar stacking sequences. Along the *c* axis, the noncoordinated $\{SiW_{12}O_{40}\}$ anions are filled on each side of the "toothed" part of these two types of zigzag chains to form a "composite chain" by intermolecular interactions. As shown in Fig. 2b, these "composite chains" stack with each other to construct a 2-D interconnecting channel system parallel to the (101) plane. The largest stacking channel along the [001] direction, filled by free DMF and water molecules, is about 10.3 × 10.3 Å in the aperture. In contrast to the POM-based coordination polymers, which are usually composed of the simple organic ligands and mononuclear metal (TM or Ln) centers,[7] these three compounds represent the first examples comprising both the metalloligands and high-nuclear metal complexes. For the coordination polymer–POM host–guest supramolecular system, the geometrical requirements of the ligands, the coordination preferences of the metal nodes and the geometry of POM anions have vital effects in our case. We propose the formation of these novel ternary vital effects on the self-assembly process. This self-assembly process in Ln–Ru–W hybrids is complex and could be attributed to the bent angle (~90°) of the ***m*-H_2L_{Ru}** metalloligand, the compact shape of the Keggin $\{SiW_{12}O_{40}\}^{4-}$ anionic template and the coordination chemistry of Ln ions.

Considering the interesting magnetic properties of Ln^{3+} ions, the variable temperature magnetic behaviors of **Gd-1**, **Dy-2** and **Er-3**, measured with polycrystalline samples at an applied field of 1000 Oe, are plotted as $\chi_m T$ *versus* *T*. The **Gd-1** and **Er-3** exhibit the normal magnetic behaviors shown in ESI.† For **Dy-2** (Fig. S10, ESI†),

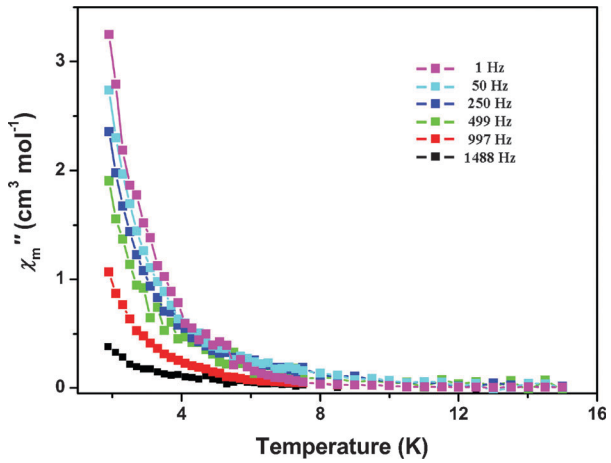

Fig. 3 The out-of-phase ac susceptibility (χ_m'') for **Dy-2** at the zero direct-current (dc) field and an ac field of 3 Oe with oscillating frequencies.

the room-temperature $\chi_m T$ value is 70.3 cm^3 K mol^{-1}, which is close to the expected value of five uncoupled Dy^{III} ions (70.8 cm^3 K mol^{-1} calculated for $^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$, $g = 4/3$). Upon cooling, the $\chi_m T$ value firstly decreases gradually and then more rapidly below 70 K, and at last reaches the minimum of 53.5 cm^3 K mol^{-1} at 2 K. Such magnetic behavior is ascribed to the combination of the excited Stark sublevels and possible interaction between the Dy^{III} ions.[10] The *M vs. H* curves for **Dy-2** at 2.0 K show a rapid increase at a low field and eventually reach a maximum value of 27.5$N\beta$ at 5 T (Fig. S11, ESI†). This value is much lower than the expected M_{sat} value of 50$N\beta$ for free five Dy^{III} ions which is indicative of anisotropy and the ligand-field effect occurring at Dy^{III}.[11] Alternating current (ac) susceptibility for these compounds was collected at the zero direct-current (dc) field with an ac field of 3 Oe with oscillating frequencies. For **Gd-1** and **Er-3**, frequency-dependent peaks did not appear at the out-of-phase susceptibility above 1.8 K (Fig. S13, ESI†). As shown in Fig. 3, frequency dependent out-of-phase signals of **Dy-2** are observed, suggesting the onset of slow relaxation of the magnetization, which is the signature of a SMM (single molecular magnet) behavior as shown in many Dy clusters.[11a,12]

In summary, a series of novel hybrid frameworks constructed by lanthanide-metalloligand-based coordination polymers and POMs anions have been successfully synthesized by an efficient synthetic strategy. These compounds represent the first hybrid examples with both the metalloligands and high-nuclear metal complexes. It is notable that POMs can act as building blocks hybridized with photo-functional semiconductor nanostructures and organic–inorganic molecules to obtain highly efficient photocatalysts and photo-electrochemical devices.[13] Future work will be focused on the development of some catalytic reactions based on these hybrids.

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