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Two kinds of 3D coordination frameworks from monometallic to 4d–4f heterometallic: Synthesis, crystal structures, photoluminescence and magnetic properties ☆

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ABSTRACT

Two kinds of three-dimensional (3D) coordination frameworks from monometallic to heterometallic, including a charming 3D monometallic complex, namely, $[Eu_2(mpda)_3(H2O)_4]_n$ (1) and the first series of novel 3D heterometallic 4d–4f coordination frameworks based on 2,6-dimethylpyridine-3,5-dicarboxylic acid, namely, $[Ln_2Cd_2(mpda)_2(bdc)_2(SO_4)_2(H2O)_6]_n$ [Ln = Sm(2), Eu(3), Gd(4), Tb(5), Dy(6); mpda = 2,6-dimethylpyridine-3,5-dicarboxylic acid; bdc = 1,4-benzenedicarboxylic acid] have been successfully synthesized under hydrothermal conditions and structurally characterized. Crystal 1 is featured by its interesting 3D chain-layer construction which is formed by the alternative arrangement of chains and layers and exhibits 2-nodal 5, 6-connected 3D network with the Schlafli symbol of $\{3^3.4^3.5^5.6^4\}\{3^6.4^6.5^3\}$. Complexes 2–6 are isostructural and it reveals that these 3D heterometallic compounds are firstly built by H_2mpda ligand. What is worth mentioning is that anionic ligand SO_4^{2-} plays a crucial function in the construction building. The two-dimensional (2D) lanthanide-transition heterometallic bilayers $[Ln_2Cd_2(mpda)_2(bdc)_2]_n$ are pillared by SO_4^{2-} subunits forming mixed-ligand complexes with a pillared-layer 3D structure. Complexes 2–6 feature 4-nodal 3, 4, 5, 6-connected 3D frameworks with $\{4.8^2\}\{4.8^4.10\}\{4^2.8^{10}.10^2.12\}\{4^2.8^8\}$ topology. All the complexes are characterized by elemental analyses, FT-IR spectroscopy, Powder X-ray diffraction (PXRD) and thermogravimetric analyses (TGA). Furthermore, the luminescence properties of compounds 1, 3, and 5 and the magnetic properties of complexes 4 and 6 were also investigated in detail.

Microporous metal-organic frameworks (MOFs) are of great interest, not only because of their aesthetically fascinating architectures, but also due to their wide range of potential applications, especially in gas separation and adsorption [1], chemical separation [2], drug delivery [3], catalysis [4], magnetism [5], luminescent materials [6], sensors [7], etc. Among them, metal-organic frameworks based on trivalent lanthanides (Ln-MOFs) are a very promising class of materials for addressing the challenges in the engineering of luminescent centers and their unique topological structures and fascinating physico-chemical properties [8]. However, lanthanide metals display larger coordination spheres and more flexible coordination geometries as well as the competitive reactions between lanthanide and transition metals, which make it difficult to control the synthesis of lanthanide complexes with desired topology, but do provide an opportunity to construct unusual frameworks with interesting magnetic and luminescent properties [9]. Furthermore, many d–f coordination polymers, which possess not only interesting structural motifs but also fascinating properties, have been successfully obtained under different reaction conditions [10]. However, the assembly of extended structures of d–f polymeric compounds, especially three-dimensional (3D) d–f heterometallic coordination polymers, is less successful and remains a challenge for chemists. Therein, the construction of 4d–4f heterometallic multifunctional coordination polymers is less reported [11].

However, based on the fact that multidentate ligands of O and N atoms have different affinities to lanthanide and transition metal ions and considering the hard-soft acid base theory, we know that lanthanide metal ions have stronger affinity to O over N, while transition

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metal ions have a strong tendency to coordinate to N [11d,12]. Furthermore, the coordination polymers based on 2,6-dimethylpyridine-3,5-dicarboxylic acid (H_2mpda) which have been built are all 3d/4d or 4f monometallic construction. In addition, the 4f monometallic coordination compounds are still rare and the luminescent properties of lanthanide-organic motifs have not been reported so far. Therefore, we would like to build monometallic Ln-MOFs based on H_2mpda. More importantly, 4d–4f heterometallic framework based on H_2mpda has never been reported up to now [13]. Taking these into consideration and inspired by our team [12b,14], we would like to use H_2mpda as the main ligand and 1,4-benzenedicarboxylic acid (H_2bdc) [15] as the second ligand because of their diverse coordination modes and bridging ability to build heterometallic coordination compounds. We hope that the O and N, respectively, coordinate with rare earth and transition atom to build the 4d–4f heterometallic framework as well as the study of the photoluminescent based on lanthanide.

Here we report six 3D polymers, containing a charming 3D monometallic complex, namely, $[Eu_2(mpda)_3(H2O)_4]_n$ (1) [mpda = 2,6-dimethylpyridine-3,5-dicarboxylic acid], which is famous for a special chain-layer construction constructed by the alternative arrangement of chains and layers and the first examples of Ln(III)–Cd(II) 4d–4f 3D heterometallic compounds based on H_2mpda, namely, $[Ln_2Cd_2(mpda)_2(bdc)_2(SO_4)_2(H2O)_6]_n$ [Ln = Sm(2), Eu(3), Gd(4), Tb(5), Dy(6); mpda = 2,6-dimethylpyridine-3,5-dicarboxylic acid; bdc = 1,4-benzenedicarboxylic acid] (Scheme 1) [16]. The structures of complexes 1–6 were determined by single-crystal X-ray diffraction analyses and characterized by elemental analyses [17], FT-IR spectroscopy, Powder X-ray diffraction (PXRD) and thermogravimetric analyses

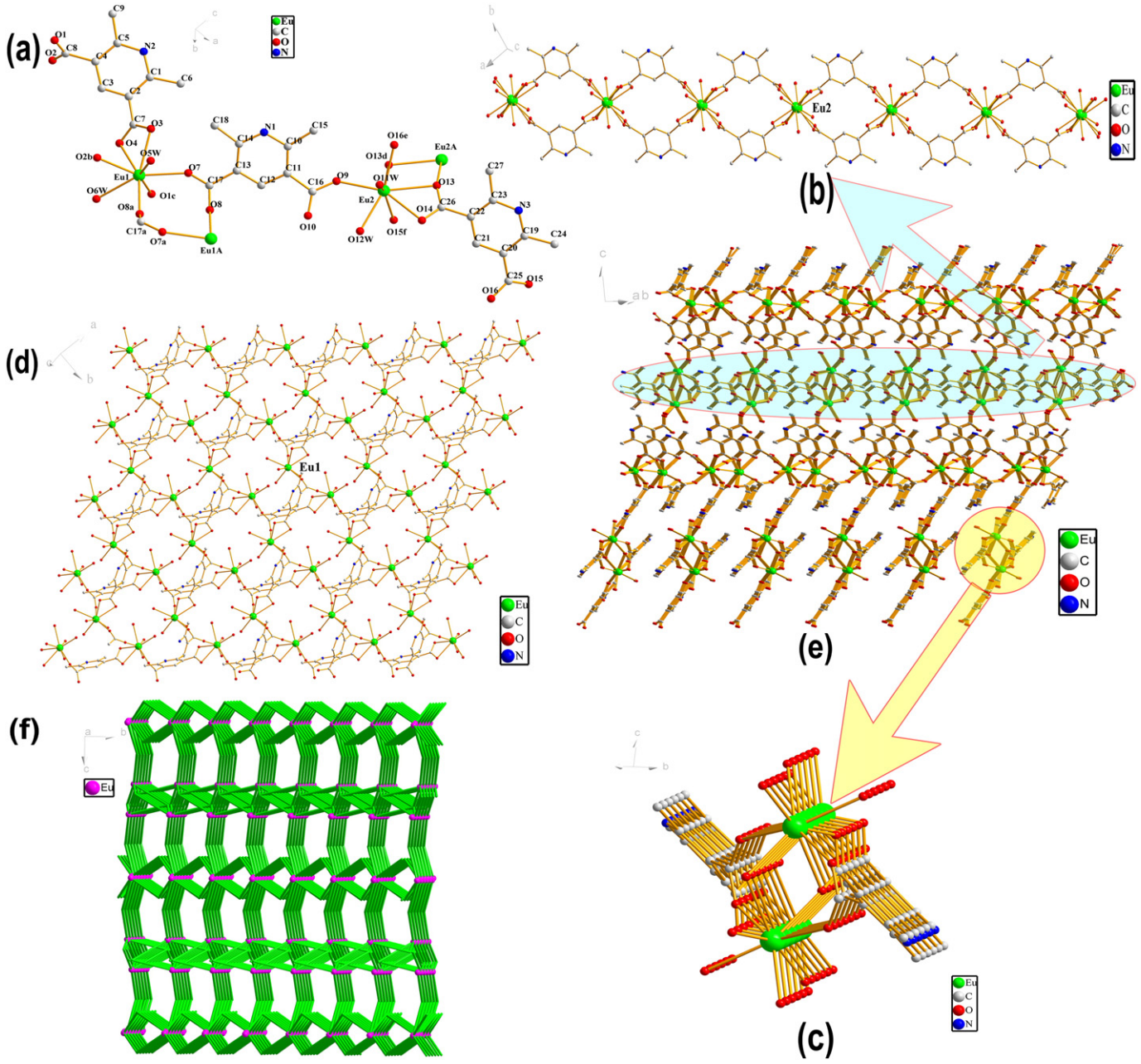

Fig. 1. (a) Coordination environments of complex 1. All H atoms and coordinated water molecules are omitted for clarity. Symmetry codes: (i) 2.5 − x, 1.5 − y, 1 − z; (ii) 2 − x, 1 − y, 1 − z; (iii) −0.5 + x, −0.5 + y, z; (iv) 0.5 + x, 0.5 + y, z; (v) 1 − x, y, 0.5 − z; (vi) −x, y, 0.5 − z. (b) and (c) two different kinds of configurations of the 1D chain motifs in the 3D chain-layer framework of complex 1. (d) View of the 2D layer formed by coordination of ligand $mpda^{2-}$ and Eu1 of complex 1. (e) View of the 3D chain-layer construction fabricated by the link of ligand $mpda^{2-}$ in mode Scheme 2b between Eu1 atoms from layers and Eu2 atoms from chains. (f) The simplified 2-nodal 5, 6-connected 3D network of compound 1.