

New organic–inorganic hybrid assemblies based on metal–bis(betaine) coordination complexes and Keggin-type polyoxometalates



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ABSTRACT

The slow diffusion reactions of a double-betaine-containing ligand with $\text{YbH}[\text{SiMo}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ and $\text{Ca}_2[\text{SiMo}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ led to the isolation of two new organic–inorganic hybrid assemblies, $[\text{Yb}(\text{O})(\text{HL})_2(\text{H}_2\text{L})_{0.5}(\text{H}_2\text{O})_3][\text{SiMo}_{12}\text{O}_{40}] \cdot 2.5\text{CH}_3\text{CN} \cdot 1.5\text{H}_2\text{O}$ (**1**) and $[\text{Ca}(\text{HL})_2(\text{L})_{0.5}(\text{H}_2\text{O})_4][\text{SiMo}_{12}\text{O}_{40}] \cdot 5\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ (**2**) ($\text{L} = 1,4\text{-bis}(\text{pyridinil-4-carboxylato})\text{-1,4-dimethylbenzene}$). Compounds **1–2** were characterized by elemental analyses, TG, IR, XPS and single-crystal X-ray diffraction. Compound **1** contains the dinuclear $[(\text{YbO})(\text{HL})_2(\text{H}_2\text{O})_3]_2$ coordination moieties and discrete protonated L ligands, which are connected together by H-bonds and $\pi\text{-}\pi$ interactions to form a 3D supramolecular framework with the Keggin-type $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ polyoxoanions and solvent molecules encapsulated. Compound **2** possesses discrete $[\text{Ca}(\text{HL})_2(\text{L})_{0.5}(\text{H}_2\text{O})_4]_2$ coordination units that are linked by the extensive intermolecular H-bonds and $\pi\text{-}\pi$ interactions to form a 3D supramolecular framework with the $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ polyoxoanions and solvent molecules are encapsulated in the interbedded cavities. The structural motifs of the metal–organic coordination units can be obviously modulated by the use of chemically different cationic nodes. The degradation of Rhodamine-B (RhB) under UV irradiation with compounds **1** and **2** as heterogeneous photocatalysts were investigated, both exhibiting good photocatalytic properties. Furthermore, these hybrid compounds display luminescent properties induced by organic ligands.

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The design and synthesis of polyoxometalate (POM)-based coordination networks have been paid much attention in recent years. The combination of POMs and metal–organic coordination moieties has not only led to more complicated and fascinating structural topologies, but also exerted their synergetic effects and converge the merits of both aspects, exhibiting potential applications in heterogeneous catalysis, selective absorption, and photonic, electronic and magnetic functional materials [1–5]. In this research field, three main building blocks, that is, POMs and metal and organic bridging ligands, have currently constituted an extensive and multiple hybrid system [2]. Especially, the analogs based on lanthanide/alkaline earth metal–organic hybrid moieties and POM building units have attracted great interest in recent years [3]. The introduction of lanthanide or alkaline earth metal into organic–inorganic hybrid compounds based on POMs may induce various topological architectures due to their different coordinated modes in comparison with transition-metals as well as new functionalities such as luminescent, magnetic, and/or catalytic properties [4]. In such a subfamily, the design and use of organic bridging ligands is one of the important factors. On the one hand, compared with O-donor bridging ligands, many N-donor linking ligands exhibit relatively low coordination ability with lanthanide or alkaline earth metal ions. On the other hand, anionic carboxyl-containing ligands

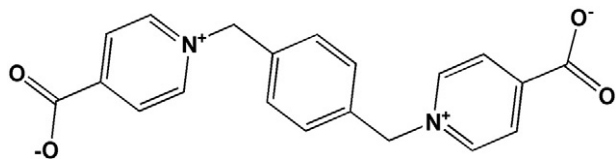
possess potential advantages of high reactivity, but the reaction competition between carboxylate groups and the polyoxoanions with the lanthanide or alkaline earth metal cations cannot be easily avoided, which always leads to unexpected results [5].

Based on aforementioned considerations, the design and synthesis of new neutral O-donor bridging ligands may be another new route for the construction of POM-based lanthanide/alkaline earth metal–organic hybrid compounds. In this aspect, the double betaine-containing ligands could be one type of suitable candidates, considering that such neutral O-donor ligands can still retain the diverse coordination modes of carboxylate groups [6]. Therefore, we chose a double-betaine-containing ligand, namely 1,4-bis(pyridinil-4-carboxylato)-1,4-dimethylbenzene (L) (see Scheme 1) to explore new type of POM-based Ln metal–organic coordination polymers and networks [7,8]. As a continuing work of this reaction system, herein, we reported two new organic–inorganic hybrid assemblies based on Ln/alkaline-earth metal–organic coordination complexes and Keggin-type POM units: $[\text{Yb}(\text{O})(\text{HL})_2(\text{H}_2\text{L})_{0.5}(\text{H}_2\text{O})_3][\text{SiMo}_{12}\text{O}_{40}] \cdot 2.5\text{CH}_3\text{CN} \cdot 1.5\text{H}_2\text{O}$ (**1**) and $[\text{Ca}(\text{HL})_2(\text{L})_{0.5}(\text{H}_2\text{O})_4][\text{SiMo}_{12}\text{O}_{40}] \cdot 5\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ (**2**) [9].

Single-crystal X-ray diffraction analysis [10,11] shows that compounds **1–2** crystallize in the triclinic space group *P*-1. The basic structural unit of **1** consists of a cationic lanthanide–organic coordination moiety $[\text{Yb}(\text{O})(\text{HL})_2(\text{H}_2\text{O})_3]^{3+}$, a half protonated double-betaine-containing L ligand, a Keggin-type $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ polyoxoanion [12], two and a half solvent acetonitrile molecules as well as one and a half water molecules (Fig. S1). In the $[\text{Yb}(\text{O})(\text{HL})_2(\text{H}_2\text{O})_3]^{3+}$ cluster, each

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Scheme 1. Structure of the double-betaine-containing ligand L (1,4-bis(pyridinil-4-carboxylato)-1,4-dimethylbenzene).

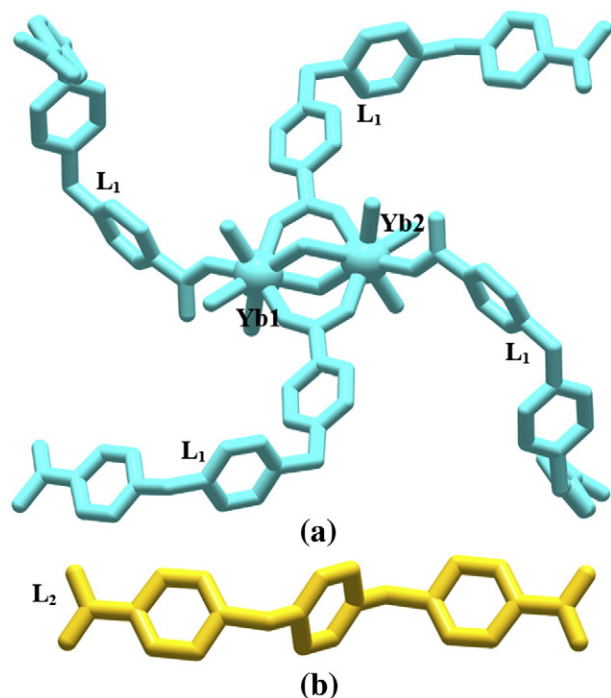


Fig. 1. (a) Structure of the di-ytterbium cluster $[\text{Yb}(\text{O})(\text{HL})_2(\text{H}_2\text{O})_3]_2$ in **1**; (b) structure of dissociative L_2 ligands adopting *trans*-configuration in **1**.

Yb^{3+} ion adopts an octa-coordinated environment with three oxygen atoms from the carboxylate groups of three different L ligands, two O groups and three coordinated water molecules (Fig. 1a). It is interesting that each Yb1 atom connects with Yb2 atom via two O groups to form a dinuclear $\{\text{Yb}_2\}$ cluster and the bond distances of Yb1...Yb2 is

3.8926(18) Å (Fig. 1a). In such a coordination moiety (Fig. 1a), all bis(betaine) ligands (labeled with L_1) adopt a *cis*-configuration and exhibit a monodentate connection mode, that is, one carboxylate group is coordinated with the Yb center while the other is protonated. Furthermore, the adjacent $\{\text{Yb}_2\}$ moieties are linked together to form a 1D supramolecular chain via hydrogen bonds along the *b* axis. The typical hydrogen bond is between the coordination water molecule (O1w) and the carboxylate group (O48) with the distance of O1w-H2aa...O48 1.882 Å (Figs. 2 and S2). In **1**, the discrete protonated bis(betaine) ligands (labeled with L_2) adopt a *trans*-configuration (Fig. 1b). They are also connected by the adjacent 1D supramolecular chains to generate a 2D supramolecular network via several kinds of hydrogen bonds, such as the coordination water molecules (O1w, O2w) and O groups (O41) on the 1D chains, and the carboxylate groups (O51, O50) on the dissociative L_2 ligands along the *a* axis (Figs. 2 and S2). The typical H-bonds are O1w-H1aa...O50, O2w-H4aa...O51 and O41...H51-O51 with the distances of 2.122 Å, 1.990 Å and 1.916 Å, respectively (Fig. S2). Moreover, π - π interactions exist between two adjacent 2D supramolecular networks and a 3D supramolecular framework is thus formed (Fig. S3). The Keggin-type $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ polyoxoanions, solvent MeCN and water molecules are encapsulated in the interbedded cavities of two adjacent 2D supramolecular networks (Fig. 3). Compared with the previously reported hybrid assemblies in such reaction system [7,8], it is found that the structural motifs of Ln metal-organic units can be modulated not only by the Keggin-type POMs with different negative charges, but also by different Ln^{3+} ions due to the well-known lanthanide contraction.

In compound **2**, the basic structural unit contains one cationic coordination moiety $[\text{Ca}(\text{HL})_2(\text{L})_{0.5}(\text{H}_2\text{O})_4]^{4+}$, one Keggin-type cluster $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ [12], five acetonitrile molecules, and one water molecule (Fig. S4). In the $[\text{Ca}(\text{HL})_2(\text{L})_{0.5}(\text{H}_2\text{O})_4]^{4+}$ moiety, each Ca^{2+} ion coordinates with three oxygen atoms from the carboxylate groups of three different L ligands and four coordinated water molecules, exhibiting a distorted hepta-coordinated antiprismatic geometry (Figs. 4 and S4). It is interesting that the L ligands adopt two different configurations and thus can be divided into two types, labeled with L_1 and L_2 , respectively (Fig. 4). The four L_1 ligands adopt the *cis*-configuration, in which one carboxylate group exhibits a monodentate coordination mode with one Ca center, while the other is protonated (Fig. 4). The L_2 ligand possesses the *trans*-configuration, in which both carboxylate groups display the monodentate coordination mode with one Ca center. Thus, the L_2 ligand acts as a bridge to join two Ca centers together, forming a $\{\text{Ca}_2\}$ -containing fragment (Fig. 4). The adjacent $\{\text{Ca}_2\}$ moieties are further

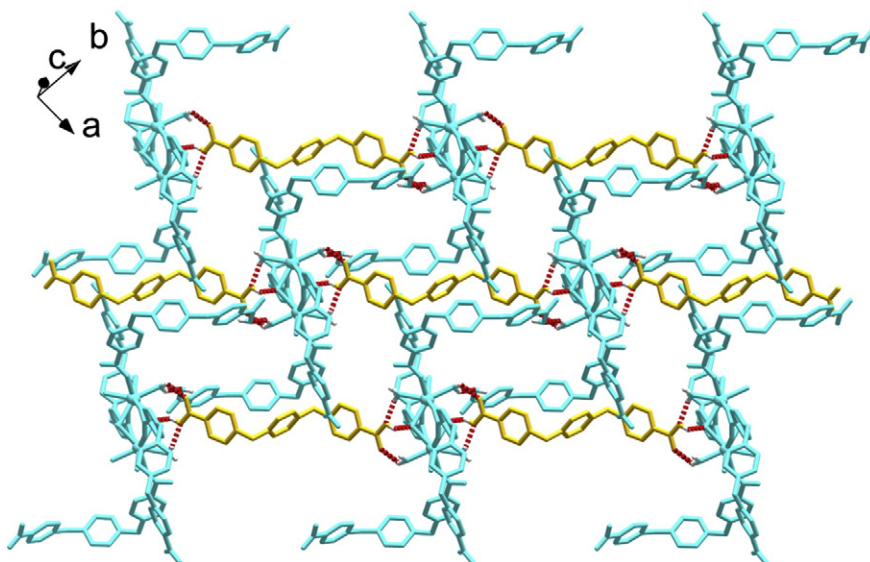


Fig. 2. View of 2D supramolecular layer constructed by adjacent 1D hybrid chains formed via H-bonds and dissociative L_2 ligands via H-bonds in **1**.

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