



Self-assembly and morphology change of four organic-polyoxometalate hybrids with different solid structures from 2D lamellar to 3D hexagonal forms



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ABSTRACT

A series of organic-polyoxometalate hybrids L-EuW₁₁, L-EuW₁₀, L-EuW₂₂ and L-Mo₁₃₂ were fabricated by the same organic cations with different polyoxometalate anions from K₅[Eu(SiW₁₁O₃₉)(H₂O)₂], K₁₃[Eu(SiW₁₁O₃₉)₂]·15H₂O, Na₉[EuW₁₀O₃₆]·36H₂O to “Keplerate” -type (NH₄)₇₂[Mo₁₃₂O₃₇₂(-SO₄)₃₀(H₂O)₇₂]. The structures of hybrids were characterized by elemental analysis, thermogravimetric analysis (TGA), infrared spectra (IR) and small-angle X-ray scattering (SAXS). Self-assembly behaviors and aggregates morphology of these hybrids in mixed solution of chloroform-methanol are obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). L-EuW₁₁, L-EuW₁₀ and L-EuW₂₂ have different aggregation morphology but the similarly layered structures. Micron-sized vesicular structures of L-Mo₁₃₂ rupture in solvent and eventually turn into approximate hexagon. SAXS analysis of L-EuW₁₁, L-EuW₁₀ and L-EuW₂₂ shows that these hybrids aggregates change from two-dimensional (2D) lamellar to three-dimensional (3D) hexagonal structure in solid state.

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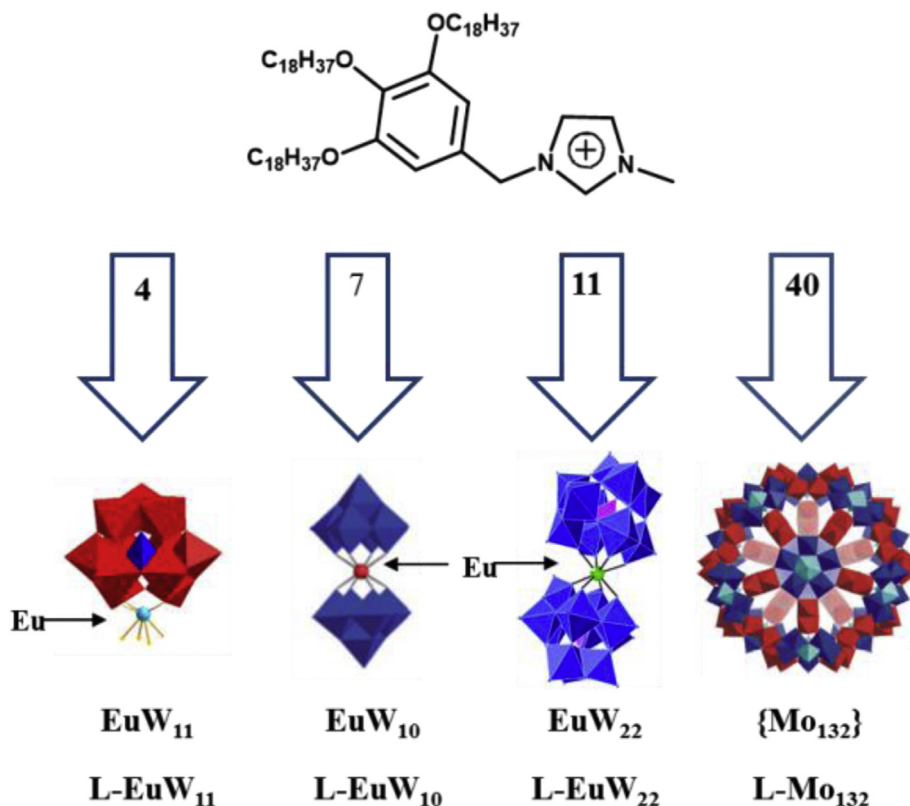
1. Introduction

Polyoxometalates (POMs) are attractive building blocks for the construction of large supramolecular structures and organic-inorganic hybrids materials in catalyst [1–3], biology [4] and optical/electronic functional devices [5–7]. In aqueous, POMs can be ionized and give high-charge delocalized anions with nano size but be insoluble in organic solvents, which limits their application in materials. Currently, the study of organic-polyoxometalates (organic-POMs) hybrid materials has drawn extensive attentions in different fields in recent years [8,9]. These hybrids depend on non-covalent bonds, such as hydrogen bonds, electrostatic interactions and van der Waals forces between the organic and inorganic interface. In organic-POMs hybrids, the physical and chemical properties of polymolybdate can be tuned by surface modification of organic cations. Organic-POMs hybrids are formed in water/organic mixed solution by replacing the anions of POMs surface with organic cations through electrostatic interaction. Organic-POMs hybrids have higher solubility in organic solvent and the negative charges of clusters surface could be neutralized by

organic cations, which is beneficial to stabilize aggregates and optimize the interfacial properties of POMs, such as self-aggregation, wettability.

In this paper, we employed the same organic cations 1-methyl-3-[3,4,5-tris(octadecyloxy) benzyl]imidazolium salts (labeled as L⁺) to encapsulate a series of POMs (as showed in Scheme 1). There are certain differences in imidazolium and other cations, such as ammonium cations as “head” moiety anchored on the surface of POMs anions. Self-assembly morphology of hybrids containing imidazolium cations mainly depends on hydrophobic force between alkyl tails and the interaction of flatted imidazolium “head” with electron-rich surface of POMs. Some lanthanide substituted POMs, such as Eu³⁺, Tb³⁺, Sm³⁺ have attracted much attention owing to their characteristic luminescent properties. These POMs possess different topologic structures, surface negative charges and chemical compositions. K₅[Eu(SiW₁₁O₃₉)(H₂O)₂] (labeled as EuW₁₁) and K₁₃[Eu(SiW₁₁O₃₉)₂]·15H₂O (labeled as EuW₂₂) are composed by one or two lacunary Keggin-type POMs linked by a europium ion. Na₉[EuW₁₀O₃₆]·36H₂O (labeled as EuW₁₀) [10] has been also known for the highest emission quantum efficiency and in skeleton two [W₅O₁₈]⁶⁻ vacancy clusters are linked by one Eu³⁺. EuW₁₁ has similar appearance with Keggin-type POMs but EuW₁₀ and EuW₂₂ are ellipsoidal shape. Among them, EuW₁₀ has highest symmetry.

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Scheme 1. The chemical structure of L^+ and schematic polyhedron of four POMs.

Combined with our previous work [11], the organic cations on the surfaces of POMs anions with different shapes and numbers of negative charges would have different distribution and arrangement in organic-POMs hybrids. The giant hollow spherical polyoxymolybdate clusters $(\text{NH}_4)_{42}[\text{MoVI}_{72}\text{MoV}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$ formed by 132 molybdenum atoms with nano-sized holes and a diameter of 2.9 nm was reported by A. Müller [12–16]. For comparison, we use $(\text{NH}_4)_{72}[\text{Mo}_{132}\text{O}_{372}(\text{SO}_4)_{30}(\text{H}_2\text{O})_{72}]$ (labeled as $\{\text{Mo}_{132}\}$) to fabricate $L\text{-Mo}_{132}$ by the L^+ replacing the cations ions of $\{\text{Mo}_{132}\}$ surface in water/chloroform mixed solution. It is emphasized that the organic cations with hydrophobic moieties used for the encapsulation POMs anions are more favorable for increasing the solubility and flexibility of the hybrid system.

Wu [17] obtained the surfactant-encapsulated polyoxometalates complex (SEPs) based on cationic surfactant dimethyldioctadecylammonium bromide (DODA) and $\{\text{Mo}_{132}\}$ by electrostatic encapsulation. SEPs complexes would aggregate into 2D or 3D ordered supramolecular structure in the gas-liquid interface [18–20]. However, self-assembly results behavior of four hybrids imply that structures of supramolecular hybrids consisting of a rigid and hydrophilic POM core and flexible hydrophobic shell main depend on the length ratio of organic cations to POMs anions whether or not the connection by non-covalent or covalent bond. The latter idea was designed into subsequent experiments.

Elemental analysis, TGA and IR were used to determine the composition of four organic-POMs hybrids. The encapsulated structures of $L\text{-EuW}_{11}$, $L\text{-EuW}_{10}$, $L\text{-EuW}_{22}$ and $L\text{-Mo}_{132}$ were confirmed. Different amounts of L^+ on surface of various POMs anions show different assembling behaviors. We try to understand the relationship between structure and aggregation morphology and its stacking in solid state.

2. Result and discussion

2.1. IR spectra

Detailed IR spectra data (Fig. 3) of $L\text{-EuW}_{11}$, $L\text{-EuW}_{10}$, $L\text{-EuW}_{22}$ and $L\text{-Cl}$ were summarized in Table 1. The three-tailed L^+ has long alkyl chains and strong absorbance bands of methylene (CH_2) emerged at 2919 and 2851 cm^{-1} . According to the relationship of CH_2 stretching vibration frequency with alkyl chain conformations [21], these sharp peaks at low wavelength region imply the highly ordered conformation of alkyl chains. Meanwhile, the absorption peaks of deformation and scissor vibration mode of CH_2 concomitantly appear at 1467 and 1442 cm^{-1} . The aromatic ring C–C asymmetric stretching vibration mode locates at 1588 cm^{-1} . Band at 1114 cm^{-1} is associated with C–N stretching mode of imidazole ring in L^+ and the same peak also appears in $L\text{-EuW}_{11}$, $L\text{-EuW}_{10}$ and $L\text{-EuW}_{22}$. In the IR spectrum of three complexes, main fine peaks between 1000 and 700 cm^{-1} are attributed to the characteristic bands of parent polyoxometalates anions structure. The bands of W–O_d, W–O_b–W, W–O_c–W and W–O_a–W asymmetric stretching modes were different for the discrepancy between polyanions $[\text{EuSiW}_{11}\text{O}_{39}]^{5-}$, $[\text{Eu}(\text{SiW}_{11}\text{O}_{39})_2]^{13-}$ and $[\text{EuW}_{10}\text{O}_{36}]^{9-}$, whereas the Si–O asymmetric stretching mode only appeared at 1014 and 922 cm^{-1} [22] in $L\text{-EuW}_{11}$ and $L\text{-EuW}_{22}$. The band around at 720 cm^{-1} is the characteristic of the methylene C–H rocking mode in long alkyl chain. The IR spectra of $L\text{-EuW}_{11}$, $L\text{-EuW}_{10}$ and $L\text{-EuW}_{22}$ proved three hybrids to be prepared successfully.

In IR spectra of $L\text{-Mo}_{132}$ (Fig. 3), the characteristic absorption peaks of $\{\text{Mo}_{132}\}$ and L^+ simultaneously appear, which confirm that the $\{\text{Mo}_{132}\}$ is successfully entrapped by organic cations L^+ . Strong absorbance bands of CH_2 emerged at 2919 and 2851 cm^{-1} , which imply the existing of ordered conformation. The signal at

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