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Using a facile experimental manipulation to fabricate and tune a polyoxometalate-cholesterol hybrid material

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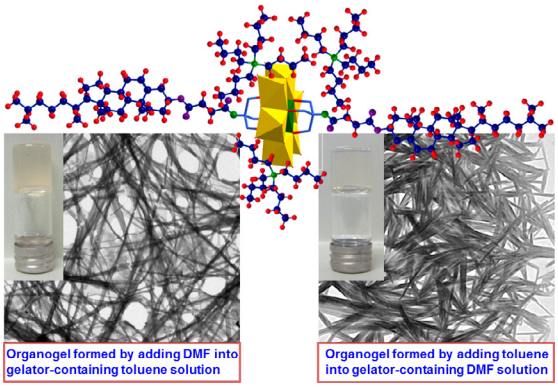
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we describe how the toluene and DMF addition order influences the gelation behaviors and supramolecular structures of a self-assembled polyoxometalate-cholesterol hybrid. Morphological studies of the dried xerogel samples were performed with transmission electron microscopy and atomic force microscopy, revealing that the order of solvent addition directed the self-assembly of polyoxometalate-cholesterol hybrids toward the formation of organogels with different supramolecular structures. In the case of organogel 1, which was formed by adding DMF dropwise into a hybrid-containing toluene solution, the characteristic organogel morphology contained a three-dimensional fibrous network structure. Meanwhile, organogel 2, which was prepared by adding toluene dropwise into a hybrid-containing DMF solution, had a supramolecular structure made up of short ribbons. Based on these results, a mechanism is proposed to illustrate the distinctly different self-assembly mechanisms of hybrid molecules in the formation of organogels 1 and 2. Importantly, the order of solvent addition plays a central role in the aggregation process. This study provides a rational method for the construction of supramolecular soft materials, and can be extended to other self-assembled systems.

1. Introduction

Hybrid organic-inorganic materials, such as those created through the combination of inorganic clusters and organic components at the nanometer or the molecular scale, have attracted widespread attention from a range of scientific fields [1–4]. Because of the versatility and synergistic effects of combined inorganic and organic components, the comprehensive properties and performances of self-assembled materials are often superior to those of the individual components on their own [5,6]. Until now, a variety of self-assembled nanomaterials with unique

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functions have been constructed using molecular self-assembly via weak noncovalent interactions, such as hydrogen bonding, π–π stacking, van der Waals interactions, dipole–dipole interactions, and electrostatic interactions [7–11]. Indeed, self-assembled materials have facilitated the development of new materials with promising applications in the fields of catalysis, nano-devices, photochemistry, electrochemistry, and biomedicine [12–16].

As a typical inorganic component, polyoxometalates (POMs) are a unique class of early transition metal-oxygen anion clusters in high oxidation states and have received considerable attention because of their widespread applications in catalysis, biology, electrochemistry, materials science, nanoscience and nanotechnology [17–20]. POM clusters are frequently used as molecular building blocks in the design of self-assembled materials, because of their versatile structures, diverse functions and remarkable self-assembly properties [21–24]. Through the appropriate selection of POM clusters and the effective regulation of self-assembly conditions, ordered nano- and micro-structured materials with tunable structures and properties can be formed through self-assembly. This ability has led to a growing interest in the design and preparation of self-assembled materials with desired properties [25–27]. Much effort has also been devoted to their preparation [28–35]. Among the available methods to prepare well-organized nanomaterials, one of the most promising is the regulation of solvent composition, which can be used to easily control the solubility as well as the self-assembled structures of organic-POM hybrids, because the POM clusters and organic components have different solubilities [30–32]. By controlling temperature, an organic-POM hybrid is conveniently and effectively created with ordered supramolecular nanostructures, because temperature influences the driving forces of assembly, such as hydrogen bonding, van der Waals interactions, and π–π stacking [33–35]. Moreover, replacing counter-cations outside of POM cluster with different ions is a powerful method to prepare well-defined supramolecular structures. Because it can greatly affect the resulting hierarchical structures as well as the physical and chemical properties of organic-POM hybrids [36–38].

Nanostructured assemblies are known to be efficiently created by metal-ion coordination. Specifically, organic-POM hybrids can spontaneously assemble into discrete supramolecular species or dense monodisperse nanoparticles via metal ion-directed self-assembly [39,40]. Electrostatic interactions are also used for the layer-by-layer assembly of organic-POM hybrids. The layer-by-layer deposition of functional POMs on a carbon support (e.g., carbon nanotubes and graphene oxide) has been achieved using various cations on the support surfaces, as linker molecules to build up electrostatically stabilized thin films [23,41–43]. In addition, pH can be tuned or an optical trigger can be used to regulate the supramolecular structures of organic-POM hybrids, these methods are both well-suited for the formation of POM-based hybrid materials [44–47].

Currently, the preparation of nanomaterials based on supramolecular assemblies of organic-POM hybrids is well understood. However, how to control the morphologies, shapes and dimensions of nanostructures via self-assembly is still a major challenge in supramolecular chemistry. Also, studies focused on resolving these structural control issues using self-assembly are limited in the literature. Therefore, new methods for the controlled preparation of self-assembled materials are still needed.

In a recent preliminary attempt at the design and preparation of POM-based self-assembled materials, the self-assembly of a POM-cholesterol hybrid was controlled via a temperature-directed method [48]. In this work, a new method is described for the construction of POM-based soft materials through spontaneous supramolecular self-assembly using different experimental manipulations. Specifically, a POM-cholesterol hybrid with a cholesterol-POM-cholesterol molecular structure (see Scheme 1) was used to prepare the organogels. The thermal stabilities and supramolecular structures of the resulting organogels were greatly affected by the preparation method.

2. Experimental section

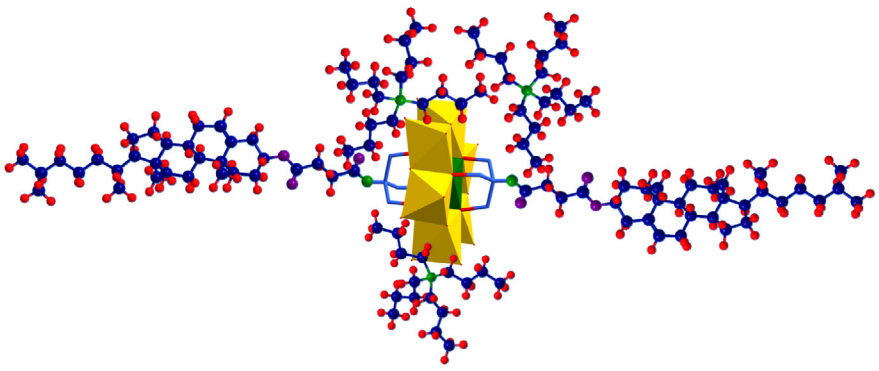
2.1. Materials

All starting materials were purchased from Alfa Aesar and used as received without further purification. The POM-cholesterol hybrid was prepared as previously reported and details of its synthesis are provided in the supplementary material [49]. Analytical grade solvents were purchased from Beijing Chemical Reagent Industry and used without further purification except for *N*,*N*-dimethylformamide (DMF) and toluene, which were dried and freshly distilled prior to use.

2.2. Preparation of organogels

Preparation of organogel 1. In a typical procedure, a POM-cholesterol hybrid was mixed with 900 μL of toluene in a sealed screw-cap vial, and the mixture was heated until the hybrid was dissolved. The resulting solution was then cooled to 20 °C, and 100 μL of DMF was slowly added dropwise into the solution. The resulting mixture was homogenized by shaking before being aged for five days at 20 °C. The vial was inverted to determine if the solution could still flow, and an organogel was confirmed to have formed when the solution solidified under gravity.

Preparation of organogel 2. In a typical procedure, a POM-cholesterol hybrid was mixed with 100 μL of DMF in a sealed screw-cap vial, and the mixture was heated until the hybrid was



Scheme 1. Chemical structure of the POM-cholesterol hybrid.