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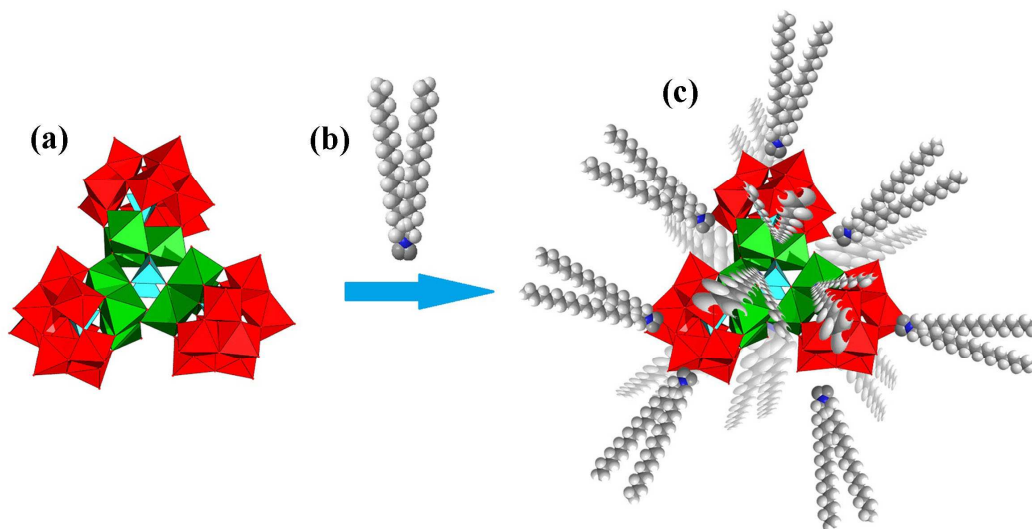
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Graphical



The dimethyldioctadecylammonium (DODA^+) was used as the surfactant to react with polyoxoanion $[\text{Ni}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$, resulting an organic-inorganic hybrid complex **SEP-1**, representing the first liquid crystal materials based on the high-nuclear transition-metal cluster-substituted polyoxoanions.

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ARTICLE TYPE

Design and construction of thermotropic liquid crystal material based on high-nuclear transition-metal cluster-containing polyoxometalate

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The dimethyldioctadecylammonium (DODA⁺) was used as the surfactant to react with the high-nuclear transition-metal cluster-containing polyoxometalate $K_5Na_{11}[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3] \cdot 52H_2O$ (POM-1), resulting a organic-inorganic hybrid complex (DODA)₁₆[Ni₉(OH)₃(H₂O)₆(HPO₄)₂(PW₉O₃₄)₃]₃·36H₂O (SEP-1), which exhibits characteristic thermotropic liquid crystalline behavior. Here, the high-nuclear transition-metal cluster-substituted polyoxoanions were firstly introduced into liquid crystalline materials. The chemical composition of the obtained SEP-1 was determined by IR spectra, elemental analysis, and thermogravimetric (TG) analysis. Also, polarized optical microscopy, differential scanning calorimetry (DSC), variable temperature X-ray diffraction (VT-XRD) were performed on SEP-1 to confirm its thermotropic liquid crystalline behavior.

1. Introduction

Polyoxometalates (POMs), as one kind of important molecule-based nanomaterials composed of the early transition-metal (TM) oxides, such as the elements of Mo, W, V, Nb and Ta, have attracted great attention owing to their structural variety and interesting physicochemical properties.¹⁻⁶ In the POM family, an important subfamily is the high-nuclear TM cluster-substituted POMs. In this subfamily, the introduction of the TM cations into the POM clusters can efficiently introduce the magnetic centers, electrochemical active centers, as well as the catalytic active center into the POMs. Thanks to the prominent work of POM chemists in the past decade, numerous high-nuclear TM cluster-containing POMs have been synthesized by reaction of lacunary POMs with 3d TM cations. For example, the {Mn₆}, {Mn₇}, {Mn₁₂}, {Fe₂₇}, {Co₁₆}, {Ni₇}, {Ni₁₃}, {Ni₄₈}, {V₆}, {Cu₉} and {Cu₂₀}-containing POMs were all synthesized and exhibited interesting magnetic and catalytic properties.⁷⁻¹⁸ Recently, these molecular nanomaterials composed of the TM clusters and lacunary POM units have been widely used as the useful individual functional components for constructing functional devices and materials.¹⁹⁻²¹ It has become a hot and important research field in the POM chemistry.

Recently, organic-inorganic hybrid materials have attracted wide attention as their intriguing topological structures and potential applications in various fields.²²⁻²⁵ POMs are usually

built into the organic-inorganic hybrid materials via two strategies. First, the polyoxoanions were covalently decorated by the organic ligands, which has supplied a series of POM-based organic-inorganic hybrid materials.^{26,27} Second, the polyoxoanions were encapsulated by the surfactant to construct the supermolecular materials. Liquid crystalline are a kind of organic-inorganic hybrid supermolecular materials, which can be automatically self-assembled via various kinds of materials and provide extra features.²⁸⁻³⁰ Many previous reports have shown that incorporating POMs into the organic liquid crystalline system could lead to novel hybrid liquid crystalline materials. This research field has attracted broad interest in the past few decades and a great progress has been achieved in constructing POM-based liquid crystalline materials.³¹⁻³⁶ For example, Wu *et al.* reported that the typical Keggin-type POMs (H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀) could be widely used as the building blocks for constructing organic-inorganic hybrid liquid crystalline materials.³⁴ They also used cationic surfactants to equip the Tb-substituted sandwich cluster [Tb(SiW₁₁O₃₉)₂]¹³⁻, resulting in the ionic liquid crystalline materials.³⁵ Faul and coworkers described the liquid crystalline behaviors of surfactant-encapsulated polyoxometalate (SEP) materials based [EuP₅W₃₀O₁₁₀]¹²⁻ and [Eu(SiW₉Mo₂O₃₉)₂]¹³⁻. Wang *et al.* used the DODA⁺ as the surfactant to encapsulate organic-inorganic hybrid POMs {Mo₂^VO₄[(Mo₂^{VI}O₆)NH₃CH₂CH₂CH₂C(O)(PO₃)₂]₂}⁶⁻ and {Mo₂^VO₄[(Mo₂^{VI}O₆)CH₃C(O)(PO₃)₂]₂}⁸⁻, resulting in two new SEP compounds with characteristic thermotropic liquid crystalline behavior.³⁷ Further, they also demonstrated the first example of Waugh- and Silverton-type POM-based thermotropic liquid crystalline materials.³⁸ Obviously, these liquid crystalline materials are mostly based on typical structural POMs (Keggin, Waugh, Silverton and Preyssler-type POMs *et al.*) and the sandwich-type POMs. As mentioned above, the synthetic

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† Electronic Supplementary Information (ESI) available: the TGA curve, ¹H NMR spectra and the optical textures. See <http://dx.doi.org/10.1039/b000000x/>

chemistry of POMs has made great progress in the past few decades, and thousands of novel high-nuclear TM cluster-substituted POMs have been obtained.⁷⁻¹⁸ However, no high-nuclear TM cluster-substituted POMs were used for constructing POM-based liquid crystalline materials. Here, a Ni₉ cluster-substituted trimeric high-nuclear POM cluster [Ni₉(OH)₃(H₂O)₆(HPO₄)₂(PW₉O₃₄)₃]¹⁶⁻ was encapsulated by surfactant DODA⁺ to construct thermotropic liquid crystalline materials (Fig. 1). The liquid crystalline behavior was determined by polarized optical microscopy, DSC, and VT-XRD, respectively.

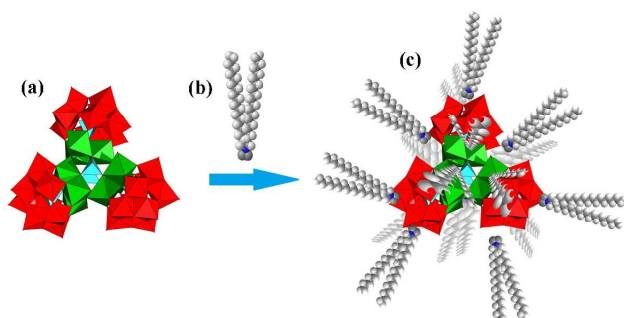


Fig. 1. Schematic view of the synthesis of **SEP-1**, (a) **POM-1**, (b) surfactant DODA⁺, (c) **SEP-1**.

2. Experimental section

2.1 Materials and Methods

The dimethyldioctadecylammonium chloride (DODACl) and chloroform were obtained from Aladdin Reagent Co. Ltd. (Shanghai, China) and used without further purification. **POM-1** was prepared according to literature procedure,³⁹ and identified by using IR spectroscopy. IR spectra were carried out on an Alpha Centaur FT/IR Spectrophotometer with KBr pellets. TGA was performed with the powder sample on a Perkin-Elmer TGA instrument flowing N₂ with a heating rate of 10 °C min⁻¹. DSC measurement was performed on a Netzsch DSC 204. The optical images were observed using a polarizing optical microscope (XP-400E, China) with a hot stage. For VT-XRD measurements, a Bruker AXS D8 ADVANCE X-ray diffractometer using CuK_α radiation of a wavelength of 1.54 Å with an mri Physikalische Geräte GmbH TC-Basic temperature chamber was used. Elemental analyses (C and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. W and Ni were determined by a Leaman inductively coupled plasma (ICP) spectrometer.

2.2 Preparation of SEP-1

POM-1 (716 mg, 0.08 mmol) was dissolved in 20 mL of distilled water resulting in a light green-yellow solution, and a 30mL light yellow chloroform solution of DODACl (751 mg, 1.28 mmol) was added dropwise to this aqueous solution with slowly stirring at about 150 r/min. The color of the organic phase turned to yellow after several minutes. After 5 h stirring at room temperature, the organic phase was separated, and the yellow powder was obtained by evaporation of chloroform to dryness. And then, the target product was further dried under vacuum. After 24 h, the weight remained constant. Combining the IR spectra of **POM-1**, DODA and **SEP-1** (Fig. 2, S5), it could be concluded that the surfactant replaced the counter cations around

polyoxoanion successfully, forming a complex with core-shell structure.²⁸ TGA analysis suggests a mass loss of 3.78% in the range of 20-100 °C (Fig. S1) resulting from loss of the water molecules in **SEP-1**. The ¹H NMR spectra of DODACl (Fig. S2) and **SEP-1** (Fig. S3) indicated that **SEP-1** contains DODA⁺ cation. Anal. Calcd for C₆₀₈H₁₃₆₉N₁₆O₁₅₅P₅W₂₇Ni₉: C 42.87; N, 1.32; Ni 3.10; W 29.14. Found: C 43.35; N, 1.58; Ni 2.92; W 28.73. According to the elemental analysis, TG analysis and the charge balance consideration, the chemical formula of **SEP-1** was determined as (DODA)₁₆[Ni₉(OH)₃(H₂O)₆(HPO₄)₂(PW₉O₃₄)₃]•36H₂O.

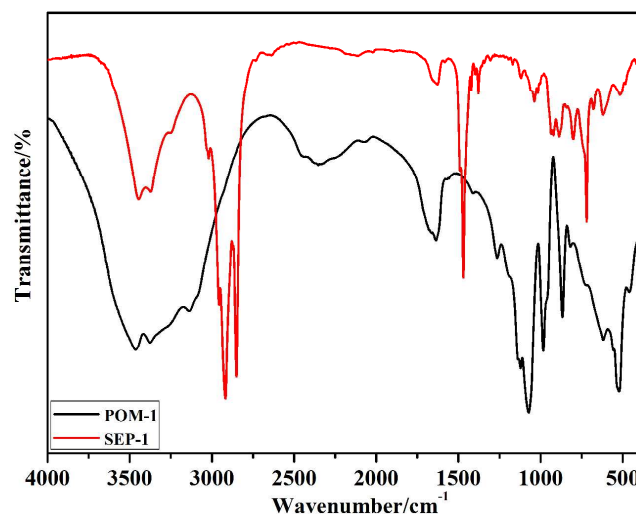


Fig. 2. IR spectra of **POM-1**, and **SEP-1**.

3. Results and discussion

Polyoxoanion [Ni₉(OH)₃(H₂O)₆(HPO₄)₂(PW₉O₃₄)₃]¹⁶⁻ is a high-nuclear TM cluster-substituted cluster, composed of nine nickel cations and three trivacant Keggin POM units (Fig. 1a).³⁹ These trimeric polyoxoanion was charge balanced by 16 alkali metal cations. Here, the potassium and sodium cations were replaced by the surfactant DODA⁺ via a simple ion exchange reaction, resulting in high-nuclear TM cluster-containing POM-based liquid crystal material. As shown in the DSC curves, **SEP-1** exhibits three phase transitions at 120 °C, 54 °C and 24 °C during its first cooling (Fig. 3), which can be assigned to the changes from isotropic liquid to liquid-crystalline phase, liquid-crystalline phase to the solid state, and a transition between two kinds of solids (solid 1 and solid 2), respectively. As shown in Fig. 3, **SEP-1** displays four phase transitions at 30 °C, 55 °C, 75 °C and 125 °C during its second heating. The first two peaks at 30 °C and 55 °C can be attributed to the changes from solid state 1 to solid state 2, and solid state 2 to SmX, respectively.³⁴ The last two peaks at 75 °C and 125 °C are attributed to SmX to SmA and SmA to isotropic liquid, respectively.³⁰ The phase transition temperatures, enthalpies and assignments of the phase transitions for **SEP-1** are summarized in Table 1. The phase transition from mesophases to isotropic phase during the second heating process could be confirmed by using the polarizing optical microscopy with a hot stage (Fig. 4). A hysteresis phenomenon is also presence in this transition process. The liquid birefringence phenomenon was observed at 102 °C on polarized optical

microscopy when complex was cooled from the isotropic phase (Fig. 4, S4), implying that the formation of the liquid-crystalline phase.

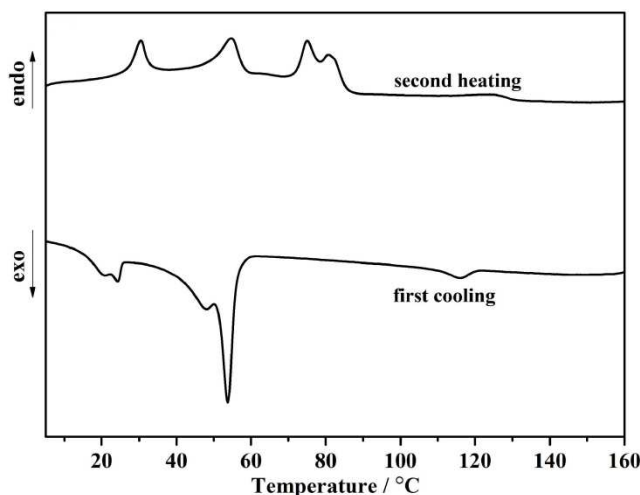


Fig. 3. DSC curves of **SEP-1** on its first cooling and second heating processes.

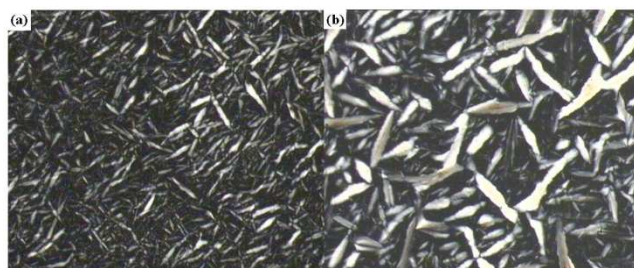


Fig. 4. The optical images of **SEP-1** at 110 °C (a) and 102 °C (b), respectively, during the cooling process (100×).

The liquid crystalline behavior of the **SEP-1** was further investigated by the VT-XRD measurement. As shown in Fig. 5, when the complex slowly cooled down from its isotropic state, strong equidistant diffractions in the small-angle region emerge along with a sharp diffraction at $2\theta = 2.56^\circ$ and diffuse peak in the wide-angle region at $2\theta \approx 20^\circ$ at 110 °C. This result confirms the formation of a layer structure, and the layer distance is 3.45 nm calculated from the Bragg equation. Considering the shortaxis diameter ($L_{\text{POM-1}}$) of polyoxoanion $[\text{Ni}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ is about 1.04 nm and the normal length (L_{DODA^+}) of DODA^+ is 2.25 nm, so the theoretical layer of **SEP-1** is about 5.54 nm. The distance of two neighboring layers ($d = 3.45$ nm) calculated from X-ray diffraction at 110 °C is ($L_{\text{DODA}^+} + L_{\text{POM-1}}$) $< d < (2 L_{\text{DODA}^+} + L_{\text{POM-1}})$, which indicates the alkyl chains are partially interdigitated (or tilted) in the smectic A structure of **SEP-1**.^{30,32,35} A possible packing structure of **SEP-1** is shown in Fig. 6. When the temperature decreases to 55 °C, we can clearly see the equidistant diffractions in the small-angle region and several sharp peaks in the wide-angle region. This heating process leads to a smectic X to solid transition. As shown in Fig. 5, the **SEP-1** in its solid state exhibits equidistant diffractions in the small-angle region and a sharp diffuse peak in the wide-angle region at $2\theta \approx 20^\circ$. Accordingly, it could be concluded that the

alkyl chains of **SEP-1** at 110 °C are more relaxed and exhibit a deeper interdigitated structure.^{30,34}

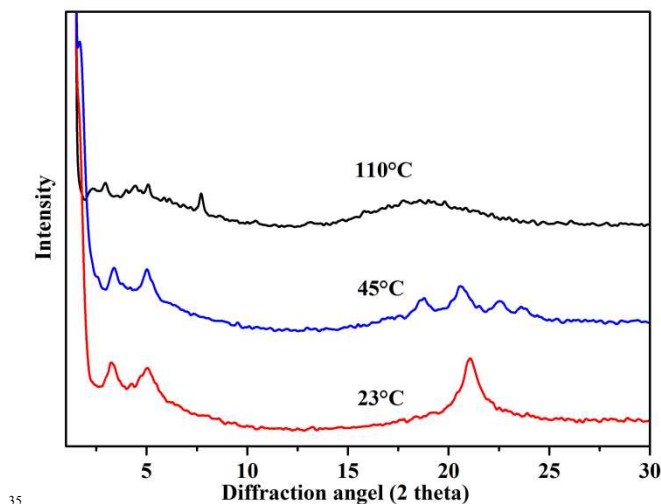


Fig. 5. The VT-XRD of **SEP-1** at 23°C, 45°C, and 110°C.

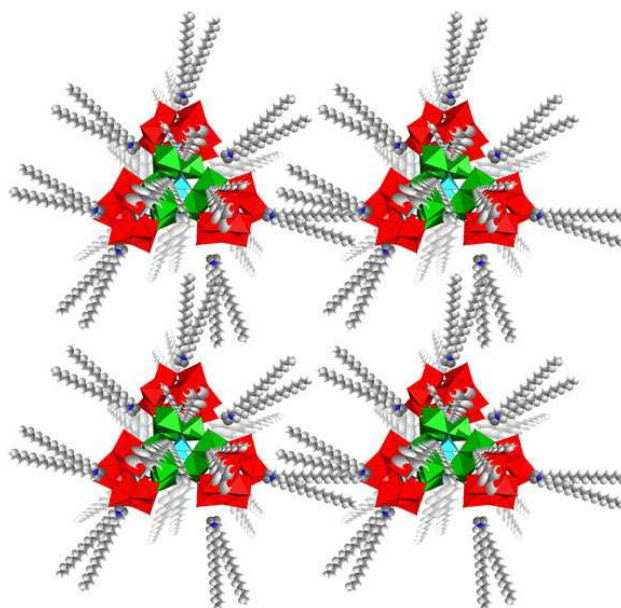


Fig. 6. Schematic drawing of the packing model of **SEP-1** at liquid crystal state.

Table 1 The phase transition temperatures (°C), enthalpies (kJ/mol), and assignments of the phase transitions for **SEP-1** (S = solid, S1 = solid 1, S2 = solid 2, SmX = smectic X, SmA = smectic A, Iso = isotropic phase).

Sample	Transition	Temperature/°C	$\Delta H/\text{KJ mol}^{-1}$
SEP-1	S1-S2	30	91.7
	S2-SmX	55	113.4
	SmX- SmA	75	199.1
	SmA-Iso	125	—

Conclusions

In this article, the high-nuclear TM cluster-substituted POM was firstly used as the building blocks to construct the SEP complex. Polarized optical microscopy, differential scanning

calorimetry and variable temperature X-ray diffraction study revealed that **SEP-1** shows thermotropic liquid crystalline behavior. The synthesis of the title material not only obtained a new POM-based liquid crystalline material, but also supplied a strategy for constructing the liquid crystalline materials with employing the high-nuclear TM cluster-substituted POMs as the building blocks. Further study will focus on the design and synthesis of the high-nuclear cluster-based liquid crystalline material.

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