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Anisotropic ionic liquids built from nonmesogenic cation surfactants and Keggin-type polyoxoanions†

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Non-mesogenic unit bearing Keggin-type polyoxoanions with tetra-*n*-octylammonium counterions exhibit an ionic liquid crystalline structure via ionic self-assembly in a certain temperature range.

Polyoxometalates (POMs), a class of discrete, negative charge early transition metal oxide clusters, possess a wealth of topologies and physical and chemical properties.¹ The POMs-based hybrid materials have attracted much attention during the past few years because such hybrid materials exhibit diverse interesting electronic, magnetic, redox, medicine and photonic properties, *etc.*² Among the variety of routes described to prepare these materials, ionic self-assembly has been successfully introduced to organize POMs with surfactants into ordered assemblies. The self-assemblies of these tectons are often accompanied with the formation of Langmuir–Blodgett (LB) films,³ bilayer or multilayer membranes,⁴ different kinds of mesophases,⁵ and ionic liquids (ILs).⁶ In the preparation of organic/POMs mesostructured materials, an effective method is that using the mesomorphic cation surfactant to encapsulate POMs through electrostatic interaction forming liquid crystals (LCs) hybrid materials. However, it is difficult to obtain the surfactant with mesogenic units because there is need to strictly control the complex multiple-steps. In these cases, the liquid crystallinity is completely provided by the predesigned mesomorphic cations. As we know, there are merely three examples of POMs-based liquid crystalline hybrid materials composed of non-mesogenic unit bearing surfactants and polyoxoanions reported so far.^{5a,h,k} Moreover, the surfactants with two long alkyl chains were mostly used as the structure-directing agents in such systems, few other surfactants were used. Therefore, the extension of such investigations should provide further insight into the structure–property–function relationships that exist in such nanostructured organic–inorganic hybrids. Furthermore, the controlled spatial assembly of

defined size and shape POMs in different surfactants promises new synergistic properties of materials.

We now chose tetra-*n*-octylammonium (TOA) cation containing four equivalent *n*-alkyl chains ($n = 8$) and Keggin-type polyoxoanions (PW₁₂O₄₀³⁻, GeW₁₂O₄₀⁴⁻ and BW₁₂O₄₀⁵⁻) to prepare three new surfactant/POM hybrids: [(C₈H₁₇)₄N]₃[PW₁₂O₄₀] (TPW), [(C₈H₁₇)₄N]₄[GeW₁₂O₄₀] (TGeW) and [(C₈H₁₇)₄N]₅[BW₁₂O₄₀] (TBW) by a straightforward ion exchange reaction, respectively. The obtained complexes are highly insoluble in water and are viscous at room temperature except TPW. Single crystals of TPW were only obtained from ethanol/dichloromethane mixture (1:1 by volume, 20 mL) by slow evaporation at room temperature. TPW does not exhibit mesomorphism, however, TGeW and TBW exhibit thermotropic LC behaviors despite the fact that neither the Keggin-polyoxoanions nor TOA cation are mesogenic unit containing components.

The packing in the crystal structure of TPW can be described as a pseudo-lamellar system with a stacking direction along the *b* axis (Fig. S11, ESI†). The electrostatic forces associate the rigid POM anions with TOA cations and each POM anion is surrounded by the surfactants. These units, POM anions, comprise layers that are completely segregated by the flexible alkyl chains. The layers are stacked along the *b* axis at a repeat distance of approximately 14.37 Å.

The LC properties of TGeW and TBW were analysed by differential scanning calorimetry (DSC) (Fig. S7 and S8, ESI†). The LCs state of TGeW was observed between 80.2 °C to 115 °C during the second heating run, however, a broad peak at about 75 °C was only observed upon cooling that should correspond to a slow phase transition from the isotropic phase to a crystal phase. During the first heating, complex TBW, as obtained from the synthesis, shows a clear melting transition. However, the reverse process is not observed in the cooling run. Instead, a glass transition is observed around 0 °C. Because the glass transition temperature is relatively low, the LCs phase of TBW shows a wide temperature range including room temperature, which is beneficial for the applications. The phase transition temperatures of TBW and TGeW are below 100 °C and 150 °C,^{7,8} therefore they can formally be considered as the ILs.

TGeW and TBW are viscous fluids on heating with clearly birefringence and can be spread on the glass. TGeW exhibited a focal conic fans texture at 85 °C, as shown in Fig. 1(a).

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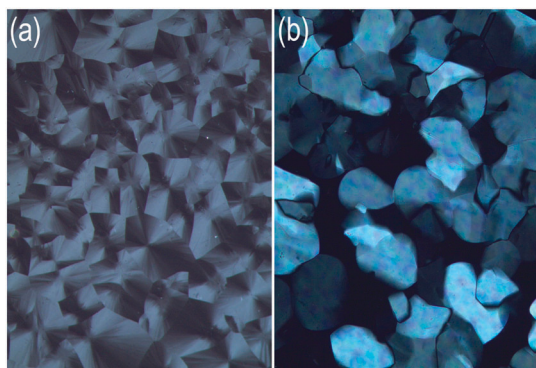


Fig. 1 Optical textures of complexes are obtained under an optical polarized microscope. (a) TGeW at 85 °C on heating, and (b) TBW at 45 °C on cooling from isotropic liquid (100 \times).

TBW crystallizes slowly, and a well mesophase texture could be obtained in 1 hour after cooling from the isotropic liquid state at 45 °C (Fig. 1(b)).

The temperature dependence of IR spectra provides evidence of the structure and dynamics of alkyl chains in the LCs state, especially the antisymmetric (d^-) and symmetric (d^+) stretching vibrations of the methylene groups. In the range of 35–170 °C, the spectra of TGeW at high wavenumbers, which has eliminated thermal history, are shown in Fig. S9 (ESI †). To further analyze the temperature dependence of the packed alkyl chain structure, we quantify the frequency changes of d^- and d^+ as a function of the temperature (Fig. 2). Upon heating, the initial plateau at 2925.84 cm^{-1} is retained until 80 °C, suggesting little change in the d^- conformation in this temperature region. An obvious shift of the methylene anti-symmetric stretching mode to higher wavenumbers is observed in the 80–90 °C range. The absorption band shift illustrates an increasing accumulation of *gauche* conformers in the alkyl chain ensembles, and corresponds to the phase transitions of crystals to LCs observed from DSC measurements. After that the band position keeps unchanged, because the alkyl chains are highly disordered. The symmetric stretching mode of methylene does not appear very sensitive to the aggregated structural change as its wavenumber remains constant through phase transitions.

The mesophases and structures of TGeW and TBW are further identified by using XRD. The characteristic lamellar

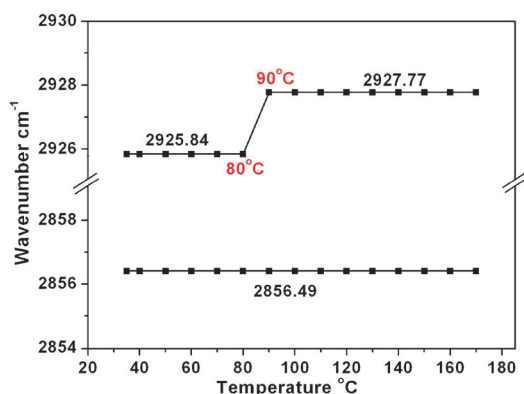


Fig. 2 Temperature dependence of the positions of IR bands of antisymmetric and symmetric stretching vibrations of CH_2 .

structures in the diffraction patterns are obtained for temperature ranges corresponding to the mesophases detection by DSC. The diffraction patterns contain a strong fundamental reflection in the small-angle region, which arises from the regular arrangement of the molecules in layers. A diffuse reflection around 4.5 Å in the wide-angle region of the patterns is related to the disordered conformation of the alkyl chains in the LCs phase. In addition, there appeared more significant small peaks with d -spacing values of 14.6, 13.0 and 9.8 Å as the temperature decreases in the diffraction patterns of TGeW, which may be due to the regularity of the positions of Keggin-polyoxoanions within the layer (seen in Fig. 3). It suggests that a smectic-type phase of the complex is formed more structurally ordered than the conventional SmA and SmC.⁹

Inspired by the single-crystal results of TPW and the XRD data of TGeW and TBW, we presumed that the superstructures of the complexes show a tendency to layered aggregation in the LCs state. A layer stacking with alternating polar anions and apolar cations may be assumed, as shown in Fig. 4. Considering the tetrahedral conformation of TOA and the length of alkyl chain (C8) is 10 Å in the LCs state according to previous studies,¹⁰ the perpendicular height of C8 is about 5.77 Å. Combining the diameter (10.4 Å) of Keggin-polyoxoanions and the double perpendicular height of C8, the total thickness of a single layer should be around 21.95 Å. This value is larger than the layer distance measured by XRD in the mesophase. We believe that there is partial interdigitation of TOA alkyl in the smectic structures or conformational disorder of chains. Such a structure is expected to be energetically favorable due to the resulting maximization of the hydrophobic interaction between the interdigitated chains.¹¹

In contrast to classic LC materials, the architectures of TGeW and TBW are unconventional, as the POMs cluster is a polarizable rigid group that is suitable as a potential mesogenic core, similar to the ionic liquid crystals containing rigid cores.¹² The TOA cation is a hydrophobic flexible group and increases conformational freedom. In such ionic amphiphiles, electrostatic interactions, microsegregation and the minimization of volume can give rise to an ionic self-assembly formation ordered supramolecular structure. In the light of the low phase

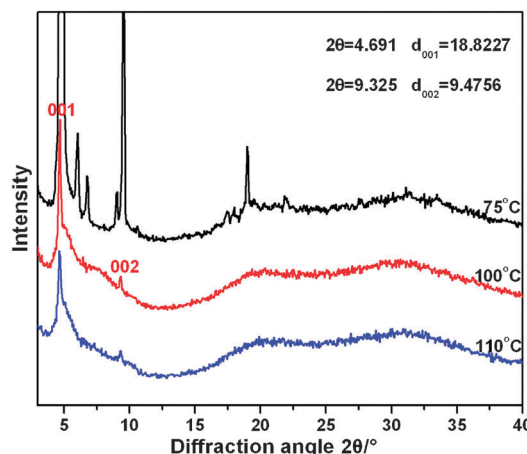


Fig. 3 X-ray diffraction patterns obtained from the 2nd heating as a function of temperature for TGeW.

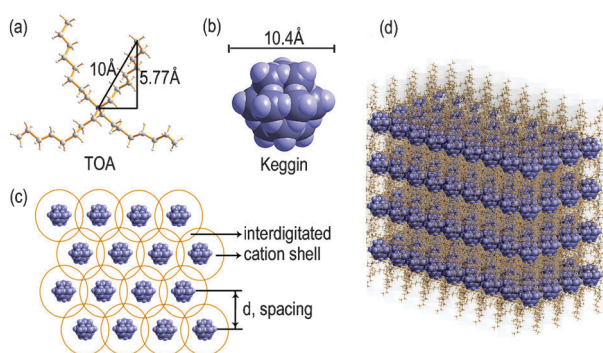


Fig. 4 (a) The tetrahedral conformation of TOA cation; (b) Keggin-polyoxoanion of the space-filling mode; (c) representation of arrangement of molecules with partial interdigitation of TOA alkyl in the LCs state; (d) a proposed lamellar structure of the complexes in the LCs state.

transition temperatures and anisotropic properties, TGeW and TBW can also be regarded as the ordered ILs.

In conclusion, in this work a new class of POMs-based ionic liquid crystals without mesogenic units has been obtained by a straightforward ion exchange reaction. These salts exhibit a lamellar structure in the LCs state revealed by X-ray diffraction. The property combined with the well-known ionic liquid crystal features and the variety of polyoxoanions makes these materials of great potential in areas ranging from optics devices, electrolytes of fuel cells and solar cells to catalysts. Our future work will focus on exploring the simple preparation and possible application of the kind of materials.

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