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Research Paper

# Photoluminescent lyotropic liquid crystals formed by Tyloxapol and *n*-dodecyl tetraethylene monoether

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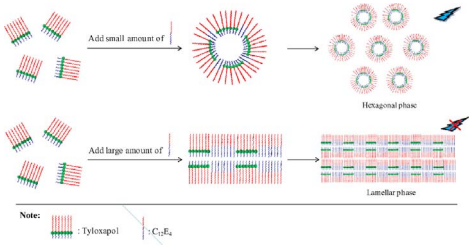
## GRAPHICAL ABSTRACT

The schematic illustrations of the interaction between 30 wt% Tyloxapol with different concentrations of $C_{12}E_4$ to form hexagonal and $L_\alpha$ phases.

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## ABSTRACT

Photoluminescent lytropic liquid crystals (LLCs) were prepared in aqueous solutions from *n*-dodecyl tetraethylene monoether ($C_{12}E_4$) and Tyloxapol, which is an oligomer of polyoxyethylene *tert*-octylphenyl ether (TX-100) with a polymerization degree below 7. The close packing of the seven benzene rings in Tyloxapol induces a strong π–π interaction, which makes Tyloxapol fluorescent. The Tyloxapol/$C_{12}E_4$ mixed system were characterized by polarized optical microscopy (POM) observations, small-angle X-ray scattering (SAXS), rheological and fluorescence measurements with close comparison to the TX-100/$C_{12}E_4$ mixture. It was found that the type of LLCs transfered gradually from lamellar phase to hexagonal phase with increasing mass ratio of Tyloxapol to $C_{12}E_4$, during which an enhanced photoluminescence was observed. Our results showed that encapsulation of fluorescent molecules into the matrix of traditional surfactants could be an effective way for the preparation of photoluminescent LLCs.

## 1. Introduction

Supramolecular self-assembly, which has attracted growing attention in recent years, is a branch of smart chemistry and offers a bottom-up approach to construct new materials without complex organic synthesis [1–4]. Amphiphiles with low molecular weights are widely used for supramolecular self-assembly where the process is driven mainly by noncovalent interactions such as electrostatic interaction, hydrogen bonding, host-guest interaction, π–π stacking, van der Waals force and hydrophobic/hydrophobic interaction [5–10]. These interactions can be adjusted through a smart design of the molecular structure, which results in the formation of various self-assemblies

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including micelles, vesicles and lyotropic liquid crystals (LLCs) [11–22].

Among various supramolecular self-assemblies, LLCs have attracted increasing interest for their potential applications in biomaterials and templated synthesis of functional materials [15,23–26]. The structures of the LLCs can be tuned and their functionalities can be expanded by the introduction of guest molecules, resulting in the formation of multifunctional soft materials. Specifically, introduction of π-conjugated molecules has attracted considerable attention due to the great potential applications of the hybrid materials in optoelectronics and fluorescence sensors [27–33]. There are a few examples by integrating π-conjugated molecules with thermotropic liquid crystals (TLCs). For example, Yuan et al. reported the incorporation of europium substituted polyoxometalate (PM) into chiral surfactant (CS) to construct multifunctional chiral photoluminescent TLCs [34]. They demonstrated that the CS-PM complex displayed intrinsic photoluminescence that could be adjusted by accurately controlling the temperature. The electrostatic encapsulation of PM with chiral mesomorphic promoters provides an effective method for constructing PM-based chiral photoluminescent TLCs. For another example, Nguyen et al. self-assembled semiconductor quantum dots into cellulose nanocrystal-templated silica to construct TLCs by a straightforward, one-pot approach [35]. They demonstrated that by regulating the intermolecular interactions between polyacrylic acid/mercaptopropionic acid-stabilized CdS quantum dots and tetraalkoxysilane/cellulose nanocrystal dispersion to get a balance, CdS/silica/nanocellulose composites can be successfully prepared which retain both chiral nematic order of the cellulose nanocrystals and the emission properties of CdS quantum dots. However, examples about the construction of photoluminescent LLCs through the introduction of π-conjugated molecules are quite rare.

Herein, photoluminescent LLCs were constructed in aqueous solutions by mixing *n*-dodecyl tetraethylene monoether ($C_{12}E_4$) and Tyloxapol, which is an oligomer of polyoxyethylene *tert*-octylphenyl ether (TX-100). In comparison, TX-100/$C_{12}E_4$ LLCs were also prepared under similar conditions. The properties of both systems have been investigated in detail by a variety of techniques including small-angle X-ray scattering (SAXS), polarized optical microscopy (POM), rheological and fluorescent measurements. Change of the LLCs from a lamellar phase to a hexagonal one with increasing mass ratio of Tyloxapol to $C_{12}E_4$ has been revealed, during which the photoluminescence of the mixed system was greatly enhanced.

## 2. Experimental section

### 2.1. Materials

$C_{12}E_4$ was purchased from Acros Organics (USA, > 99%). Tyloxapol and TX-100 were purchased from Sigma. Their chemical structures are shown in Fig. 1. All the reagents were used without further purification. Ultra-pure water was triply distilled by a quartz water purification system.

### 2.2. Sample preparation method

Samples were prepared by mixing Tyloxapol and $C_{12}E_4$ in water. The total weight percentage of Tyloxapol and $C_{12}E_4$ is at 50 wt% while their mixing ratio was changed. Totally six samples were prepared where the weight percentage of Tyloxapol is 0, 20%, 40%, 60%, 80% and 100%, respectively. Samples in TX-100/$C_{12}E_4$ system were prepared in the same way.

### 2.3. Characterizations

POM observations were performed using an AXIOSKOP 40/40 FL (ZEISS, Germany) microscope. SAXS measurements were carried out on an HMBG-SAX system (Austria) with a Ni-filtered CuKa radiation

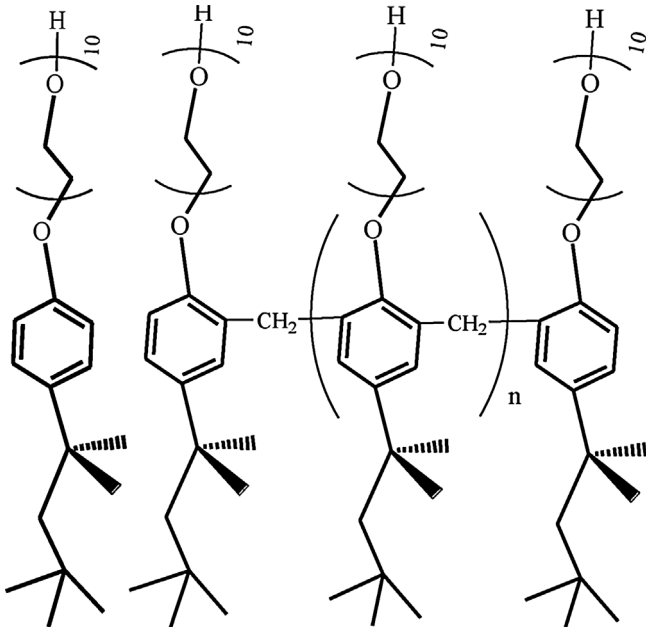


**Fig. 1.** The chemical structures of TX-100 and Tyloxapol.

(0.154 nm) operating at 50 kV and 40 mA. The fluorescence spectra were recorded on a lumina fluorescence spectrometer (Thermo Scientific). The quantum yield was measured on a FLS920 with a time correlated single photon counting (TCSPC) method by excitation with 360 nm.

Rheological measurements were carried out on a HAAKERS75 rheometer with a cone-plate system (Ti, diameter, 35 mm; cone angle, 1°) at 20.0 ± 0.1 °C with the help of a cyclic water bath. Steady-shear measurements were performed from 0 to 1000 $s^{-1}$. In oscillatory measurements, an amplitude sweep at a fixed frequency (1 Hz) was performed prior to the following frequency sweep (0.01–20 Hz).

## 3. Results and discussion

### 3.1. Tyloxapol/$C_{12}E_4$ photoluminescent LLCs

#### 3.1.1. SAXS and POM observations

First, the influence of the weight percentage of Tyloxapol and $C_{12}E_4$ on the properties of Tyloxapol/$C_{12}E_4$ LLCs were investigated and the phase behavior of the ternary Tyloxapol-$C_{12}E_4$-$H_2O$ system was performed. We fixed the total weight percentage of Tyloxapol and $C_{12}E_4$ at 50 wt% and changed their mixing ratio. The type of LLCs was checked by SAXS and POM observations.

The results obtained from SAXS are summarized in Fig. 2A. The lattice parameter of the lamellar (*d*-spacing) or the hexagonal lattice (*a*) can be calculated from the q value of the first peak ($d = 2\pi/q_{max}$). Pure 50 wt% Tyloxapol in water shows diffraction peaks with *q* values in a ratio of 1:√3:2, which indicates the formation of a hexagonal phase [36,37]. The lattice parameter *a* is calculated to be 4.95 nm (curve a). Pure 50 wt% $C_{12}E_4$ in water shows diffraction peaks with *q* values in 1:2 ratio (curve f). From POM observations, the Maltese crosses and oil steaks were observed (Fig. 3). These results indicate the formation of a lamellar ($L_\alpha$) structure [25]. The *d*-spacing is calculated to be 6.74 nm. The asymmetry and broadening of the first peak could be caused by the Helfrich undulation which would cause an uneven distribution of the *d*-spacing [24].

Then we fixed the total weight percentage of surfactant at 50 wt% and varied the ratio of Tyloxapol and $C_{12}E_4$. When the weight percentage of $C_{12}E_4$ ($c_{C12E4}$) is 10 wt%, 20 wt%, and 30 wt% (curve b–d), the *q* values of the Bragg peaks remain in a 1:√3:2 ratio, but shift to lower values corresponding to larger lattice parameters which are