Photoresponsive Supramolecules: Fibers and Vesicles Formed by Self-assembled Azobenzene-Containing Amphiphilic Phosphates

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Lyotropic liquid crystal (LLC), one of the liquid crystalline phases, commonly was used to describe materials composed of amphiphilic molecules and solvents. The amphiphilic molecules comprise a hydrophilic head group and a hydrophobic group, whose typical example is phospholipid. In recent years, LLC, as a form of supramolecule, has attracted many researchers’ attention owing to their excellent potential as drug delivery systems [1-2]. In this work, stimuli-responsive azobenzene-containing amphiphilic phosphate derivatives (X-Az-Y-6-PC), showing a LLC phase in water, were designed and prepared. Then, by mixing 2 different kinds of X-Az-Y-6-PC, vesicles or fibers were obtained. Finally, the effect of light on self-assembled supramolecules was investigated.

Figure 1. The molecular structure of azobenzene-containing amphiphilic phosphates with various functional groups (X-Az-Y-6-PC): [X,Y] = [CH₃O, O], [O₂N, O], [O₂N, N(CH₃)]

Synthesis of azobenzene-containing amphiphilic phosphates
Azobenzene-containing amphiphilic phosphates: CH₃O-Az-O-6-PC, O₂N-Az-O-6-PC and O₂N-Az-N(CH₃)-6-PC were successfully synthesized [³], respectively. Typical synthetic route was shown in Fig. 2.

Figure 2. Typical synthetic route of azobenzene-containing amphiphilic phosphates (X-Az-Y-6-PC)

Effect of the molecular structure on the formation of supramolecules
Supramolecular assemblies as fibers and vesicles formed from spontaneous self-assembly of
azobenzene-containing amphiphilic phosphates aqueous solution were explored. As shown in Fig. 3, combination of \( \text{CH}_3\text{O-Az-O-6-PC} \) and \( \text{O}_2\text{N-Az-N(CH}_3\text{)_6-PC} \) led to aggregation of fibers, and combination of \( \text{CH}_3\text{O-Az-O-6-PC} \) and \( \text{O}_2\text{N-Az-O-6-PC} \) led to aggregation of vesicles in the progress of electrostatic interaction.

**Figure 3.** The formation of supramolecules: A. fibers made by \( \text{CH}_3\text{O-Az-O-6-PC} \) (5mM) and \( \text{O}_2\text{N-Az-N(CH}_3\text{)_6-PC} \) (5mM) (taken by microscope); B. vesicles made by \( \text{CH}_3\text{O-Az-O-6-PC} \) (2mM) and \( \text{O}_2\text{N-Az-O-6-PC} \) (2mM) (taken by microscope); C and D. SEM of fibers made by \( \text{CH}_3\text{O-Az-O-6-PC} \) (5mM) and \( \text{O}_2\text{N-Az-N(CH}_3\text{)_6-PC} \) (5mM);

Light-stimuli-responsive behavior of the supramolecules

The irradiation of UV and visible light were carried out to study their light-stimulus-responsive behavior of the supramolecules. The irreversible disassembly of fibers occurred upon UV light, while the reversible disassembly and reassembly of vesicles could be induced by UV and visible light.

**Literature**


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