



Preparation and photochromic properties of layer-by-layer self-assembly films and light-responsive micelles based on amphiphilic naphthopyran derivative



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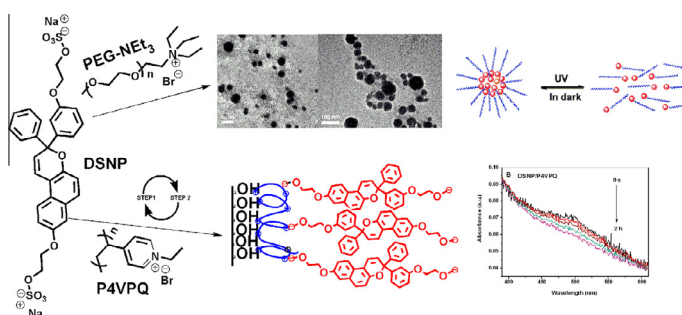
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HIGHLIGHTS

- An amphiphilic naphthopyran derivative (DSNP) was designed and prepared.
- DSNP can self-assemble into the LBL films with cationic quaternized poly(4-vinylpyridine).
- DSNP also assemble into light-responsive micelles with polyethylene glycol–triethylamine bromide.
- Naphthopyran displayed a markedly slower fading rate in LBL films.
- The photochromic reaction of naphthopyran induced disassembly and re-assembly of micelles.

GRAPHICAL ABSTRACT



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ABSTRACT

An amphiphilic naphthopyran derivative (DSNP) with negative-charged di-sulfatoethoxy was first designed and synthesized. DSNP was used to prepare the LBL self-assembly films with cationic quaternized poly(4-vinylpyridine) (P4VPQ). The multilayer assembly process was monitored via UV–Vis spectra and the DSNP displayed a significant slow fading rate in film. In addition, DSNP was also used as the light-responsive group to fabricate light-responsive micelles with polyethylene glycol–triethylamine bromide (PEG–NEt₃). The photoisomerization of naphthopyran moieties can rapidly and reversibly tune the disassembly and re-assembly of the micelles. The changes of fluorescent spectra of Nile Red (NR) in water solution of polymeric micelles demonstrated that the polymeric micelle can be used as nanocarriers to encapsulate, release and re-encapsulate guest solutes on demand controlling of light irradiation. The results indicate that the amphiphilic naphthopyran can be used in both optical-switches and biomedical area for drug delivery.

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1. Introduction

Photochromic materials are of considerable interest due to their potential applications in optical-switches memories, precision

machining, triaxial data storage and nonlinear devices [1–3]. Photochromic compounds, such as diarylethenes, spiropyrans, spirooxazines, azobenzenes, naphthopyrans have attracted considerable research attention [4–6] because they display a reversible molecular structure transformation, which results in a reversible change from colorless to colored states upon alternative irradiation of ultraviolet (UV) light and visible light. Among them,

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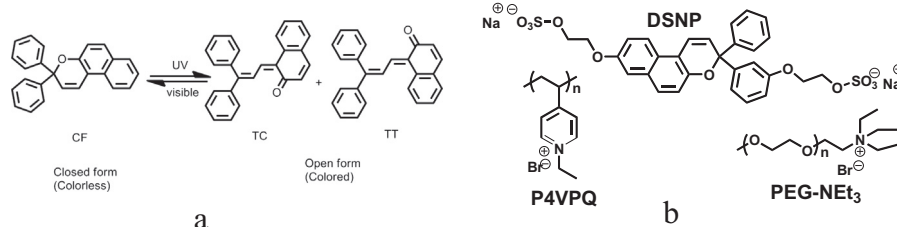
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naphthopyrans (NP) are one type of important photochromic compounds with special properties, such as the absence of background color and good thermal reversibility, etc [7].

When exposed to UV light, the photochromic reaction of the naphthopyrans occurs via the heterolytic cleavage of the C–O bond in the pyran moiety (Scheme 1). Two main isomeric open-forms (merocyanines, MC) are produced in the process, which present intense color due to their extended conjugation and quasi-planar structures. Ceasing UV irradiation leads the colored forms to thermally or photochemically return back to the original colorless state and the molecules undergo an important intramolecular rotation in the process [8,9]. The fading speed, that is the change rate of color, plays a crucial role for their practical application. Therefore, it is of great importance to tune the fading speed simply and efficiently to meet the demand requirements of the applications. Another researchful field is that the deformation of photochromic molecules on a micro level can cause the macroscopic change of matrices in which the photochromic molecules are incorporated, such as photo-controlled actuators or disassembly of micelles [10–13]. Until now, naphthopyran has not been studied in this particular field except in one of our report [14]. Most of research works on naphthopyran are based on modification of naphthopyran molecule with different functional groups [15–17] or incorporating naphthopyran into polymers in which the dyes are incorporated to modulate the fading rate of open-form NP [18–20]. Modification on naphthopyran molecules with different substitution groups is an adaptable strategy because it can change the intrinsic electronic nature or structure to further influence the fading speed. What is more, in polymers, the changing of the local host environment and the media can also tune the photochromic kinetics of naphthopyran units.

Our research group has always been committed to explore the new applications of naphthopyran in three fields and got some pioneering results. The first one is about photo-controlled fluorescence switching [21–23], in which the photoisomerization of naphthopyran molecules can modulate the fluorescent intensities of fluorophores. The second is about the introduction of naphthopyrans into nanostructures (layer-by-layer (LBL) self-assembly films and nanoparticles). It has been revealed that naphthopyran in nanostructures displayed a significant slow fading speed and the merocyanine structures are more stable than those stated in previous reports [24–26]. The third is the first time to use the photochromism of naphthopyrans to tune the assembly and disassembly of polymer micelles [14].

Based on the findings of our previous works, in this paper, we designed and synthesized an amphiphilic naphthopyran derivative with negative-charged di-sulfatoethoxy and this di-sulfatoethoxy naphthopyran compound was denoted as DSNP (Scheme 1). DSNP can be used in two main applications, viz, to prepare the LBL self-assembly films with cationic quaternized poly(4-vinylpyridine) (P4VPQ) and as the light-responsive group to fabricate light-responsive micelles with polyethylene glycol-triethylamine bromide (PEG-NEt₃).



Scheme 1. (a) Generic photochromic process of the naphthopyran, (b) the molecular structure of DSNP and polymers used to fabricate the LBL films and micelles.

2. Experimental

2.1. Materials and instrumentation

Poly(4-vinylpyridine) (P₄VP, $M_w = 60,000$), triphenylphosphine, pyridine-SO₃ complex, p-toluene sulfonic acid (PTSA), and CBr₄ were purchased from Aladdin. methoxypolyethylene glycol 5000 (PEG, Fluka), bromoethane (J&K Scientific), Nile Red (99%, J&K Scientific) were all used as received. Sulfuric acid (98%), hydrogen peroxide (30%), triethylamine, and tetrahydrofuran (THF) were all analytical grade products from Beijing Chemical Reagent Company and used without any further purification. Deionized water (Millipore) was used for all experiments. All chromatography examinations were performed using silica gel, and thin layer chromatography was performed on silica plates (made in China). The synthesis of 2-hydroxy-6-(2-hydroxyethoxy)naphthalene and 1-(4-(2-hydroxyethoxy)phenyl)-1-phenyl-2-propyn-1-ol has been described in the literature [18].

A CHF-XM35 parallel light system with a 500 W xenon lamp was used as the light source for irradiation. The photochromic properties of the polymeric films were examined using a Varian Cary 500 UV-Vis spectrophotometer. The film samples were placed on the sample holder in the spectrophotometer at a slope of about 45 °C and their absorbance was measured. The maximum absorption wavelength (λ_{max}) of the opened-ring naphthopyran was obtained by plotting the UV spectrum of the sample. Fluorescence emission spectra were recorded from Cary Eclipse Fluorescence Spectrophotometer and the excitation wavelength was 565 nm. All of the experiments were carried out at room temperature. The ¹H NMR spectroscopy spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz) at room temperature. Here d-chloroform and DMSO were used as the solvents. Transmission Electron Microscopy (TEM) analysis was performed on a JEOL-2011F microscope operating at an accelerating voltage of 200 kV. Samples were prepared by placing a drop of the solutions on a 400-mesh carbon-coated copper grid.

2.2. Synthesis of DSNP

DSNP was synthesized according to the synthetic route shown in Fig. S1A. A mixture of 2-hydroxy-6-(2-hydroxyethoxy)naphthalene (2.0 g, 10.0 mmol), 1-(4-(2-hydroxyethoxy)phenyl)-1-phenyl-2-propyn-1-ol (3.0 g, 11.0 mmol), and PTSA (0.2 g) in 20 mL of dry CH₂Cl₂ solution were stirred at room temperature under nitrogen atmosphere for 48 h. The reaction mixture was washed with water (3 × 50 mL) and organic solution was dried with anhydrous sodium sulfate. The crude product was further purified by column chromatography on silica gel (petroleum ether:ethyl acetate = 2:1), orange solid 2.7 g, 60% yield. ¹H NMR (500 MHz, CDCl₃, δ): 8.59 (s, 1H, OH), 7.87 (d, $J = 9.0$ Hz, 1H, Ar-H), 7.53 (d, $J = 9.0$ Hz, 1H, HC=CH), 7.47 (d, $J = 7.0$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.33–7.30 (m, 2H, Ar-H), 7.24 (d, $J = 7.0$ Hz, 1H, Ar-H), 7.18–7.15 (m, 2H, Ar-H), 7.05 (d, $J = 2.0$ Hz, 1H, Ar-H),

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