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Full Length Article

Fluorescent sensitization of gemini surfactant micellar-hybridized supramolecular hydrogels

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ABSTRACT

Fluorescence enhancement of the fluorescence probe 1,8-anilinonaphthalenesulfonicacid (ANS) in micellar-hybridized supramolecular hydrogels consist of micelles formed by gemini surfactant (GS) and supramolecular hydrogels formed by self-assembly of hydrogelator *N,N′-Dibenzoyl-L-cystine* (DBC) was investigated by steady state fluorescence and time-resolved fluorescence. An optimum ratio of GS/DBC was obtained by maximum fluorescence quantum yield of ANS. The fluorescence images show that ANS were dispersed in the micellar-hybridized supramolecular hydrogels. The fluorescence intensity of ANS in the micellar-hybridized supramolecular hydrogels was significantly increased in comparison with that in corresponding aqueous solutions and DBC hydrogels. SEM images indicated that the microscopic morphology of micellar-hybridized DBC gels possessed a three-dimensional network structure. The results implied that the micellar-hybridized supramolecular hydorgels can form more complex structure compared to hydrogels. It is suggested that the fluorescence of the probe within the hybridized system is a facile and sensitive method to monitor the structure of the micellar-hybridized supramolecular hydrogels.

1. Introduction

Hybrid assembled systems usually consist of the different components with specific structures and functionalities to meet the promising applications such as multi-channel response [1], microstructure control [2] and so on. Supramolecular hydrogels formed by the self-assembly of hydrogelators in aqueous media are novel soft materials and show potential applications such as regenerative medicine and drug delivery [3–6]. Since surfactants can form micelles with various morphologies, the micellar-hybridized systems are recently a subject of increasing attention, such as micellar-hybridized polymer [7,8] and micellar-hybridized supramolecular gels [9,10]. Gemini surfactant which have possess better surfactant properties in comparison with the traditional surfactant exhibits a smaller critical micelle concentration (CMC) and superior wetting ability. The hybrid systems formed by the aggregates of gemini surfactant and hydrogelator which can provide synergistic behavior resulting in special feature such as fluorescence sensitization effect.

In recent years, the luminescence enhancement of typical organic fluorescent molecules trapped in supramolecular assemblies has been extensively studied [11]. For instance, 1,8-anilinonaphthalenesulfonicacid (ANS) is an organic fluorescence probe which is sensitive to the microenvironment, the change of intensity such as fluorescence enhancement or quenching of fluorescent probe can describe the variation of microenvironment, it has been extensively used to monitor the CMC, biological macromolecular folding and thermo-reversibility macromolecule [12–14]. However, very few investigations of fluorescence enhancement by micellar-hybridized hydrogels have been reported.

In this work, micellar-hybridized supramolecular hydrogels consist of micelles formed by *N′-((methylazanediyl)bis(ethane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminium)* (GS, Scheme 1) and supramolecular hydrogels formed by self-assembly of hydrogelator *N,N′-Dibenzoyl-L-cystine* (DBC, Scheme 1) was prepared, and the fluorescence sensitization mechanism of ANS in hybrid system was investigated using field transmission electron microscopy, fluorescence microscopy as well as steady-state and time-resolved fluorescence techniques. Because the fluorescence of ANS can respond to variation of the microenvironment within this system, the fluorescent behavior of ANS in hybrid system can be

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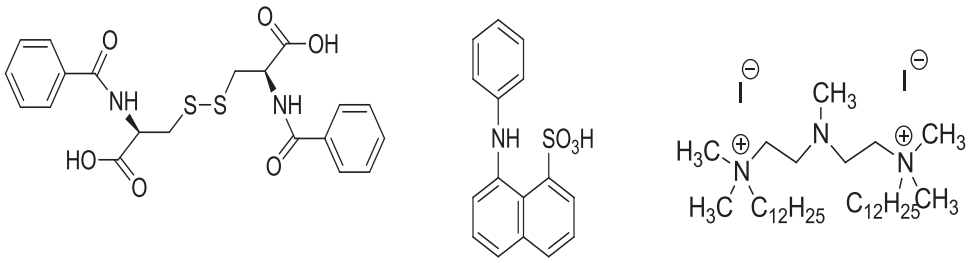

Scheme 1. Molecular structure of DBC, ANS and GS, respectively.

used to monitor the structure of the micellar-hybridized supramolecular hydrogels, and it is a facile and sensitive strategy compared with other methods.

2. Material and methods

2.1. materials

N,N-Dibenzoyl-L-cystine (denoted as DBC, purity 99%) was purchased from Fluka and used as received., Cationic Gemini surfactant, *N,N′*-didodecyl-*N,N,N′,N′,N″*-pentamethy l-1,4,7-triazaheptane diiodide (denoted as GS) was synthesized according to the literature reported procedures [15,16]. 8-anilino-1-naphthalenesulfonic acid (denoted as ANS) was purchased from TCI (Shanghai) Development Co., Ltd, dimethyl sulfoxide (denoted as DMSO) and cetylpyridinium chloride(denoted as CPC) were purchased from Sinopharm Chemical Reagent Co., Ltd. All water used in this work is ultrapure produced by a Millipore Direct-Q system.

2.2. Preparation of micellar-hybridized supramolecular hydrogels

Firstly, a designed amount of GS was mixed with an ANS (1.9×10^{-6} mol/L) aqueous solution. The mixture was heated in a water bath (ca. 60 °C). Then, a designed amount of DBC was added to a small amount of DMSO. In addition, the hot solution mixture was added into DMSO solution with the final ratio of DMSO/H_2O was 1/10 (v/v). Subsequently, both mixtures were poured into a vessel equipped with stirring. The hot solution mixtures were allowed to cool to room temperature to form a stable gel (denoted as the ANS/GS/DBC gel). Similarly, a blank gel was prepared without GS. The concentration of GS was equal to its CMC (0.2294 g/L). The mass fraction of DBC in all samples was 0.3 wt%.

2.3. Fluorescent measurements

Steady-state and polarized fluorescence measurements were performed with the spectrofluorimeter (FP-6500, Jasco). In a 5 mm cuvette, the hot solution mixtures were placed and then allowed to cool to room temperature. The anisotropy values (γ) of gels' procedure and calculation method were referred to the reference [17]. The excitation wavelength was 381 nm and the emission wavelength was 450 nm.

2.4. Scanning electron microscopy (SEM) and Fluorescent Optical Microscope (FOM)

The gel samples were frozen in liquid nitrogen and then freeze-dried. All samples were coated with Au and imaged by FE-SEM (Sirion 200, FEI). The accelerating voltage was 5 kV. The hot solution mixtures described above were dropped on a pre-heated glass plate. After cooling to room temperature, the gel samples were imaged by FOM (IX71, Olympus).

2.5. Fluorescence quenching measurements

Firstly, a designed amount of CPC was mixed with an ANS and GS aqueous solution, (10^{-4} mol/L). The mixture was heated in a water bath (ca. 60 °C). Then, the next step was prepared according to the method described in Section 2.2 and then allowed to cool at room temperature. The fluorescent measurement of gel was accorded to the method in Section 2.3.

2.6. Disassembly experiments and fluorescence measurements of GS/DBC micelles hybridized hydrogel

Time-dependent fluorescence was performed with the spectrofluorimeter. The GS/DBC micelles hybridized hydrogel was prepared according to the method described in Section 2.2. In the measurements of time-dependent fluorescence at 450 nm also, the NaF solution (0.1 mol/L) was carefully added on the top of the GS/DBC micelles hybridized hydrogel.

3. Results and discussion

3.1. Fluorescent ANS in micelles hybridized hydrogels

As shown in Fig. 1, the fluorescence of ANS in aqueous solution without GS and DBC is extremely weak (spectrum 1). In contrast, the fluorescent intensity of ANS increased significantly with a blue shift from 472 nm to 450 nm (spectrum 4) in GS/DBC micelles hybridized hydrogels in comparison with that in the corresponding GS solution (spectrum 3), it indicated that ANS was incorporated in less polar micelles environment [10], implying that the enhanced fluorescence may be caused by especially in GS/DBC micelles hybridized hydrogels in addition a weaker enhanced fluorescence of ANS was observed in DBC hydrogels (spectrum 2), which is a further indication that GS/DBC assemblies induce a synergistic sensitization effect. Therefore, enhanced fluorescence of ANS can be attributed

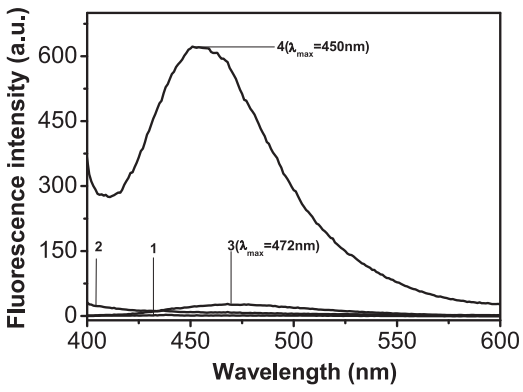

Fig. 1. The fluorescence spectra of ANS in the different matrixes. (1) aqueous solution; (2) DBC gel; (3) micelle solution; (4) GS/DBC gel.