



ELSEVIER

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Indication of critical micelle concentration of nonionic surfactants with large emission change using water-soluble conjugated polymer as molecular light switch

Lilin Sun^a, Dan Hao^a, Ping Zhang^a, Zhangsheng Qian^a, Weili Shen^a, Taili Shao^{a,b}, Changqing Zhu^{a,*}

^a Anhui Key Laboratory of Chemo-Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, China

^b Department of Pharmacy, Wannan Medical College, Wuhu 241000, China

ARTICLE INFO

Article history:

Received 8 May 2012

Received in revised form

10 August 2012

Accepted 17 August 2012

Available online 28 August 2012

Keywords:

Nonionic surfactant

Critical micelle concentration

Water-soluble conjugated polymer

Fluorimetry

Molecular light switch

ABSTRACT

A new near-infrared water-soluble conjugated polymer, i.e. poly [2,5-di (propyloxysulfonate)-1,4-phenylene-ethynylene-9,10-anthrylene] (PPEASO3) was synthesized to investigate its interaction with surfactants. It was found that PPEASO3 has only a weak fluorescence emission at about 670 nm due to its self-aggregation in water and in aqueous solution containing a low concentration of nonionic surfactants, i.e. below their critical micelle concentration (CMC). However, a dramatic fluorescence enhancement with a large emission blue-shift (> 40 nm) was found once the concentration of nonionic surfactants reached the CMC (especially for Triton X-100). An orange fluorescence could be observed even with naked-eyes under UV-lamp, which gave a direct indication for the micelle forming process and provided a simple method for the CMC determination of the nonionic surfactants. The CMC values determined by this method were in good agreement with those obtained by other techniques. The dramatic emission change observed could be ascribed to the intensive hydrophobic interaction between PPEASO3 and surfactants micelle, which greatly disrupts the aggregation of the polymer and increase the fluorescence efficiency of PPEASO3.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The minimum concentration of surfactants associate in aqueous solution is the critical micelle concentration (CMC). It is one of the most important physical parameters for preparing, solubilizing and characterizing liposomes, surfactants and other self-aggregating amphiphiles [1]. For example, surfactant solutions with a concentration above their CMC are frequently utilized in fluorescence spectrometry to solubilize the dye and enhance its photophysical properties [2–4]. Moreover, the CMC value is probably the simplest way of describing the colloid and surface behavior of a surfactant solution and reflects information about the industrial usefulness and biological activity of a detergent [5]. It can also be used to study kinetics and mechanism of reactions in some cases. Therefore, the determination of CMC of surfactants is very important.

The CMC is the relatively narrow concentration range over which amphiphile dispersions show an abrupt change in physical properties such as electrical conductivity, surface tension, osmotic pressure, light scattering, and sound velocity [1]. So, some detective

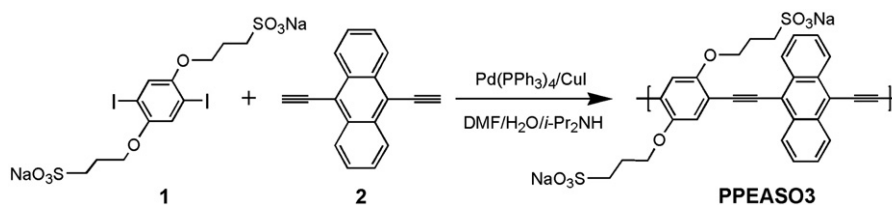
methods, such as surface tension, electrical conductivity, dynamic light scattering and resonance Rayleigh scattering technology have been developed for the CMC determination [5–9]. Meanwhile, as one of the most convenient and fast method, fluorimetry is often employed to determine the CMC values [10–14], based on the fluorescence changes at CMC. For obtaining a clear break point in the CMC measurement, it is critical to find a suitable probe which is sensitive to micro-environmental changes and tends to change its fluorescent properties (not only fluorescence intensity) dramatically at CMC.

In recent years, fluorescent conjugated polymers (FCPs) have attracted many attentions due to their unique properties [15–21]. One of the most important properties of FCPs is intrinsic fluorescence signal amplification. Many chemo- and biosensors based on the superquenching of conjugated polymers have been developed for the assays of metal ions [22–24], proteins [25–27] and enzymes [28–30]. Meanwhile, it was noted that both the turning properties of FCPs through surfactants and the determination of surfactant by using FCPs have been studied intensely [31–42]. However, the estimation of CMC of surfactants by using FCPs as probe has not been reported so far.

Recently, we synthesized a new water-soluble conjugated polymer, i.e. poly (2,5-dipropyloxysulfonate-1,4-phenylene-ethynylene-9,10-anthrylene) (PPEASO3) [43], and investigated the

* Corresponding author. Tel.: +86 553 3937137; fax: +86 553 3869303.

E-mail addresses: sunlilin126@126.com (L. Sun), zhucq@mail.ahnu.edu.cn (C. Zhu).



Scheme 1. Synthesis of the conjugated polymer PPEASO3.

influence of various surfactants on the properties of PPEASO3. The results showed that PPEASO3 is an ideal probe for the indication of the CMC of nonionic surfactants. In water and in aqueous solution containing a low concentration (below the CMC) of nonionic surfactants, PPEASO3 displayed a weak fluorescence emission at 670 nm due to its self-aggregation. However, a dramatic fluorescence enhancement with a large emission blue-shift (> 40 nm) was found once the surfactants concentration reached the CMC. An orange fluorescence could be observed even with naked-eyes under UV-lamp, which gave a direct indication for the micelle forming process and provided a simple method for the CMC determination of the nonionic surfactants.

2. Experimental

2.1. Materials

All the reagents were of analytical grade, and all solutions were prepared with double deionized water (DDW). $\text{Pd}(\text{PPh}_3)_4$ (99.8%), and 9,10-dibromoanthracene (98%) were purchased from Alfa Aesar. Trimethylsilylacetylene was purchased from J&K Chemical Ltd. Cuprous iodide was purchased from Zhengxing Reagent Factory of Shanghai. 1,3-propane sultone was purchased from Suzhou Yacoo Chemical Reagent Co., Ltd. Polyoxyethylene (20) sorbitan monolaurate (Tween-20), polyoxyethylene (20) sorbitan monopalmitate (Tween-40), polyoxyethylene (20) sorbitan monostearate (Tween-60), and polyoxyethylene (20) sorbitan monooleate (Tween-80) were purchased from Alfa Aesar. Cetyltrimethylammonium bromide (CTAB), polyoxyethylene (10) isocetylphenylether (Triton X-100), sodium *n*-dodecylbenzenesulfonate (SDBS), diisopropylamine, hydroquinone and other routine chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. Those surfactants were used without further purification.

2.2. Measurements

The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV300 or AV400 spectrometer. The solid state ^{13}C NMR spectra were recorded on a Bruker Avance III 400 WB Plus solid state spectrometer. FTIR data were obtained by an IRPrestige-21 FTIR spectrophotometer (Shimadzu, Japan). Ubbelohde viscometer, with an external temperature controlled water thermostat (20 ± 0.1 °C), was employed to assessment of molecular weight of PPEASO3. All fluorescence measurements were made with a Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan) equipped with a plotter unit and a 1-cm quartz cell. Absorption spectra were recorded with a Hitachi U-3010 spectrophotometer (Tokyo, Japan). The pH values were measured with a model PHS-3C pH meter (Hangzhou, China).

2.3. Preparation and characteristic of PPEASO3

1,4-diiodo-2,5-di(propoxysulfonate) benzene (**1**) was synthesized according to the literature [44]. ^1H NMR (DMSO- d_6 , ppm), δ : 1.99 (m, 4H, $-\text{CH}_2-$), 2.61 (t, 4H, $-\text{CH}_2-\text{SO}_3^-$), 4.04 (t, 4H, $-\text{OCH}_2-$),

7.30 (s, 2H, Ar-H). ^{13}C NMR (DMSO- d_6 , ppm), δ : 26.26, 49.03, 69.92, 87.94, 123.44, 153.27. IR (KBr, cm^{-1}): 3088 (Ar-H), 2939 ($-\text{CH}_2-$), 2870 ($-\text{CH}_2-$), 1626, 1489, 1464 (Ar($c=c$)), 1437 ($-\text{CH}_2-$), 1391, 1354, 1261, 1213, 1180, 1157, 1057, 1032, 935, 849, 812, 795, 739, 625, 554.

9,10-diethynylanthracene (**2**) was synthesized according to the literature [45]. ^1H NMR (CDCl_3 , ppm), δ : 4.05 (s, 2H, $\equiv\text{C}-\text{H}$), 7.61 (m, 4H, β -H of anthracene ring), 8.59 (m, 4H, α -H of anthracene ring). ^{13}C NMR (CDCl_3 , ppm), δ : 80.22, 89.87, 117.81, 127.03, 127.43, 132.47. IR (KBr, cm^{-1}): 3300 ($\equiv\text{C}-\text{H}$); 2100 ($-\text{C}\equiv\text{C}-$); 760 (substituted anthracene ring).

The polymer PPEASO3 was synthesized by Sonogashira coupling reaction of **1** and **2** using $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$ as catalyst (see Scheme 1). ^1H NMR (DMSO- d_6 , ppm), δ : 2.05 (broad, 4H, $-\text{CH}_2-$), 2.70–2.85 (broad, 4H, $-\text{CH}_2-\text{SO}_3^-$), 4.20–4.45 (broad, 4H, $-\text{OCH}_2-$), 7.67 (broad, 2H, H of benzene ring), 7.93 (broad, 4H, β -H of anthracene ring), 8.91 (broad, 4H, α -H of anthracene ring). ^{13}C NMR (DMSO- d_6 , ppm), δ : 26.78, 49.60, 69.44, 93.80, 101.43, 114.23, 119.12, 128.12, 129.02, 131.44, 132.32, 154.60. Solid-state ^{13}C NMR (ppm), δ : 24.90, 48.58, 66.78, 92.45, 100.05, 113.10, 118.25, 125.75, 130.78, 151.68. IR (KBr, cm^{-1}): 3057 (Ar-H), 2953 ($-\text{CH}_2-$), 2851 ($-\text{CH}_2-$), 2106 ($-\text{C}\equiv\text{C}-$), 1620, 1468 (Ar($c=c$)), 1435 ($-\text{CH}_2-$), 1396, 1184, 1042, 770 (substituted anthracene ring), 640, 615, 521. Full details of synthesis have been given elsewhere in Ref. [43].

In addition, the experimentally obtained value of $[\eta]$ for PPEASO3 in 0.1 M NaNO_3 aqueous solution has been used to compute the polymer's M_η value by use of the Mark-Houwink relation ($[\eta]=KM_\eta^\alpha$) and the values of K and α obtained from the literature for three different reference polyelectrolytes [46–48].

The viscometry data obtained for PPEASO3 in water with NaNO_3 suggest that for this polymer viscosity average molecular weight $M_\eta \approx 150$ kD (see Fig. S1 and Table S1).

2.4. Analytical procedure

Fresh working solution of PPEASO3 5.0×10^{-4} mol L^{-1} (in terms of repeating unit of the polymer) was prepared in DDW. Into a 10 mL volumetric bottle was transferred appropriate volumes of surfactant solution, 0.1 mL of pH 8.9 Tris-HCl buffer solution and diluted the mixture with DDW to the mark, then 200 μL 5.0×10^{-4} mol L^{-1} PPEASO3 solution was added and mixed thoroughly. The fluorescence intensities of PPEASO3 in the presence and absence of surfactants were measured with the excitation at 520 nm.

3. Results and discussion

3.1. Spectral behaviors of PPEASO3 in the presence of TX-100

From Fig. 1, it can be seen that PPEASO3 had a strong fluorescence in DMSO with the excitation and emission peaks at 520 nm and 605 nm, respectively ($\phi_f=0.51$, fluorescence quantum yield was measured relative to Rhodamine B). In aqueous solution, it displayed a very weak fluorescence emission at 670 nm ($\phi_f=0.12$), suggesting an obvious aggregation tendency

Download English Version:

<https://daneshyari.com/en/article/5401163>

Download Persian Version:

<https://daneshyari.com/article/5401163>

[Daneshyari.com](https://daneshyari.com)