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Effects of anionic surfactant SDS on the photophysical properties of two fluorescent molecular sensors

Junhong Qian, Yufang Xu, Xuhong Qian*, Jiaobing Wang, Shenyi Zhang

State Key Laboratory of Bioreactor Engineering and Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

Two fluorescent molecular sensors CS1 and CS2 were designed and synthesized to probe the aggregate behavior of anionic surfactant SDS. CS1 was based on the photo-induced electron transfer (PET) mechanism, while CS2 was founded on the intramolecular charge transfer (ICT) mechanism. The photophysical properties of CS1–2 in anionic surfactant sodium dodecyl sulfate (SDS) solution were studied by fluorescence and UV–vis methods. The experimental results show that significant absorption and emission spectral responses of CS1 were observed with the addition of SDS: the absorbance and fluorescence intensity decreased first and then increased. The plot of fluorescence intensity of CS1 versus SDS concentration showed two break points, which might be ascribed to the critical micellar concentration (cmc) and the formation of premicelle (cac) aggregate, respectively. But the solution's color of CS2 changed from yellow to red with increasing SDS concentrations. The large red-shift in both absorption (50 nm) and emission (55 nm) spectra of CS2 was resulted from the protonation of the electron accepting moiety (N=C nitrogen), which enhanced the "push–pull" interaction of the ICT fluorophore. This was facilitated by the increase of local H^+ concentration around SDS premicelle and micelle. As a consequence, pK_a values of CS1 and CS2 were elevated in SDS micelle.

1. Introduction

Developing fluorescent chemosensors used for detecting the variations in environment or physiological phenomena has been extensively pursued because these sensors can provide real-time, in situ and non-invasive monitoring information with fast response [1–5]. Many fluorescent sensors utilizing the following two distinct design principles: internal charge transfer (ICT) [6–10] and photoinduced electron transfer (PET) [11–13]. These two design principles have different characteristics: the attractiveness of the ICT sensors lies on their two-channel output signals (color change and fluorescence variation), which are convenient and sensitive for the practical utilization; whereas "off-on" or "on-off" fluorescence would occur when a PET sensor binds the guest (Scheme 1).

In the present study, we used a PET sensor CS1 and an ICT sensor CS2 to study the aggregation behavior of anionic surfactant SDS. For CS1, a tertiary amine group (pK_a ~8.0) [14,15] is appended, which should be protonated in neutral aqueous solution, thus making CS1 more like a cationic amphiphilic molecule and facilitating electrostatic attraction with anionic SDS [16–23]. 4-aminonaphthalimide fluorophore is expected to produce an optical signal upon changing its microenvironmental properties when interactions between CS1 and SDS assemblies occur. Much attention should be paid to the structural modification on the electron deficient "imide" moiety of CS2, where the O=C oxygen is displaced by a cyclized imine. This modification is expected to elevate the pK_a of the "imine" moiety, which (N=C nitrogen) will be protonated in the slightly acidic microenvironment around anionic SDS micelle (proton is attracted and concentrated there due to electrostatic interaction [21,22]). Consequently, when CS2 is located in SDS micelle, the protonation at the imine nitrogen will enhance the ICT process and results in a spectral shift to the longer wavelength both in the absorption and emission spectra. The plot of fluorescence intensity of CS1 versus SDS concentration presents two break points corresponding to the cmc and critical aggregate concentration (cac) of SDS, respectively. The plot of fluorescence intensity of CS2 shows a break point corresponding to cmc, but distinct wavelength shifts (~50 nm) in both absorption and emission spectra of CS2 are observed with the addition of SDS. pK_a values of CS1 and CS2 are elevated in SDS micelle due to its "proton-sponge" effect [21,22].

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* Corresponding author. Tel.: +86 514 87875805.
E-mail address: xhqian@ecust.edu.cn (X. Qian).

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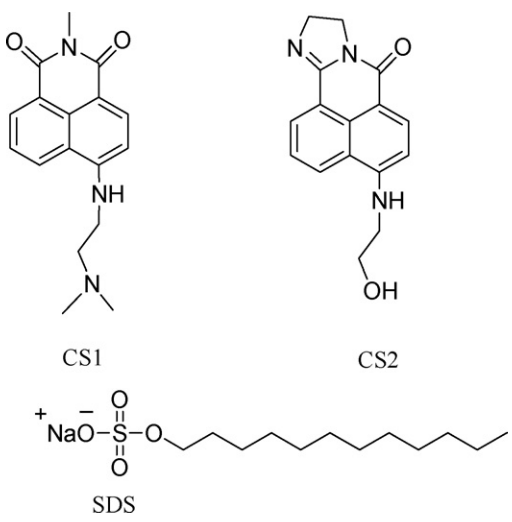


Scheme 1. Molecular structures of CS1, CS2 and SDS.

2. Experimental

2.1. Reagents

All the solvents and reagents were of analytic grade and used as received, Sodium dodecylsulfate (SDS, Sigma, 99%). Water used was twice distilled.

2.2. Absorbance and fluorescence titration

Dye and SDS aqueous solution were prepared with water. Appropriate aliquots of 0.606 M SDS aqueous solution were added to the dye solution followed by stirring and stabilization period before spectral measurements. The pH values were adjusted with 5 M NaOH and HCl aqueous solution and recorded after stable for 1 min. The pH was determined with a pH meter (Shanghai Rex Instrument Factory, China; model PHS-3C), which was standardized with Aldrich buffers. Absorption measurements were performed with a Varian Cary 500 spectrophotometer (1 cm quartz cell) and fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell). Mass spectra (MS) were recorded on a MA1212 instrument using standard conditions (ESI, 70 eV). All the experiments were performed at 25.0 ± 0.1 °C.

2.3. Synthesis

The synthesis of CS1–2 from commercially available starting materials is illustrated in Scheme 2.

2.3.1. *N-methyl-4-bromonaphthalene-1,8-dicarboximide (**1**)*

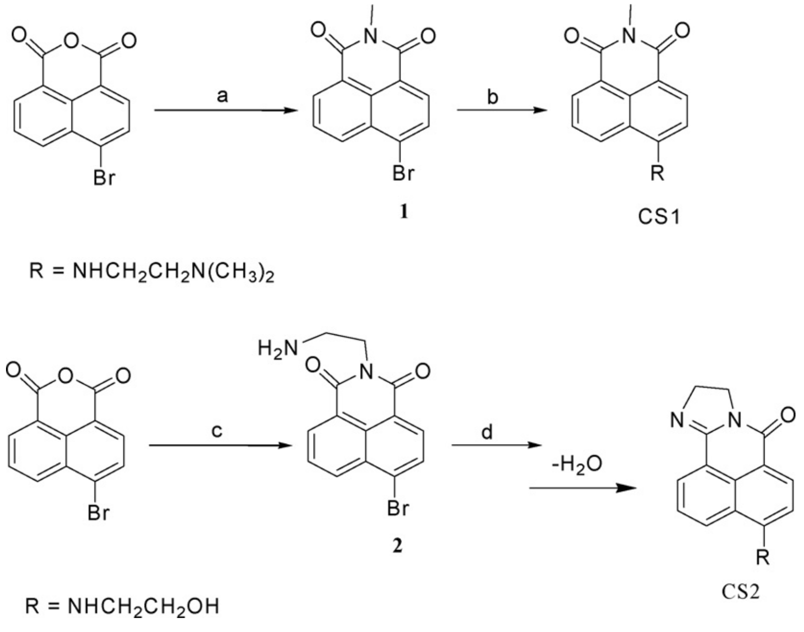
4-Bromo-1,8-naphthalic anhydride (1.11 g, 4 mmol) was suspended in 33% methyl amine aqueous solution. The mixture was stirred for 10 h at room temperature. The product was obtained by filter and crystallized from ethanol, yield 90%. m.p. 150.3–151.2 °C; 1H NMR (400 MHz, $CDCl_3$): δ8.68–8.65 (d, J = 7.5 Hz, 1H), 8.56 (d, J = 7.9 Hz, 1H), 8.41 (d, J = 7.9 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.84 (t, J = 7.9 Hz, 1H), 3.57 (s, 3H); MS: m/z (%) 289 (100%).

2.3.2. *CS1*

0.2 g (0.69 mmol) of **1** and excess N,N-dimethyl ethylenediamine (1 mL) were added to a solution of 5 mL of ethylene glycol monomethyl ether. The mixture was refluxed for 3 h under N_2 atmosphere and then the solvent was evaporated under vacuum. The product was purified by chromatography using methanol/dichloromethane (1:10, v/v) as eluant to give 164 mg (80%) of CS1 as yellow solid. 1H NMR (400 MHz, $CDCl_3$): δ8.68 (d, J = 7.6 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.55 (s, 1H), 3.63 (s, 3H), 3.54 (t, J = 4.8 Hz, 2H), 2.92 (t, J = 4.4 Hz, 2H), 2.52 (s, 6H). HR-MS (ES^+) Calcd. for $([M+H])^+$, 298.1556; Found, 298.1555.

2.3.3. *N-(aminoethyl)-4-bromonaphthalene-1,8-dicarboximide (**2**)*

Ethylenediamine (2.0 g, 33.3 mmol) was added to a suspension of 4-bromo-1,8-naphthalic anhydride (5.54 g, 20 mmol) in ethanol (50 mL). The mixture was then refluxed for 4 h, after which the solvent was evaporated under vacuum. The product was crystallized



Scheme 2. Preparation of CS1–2. Reagents: (a) 33% methyl amine aqueous solution, (b) N,N-dimethyl ethylenediamine, ethylene glycol monomethyl ether; (c) ethylenediamine, EtOH; (d) ethanolamine, ethylene glycol monomethyl ether.