



Colorimetric and fluorometric detection of anionic surfactants with water soluble sensors



Yingyuan Zhao^b, Xiyou Li^{a,b,*}

^a Xinjiang Technical Institute of Physics and Chemistry, CAS, Urumqi, China

^b Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, Department of Chemistry, Shandong University, China

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ABSTRACT

Five amphiphilic naphthalimide derivatives were synthesized and applied as colorimetric and fluorometric probes for the detection of anionic surfactants. Because of electrostatic and hydrophobic interactions, the probe and anionic surfactant can form complex in water. The formation of the probe–anionic surfactant complex induces distinctive changes on color and optical properties. Therefore, these derivatives can be used as sensors for anionic surfactants. Besides the advantage of visual detection, the detection of anionic surfactant can be realized by both absorption and fluorescence methods with high selectivity and sensitivity.

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1. Introduction

Because of their highly potent detergency and low cost of manufacture, anionic surfactants are used in greater volume than any other surfactants in the detergent industry [1–3]. Hence anionic surfactants are becoming one of the major components of environmental pollutants. Apart from the efforts in studying methods to reduce their environmental impact, another important aspect is the development of new and improved detecting methods in environment.

Although many well-known techniques in surfactant analysis, including methylene blue method [4], ion-selective electrodes capillary electrophoresis method [5], and so forth [6], have been developed, there exist still some limitations in their applicability, such as tedious procedures, large amount of toxic solvents, irreproducibility, signal instability, temperature and pH sensitivity [7–10]. Therefore, it is still attractive to find new simple and sensitive approaches for in site anionic surfactant detection.

An and co-workers developed an anionic surfactant detection method based on the disassembly of the complex between a

cationic conjugated polyelectrolyte (CPE), poly(3-(4-methyl-3'-thienyloxy)propyltrimethylammonium (PMTTPA) and an anionic dye, 8-hydroxy-1,3,6-pyrenetrisulfonic acid risodium salt (HPTS) [11]. Coll and co-workers used hybrid systems for colorimetric signaling of anionic surfactants in water [12,13]. Chen and co-workers developed an imidazolium-based conjugated polydiacetylene sensor for colorimetric and fluorescent detection of anionic surfactants [14]. These methods mentioned above are all based on supramolecular interactions of anionic surfactants with conjugated polymers. The difficulty on the synthesis and quality control of the polymers is the main drawback for these methods. Qian and co-workers reported a series of relatively simple molecular “on–off–on” fluorescent sensors for detecting anionic surfactants based on the electrostatic and hydrophobic interactions between sensors and anionic surfactants [15]. However, the solubility of these molecular sensors in water is small, therefore, polar non-protonic solvents, such as DMF, must be employed in the sensing process. For the purpose of simplifying the sensing process and avoiding the use of expensive and poison solvents, water soluble fluorescent probes are most desired.

Herein, five naphthalimide-based cationic dyes (**1a**, **1b**, **1c**, **2b** and **3b** shown in Chart 1) were designed and synthesized for the purpose of applying as probes for the detection of anionic surfactants with both absorbance and fluorescence changes. The cationic hydrophilic headgroups endow the sensors with a strong electrostatic interaction with anionic surfactant. Meanwhile, the n-alkyl hydrophobic chains endow these dyes with a comparatively

* Corresponding author at: Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, Department of Chemistry, Shandong University, China.

Tel.: +86 0531 88369877; fax: +86 0531 88564464.

E-mail address: xiyouli@sdu.edu.cn (X. Li).

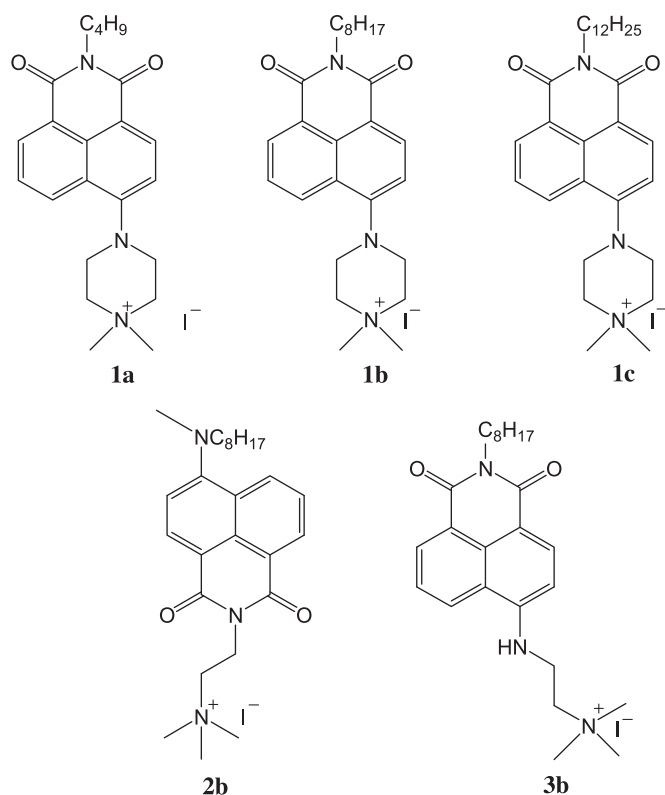


Chart 1. Molecular structures of the probes.

strong hydrophobic interaction with anionic surfactants. A stable complexes of dye-anionic surfactant based on static attraction is expected. Accordingly, the spectroscopic properties of the probes will change significantly in the presence of anionic surfactants and thus successfully achieve the sensing of anionic surfactants.

2. Experimental

2.1. Reagents

Sodium dodecylsulfate (SDS, 99%) was obtained from Alfa Aesar, while sodium dodecylsulfonate (SDSO, 99%) was bought from J&K. Sodium dodecylbenzenesulfonate (SDBS, 95%), sodium dodecanoate (SD, 98%) and hexadecyltrimethylammonium bromide (CTAB, 99%) were purchased from Aladdin. Triton X-100 (TX-100 AR) was bought from Sinopharm Chemical Reagent Co., Ltd. Pluronic P123 (AR) was a product of Sigma. Triply distilled water was used as solvent throughout the experiments. All other chemicals are of analytical grade and were purchased from commercial source and used as received without further purification.

2.2. Synthesis

1a, **1b**, **1c** were synthesized according to the procedure reported in our previous work [16]. The synthetic procedures of **2b** and **3b** are presented in Supporting Information. All the products were characterized by ^1H NMR and mass spectrometry (MS).

1a ^1H NMR (CDCl_3): δ 8.24 (m, 3H, H_{naph}), 7.63 (t, $J=10.0$ Hz, 1H, H_{naph}), 7.28 (d, $J=10.0$ Hz, 1H, H_{naph}), 3.88 (t, $J=8.1$ Hz, 2H, $\text{C}_3\text{CH}_2\text{N}$), 3.75 (t, $J=6.6$ Hz, 4H, $\text{NaphNCH}_2\text{CH}_2$), 3.57 (t, $J=5.2$ Hz, 4H $(\text{CNCH}_2\text{CN})_2$), 3.28 (s, 6H, CH_3NCH_3), 1.52 (m, 2H, $\text{C}_2\text{CH}_2\text{C}$), 1.30 (m, 2H, CCH_2C_2), 0.86 (t, $J=8.0$ Hz, 3H, CH_3C_3). ESI-MS (Q-TOF): calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_3\text{O}_2$: 366.2176; found: 366.2122 (M^+).

1b ^1H NMR (CDCl_3): δ 8.55 (d, $J=8.2$ Hz, 1H, H_{naph}), 8.50 (d, $J=9.0$ Hz, 1H, H_{naph}), 8.45 (d, $J=9.1$ Hz, 1H, H_{naph}), 7.77 (t, $J=9.1$ Hz,

1H, H_{naph}), 7.41 (d, $J=8.1$ Hz, 1H, H_{naph}), 4.16 (m, 2H, $\text{C}_7\text{CH}_2\text{N}$), 4.11 (s, 4H, $\text{NaphNCH}_2\text{CH}_2$), 3.76 (s, 6H, CH_3NCH_3), 3.62 (s, 4H $(\text{CNCH}_2\text{CN})_2$), 1.70 (m, 2H, $\text{C}_6\text{CH}_2\text{C}$), 1.38 (m, 10H, $(\text{CH}_2)_5$), 0.86 (t, $J=8.0$ Hz, 3H, CH_3C_7). ESI-MS (Q-TOF): calcd. for $\text{C}_{26}\text{H}_{36}\text{N}_3\text{O}_2$: 422.2808; found: 422.2769 (M^+).

1c ^1H NMR (CDCl_3): δ 8.55 (d, $J=8.2$ Hz, 1H, H_{naph}), 8.50 (d, $J=8.2$ Hz, 1H, H_{naph}), 8.45 (d, $J=9.0$ Hz, 1H, H_{naph}), 7.76 (t, $J=9.1$ Hz, 1H, H_{naph}), 7.40 (d, $J=9.0$ Hz, 1H, H_{naph}), 4.15 (t, $J=7.9$ Hz, 2H, $\text{C}_{11}\text{CH}_2\text{N}$), 4.11 (s, 4H, $\text{NaphNCH}_2\text{CH}_2$), 3.73 (s, 6H, CH_3NCH_3), 3.60 (s, 4H, $(\text{CNCH}_2\text{CN})_2$), 1.70 (m, 2H, $\text{C}_{10}\text{CH}_2\text{C}$), 1.25 (m, 18H, $(\text{CH}_2)_9$), 0.87 (t, $J=7.6$ Hz, 3H, CH_3C_{11}). ESI-MS (Q-TOF): calcd. for $\text{C}_{30}\text{H}_{44}\text{N}_3\text{O}_2$: 478.3434; found: 478.3450 (M^+).

2b ^1H NMR (CDCl_3): δ 8.58 (d, $J=7.5$ Hz, 1H, H_{naph}), 8.46 (m, 2H, H_{naph}), 7.68 (t, $J=8.0$ Hz, 1H, H_{naph}), 7.14 (d, $J=9.2$ Hz, 1H, H_{naph}), 4.66 (t, $J=7.3$ Hz, 2H, NCH_2CNCO), 3.90 (t, $J=7.1$ Hz, 2H, NCCH_2NCO), 3.60 (s, 9H, $(\text{CH}_3)_3\text{N}$), 3.38 (t, $J=8.0$ Hz, 2H, CNCH_2C_7), 3.11 (s, 3H, CH_3NC_8), 1.74 (m, 2H, CCH_2C_6), 1.29 (m, 10H, $(\text{CH}_2)_5$), 0.87 (t, $J=7.8$ Hz, 3H, CH_3C_7). ESI-MS (Q-TOF): calcd. for $\text{C}_{26}\text{H}_{38}\text{N}_3\text{O}_2$: 424.2958; found: 424.3062 (M^+).

3b ^1H NMR (CDCl_3): δ 8.74 (d, $J=10.1$ Hz, 1H, H_{naph}), 8.44 (d, $J=8.1$ Hz, 1H, H_{naph}), 8.28 (d, $J=10.2$ Hz, 1H, H_{naph}), 7.57 (t, $J=9.2$ Hz, 1H, H_{naph}), 6.58 (d, $J=9.2$ Hz, 1H, H_{naph}), 4.17 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 4.07 (t, $J=7.1$ Hz, 3H, C_7CH_2), 3.55 (s, 9H, $(\text{CH}_3)_3\text{N}$), 1.65 (m, 2H, $\text{C}_6\text{CH}_2\text{C}$), 1.28 (m, 10H, $(\text{CH}_2)_5$), 0.86 (t, $J=7.2$ Hz, 3H, CH_3C_7). ESI-MS (Q-TOF): calcd. for $\text{C}_{26}\text{H}_{38}\text{N}_3\text{O}_2$: 410.2802; found: 410.2811 (M^+).

2.3. Apparatus

Electronic absorption spectra were recorded on a UV-2450 spectrophotometer (SHIMADZU, Japan). The steady-state fluorescence measurements were carried out on a FLS920 fluorescence spectrometer (Edinburgh Instruments). ESI-MS were measured on Q-TOF LC/MS 6510 (Agilent). ^1H NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer with the solvent peak as internal standard (in CDCl_3).

3. Results and discussion

3.1. Optical properties of the dyes

The photophysical properties of 1,8-naphthalimide compounds are governed by the nature of the substituent [17]. Connection of electron donating groups at C-4 position of the naphthalic ring gives a “push-pull” electronic configuration and generate an internal charge transfer (ICT) excited state [18,19]. The five dyes investigated in this article are all quaternary ammonium salt and the presence of positive charge center (N^+) could influence the dipole moment and then affect their optical properties, such as the wavelength of the maximal absorption and emission bands (λ_{max}) and the fluorescence quantum yield. This has been successfully demonstrated by the comparison of the absorption and emission spectra of **1b** with that of **5b**, a compound without quaternary ammonium headgroup, as shown in Fig. 1. The spectra revealed that the presence of N^+ leads to a remarkable blue-shift on ICT absorption and emission band. Simultaneously, the fluorescence quantum yield of **1b** is much greater than that of **5b**. These can be attributed to the strong electron withdrawing ability of N^+ , which induces a “pull-push-pull” electronic configuration [20–23]. But in **5b**, due to the absence of N^+ , the photoinduced electron transfer from the amino group to the naphthalic ring gets efficient and the fluorescence is quenched significantly.

The fluorescence properties of these five dyes in H_2O and CH_2Cl_2 at the concentration of 1×10^{-5} M are summarized in Table 1. The fluorescence quantum yields of these five dyes are also measured

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