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Synthesis and characterization of novel fluorescent surfactants

Jianxin Wang, Zhigang Xu, Yu Zhao, Weihong Qiao, Zongshi Li*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, PR China

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Abstract

A series of compounds $\mathbf{III_a}$ and $\mathbf{III_b}$ containing fluorescent group were designed, synthesized and characterized and their surface and fluorescence properties were measured. As the polarity of solvent increased, the absorption maxima (λ_{max}) and the fluorescence maxima (λ_{em}) exhibited a red-shifted and decreased fluorescence emission, but showed no appreciable change with the increase of pH values. The $\mathbf{III_b}$ liposome gave small particles with spherical structures about 20–50 nm in diameter as observed by transmission electron microscopy.

Keywords: Critical micelle concentration; Fluorescent surfactant; Vesicles

1. Introduction

Surfactants have been widely used in various chemical industries, for example, cosmetics, environment protection, enhanced oil recovered operation, as a carrier in enzyme and drug industry[1–4], gene-infection [5–7], and so on. Fluorescent compounds applied as fluorescence probe [8,9] in surfactant field have become an important area of research because of their sensitive fluorescent signals and convenient detection. But there were few reports of such surfactants dealing with their fluorescence properties. It was hypothesized that by introducing a fluorescent group into a surfactant molecule by an appropriate method to get a series of surfactants, which would provide not only the surface properties (CMC, γ_{cmc}), but also the fluorescence properties as well. Thus, they might lead to some potential applications in special fields. $\mathbf{III_a}$ and $\mathbf{III_b}$ as shown in Scheme 1 were designed, synthesized and both their fluorescence emission spectra and surface properties were measured. Moreover, $\mathbf{III_b}$ would possibly form vesicles in aqueous solution for its particular dual-hydrophobic-tail structure.

* Corresponding author. Tel.: +86 411 88993878; fax: +86 411 83683229.
E-mail address: lizs1216@163.com (Z. Li).

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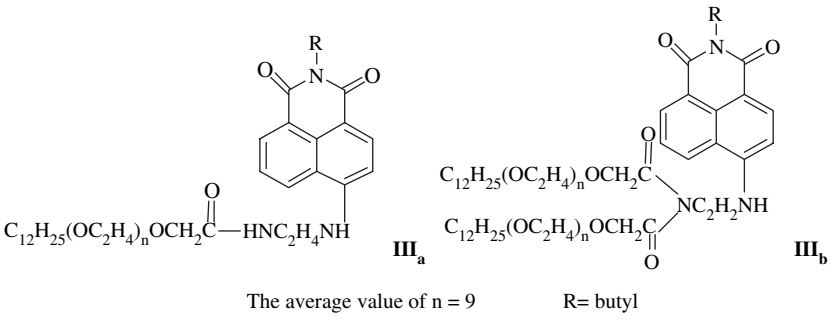
2. Results and discussion

2.1. Synthesis

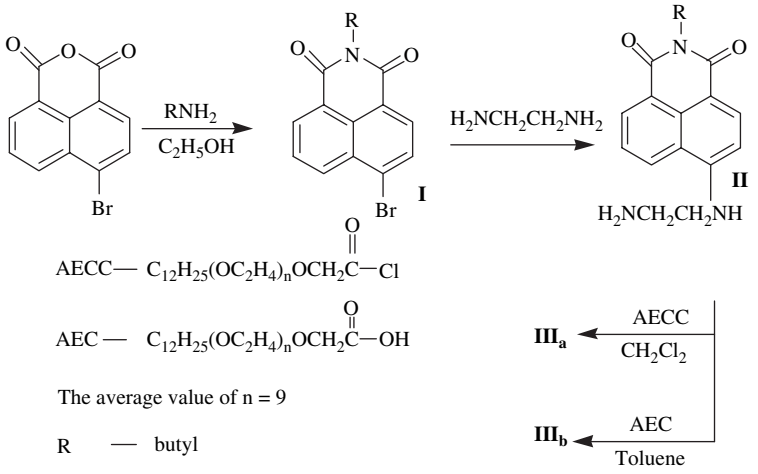
Compounds $\mathbf{III_a}$ and $\mathbf{III_b}$ were synthesized according to the route shown in Scheme 2 and characterized by IR and ^{1}H NMR. The obtained $\mathbf{III_a}$ and $\mathbf{III_b}$ were confirmed to be the above-designed compounds according to the data of IR and ^{1}H NMR as described below.

2.2. Fluorescence properties

Table 1 shows the spectral data of $\mathbf{III_a}$ (0.162 mg/ml) and $\mathbf{III_b}$ (0.051 mg/ml) in different solvents excited at 424 nm. The absorption maxima (λ_{max}) and fluorescence emission maxima (λ_{em}) exhibited a bathochromic shift and decreased fluorescence emission as both the compounds $\mathbf{III_a}$ and $\mathbf{III_b}$ were introduced into more polar solvents. The absorption and fluorescence emission maxima of $\mathbf{III_a}$ were shifted from $\lambda_{max} = 416–445$ nm and $\lambda_{em} = 479–544$ nm; for $\mathbf{III_b}$ from $\lambda_{max} = 365–446$ nm and $\lambda_{em} = 487–542$ nm (Table 1). The long-wavelength bands of the absorption spectrum in the UV region would be attributed to the $\pi–\pi^*$ electron transfer on $S_0 \rightarrow S_1$ transition [10]. As the molecule is excited, the dipole



Scheme 1. Molecular structures of novel fluorescent surfactants **III$_a$** and **III$_b$**.



Scheme 2. Synthetic routes to both the compounds **III$_a$** and **III$_b$**.

moments and polarity of C=C tend to be larger in the excited state than in the ground state. The more polar the solvent is, the more stable is the interaction between molecules in the excited state and the smaller is the difference of energies between the excited state and the ground state. That is why the absorption maxima (λ_{max}) and the fluorescence emission maxima (λ_{em}) were bathochromically shifted and decreased. As could be seen, both **III$_a$** and **III$_b$** were environment-sensitive because their fluorescence spectra were highly dependent on the solvent.

In order to study the environment-sensitivity of **III$_a$** and **III$_b$** further, their fluorescent emission spectra were measured in different ratio ranging from 9:1 to 1:9 (ethanol:water, v/v) excited at 454 nm as shown in Table 2. Similarly, the fluorescence emission maxima of both **III$_a$** and **III$_b$** exhibited a red-shifted and decreased fluorescence emission as the polarity of solvent increased. Especially, the fluorescence emission maxima of **III$_b$** were shifted 13 nm from 530 nm (9:1) to 543 nm (9:1) and fluorescent intensity dropped from 302 to 49.

The spectral data of **III$_a$** and **III$_b$** at different pH values are summarized in Table 3 and Table 4. As can be seen from the tables, as a whole, the absorption spectra of **III$_a$** and **III$_b$** showed irregular changes and their maximal fluorescence wavelengths almost did not change as the pH values increased. The explanation would be that, in **III$_a$** or **III$_b$**, the amido group (−NH−CO− or −N=(CO−)$_2$) played a role to connect the fluorescent group and the hydrophilic group (−CH_2−CH_2−O−)$_n$, due to the inductive effect, the electron density

Table 1
Spectral data of **III$_a$** (0.162 mg/ml) and **III$_b$** (0.0712 mg/ml) at 424 nm excitation in various solvents

Solvent	**III$_a$**				**III$_b$**			
	λ_{max} (nm)	Abs (AU)	λ_{em} (nm)	I_F	λ_{max} (nm)	Abs (AU)	λ_{em} (nm)	I_F/E + 6
Hexane	416	0.51	479	223	365	0.22	487	1.22
Tetrahydrofurane	429	2.30	505	280	428	0.32	502	1.43
Dichloromethane	427	2.43	506	298	426	0.42	504	1.48
Acetone	430	2.35	513	270	426	0.12	510	1.30
Ethanol	435	2.31	523	197	437	0.34	525	0.98
Methanol	435	2.26	528	158	437	0.36	530	0.84
Water	445	0.85	544	135	446	0.46	542	0.78

Table 2
Fluorescence spectral data of **III$_a$** (0.121 mg/ml) and **III$_b$** (0.099 mg/ml) in different ratios of ethanol and water at 454 nm excitation

Ethanol:water		9:1	8:2	7:3	6:4	1:1	4:6	3:7	2:8	1:9
III$_a$	λ_{em} (nm)	529	531	531	534	535	536	539	542	543
	I_F	157	156	151	144	133	134	130	118	117
III$_b$	λ_{em} (nm)	530	530	533	532	533	535	537	541	543
	I_F	302	289	288	282	267	262	164	67	49

of nitrogen atom would decrease, then it would be unlikely to form hydrogen bonding with the proton, so the pH values would have little influence on fluorescence emission spectra.

2.3. Surface properties

The critical micelle concentration (CMC) and surface tension (γ_{cmc}) at CMC of the surfactant are the major performance parameters to be studied. The CMCs and γ_{cmc} of AEO_9 ($C_{12}H_{25}(OCH_2CH_2)_nOH$, the average value of $n = 9$), **III$_a$** and **III$_b$** were measured at 25 °C. The surface tension of de-ionized water was 71.50 mN/m (25 °C). Surface tensions (γ) of AEO_9, **III$_a$** and **III$_b$** plotted against the logarithmic concentrations of surfactant in aqueous solution are shown in Fig. 1. The results obeyed the general surfactant behaviors. Surface tensions normally decreased linearly with the increase of the concentrations of surfactant and then flattened out. The inflection point, corresponding to the CMC, could be distinctly observed for each of AEO_9, **III$_a$** and **III$_b$**.

The CMC and γ_{cmc} for AEO_9, **III$_a$** and **III$_b$** are summarized in Table 5. As shown in Table 5, the values of CMCs for AEO_9, **III$_a$** and **III$_b$** decreased from 25.12×10^{-6} mol/l to 4.07×10^{-6} mol/l and surface tensions (γ_{cmc}) at CMC increased from 28.26 mN/m to 31.73 mN/m, respectively. The reason for this result could be that at lower concentrations, the long chains of **III$_a$** and **III$_b$**, which might arbitrarily stretch itself so as to promote the chains in the molecules intertwist each other to form micelles. Moreover, in comparison with AEO_9, **III$_a$** and **III$_b$**, the introduction of fluorescent group would increase the bulkiness of the molecules and have the aromatic rings and hydrophobic carbon chains aligned at outer surface layers of their aqueous solutions. Consequently the consistency and saturation adsorption values of **III$_a$** and **III$_b$** would therefore decrease and the molecular arrangements get loosened. Thus, it would be understandable why the CMCs of AEO_9, **III$_a$** and **III$_b$** would decrease and surface tensions (γ_{cmc}) at CMC increase stepwise in this study. The introduction of fluorescent group in the molecule also made the compounds **III$_a$** and **III$_b$** less hydrophilic than AEO_9. They showed lower cloud points than AEO_9 though they contained the same hydrophilic group; meanwhile, **III$_b$**, having one more long carbon chain than **III$_a$**, contained a relatively large amount of ($-CH_2-CH_2-O-$) groups in the molecule, so the cloud point of **III$_b$** was higher.

To examine the shape and size distribution of liposome, transmission electron microscopy was introduced. As expected, compound **III$_b$** formed closed vesicles spontaneously in aqueous solution. Small particles with spherical structures of about 20–50 nm in diameter are shown in Fig. 2.

Compounds **III$_a$** and **III$_b$** not only behaved normally as other conventional surfactants, but also exhibited good fluorescence properties. Consequently, the closed vesicles of **III$_b$** in aqueous solution also provided fluorescence properties. These additional fluorescence properties will lead **III$_b$** to provide a good opportunity in application as a potential carrier in drug and gene-infection industries.

3. Conclusions

A series of compounds **III$_a$** and **III$_b$** were synthesized and characterized. As the polarity of solvent increased, their absorption maxima (λ_{max}) and fluorescence emission maxima (λ_{em}) exhibited a bathochromic shift and decreased fluorescence emission. **III$_a$** and **III$_b$** both were environment-sensitive because their fluorescence spectra were highly dependent on the solvent. The pH values of the solutions caused little influence on their fluorescence emission spectra. In **III$_a$** or **III$_b$**, the amido group ($-NH-CO-$ or $-N{=}(CO)_2$) played a role to connect the fluorescent group and hydrophilic group ($-CH_2-CH_2-O-)_n$. Due to the inductive effect, the electron density of nitrogen atom decreased and it was rather difficult to form hydrogen bonding with the proton, so the pH values would have little influence on fluorescence emission spectra.

It was found that the CMCs of AEO_9, **III$_a$** and **III$_b$** would decrease while their surface tensions (γ_{cmc}) at CMC increase stepwise. Moreover, compound **III$_b$** formed closed vesicle in

Table 3
Spectral data of **III$_a$** (0.0087 mg/ml) at different pH values when excited at 384 nm

pH	2.10	2.64	3.32	4.05	5.21	6.64	7.10	8.82	10.21	11.45
λ_{max} (nm)	447	445	450	451	451	449	449	447	445	441
Abs (AU)	0.022	0.024	0.028	0.026	0.021	0.017	0.028	0.025	0.024	0.021
λ_{em} (nm)	544	542	544	542	542	541	544	543	545	544
I_F	258	289	319	321	329	307	305	302	229	217

Table 4
Spectral data of **III$_b$** (0.0712 mg/ml) at different pH values when excited at 454 nm

pH	2.21	2.46	3.03	3.40	5.98	6.30	8.80	11.17
λ_{max} (nm)	441	438	442	445	448	446	448	437
Abs (AU)	0.20	0.21	0.14	0.12	0.40	0.46	0.43	0.42
λ_{em} (nm)	544	541	542	542	543	544	544	544
I_F	155,332	158,330	166,182	164,865	170,698	169,790	172,948	165,297

aqueous solution spontaneously and **III$_b$** liposome would give small particles with spherical structures about 20–50 nm in diameter.

Compounds **III$_a$** and **III$_b$** not only behaved normally as other conventional surfactants, but also exhibited good fluorescence properties. Consequently the closed vesicles of **III$_b$** in aqueous solution also provided fluorescence properties. These additional fluorescence properties will lead **III$_b$** to have a good opportunity in application as a potential carrier in drug and gene-infection industries.

4. Experiment

4.1. Synthesis and characterization

4.1.1. Synthesis of compound I

A solution of *n*-butylamine (0.27 ml, 2.73 mmol) in 5 ml ethanol was added dropwise to a mixture of 0.7 g (2.53 mmol) of 4-bromo-1,8-naphthalic anhydride and 35 ml of ethanol at 60–70 °C under vigorous stirring. The mixture was refluxed for 8 h until the mixture became clear, then cooled and filtered to give the crude product. After recrystallization from anhydrous ethanol, compound I was obtained in 91.2% yield, mp: 103.8–105.3 °C, EIMS *m/z* 332 (^{79}Br M+1 100), 334(^{81}Br M+1 99.8).

4.1.2. Synthesis of compound II

In a three-necked flask of 100 ml, equipped with a mechanical stirrer and a reflux condenser, 10 ml of ethylene diamine was added. With continuous stirring at 50 °C and within an interval of 1 h, 0.8 g (2.41 mmol) of I was evenly added. After heating at the same temperature for 4 h, the mixture was cooled and poured into 20 ml of ice water. The residue was filtered and dried. After recrystallization from acetone, compound II was obtained in 71.4% yield, mp: 129.4–131.8 °C (lit. [11] provided appropriate IR, ^{1}H NMR , ^{13}C NMR, UV–visible and fluorescence spectra).

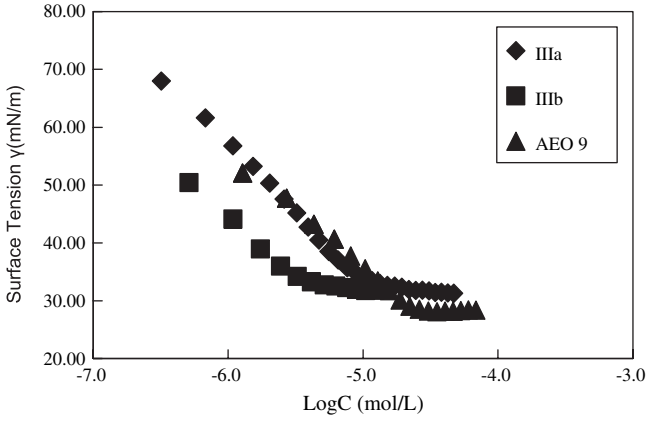


Fig. 1. Plots of surface tension of aqueous solutions against the logarithmic concentrations of **III$_a$**, **III$_b$** and AEO_9 at 25 °C.

4.1.3. Synthesis of compound *III$_a$*

Compound **II** (1.4g, 4.5 mmol) was dissolved in 30 ml of dichlorumethane and a few drops of triethylamine was added. To the suspension with continuous stirring at room temperature AECC was added dropwise until the smoke disappeared. After that, the solution was stirred for 5 h at the same condition and the solvent was evaporated under reduced pressure. The residue was washed with petroleum ether and separated by column chromatography on silica gels (dichloromethane: methanol = 5:1). The brown liquid was obtained in 40.4% yield.

IR (ν_{max}) 3349, 2924, 2858, 1683, 1646, 1581, 1122 cm^{-1}. ^{1}H NMR (δ ppm): 8.55 (1H, d, J = 6.8 Hz), 8.42 (1H, d, J = 8.4 Hz), 8.32 (1H, d, J = 8.4), 7.60 (1H, t, J = 8.4, 7.2 Hz), 6.59 (1H, d, J = 8.4 Hz), 4.05(2H, s), 4.20–3.30 (46H, complex), 1.80–1.10 (24H, complex), 0.96 (3H, t, J = 7.2, 7.6 Hz), 0.87(3H, t, J = 5.6, 6.8 Hz).

4.1.4. Synthesis of compound *III$_b$*

Compound II (1.4 g) was reacted with 6 g (9.38 mmol) of AEC in 30 ml boiling toluene for 6 h and water was gradually separated from the mixture. After the solvent was evaporated under reduced pressure, compound **III$_b$** could be obtained by the same separation procedure as **III$_a$** in 51.2% yield. IR (ν_{max}) 3324, 2923, 2855, 1685, 1648, 1581, 1116 cm^{-1}. ^{1}H NMR (δ ppm): 8.56(1H, d, J = 6.8 Hz), 8.43 (1H, d, J = 8.4 Hz), 8.32 (1H, d, J = 8.0 Hz), 7.61 (1H, t, J = 8.0, 8.0 Hz), 6.60 (1H, d, J = 8.4 Hz), 4.05 ($2CH_2$, s), 4.20–3.30 (83H, complex), 1.80–1.10 (44H, complex), 0.96 (3H, t, J = 7.2, 7.2 Hz), 0.87 ($2CH_3$, t, J = 5.6, 6.8 Hz).

4.2. Liposome preparation

Compound **III$_b$** in dichloromethane was evaporated under reduced pressure and further dried in vacuo. De-ionized water was added to the dried **III$_b$** and the vortex mixed. After that,

Table 5
Surface properties of AEO_9, **III$_a$** and **III$_b$**

Surfactant	CMC × 10^{-6} (mol/l)	γ (mN/m)	Cloud point (°C)
AEO_9	25.12	28.26	77.9
III$_a$	11.48	31.29	40.1
III$_b$	4.07	31.73	44.2

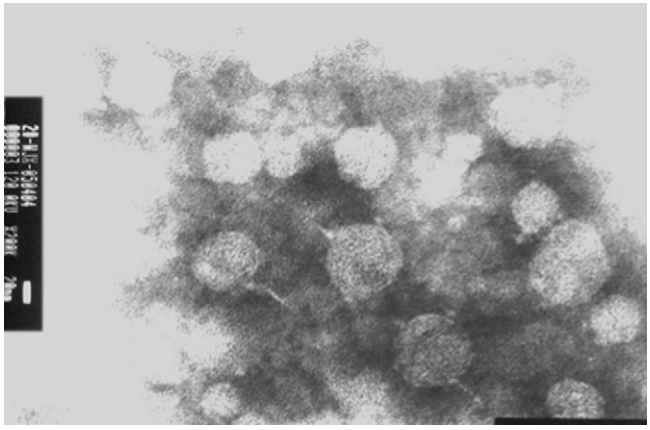


Fig. 2. Images of compound $\mathbf{III_b}$ liposome.

the mixture was sonicated using a bath-type sonicator. The shape and size distribution of liposome were determined by transmission electron microscopy as described above.

4.3. Method of measurements

^{1}H NMR spectra were obtained at 400 MHz by a Varian Avance-400 spectrometer. Mass spectra were performed on an HP1100-MS and infrared spectra were recorded on an FTIR Nicolet 20DXB. Melting points were taken using a hot-stage microscope and uncorrected. UV–visible-spectrophotometric investigations were carried out on a TU-1901 spectrophotometer (Beijing, China). The fluorescence spectra were taken on an F-4500 spectrofluorimeter (Japan). For fluorescence emission experiments, the solutions of different pH were adjusted with $HClO_4$ and NaOH.

Surface tensions of aqueous surfactant solutions were measured at 25 °C, using a Krüss 12 surface tensionmeter (Krüss GmbH, Germany). The platinum plate was cleaned by flaming, while the glassware was cleaned with strong alkaline solution and rinsed by ethanol and distilled water, respectively. Surface tensions were measured three times for each concentration, and an average error of less than 0.5 mN/m is obtained. A JEM-2000EX transmission electron microscope (JOEL, Japan) was used for imaging the shape and particle size of the liposome.

Acknowledgments

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