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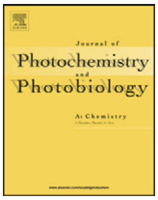

A new strategy for the ratiometric fluorescence detection of Zn(II) in the surfactant solution

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ABSTRACT

A new strategy derived from the intramolecular charge transfer mechanism was employed to create a ratiometric sensing system for Zn^{2+} in aqueous solution by using sodium dodecyl sulfate (SDS) micelles as the scaffold. The amphiphilic carboxamidoquinoline-based sensor (**AQZ2Cl**) was simultaneously solubilized at different locations in the SDS micelle. Some **AQZ2Cl** molecules were adsorbed at the micelle–water interface and emitted a fluorescence-enhancing and red-shifted signal upon binding Zn^{2+}. And the others were incorporated into the palisade layer of the micelle, in which the produced bands had no appreciable changes with the addition of Zn^{2+}, thus acting as an internal standard and allowing **AQZ2Cl** as a ratiometric sensor for the detection of Zn^{2+}.

1. Introduction

Fluorescence sensors are becoming increasingly popular due to the simplicity in applications as well as the high sensitivity and selectivity for biologically and environmentally important metal ions [1,2]. During the past decades, a variety of sensors have been fabricated to detect cations in special systems, such as organic solvents, buffer solutions, or biological cells [3–6].

Recently, the research on the utilization of amphiphilic surfactants in the field of supramolecular chemistry has made great progress [7–9]. Surfactants in aqueous solution can offer a special phase or microenvironment, such as a micelle. Micelles have been widely used as nanosized containers for molecular self-assembly, in which separated fluorophores and receptors are kept together and communicate inside the micelle without a covalent spacer [10–12]. In addition, the enhanced sensing capabilities have been observed by confining traditional sensors inside micelles [13–16] because of a change in the micropolarity and rigidity in micelles compared to the situation in the bulk aqueous phase [17]. It should be mentioned that the exact location in micelles at which the solubilization occurs varies with the nature of solubilized sensors [18]. We reasoned, if sensors are located at different solubilizing sites of the micelle and produce various fluorescence signals for cations, a ratiometric sensing system will be created through the solubilization effect of surfactants.

Generally, ratiometric sensors can be designed to follow two main strategies: fluorescence resonance energy transfer (FRET) and intramolecular charge transfer (ICT) mechanism. The FRET process is defined as an excited-state energy interaction between two different fluorophores, in which the excited donor energy is transferred to the proximal ground-state acceptor [19–21]. And the ICT-based sensors with only one type of fluorophore have two distinct emissive states (object-free and object-bound), which lead to the shift of the emission maxima upon binding objects [22–25]. However, the FRET-type sensors usually need synthetic efforts to covalently link two fluorophores, resulting in the difficulties in syntheses [26]. And the accuracy of the ICT-type sensors is also potentially decreased in applications owing to the difficultly determined bands of the object-free sensors after full complexation [19].

Theoretically, these problems can be avoided by using micelles as the scaffold. Recently, Zeng et al. developed a class of the FRET-type ratiometric systems for cations, in which two separated fluorescent compounds with different hydrophilicity resided at different sites of the micelle [27,28]. But there appear still no exploration on one amphiphilic sensor simultaneously emitting various signals for objects through the micellar solubilization. And using one molecule instead of two fluorescent compounds would also efficiently reduce the complexity of measurements.

Carboxamidoquinoline as a popular moiety was widely applied to the design of ratiometric sensors through the ICT process [29–33]. Previously, we published our contribution to this

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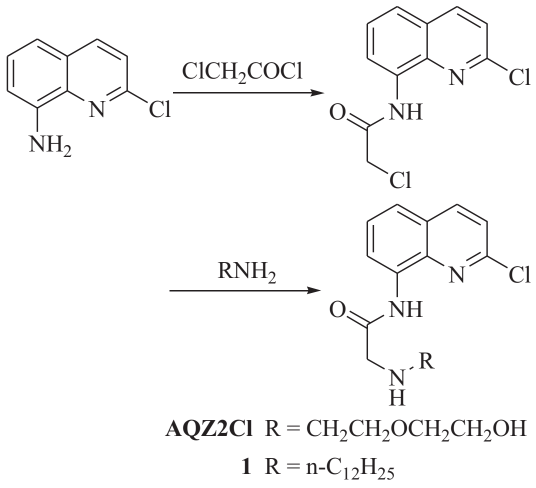

Scheme 1. The synthesis of carboxamidoquinoline-based fluorescent sensors.

field describing the carboxamidoquinoline-based sensor (the **AQZ** family) for sensing Zn^{2+} [29,33]. Herein, the amphiphilic carboxamidoquinoline derivative (**AQZ2Cl**), which contains a hydrophobic 2-chloroquinoline ring and a hydrophilic 2-(2-hydroxyethoxy)ethylamino group, was synthesized (Scheme 1) and chosen as the target of the current research.

2. Experimental

2.1. Chemicals and instruments

All of the solvents were of analytic grade and used as received. Water was twice distilled. NMR spectra were recorded on a Bruker AV-400 spectrometer using $CDCl_3$ as the solvent. Mass spectra were measured on a Micromass HPLC-Q-Tof MS spectrometer. IR spectra were obtained on a Nicolet AVATAR-370 FT-IR instrument, and samples were prepared as KBr pellets. Melting points were determined by an X-6 micro-melting point apparatus and uncorrected. All pH measurements were made with a Sartorius basic pH-meter PB-10. Fluorescence and absorption spectra were recorded on a Hitachi F-4500 fluorescence spectrometer and a Pgeneral TU-1901 UV–vis spectrophotometer.

2.2. Synthesis

2.2.1. 2-Chloro-N-(2-chloroquinol-8-yl)acetamide

2-Chloroacetyl chloride (461 mg, 2.4 mmol) was dissolved in 5 mL of chloroform, then added dropwise to a cooled, stirred solution of 2-chloro-8-aminoquinoline (356 mg, 2.0 mmol) and pyridine (222 mg, 2.8 mmol) in 10 mL of chloroform within 1 h, after stirred 2 h at room temperature, the mixture was removed under reduced pressure to obtain a white solid, which was purified by silica gel column chromatography using dichloromethane as the eluent. Yield: 447 mg (88%), mp: 148.9–149.1 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 10.90 (NHCO, s, 1H), 8.82 (d, J = 7.6 Hz, 1H), 8.72 (d, J = 4.8 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 8.2 Hz, 1H), 7.58 (d, J = 4.8 Hz, 1H), and 4.32 ($COCH_2$, s, 2H) ppm.

2.2.2. Carboxamidoquinoline-based sensors

2-Chloro-*N*-(2-chloroquinol-8-yl)acetamide (100 mg, 0.39 mmol), corresponding amine (3.9 mmol), *N*,*N*-diisopropylethylamine (504 mg, 3.9 mmol), and KI (10 mg) were added to 30 mL of acetonitrile, after stirred and refluxed for 10 h under nitrogen atmosphere, the mixture was cooled to room temperature and removed under reduced pressure to obtain a brown oil, which was purified by silica gel column chromatography using the chloroform/methanol mixture as the eluent.

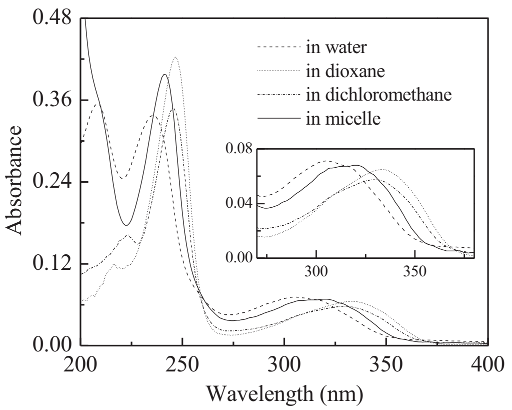

Fig. 1. Absorption spectra of 10 μM **AQZ2Cl** in the SDS solution or different solvents. Maximum absorption bands of **AQZ2Cl** are about 305 nm in water, 320 nm in micelle, 330 nm in dichloromethane, and 333 nm in dioxane.

2-(2-(2-Hydroxyethoxy)ethylamino)-*N*-(2-chloroquinolin-8-yl)-acetamide (**AQZ2Cl**). Yield: 101 mg (80%). ^1H NMR ($CDCl_3$, 400 MHz): δ 11.23 (NHCO, s, 1H), 8.86 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 4.8 Hz, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.63 (t, J = 8.2 Hz, 1H), 7.54 (d, J = 4.8 Hz, 1H), 3.74 (OCH_2CH_2OH, m, 4H), 3.59 ($COCH_2$, $NHCH_2CH_2$, m, 4H), and 2.98 (CH_2NHCH_2, t, J = 4.8 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 147.4, 142.6, 139.3, 134.1, 127.9, 125.9, 121.3, 117.6, 117.0, 71.9, 70.1, 61.4, 53.2, and 48.9 ppm. HRMS m/z (TOF MS ES^+) calcd for $C_{15}H_{19}ClN_3O_3{}^+$ ($M+H^+$) 324.1109, found 324.1115. FT-IR (KBr): ν_{max} 3275.65, 2920.30, 2860.27, 1683.91, 1518.07, 1482.71, 1303.29, 1116.59, 1065.91, 811.85, and 755.02 cm^{-1}.

2-Dodecylamino-*N*-(2-chloroquinolin-8-yl)-acetamide (**1**). Yield: 119 mg (76%), mp: 42.7–43.3 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 11.44 (NHCO, s, 1H), 8.89 (d, J = 8.8 Hz, 1H), 8.70 (d, J = 4.8 Hz, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.64 (t, J = 8.2 Hz, 1H), 7.54 (d, J = 4.8 Hz, 1H), 3.54 ($COCH_2$, s, 2H), 2.74 ($NHCH_2CH_2CH_2(CH_2)_8CH_3$, t, J = 7.0 Hz, 2H), 1.60 ($NHCH_2CH_2CH_2(CH_2)_8CH_3$, m, 2H), 1.43 ($NHCH_2CH_2CH_2(CH_2)_8CH_3$, m, 2H), 1.25 ($NHCH_2CH_2CH_2(CH_2)_8CH_3$, m, 16H), and 0.90 ($CH_3$, t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0, 147.7, 143.0, 139.9, 134.8, 128.4, 126.4, 121.7, 117.8, 117.3, 53.9, 50.4, 31.9, 30.3, 29.7, 29.6, 29.4, 27.2, 22.7, and 14.1 ppm. HRMS m/z (TOF MS ES^+) calcd for $C_{23}H_{35}ClN_3O^+$ ($M+H^+$) 404.2463, found 404.2455. FT-IR (KBr): ν_{max} 3270.41, 2921.82, 2850.71, 1677.29, 1519.02, 1480.98, 1300.89, 821.92, and 750.68 cm^{-1}.

3. Results and discussion

3.1. Incorporation of carboxamidoquinoline in micelles

In this study, the anionic surfactant SDS was chosen as the scaffold to construct the ratiometric system. The critical micelle concentration of SDS is 8.2 mM at 25 °C, and the aggregation number is about 62 [34]. So the micelle concentration was calculated to be about 60 μM in the presence of 12 mM SDS.

To verify the locations of the sensor in micelles, absorption spectra of **AQZ2Cl** in the SDS solution or different solvents were measured (Fig. 1). The relatively broad absorption maxima of **AQZ2Cl** obtained in the SDS solution is at around 320 nm, which is between that in pure water (to mimic the micelle–water interface) and that in apolar organic solvents (to mimic the interior of the micelle). Thus, the formation of the broad peak may be due to the combination of two absorption bands, indicating that **AQZ2Cl**