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Study on Fluorescence Properties of Boradiazaindacenes (BODIPY) in Different Surfactant Solutions

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A novel yellow-green fluorescent BODIPY dye (**1**) was synthesized and its fluorescence properties were investigated in various surfactant solutions, including myristyltrimethylammonium bromide, sodium dodecylbenzenesulphonate, sodium dodecylsulfate and triton X-100. The results show that BODIPY dye (**1**) displays an obvious fluorescence sensitizing effect in the presence of myristyltrimethylammonium bromide, which can be attributed to the entrance of **1** into myristyltrimethylammonium bromide micelle. Furthermore, there is a good linear relationship between fluorescence intensity and myristyltrimethylammonium bromide concentration in the range of 0-2.1 × 10^{-3} mol/L, with the association constant of 3.71 × 10^{4}.

Keywords: Fluorescence, BODIPY, Surfactant, Sensitizing effect.

INTRODUCTION

Because of high sensitivity, good selectivity, turn on-off convertibility and ease of use, fluorescent sensors have caused considerably concern[1-4]. Such a system generally consists of two parts *i.e.*, a binding site and a fluorescent part. During myriad fluorescent parts, boradiazaindacenes (BODIPY) possess remarkable properties such as high absorption coefficient, high quantum yields, *etc.*[5,6]. Therefore, boradiazaindacenes are widely applied as fluorescent probes for anions, cations and neutral molecules. However, boradiazaindacenes-based sensors have limited utility due to poor solubility in water[7-9]. For most biological conditions good water solubility of probe is essential. Considerable tactful synthetic methods have to import the solubility by introducing hydrophilic groups within the core structure of boradiazaindacenes[10-12]. Such synthetic strategies are obviously strenuous and time-consuming to obtain desired water-soluble analogues. As a result, it is necessary to develop novel recognition system of boradiazaindacenes solution to circumvent redundancy synthetic difficulties. Surfactant solutions should be very competitive candidates in the choice of sensing system[13]. Surfactant can reduce surface tension and form micelle, which might facilitate water-soluble capacity and enhancement of fluorescence intensity, namely sensitizing effect[14-16]. In this paper, we have selected four surfactants, including myristyltrimethyl-ammonium bromide, sodium dodecylbenzenesulphonate, sodium dodecylsulfate and triton X-100[17] in ordet to investigate the properties of **1**. Results show that **1** illustrates dramatic sensitizing effect in myristyltrimethylammonium bromide solution, while in other surfactants **1** displays relative weak or no fluorescence enhancement. myristyltrimethylammonium bromide is therefore potential for a BODIPY sensing solution.

EXPERIMENTAL

All materials were purchased commercially and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were using a Varian INOVA 400 MHz spectrometer. ESI-MS were recorded using a Waters Micromass ZQ-4000 spectrometer. Fluorescence were recorded on a Perkin Elmer LS55 spectrometer. Surfactant solutions of **1** were made as follows. 3.1 × 10^{-6} mol/L of 1 (0.20 mL) in CH_3CN was firstly added to 5mL volumetric flask and then CH_3CN solvent was removed by N_2 flow. Surfactants in corresponding concentration were added and stirred to garner target solutions.

Compound **1** was prepared according to the synthetic route, as shown in Fig. 1[18]. 4-Bromobenzoyl chloride (5.8 g, 0.026 mol) and 2,4-dimethylpyrrole (5 g, 0.05 mol) were refluxed in CH_2Cl_2 under N_2. Triethylamine (15 mL, 0.11 mol) followed by BF_3Et_2O (15 mL, 0.12 mol) was added and continued stirring for additional 3 h. The reaction mixture was washed with 0.1 M NaOH solution and water thoroughly. Combined organic layers were dried over $MgSO_4$, filtered and evaporated. The crude product was purified by silica gel column chromatography using hexane/dichloromethane (1:1) to afford **1** as a

red solid. Compound **1**: Yield 30 %. m.p. = 176-177 °C. ESI-MS: 403.1 $[M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.392 (s, 6 H, 2 CH_3), 2.530 (s, 6 H, 2 CH_3), 5.970 (s, 2 H, 2 CH), 7.158 (d, *J* = 6.4 Hz, 2 H, ArH), 7.624 (d, *J* = 6.4 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.63, 121.42, 123.23, 129.79, 131.14, 132.42, 133.92, 139.98, 142.89, 155.87.

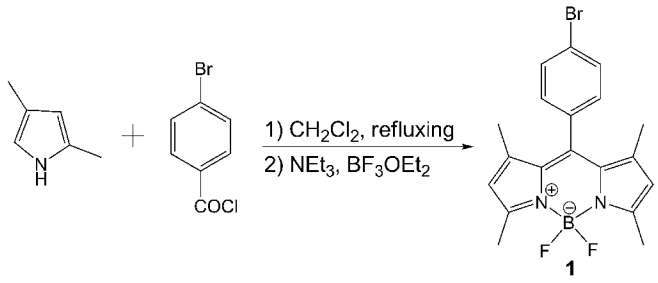

Fig. 1. Synthetic route of BODIPY dye **1** [Ref. 18]

RESULTS AND DISCUSSION

The fluorescent properties of **1** were studied by emission spectra in different surfactants with excitation at 490 nm. Compound **1** itself displayed a yellow-green fluorescence centered at 510 nm, with a nice mirror symmetry with the lowest-energy absorption band at 490 nm, in keeping with classical BODIPY derivatives. As shown in Fig. 2, fluorescence spectra of **1** changed with different surfactant solutions. About 3-6 nm red-shift of the maximum were observed in four surfactants, which could be assigned to the stronger polarity of surfactant solutions than CH_3CN[19]. Moreover, intensity at 513 nm increased by 11-fold in myristyltrimethylammonium bromide solution. Fig. 3 illustrated the intensity gradually increased along with increasing the concentration of myristyltrimethylammonium bromide. When the concentration reached 2.1×10^{-3} mol/L, closely to critical micelle concentration[20], intensity value was almost constant. This might be due to the formation of myristyltrimethyl-ammonium bromide micelle, allowing the entrance of BODIPY molecule, which rendered fluorescence significantly enhancing. The intensity is in good line with myristyltrimethylammonium bromide concentration in the range of 0-2.1 $\times 10^{-3}$ mol/L, with the association constant (K_M) of 3.71×10^4.

By contrast, sodium dodecylbenzenesulphonate only induced 3-fold fluorescence enhancement in Fig. 4a. Association constant ($K_S = 1.22 \times 10^3$) was smaller than K_M. This order might be ascribed to the looser structure of myristyltrimethylammonium bromide micelle than sodium dodecylbenzenesulphonate micelle[21], which would favor the approach of BODIPY. As for sodium dodecylsulfate and X-100, there was only a small red-shift and no obvious intensity change in Fig. 4b and 4c.

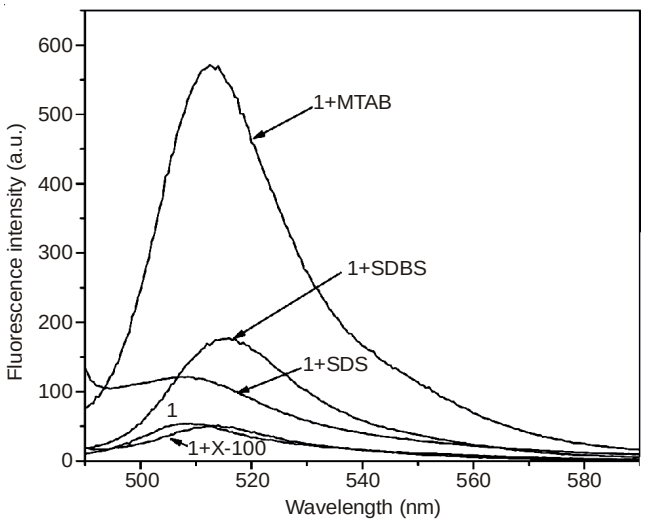

Fig. 2. Fluorescence spectrum of **1** (1.24×10^{-6} M) in various surfactant solutions 2.1×10^{-3} M

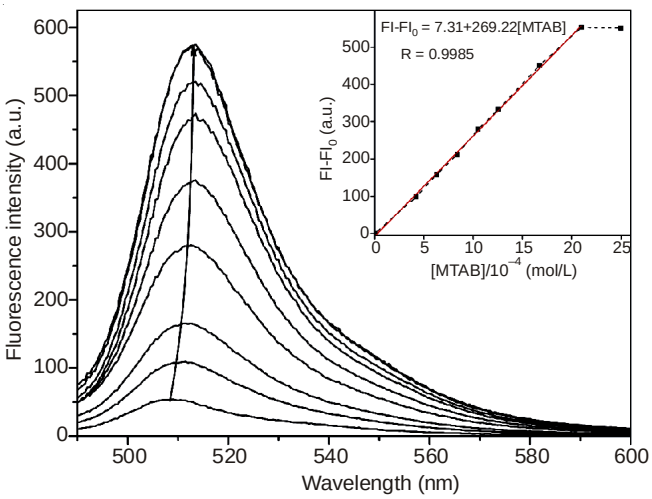

Fig. 3. Fluorescence spectrum of **1** (1.24×10^{-6} M) in myristyltrimethyl-ammonium bromide solutions from 0 to 2.5×10^{-3} M; **Inset**: Intensity changes as a function of [myristyltrimethylammonium bromide] monitored at 513 nm

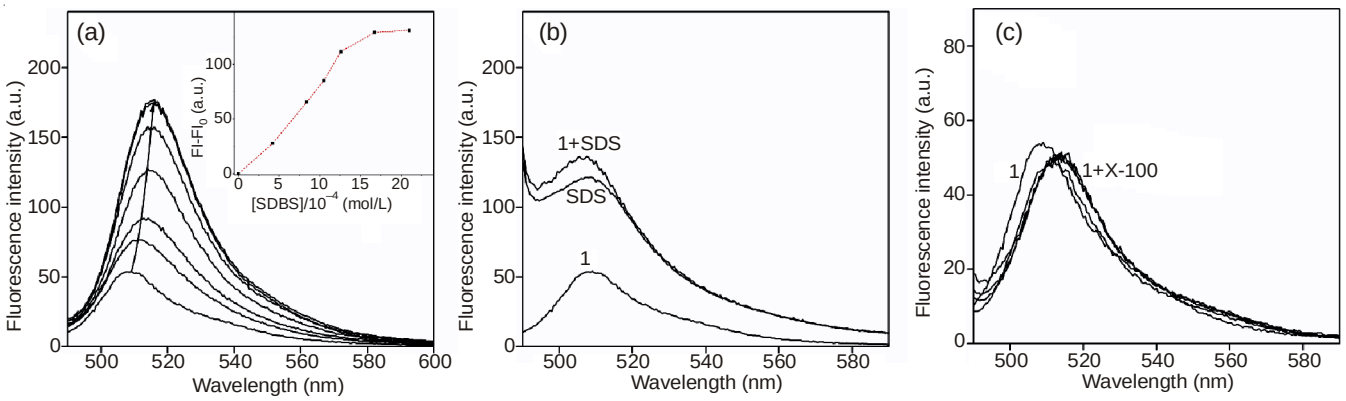

Fig. 4. Fluorescence spectrum of **1** (1.24×10^{-6} M) in various surfactant solutions from 0 to 2.1×10^{-3} M

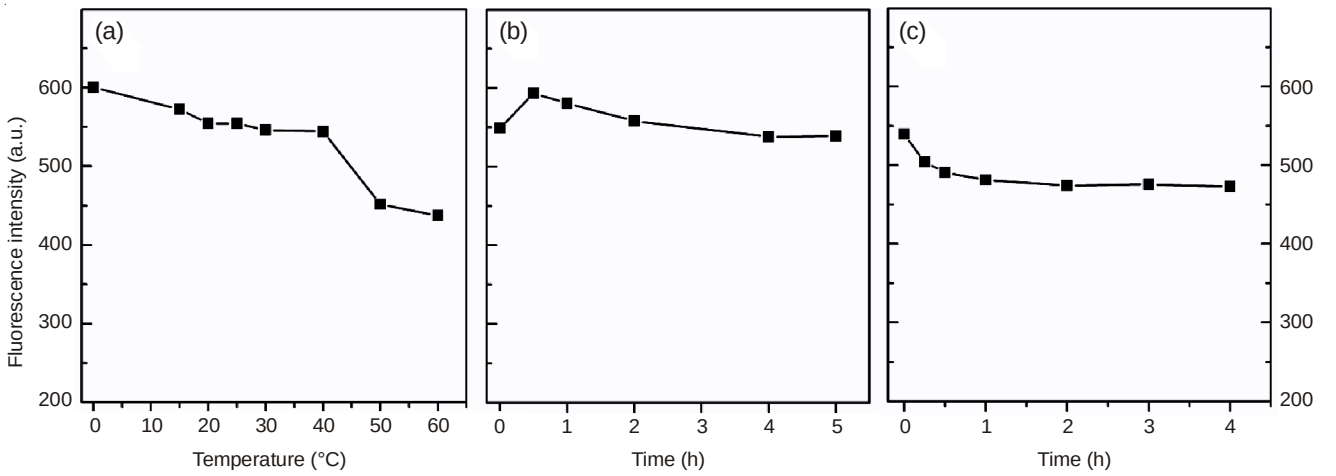

Fig. 5. Effect of temperature (a), equilibrium time (b) and sunlight time (c) on the fluorescence intensity of **1** (1.24×10^{-6} M) in the myristyltrimethylammonium bromide solution 2.1×10^{-3} mol/L

The influences of temperature, equilibration time and light application time on the fluorescence intensity of **1** in myristyltrimethylammonium bromide solution were also conducted in Fig. 5. The intensity remained stable in the temperature range of 15-40 °C and it decreased at high temperature inducing fluorescence quenching. The equilibrium between BODIPY and myristyl-trimethylammonium bromide could rapidly attain after 20 min. Besides, this mixture exhibited basically stable intensity even exposure for 4 h. This stability was likely related to the protection of BODIPY molecule given by myristyltrimethylammonium bromide micelle. Thus surfactant-containing system has the potential to be utilized in the field of fluorescence sensing and recognizing. Further work to that goal is now in progress.

Conclusion

In summary, a BODIPY dye was constructed and its fluorescence characteristics in four surfactant solutions were studied. **1** suggested 11-fold fluorescence enhancement in the myristyltrimethylammonium bromide solution, resulting from the entrance of **1** into the myristyltrimethylammonium bromide micelle. Furthermore, fluorescence intensity and myristyltrimethylammonium bromide concentration revealed a good linear relationship in the range of 0-2.1×10^{-3} mol/L. Association constants were calculated in the order: $K_M > K_S$, which indicated that **1** was inclined to enter a looser myristyltrimethylammonium bromide micelle compared to sodium dodecylbenzenesulphonate micelle. Furthermore, 1-MTAB system remained stable at room temperature, rapidly equilibrated and remained light-stable. Thus, such a surfactant-containing solution would be a good alternative to evade sophisticated synthesis. Further work to explore the potential is under way.

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