

## Novel surfactant-like pyrene derivatives: synthesis, fluorescent properties and sensing applications



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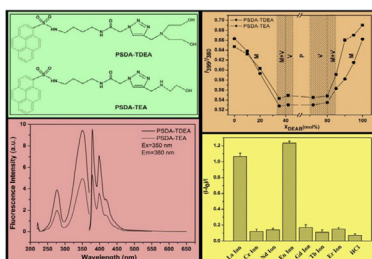
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### HIGHLIGHTS

- Prepared two novel surfactant-like pyrene derivatives.
- Monitored the transition between different surfactant aggregates.
- One of them shows selective sensing to the presence of lanthanum and europium ions.
- The compounds are more powerful multifunctional fluorescent probes.

### GRAPHICAL ABSTRACT

The application of two novel newly designed and prepared surfactant-like pyrene derivatives in the transition of the aggregates of amphiphilic compounds, especially between micelles and vesicles, were investigated systematically by using the compounds as probes. Meanwhile, one of them also shows selective sensing to the presence of lanthanum ion and europium ion, and the detection limits (DL) are 1.48 and 1.14 ppm, respectively.



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### ABSTRACT

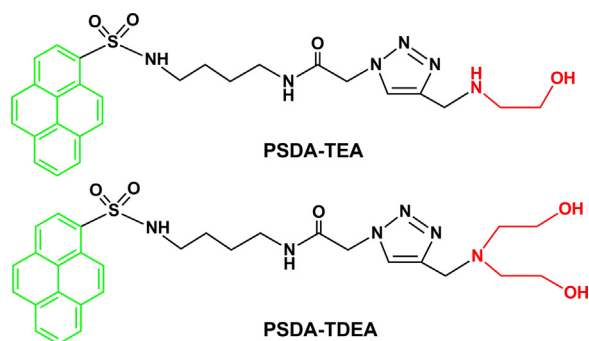
Two novel non-ionic surfactant-like pyrene derivatives containing a triazole unit, 2-(4-((bis(2-hydroxyethyl)amino)methyl)-1H-1,2,3-triazol-1-yl)-N-(4-(pyrene-1-sulfonamido)butyl)acetamide (PSDA-TDEA) and 2-(4-(((2-hydroxyethyl)amino)methyl)-1H-1,2,3-triazol-1-yl)-N-(4-(pyrene-1-sulfonamido)butyl)acetamide (PSDA-TEA) were designed and synthesized. Fluorescence studies revealed that the two fluorophores aggregate in aqueous phase, and the critical aggregation concentrations (CACs) of them are  $\sim 1.2 \times 10^{-4}$  M and  $\sim 8.5 \times 10^{-5}$  M, respectively. It was demonstrated that the profiles of the emission spectra of the two compounds are both dependent on the micro-polarities of their mediums. Specifically, the ratio of  $I_{399}/I_{380}$ , of which the two emissions appearing at 399 and 380 nm, respectively, are both coming from the monomer emissions of the pyrene residue of the compounds, increases gradually and significantly with increasing the micro-polarity of the medium at which the probes stay. As expected, PSDA-TDEA and PSDA-TEA could probe the formation and transformation of the aggregates of some typical amphiphiles. Meanwhile, PSDA-TDEA also shows selective sensing to the presence of lanthanum ion and europium ion, and the detection limits (DL) are 1.48 and 1.14 ppm, respectively. Clearly, PSDA-TDEA and PSDA-TEA as created could be used as multi-functional fluorescent probes, at least for sensing polarity and some lanthanide ions. These probes are superior to others in using due to their better solubility in aqueous phase, which must bring convenience for pre-treatment of the samples under test.

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### 1. Introduction

In recent years, with continuous development of fluorescence techniques, creation of new fluorescent probes has been oriented to multi-functionality, great-sensitivity and high selectivity [1–7]. As

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**Scheme 1.** Structures of PSDA-TDEA and PSDA-TEA.

a normal practice, to achieve high selectivity and sensitivity, special binding/sensing units and reporting elements, actually fluorophores, have to be elaborately chosen, and chemically bonded via some special linkers. In this way, new fluorescent probes with expected properties may be produced. As for the development of multifunctionality, new functional structures have to be introduced to a known fluorescence probe or to the one as to be developed with one fold functionality. According to this strategy, a variety of new multi-functional fluorescent probes has been developed and utilized for sensing and imaging in chemistry, biology, and clinical diagnoses [8–16].

In a very recent publication, we reported a non-ionic surfactant-like fluorophore based on pyrene [17]. As revealed in the studies, this probe is rich in detectable parameters and more adaptive to mediums of different properties, and provides much more information than conventional and ionic probes do. The work to be reported in the present article is a continuation of the one aforementioned. Similarly, pyrene was also chosen as the reporting fluorophore, hydrophilic hydroxyl group and triazole are chosen as the binding or sensing structures, which are expected to bind some metal ions via coordination interaction, and furthermore provide the fluorophores to be developed surfactant-like properties. Specifically, the compounds are 2-(4-((bis(2-hydroxyethyl)amino)methyl)-1H-1,2,3-triazol-1-yl)-N-(4-(pyrene-1-sulfonamido)butyl)acetamide (PSDA-TDEA) and 2-(4-(((2-hydroxyethyl)amino)methyl)-1H-1,2,3-triazol-1-yl)-N-(4-(pyrene-1-sulfonamido)butyl)acetamide (PSDA-TEA), respectively (c.f. Scheme 1). It was expected that the molecules as designed would function as a fluorescent probe to sense the polarity of their micro-environment and even the structural changes of their surroundings. Furthermore, the triazole and hydroxyl structures contained in the molecules may also provide them metal ions sensing properties. Actually, the two compounds as created do exhibit the abilities to show the formation and transformation of the aggregates of some surfactants in aqueous phase sensitively and selectively. Moreover, one of the compounds, PSDA-TDEA is also sensitive to the presence of lanthanum and europium ions in aqueous phase, and the minimum detection limits (DL) to them are 1.48 and 1.14 ppm, respectively.

## 2. Experimental

### 2.1. Materials

Bromoacetyl bromide (BB, 98%), propargyl bromide (PB, 80 wt% solution in toluene, 0.3% magnesium oxide as stabilizer), and sodium ascorbate (99%) were purchased from J&K CHEMICAL. Sodium azide, lanthanum oxide and europium oxide were purchased and used without further purification. Pyrenesulfonyl chloride (PSC) was synthesized by adopting a literature method [18]. 1,4-Diaminobutane (Acros, 99%) and diethanolamine (DEA, 99%) were used as received without further purification.

Triethylamine (TEA) was vacuum distilled over CaH<sub>2</sub>. Sodium dodecyl sulfate (SDS, 99%) and polyoxyethylene (10) isooctylphenyl ether (Triton X-100, 99%) were purchased from Acros, and were used as received without further purification. Dodecyltrimethylammonium bromide (DTAB, 99%), dodecyltriethylammonium bromide (DEAB, 99%) were synthesized from *n*-alkyl bromide and corresponding trialkylamine. These two products were recrystallized from acetone–ethanol for five times. The purity of all the synthesized cationic surfactants was examined and no surface tension minimum was found in the surface tension curve. Other starting materials were purchased commercially and used as received. Solvents were analytical grade and used as purchased, unless otherwise noted. Water used throughout is de-ionized and then double distilled.

### 2.2. General instruments

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded by using a Fourier Digital NMR spectrometer (AVANCE 300 MHz, 300 MHz) in CDCl<sub>3</sub>, and chemical shifts are reported in parts per million relative to TMS in proton spectra. All <sup>13</sup>C NMR spectra were determined with complete proton decoupling.

All of the fluorescence measurements were conducted with a time-correlated single photon counting Edinburgh FLS 920 fluorescence spectrometer at room temperature (25 °C). The path length of the quartz cell is 1 cm. The samples containing PSDA-TDEA and PSDA-TEA were both excited at 345 nm and the intensities were determined at 380 nm. All Fourier Transform infrared spectroscopy (FTIR) measurements were performed on a Bruker VERTEX 70V infrared spectrometer in an attenuated total reflectance (ATR) mode. Solution samples for FTIR measurements were prepared by dropping a very dilute solution of the sample on a hot KBr disc, and then evaporating the water in an oven at 50 °C. If necessary, the process could be repeated so that more samples were coated on the disc.

### 2.3. Experimental method

Stock solutions (1.0 × 10<sup>-3</sup> M) of the two compounds were prepared in water and ethanol, respectively. Standard solutions of them with different concentrations were obtained by direct dilution of the stock solutions with water or ethanol. Lanthanum ion and europium ion solutions were prepared by dissolving the corresponding metal oxides into hydrochloric acid.

### 2.4. Synthesis

#### 2.4.1. Synthesis of *N*-(4-aminobutyl)pyrene-1-sulfonamide (PSDAB)

1,4-Diaminobutane (0.5 mL, 5 mmol) was dissolved in 50 mL CHCl<sub>3</sub> under a N<sub>2</sub> atmosphere, and then 50 mL CHCl<sub>3</sub> solution of PSC (0.15 g, 0.5 mmol) was added drop-wise under stirring in an ice-bath, which is generally last for more than 10 h. After the addition, the mixture was stirred for 2 h, then the mixture was washed with plenty of water (150 mL) and 5% NaCl aqueous solution for at least 10 times. The organic phase was separated and dried by using anhydrous MgSO<sub>4</sub>, then the mixture was filtered, and then the filtrate was evaporated in vacuum to dryness. Finally, the solid as obtained was purified via Soxhlet extraction with water as the solvent for 24 h. The solid was further concentrated in vacuum to dryness for 18 h. A desired product (PSDAB) was obtained as a yellow powder in 73% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si, 300 MHz): δ (ppm) 9.04 (1H, d, ArH), 8.72 (1H, d, ArH), 8.11–8.30 (7H, m, ArH), 3.04 (2H, t, CH<sub>2</sub>), 2.56 (2H, t, CH<sub>2</sub>), 1.45 (2H, t, CH<sub>2</sub>), 1.31 (2H, t, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si, 76 MHz): δ (ppm) 134.63, 130.99, 130.18, 129.99, 129.71, 127.44, 127.10, 126.85, 126.74, 123.86, 123.41 (11C,

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