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A simple fluorophore/surfactant ensemble as single discriminative sensor platform: Identifying multiple metal ions in aqueous solution



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ABSTRACT

A simple imidazolium-modified mono-pyrene derivative (**Py-IM**) is synthesized. SDS assemblies modulate its fluorescence emission from monomer emission in neat aqueous solution to monomer-excimer co-emission in pre-micelles and to monomer emission again in micellar solutions. The ensemble based on **Py-IM** and SDS assemblies exhibiting both monomer and excimer emission displays multiple-wavelength cross-reactive responses to cationic metal ions. This single sensor system could well discriminate 6 quenching metal ions (Fe^{3+} , Cu^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , and Mn^{2+}) through principal component analysis method. Control experiments with **Py-IM** in the absence of SDS assemblies and in SDS micellar solutions reveal that the modulation effect of surfactant assemblies plays an important role in the cross-reactive responses of the cationic probe, which provides a general way of fabricating discriminative single sensor systems.

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1. Introduction

Discrimination of structurally or chemically similar analytes is challenging but of great significance since it provides promises of high-throughput detection or analyzing mixture samples. Such tasks can be accomplished by using sensor arrays inspired by mimicking the mammalian systems of taste and smell [1]. Usually, sensor arrays comprise a series of cross-reactive sensing elements and generate a fingerprint recognition pattern for each specific analyte by combining the response signals from all sensor elements [2]. According to the output signals of the used sensor elements, sensor arrays could be divided into electrochemical [3], colorimetric [4], and fluorescent ones [5]. By comparison, fluorescent sensor arrays have advantages in term of sensitivity and have been extensively developed for identification of multiple analytes [2], such as metal ions [6], anions [7], amino acids [8], and proteins [9].

However, there are some limitations accompanying the use of sensor arrays [10]. For example, the discrimination ability is highly dependent on the number of sensor elements, which leads to a

high consumption of samples. In the case of fluorescent sensor arrays, different fluorophore-based sensor elements are usually used to provide cross-reactivity [5,11,12]. This leads to complexity of collecting data by scanning the emission spectra of all the sensor elements. Different excitation wavelengths (if needed) further increase the tedious extent of data collecting. Therefore, more efficient methods of developing discriminative sensors or arrays are attracting increasing attention.

Recently, various single system-based fluorescent sensors with multi-wavelength cross-reactivity and fingerprint recognition capabilities have been developed through different approaches. Lavigne et al. has reported using cross-reactive fluorescent polyelectrolyte to differentiate structurally similar diamines by collecting absorption signals at different wavelengths of the UV-vis spectra to generate recognition pattern [13]. Using similar strategy, they have developed single cross-reactive sensors for discriminating biogenic amines [14], detecting food freshness [15], and identification of divalent metal ions [16]. Severin and co-workers put forward a strategy of using dynamic combinatorial libraries (DCL) with cross-reactivity to build single discriminative sensor systems, and have realized pattern recognition of dipeptide [17], tripeptide [18], and peptide hormones [19]. They also found that the sensors based on DCL method gave in most cases better results than the sensor array [20]. Margulies et al. has designed a

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combinatorial fluorescent molecular sensor composed of four different fluorescent dyes to provide multiple fluorescence signals for pattern recognition of 13 drug molecules [21].

For these cross-reactive single sensors, each selected wavelength functions as a sensor element of traditional sensor arrays and the recognition data can be collected by one-time scanning of the spectrum. The data collecting process is significantly simplified, and the consumption of sensor samples is highly reduced. However, the developed cross-reactive single sensors have issues such as low sensitivity, tedious synthesis processes, and application in organic solvents. We recently introduced a strategy of using amphiphilic assemblies to modulate the photophysical properties of small fluorescent molecules with multiple emitting signals to realize cross-reactive responses and pattern recognition [22]. By comparison, this method provides several advantages such as easy preparation, high sensitivity and detection in aqueous solution.

To explore the universality of this methodology, herein, we specially designed and synthesized a simple cationic imidazolium-modified mono-pyrene based fluorophore, **Py-IM**. Steady-state fluorescence studies reveal that the fluorescence emission of **Py-IM** can be well modulated by an anionic surfactant, sodium dodecyl sulfate (SDS). It changes from monomer emission in neat aqueous solution to monomer and excimer co-emission in SDS pre-micelles and to monomer again in SDS micellar solutions. The selected **Py-IM**/SDS ensemble with multiple emission signals exhibits cross-reactive responses to the examined metal ions by displaying various fluorescence emission changes. The combination of fluorescence variation at four specific emission wavelengths enables the **Py-IM**/SDS ensemble to provide specific recognition fingerprint to different metal ions. Principal component analysis shows that the present single sensor system could discriminate 6 quenching metal ions, namely, Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , and Mn^{2+} .

2. Experimental

2.1. Reagents and instruments

1-Pyrenemethanol (98%), 1-methylimidazole (98%), 1,8-dibromooctane (98%), sodium hydride (dispersion in mineral oil, 60%), sodium dodecyl sulfate (SDS, 98%), and HEPES (>99.5%) were all purchased from Sigma-Aldrich company and used without further purification. HEPES buffer solution (10 mM, pH 7.4) was prepared in water and used for preparation of sensor samples. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were analytical pure and dissolved in water to obtain 2.5×10^{-3} stock solution. Aqueous samples were all prepared in Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C).

^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance 400 and 600 MHz NMR spectrometer. The high resolution mass spectra (MS) were acquired in ESI positive mode using a Bruker Maxis UHR-TOF Mass Spectrometer. The FTIR spectra were measured on a Fourier Transform Infrared Spectrometer (Vertex 70v, Bruker, Germany). Steady-state fluorescence spectra were measured on a single photon-counting fluorescence spectrometer

(FS5 and FS920, Edinburgh Instruments) using 150 W and 450 W xenon lights as excitation source, respectively, and all samples were excited at 346 nm. Time-resolved fluorescence decays were measured on time-correlated single photon-counting fluorescence spectrometers (FLS920, Edinburgh Instruments) using laser as excitation source (343.4 nm).

2.2. Synthesis of the target mono-pyrene derivative, **Py-IM**

Py-IM is a simple amphiphilic fluorescent probe containing an alkyl chain which acts as a bridge between a pyrene unit and a cationic imidazolium group. The synthesis route of **Py-IM** is illustrated in Scheme 1. The detailed synthesis procedures are described as follows:

2.2.1. Synthesis of compound **1**

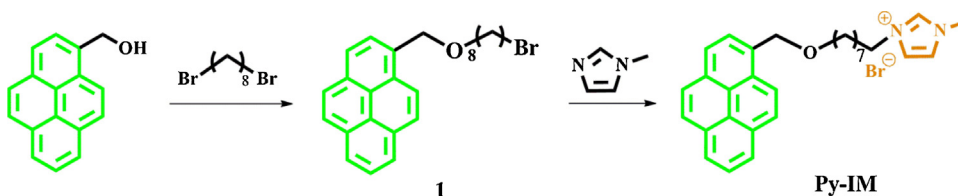
Under protection of N_2 atmosphere, a solution of 1-pyrene-methanol (1 g, 4.31 mmol) and 1,8-dibromooctane (7.95 mL, 43.05 mmol) in anhydrous tetrahydrofuran (THF, 20 mL) was added dropwise to a stirred suspension of sodium hydride (60% dispersion in mineral oil) (1.03 g, 25.83 mmol) in anhydrous THF (15 mL). The reaction mixture was refluxed for 48 h. Then the solvent was removed under reduced pressure and the excess NaH was then carefully quenched by the addition of water at 0°C . The solution was extracted with CH_2Cl_2 ($50 \text{ mL} \times 3$), and the combined organic layer was washed with water ($50 \text{ mL} \times 3$), and then dried with anhydrous Na_2SO_4 overnight. The residue after removal of the solvent was chromatographed on silica gel with ethyl acetate/petroleum ether (1:10, v/v) as eluent to give a white solid powder (1.275 g, yield 70%). ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.39 (d, $J = 9.2 \text{ Hz}$, 1H), 8.18 (s, 4H), 8.04 (s, 4H), 5.22 (s, 2H), 3.60 (s, 2H), 3.34 (s, 2H), 1.76 (t, $J = 14.3 \text{ Hz}$, 2H), 1.66 (d, $J = 28.0 \text{ Hz}$, 2H), 1.54 (s, 3H), 1.28 (d, $J = 41.9 \text{ Hz}$, 8H).

2.2.2. Synthesis of the mono-pyrene derivative, **Py-IM**

A solution of **1** (200.00 mg, 0.48 mmol) and 1-methylimidazole (0.12 mL, 1.42 mmol) in anhydrous acetonitrile (15 mL) was refluxed for 48 h under nitrogen. After removal of the solvent, a yellow precipitate appeared. The crude product was washed with diethyl ether and dried under reduced pressure to provide a yellow powder (0.212 g, yield 90%). ^1H NMR (600 MHz, DMSO, ppm) δ 9.08 (s, 1H), 8.44–8.02 (m, 9H), 7.73 (t, $J = 27.4 \text{ Hz}$, 2H), 5.18 (s, 2H), 4.08 (t, $J = 7.2 \text{ Hz}$, 2H), 3.84 (d, $J = 15.5 \text{ Hz}$, 3H), 3.58 (t, $J = 6.4 \text{ Hz}$, 2H), 1.74–1.62 (m, 2H), 1.62–1.50 (m, 2H), 1.34–1.11 (m, 8H). ^{13}C NMR (101 MHz, DMSO, ppm) δ 136.42, 132.17, 130.71, 130.52, 130.27, 128.63, 127.39, 127.34, 127.20, 126.97, 125.26, 125.21, 124.52, 123.99, 123.84, 123.58, 123.54, 122.19, 70.34, 69.60, 48.55, 29.26, 29.19, 28.49, 28.27, 25.57, 25.36. IR (cm^{-1}): 3040 (Ar-H), 2933 ($-\text{CH}_2$), 1570 and 1470 (C=C), 1352 (C-N). HS-MS (ESI) $[\text{M}-\text{Br}]^+$: calcd for $\text{C}_{29}\text{H}_{33}\text{N}_2\text{O}$, 425.2587, found, 425.2593.

2.3. Fluorescence titration measurements

For fluorescence titration measurements, the aqueous sensor solution (2.5 mL) was first put in a quartz cell ($1 \text{ cm} \times 1 \text{ cm} \times 3.5 \text{ cm}$), and the corresponding spectra were scanned; then, the



Scheme 1. Synthesis route of the mono-pyrene derivative, **Py-IM**.

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