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Ratiometric near-infrared chemosensor for trivalent chromium ion based on tricarboyanine in living cells

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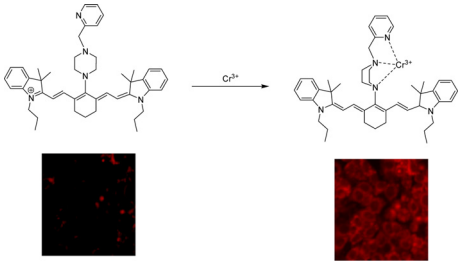
HIGHLIGHTS

- A tricarboyanine was first designed as a near-infared chemosensor for Cr^{3+}.
- The chemosensor showed ratiometric response to Cr^{3+} with well-resolved emissions.
- The chemosensor exhibited a high selectivity for Cr^{3+} over other metal ions.
- The chemosensor has been used in water samples and living cells successfully.

GRAPHICAL ABSTRACT



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ABSTRACT

A tricarboyanine derivative (**IRPP**) is applied as a ratiometric near-infrared chemosensor for detecting trivalent chromium ions (Cr^{3+}) in living cells. Upon the addition of Cr^{3+} to a solution of **IRPP**, large-scale shifts in the emission spectrum (from 755 nm to 561 nm) are observed. In the newly developed sensing system, these well-resolved emission peaks yield a sensing system that covers a linear range from 1.0×10^{-7} to 1.0×10^{-5} M with a detection limit of 2.5×10^{-8} M. The experimental results show the response behavior of **IRPP** towards Cr^{3+} is pH independent under neutral conditions (6.0–7.5). Most importantly, the fast response time (less than 3 min) and selectivity for Cr^{3+} over other common metal ions provide a strong argument for the use of this sensor in real world applications. As a proof of concept, the proposed chemosensor has been used to detect and quantify Cr^{3+} in river water samples and to image Cr^{3+} in living cells with encouraging results.

1. Introduction

Chromium ion (Cr^{3+}) is an essential micronutrient for humans as it is involved in several biochemical processes [1,2]. While chromium deficiency increases the risk factors associated with diabetes and cardiovascular disease, the excessive intake of Cr^{3+} negatively affects cellular structures and functions [3,4]. Due to its biological impact, the United States Environmental Protection Agency (USEPA) has set strict standards on the permissible concentration of Cr^{3+} in natural water (0.1 mg mL^{-1}) in an attempt to control build-up due to industrial and agricultural activities [5–7]. Therefore, there is an urgent need to develop analytical

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methods for the detection of chromium ions in environmental and biological samples.

In recent years, fluorescent chemosensors have become powerful tools for the detection of chemical species relevant to environmental and biological systems [8–10]. Currently, most fluorescent chemosensors are based on changes in emission intensity at a single wavelength (quenching or enhancement) and are thus limited by such factors as chemosensor concentration, photobleaching, optical path length, illumination intensity and microenvironment around the chemosensor molecule. In contrast, fluorescent chemosensors based on ratiometric methods offer a wider dynamic range and a built in correction for environmental factors through the measurement of emission intensity at two wavelengths upon the addition of a target [11–16]. Up until recently, only a small quantity of ratiometric Cr^{3+} chemosensors have been reported [17,18] and offer limited resolution capability and sensitivity (difference of <80 between two emission wavelengths).

At present, a number of fluorescent chemosensors for Cr^{3+} have been proposed and are based on different fluorophores such as coumarin [19], 1,8-naphthyridine (napy) [20,21], rhodamine [22–27], BODIPY [28], benzimidazole [29]. The excitation and emission wavelengths for these fluorescent dyes are generally in the ultraviolet or visible region and as a result are vulnerable to interference from background fluorescence. Near-infrared dyes, on the other hand, exhibit the long excitation and emission wavelengths needed to reduce scattering and decrease background emissions, and are more compatible with biological samples due to the penetration ability of their near-infrared photons deep into tissue samples [30–36]. Cyanine dyes have received immense attention and are widely used as near-infrared fluorescent labels for biological applications [37–40]. For example, tricarbocyanines with a rigid chlorocyclohexenyl or chlorocyclopentenyl ring in the methine chain can increase the photostability and enhance the fluorescence quantum yield [41]. While Cyanine dyes as fluorophores for the detection of Zn^{2+} [32,42,43], Hg^{2+} [34,41,44,45], Cu^{2+} [46], Ag^{+} [47] and pH [48,49] have been reported, chemosensors based on tricarbocyanine dyes for the detection of Cr^{3+} has not.

In an attempt to overcome the limitations associated with the previously developed methods, we have carried out a study aimed to create a ratiometric, near-infared chemosensor for the detection of Cr^{3+} in the environment and living cells. We report here the successful design and synthesis of tricarbocyanine-based chemosensor **IRPP** capable of producing well-resolved emission spectra in response to Cr^{3+} exposure (difference of 194 nm between emission peaks). Moreover, the proposed chemosensor has been successfully applied in the ratiometric detection and quantification of Cr^{3+} in river water and used to image Cr^{3+} in living cells.

2. Experimental

2.1. Reagents

Twice-distilled water was used throughout all experiments. IR-780 iodide, 2-(chloromethyl) pyridine hydrochloride and piperazine were purchased from Sigma–Aldrich. All other chemicals were of analytical reagent grade, purchased from Shanghai Chemical Reagent Corporation (Shanghai, China), and used without further purification. Thin layer chromatography (TLC) was carried out using silica gel 60 F254, and column chromatography was conducted over silica gel (200–300 mesh), both of which were obtained from the Qingdao Ocean Chemicals (Qingdao, China).

2.2. Syntheses

A convenient synthetic route for compound **IRPP** from commercially available compounds is depicted in Fig. 1.

Compound PP: 2-(chloromethyl) pyridine hydrochloride (0.25 g, 1.5 mmol) and piperazine (0.34 g, 4 mmol) were dissolved in dry methanol (50 mL). The reaction mixture was stirred and refluxed for 8 h at 50 °C. Then the reaction mixture was cooled to room temperature and 30 mL of 0.1 M sodium hydroxide in methanol was added. The reaction mixture was stirred for 10 min then filtered. Finally, the filtrate was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography using petroleum ether/CH_3OH (1:1, v/v) as eluent to afford yellow liquid product. Yield: 0.17 g (64.1%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.78 (t, J = 5.7 Hz, 1H), 7.63 (m, 1H), 7.26 (m, 1H), 3.70 (m, 2H), 2.98 (s, 4H), 2.54 (s, 4H), 1.93(s, 1H). MS (EI): m/z (%) = 177.1 ([M^+], 8), 162.1(9), 93.1(100), 78.0(8), Anal. calcd. for $C_{10}H_{15}N_3$ (**2**): C, 67.76; H, 8.53; N, 23.71. Found: C, 67.80; H, 8.51; N, 23.69.

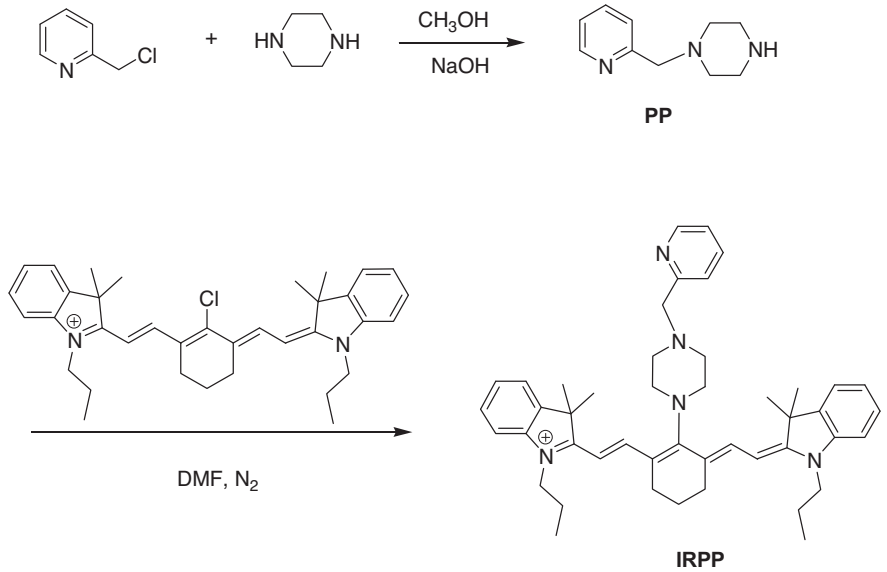

Fig. 1. Chemical structure and synthetic route for compound **IRPP**.