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Three-channel fluorescent sensing via organic white light-emitting dyes for detection of hydrogen sulfide in living cells

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ABSTRACT

To demonstrate the feasibility of development of three-channel based fluorescent sensors based on organic white light-emitting dyes, in this work, for proof-of-principle, we initially judiciously designed an organic white light-emitting dye, which was further used as a robust platform to engineer a new fluorescent sensor for monitoring H_2S with turn-on fluorescence signals in blue, green, and red emission channels in both solution and living cells. This work should open a new avenue for design of three- and multiple-channel based fluorescent sensors for various analytes.

1. Introduction

Fluorescent sensing is widely applied in diverse fields such as chemistry, biology, and medicine due to its high sensitivity and simple operation [1–3]. In addition, by combining with fluorescence microscopy, fluorescent sensing and bio-imaging can be exploited as a powerful approach to investigate biomolecules of interest with high temporal and spatial resolution. Fluorescent sensors are requisite molecular tools for sensing and bio-imaging. Up to date, a large volume of fluorescent sensors have been developed. However, most of them exhibit fluorescence signal variations only in one channel. By contrast, dual-channel based sensors have fluorescence signal changes in two distinct channels. This may reduce the potentials errors due to false positive or artifacts arising from environmental factors [4–6]. Inspired by the spectral feature of dual-channel based sensors, we reasoned that three-channel based sensors could have fluorescence signal variations in three distinct channels. Thus, in principle, three-channel based fluorescent sensors should be much more reliable to eliminate potential false positive or artifacts, as the fluorescent signals in three different channels can be used for mutual corroboration.

However, to our best knowledge, no organic three-channel based fluorescent sensors have been developed yet. Although the development of organic three-channel based fluorescent sensors is still an unmet challenge, we envisioned that this type of sensors could be constructed based on appropriate organic white light-emitting dyes, which emit light with three different channels, red, green, and blue.

In this communication, to test the hypothesis that three-channel based fluorescent sensors could be constructed based on organic white light-emitting dyes, for proof-of-principle, we initially formulated a strategy (Fig. 1) to design compound **1** (Scheme 1) as a new organic white light-emitting dye, which was further applied as a platform to develop the fluorescent sensor **4** for hydrogen sulfide (H_2S) (Scheme 1). Significantly, the fluorescent sensor **4** could respond to H_2S with turn-on fluorescence signals in blue, green, and red emission channels in both solution and living cells.

As organic white light-emitting dyes often bear excited-state intramolecular proton transfer (ESIPT) components, herein, we proposed a strategy to design organic white light-emitting dyes by conjugately connecting a blue fluorescent dye with an ESIPT dye (Fig. 1). In a typical ESIPT process, photoexcitation elicits a shift in electron density that facilitates proton migration from a dye in the enol form to the keto form. [1] Thus, an ESIPT dye normally possesses two different emission channels. We hypothesized that appropriately combing a blue light emitting dye with a dual-channel ESIPT dye may afford an organic white light-emitting dye with three emission channels.

Notably, although the ESIPT mechanism has been widely used to design dual-channel based fluorescent sensors [7–9], the

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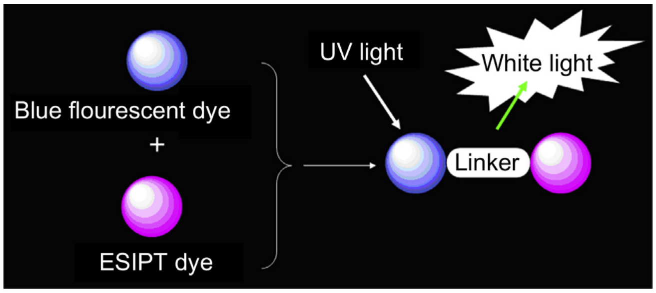


Fig. 1. The proposed design strategy of organic white light-emitting dyes.

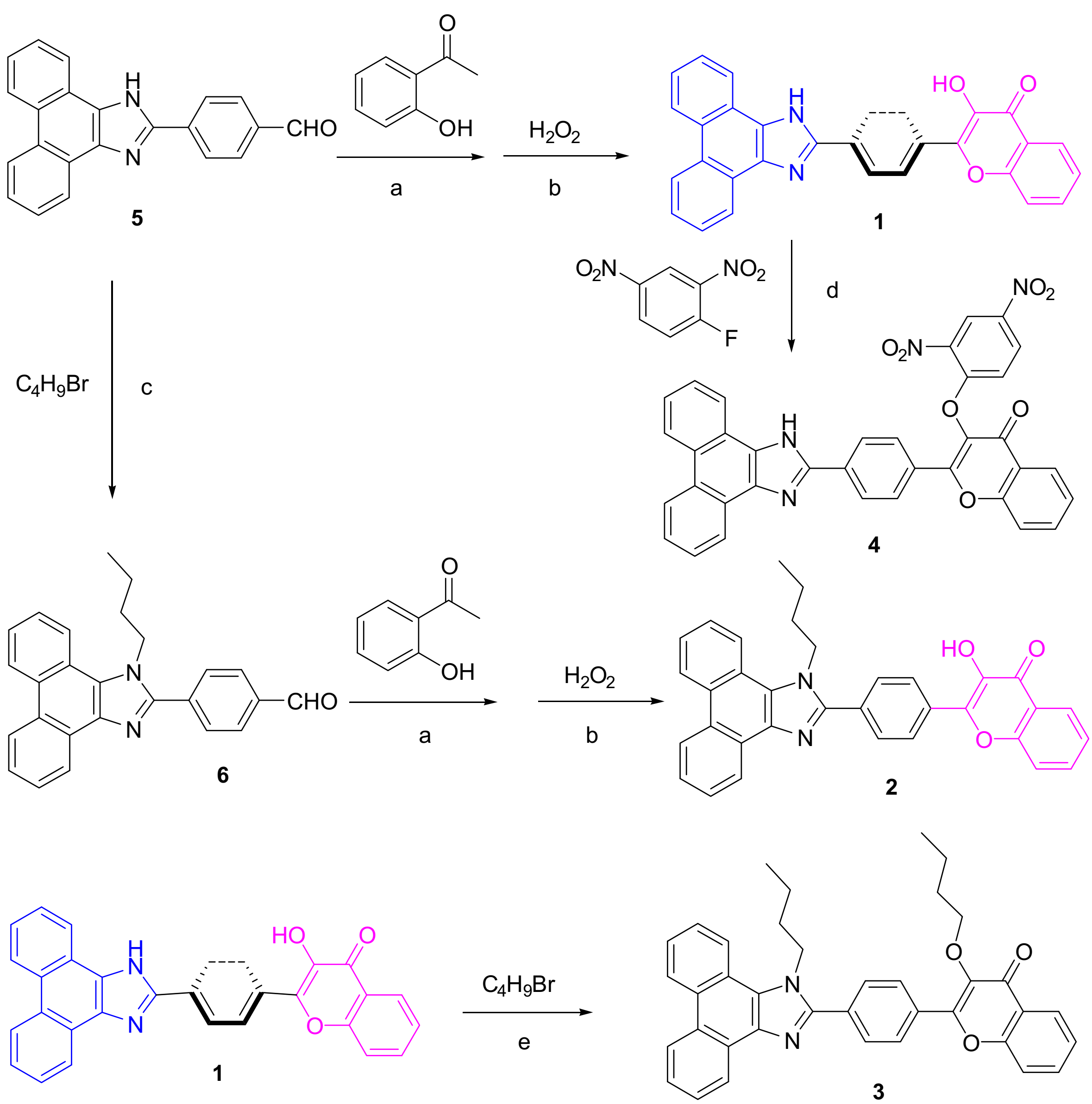
three-channel feature of organic white light-emitting dyes has not been previously exploited in the development of three-channel based fluorescent sensors. In other words, although organic white light-emitting dyes in solid state have found important applications in materials science, their three-channel characteristic in solution state has not been employed in the fluorescent sensing field.

Based on the above strategy, compound **1** was designed as an organic white light-emitting dye, which is composed of two subunits, 1H-phenanthro[9,10-*d*]imidazol and 3-hydroxychromone moieties connected by a rigid and conjugated phenyl linker. The choice of these two subunits is based on the considerations that 1H-phenanthro[9,10-*d*]imidazol dyes [10,11] emit blue light with emission from 380 to 420 nm and 3-hydroxychromone is a typical ESIPT dye with dual channel emission [12,13].

2. Experimental sections

2.1. Materials and instruments

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. Twice-distilled water was used throughout all experiments. Melting points were determined with a Beijing taike XT-4 microscopy



Scheme 1. Synthetic route to compounds **1**, **2**, **3**, and **4**. a: NaOH (10%), EtOH, 60 °C; b: NaOH (10%), EtOH, rt; c: K_2CO_3, DMF, 50 °C; d: K_2CO_3, DMF, 75 °C; e: K_2CO_3, acetone, TBAI, reflux.