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A multi-responsive diarylethene-rhodamine 6G derivative for sequential detection of Cr^{3+} and CO_3^{2-}

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ABSTRACT

A new unsymmetrical diarylethene derivative (**1o**) with rhodamine 6G as a functional group has been designed and synthesized. It displayed good physicochemical properties induced by lights and chemical stimuli. **1o** could sensitively detect towards Cr^{3+} with a 1:1 stoichiometry, and exhibit an obviously fluorescence (from dark to light cyan) and color (from colorless to pink) changes during the recognition process. The limit of detection was determined to be 27 nM and 8.5 nM via UV/vis and fluorescence methods, respectively. More importantly, the resulting complex **1o**-Cr^{3+} (**1o'**) could be served as a potential fluorescent probe to selectively and sensitively recognize toward CO_3^{2-}, the limit of detection was determined to be 0.88 μM and 0.26 μM via UV/vis and fluorescence methods, respectively. Moreover, the quenching of fluorescence intensity can reach 95% due to the perfect FRET processes between the excited open-ring rhodamine 6G moiety and the closed-ring diarylethene unit.

1. Introduction

In recent years, photochromic materials have received more and more attentions due to applications in optical information storage media and photonic switch devices, they could reversible transformation of physical properties between two molecular switches by alternative irradiation under UV or visible light.[1–3] Among the most photochromic compounds, diarylethenes have been recognized as the most promising photosensitive materials because of their fatigue resistance and thermal stability.[4,5] A series of optoelectronic parameters, such as absorption,[6] fluorescence emission,[7] chiroptical properties,[8] refractive index,[9] magnetic properties,[10] and self–assembly behaviors,[11] are subject to notable changes during the photoisomerization. The notable changes in these properties between two isomeric states, especially the fluorescence emission, have been as a tool to develop diarylethene-based multi-responsive molecular switches and chemosensor. In generally, introducing a fluorescent chromophore into the diarylethene structure, which could change either fluorescence intensity or emission wavelength. Thereinto, rhodamine 6G unit is an ideal fluorophore because of they have large molar extinction coefficient, long excitation and emission wavelengths and high fluorescence quantum yields.[12–14] In particular, it is a reversible molecular structural change between the non-fluorescent ring-closed and strongly fluorescent ring-opened amide induced by suitable metal ions or anion ions at room temperature.[15–17] Hence, it is a good choice to graft rhodamine 6G unit to diarylethene motif so as to use as multi-responsive molecular switches and chemosensors.

As is well known, chromium is a transition metals located in group elements VI-B of the periodic table and the seventh most abundant element in the earth.[18] Trivalent chromium (Cr^{3+}) is an important metal ion for human,[19,20] it play a special role in glucose metabolism and lipid metabolism.[21,22] insufficient dietary intake of Cr^{3+} leads to increases in risk factors associated with diabetes and cardiovascular disease.[23–25] Nowadays, a large amount of chromium ions exist in the environment as a persistent pollutant, due to the waste water discharged from various industrial and agriculture activities.[26,27] So, the detection of Cr^{3+} is highly demanded in above fields. Up to present, conventional methods to detect Cr^{3+} include atomic absorption spectrometry,[28] inductively coupled plasma-mass spectroscopy,[29] ion exchange,[30] liquid chromatography-mass spectrometry,[31] and so on.[32,33] However, some of these methods need sophisticated instruments with high cost, time-consuming procedures, and some needed well-controlled experimental conditions. Hence, the development of a sensitive, new convenient, rapid and real-time methods for the detection of Cr^{3+}

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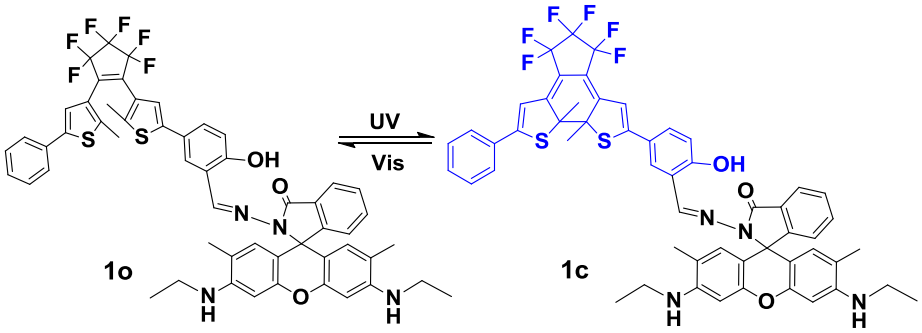
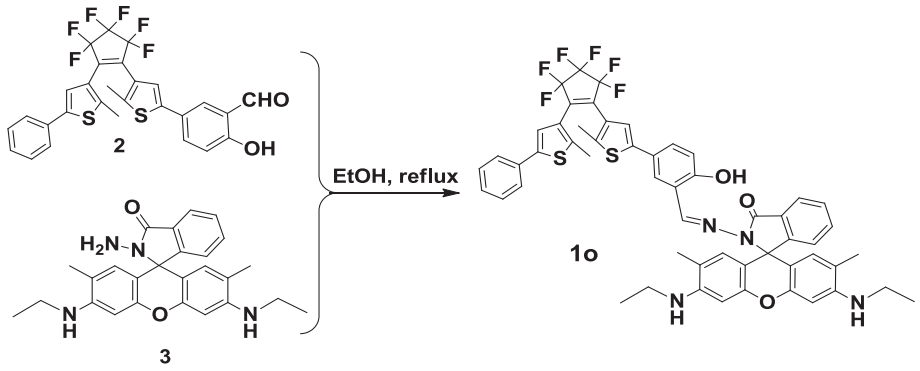


Scheme 1. Photochromism of diarylethene **1o.**



Scheme 2. Synthetic route of **1o.**

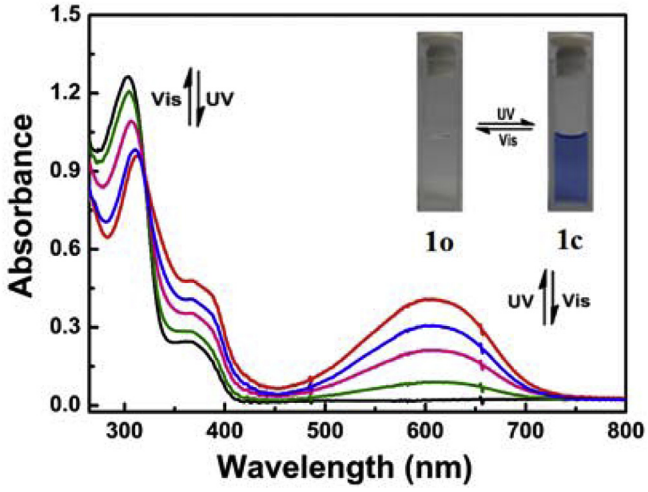


Fig. 1. Absorption spectral and color changes of **1o** by photoirradiation in methanol solution (2.0×10^{-5} mol L^{-1}) at room temperature.

ions is still a challenge.

Meanwhile, anions are very important role in the earth and life sciences. For example, Carbonate anion (CO_3^{2-}) is the main element of product synthesis required for people's life, such as glass manufacturing, rubber, plastic, paper, printing ink, cosmetics, toothpaste and food. In spite of these wide applications in various processes, the amount of carbonate anions too much or too little is likely to cause disease.[34] Therefore, development of highly selective fluorescent probes for the detection and quantification of CO_3^{2-} is of great importance in various field, including physiological analysis, fishery breeding, industrial production and environmental monitoring.[35–37] Although some sensors have been reported for the identification of metal cations and anions at the same conditions based on schiff diarylethenes, only a few sensors have been reported for the detection of CO_3^{2-} till today. Therefore, it is still a challenge to design a new multi-functional chemosensor that can highly selective and sensitive detect CO_3^{2-}.

On the basis of the mentioned facts, a new fluorescence chemosensor based on photochromic diarylethene containing hydroxyl and rhodamine 6G group was synthesized (**1o**) via a schiff base linkage. It not only could be used as a chemosensor to recognize Cr^{3+}, but also the resulted solution could be used as a versatile molecular sensor to distinguish CO_3^{2-} in the CH_3OH–H_2O solution ($C = 2.0 \times 10^{-5}$ mol L^{-1}, v/v = 4:1). The photochromism of the diarylethene are shown in Scheme 1.

2. Experimental

2.1. General methods

All chemicals were purchased from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer by using tetramethylsilane as an internal standard and with DMSO-d_6 as the solvent. Mass spectra were obtained anon AB SCIEX Triple TOF™ 4600. Infrared spectra (IR) were collected on a Bruker Vertex-70 FT-IR spectrometer. Melting point was collected on a WRS-1B melting point apparatus. UV/vis absorption were applied to the Agilent 8453 UV/vis spectrophotometer and the fluorescence spectra were determined with an F-4600 fluorescence spectrophotometer (Hitachi), the excitation and emission slit widths were 2.5 and 5.0 nm, respectively. Fluorescence quantum yield was measured with an Absolute PL Quantum Yield Spectrometer QY C11347-11.