Tetrahedron 72 (2016) 3213–3220

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A fluorescent probe for Cd^{2+} based on a diarylethene with pyridinepiperazine-linked hydroxyquinoline group

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ARTICLE INFO

Article history:
Received 12 February 2016
Received in revised form 13 April 2016
Accepted 19 April 2016
Available online 20 April 2016

Keywords:
Photochromism
Diarylethene
Pyridinepiperazine-linked
hydroxyquinoline
Ion recognition

ABSTRACT

A new diarylethene containing a pyridinepiperazine-linked hydroxyquinoline group was synthesized. Its multi-controllable switching behaviors induced by light and chemical stimuli were investigated. The diarylethene could be used as a fluorescent probe for the detection of Cd^{2+} with high selectivity. When triggered by Cd^{2+}, enhanced fluorescence intensity accompanied with color change from light blue to bright blue was observed. In addition, the diarylethene exhibited notable fluorescence enhancement upon the addition of TFA into the solution. Moreover, its fluorescence behaviors in response to light and Cd^{2+} were applied for the construction of a molecular logic circuit with four inputs and one output.

1. Introduction

Heavy metal contamination has become a serious threat to environment and human health.[1] Cadmium has been widely used in a variety of industrial and agricultural processes, such as rechargeable batteries, fertilizers, coloring agents, and electroplating.[2] However, exposure of cadmium can cause serious renal dysfunction and calcium metabolism disorder, and increase the risks of certain types of cancers.[3] Thus, cadmium has been recognized as a toxic and carcinogenic metal. It is highly desirable to develop reliable methods for monitoring the levels of cadmium in environmental samples and living cells.

Recently, fluorescence probes with various functional groups,[4] such as 8-hydroxyquinoline,[4d] pyrene,[4g] and 1,8-naphthalimide,[4i] have been synthesized and used to detect Cd^{2+} at trace level due to the characteristics of operational simplicity, high sensitivity, and real-time detection. Among these fluorophores, hydroxyquinoline has been frequently employed as a building block for the construction of functional ionophores to recognize a variety of metal ions.[5] Meanwhile, hydroxyquinoline derivatives are ideal probes because of their excellent photostability, strong binding affinity, and convenient synthesis.[6] In addition, the conformation of pyridinepiperazine not only has excellent rigidity, but also offers a tunable and suitable coordination structure to improve the selectivity to metal ions.[7] The quinoline-based probes containing a tweezer-like receptor for tuning their selectivity to Cd^{2+} in aqueous solution through simple and instantaneous reaction have been developed.[8] However, the above traditional fluorescent probes for Cd^{2+} sometimes suffer from the interference of background or Zn^{2+} with similar chemical properties,[9] and most of them are easily photobleached or only reveal the irreversible response to one event, suggesting that the detection process is a single channel and the switch can't be controlled. Therefore, the development of novel photo-controllable fluorescent probes as powerful tools for the detection of Cd^{2+} with high selectivity and sensitivity is highly desired.

Among various photochromic systems, diarylethene is believed as one of the most promising photoswitchable units because of its excellent photochromic properties, thermal stability, fatigue resistance, sensitivity, and reversible fluorescence under alternating irradiation with UV and visible light.[10] In recent years, many multifunctional diarylethene-based fluorescence chemosensors have been designed and synthesized. For example, a 1,8-naphthalimidepiperazine-tethered dithienylethene molecule with fluorescence-tunable groups to Cu^{2+}, proton, and light has been synthesized.[11] In addition, the diarylethenes with a rhodamine or a salicylidene Schiff base unit as a selective chemosensor toward Al^{3+} have been synthesized.[12] Herein, by combining the excellent optical switching property of diarylethenes and the advantages of fluorescent probes for the detection of ions, we designed and constructed a photocontrollable and highly selective fluorescent probes for Cd^{2+} based on a diarylethene with a pyridinepiperazine-

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http://dx.doi.org/10.1016/j.tet.2016.04.043
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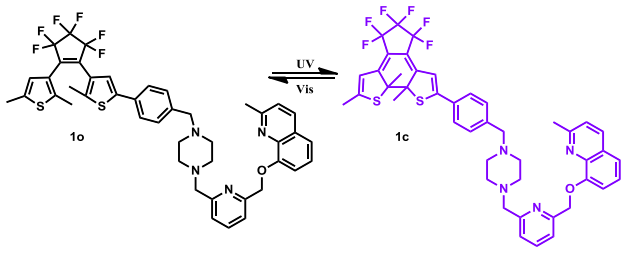
linked hydroxyquinoline unit. Its multifunctional fluorescent switching characteristics induced by light, Cd^{2+}, and proton were systematically explored. The schematic illustration of photochromism is shown in Scheme 1.

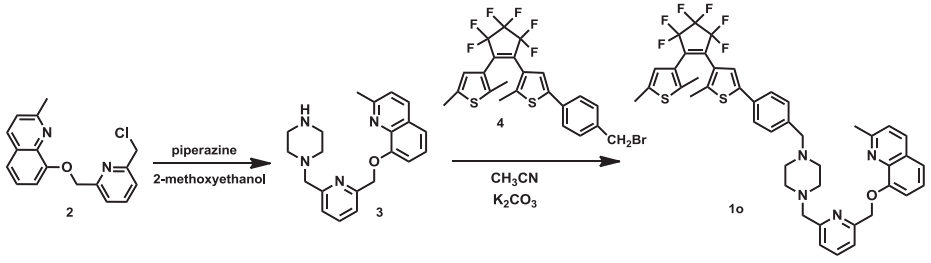


Scheme 1. Photochromism of diarylethene **1**.

was collected with an Agilent 8453 UV–visible spectrophotometer. Fluorescence spectrum was recorded with a Hitachi F-4600 fluorescence spectrophotometer with both excitation and emission slit widths of 5.0 nm. Quantum yield was measured with Absolute PL Quantum Yield Spectrometer QY C11347-11. Elemental analysis was carried out with a PE CHN 2400 analyzer. HPLC analysis was performed by an Eclipse XDB-C18 instrument equipped with a column (5 μm in particle size, 4.6 mm×150 mm). All of the materials for the synthesis of the target compound were purchased from J & K and used without further purification. Solvents for reactions were used as received with the following exceptions. Tetrahydrofuran (THF) was distilled from sodium (Na) and benzophenone. The solutions of metal ions (0.1 mol L^{-1}) were prepared by the dissolution of their metal nitrates in distilled water, except for Mn^{2+}, Hg^{2+}, and Ba^{2+} (all of their counter ions were chloride ions).

2.2. Synthesis of the target compound

The synthesis route of diarylethene **1o** is shown in Scheme 2. The intermediate compounds **2** and **4** were synthesized according to the similar procedures as previous descriptions.[13]



Scheme 2. Synthetic route for diarylethene **1o**.

2. Experimental

2.1. General methods

NMR spectrum of this probe was recorded on a Bruker AV 400 (400 MHZ) spectrometer by using TMS as an internal standard and $CDCl_3$ as the solvent. Mass spectrum was performed using an Agilent 1100 ion trap MSD spectrometer. Melting point was measured on a WRS-1B melting point apparatus. Infrared (IR) spectrum was collected on a Bruker Vertex-70 spectrometer. Absorption spectrum

*2.2.1. Synthesis of compound 2-methyl-8-((6-(piperazin-1-ylmethyl) pyridin-2-yl)methoxy)quinoline) (**3**).* Compound **2** (893 mg, 3 mmol) and piperazine (1806 mg, 21 mmol) were dissolved in 2-methoxyethanol (18 mL). The mixture was refluxed for 6 h under a nitrogen atmosphere, and then cooled to room temperature to remove 2-methoxyethanol under reduced pressure. The product was purified by extraction, evaporation, and separation on silica gel using dichloromethane–methanol at the ratio of 10:1 (v/v) as the eluent to obtain the compound **3** (637.6 mg, 61%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (t, J=8.4 Hz, 1H), 7.63 (d,

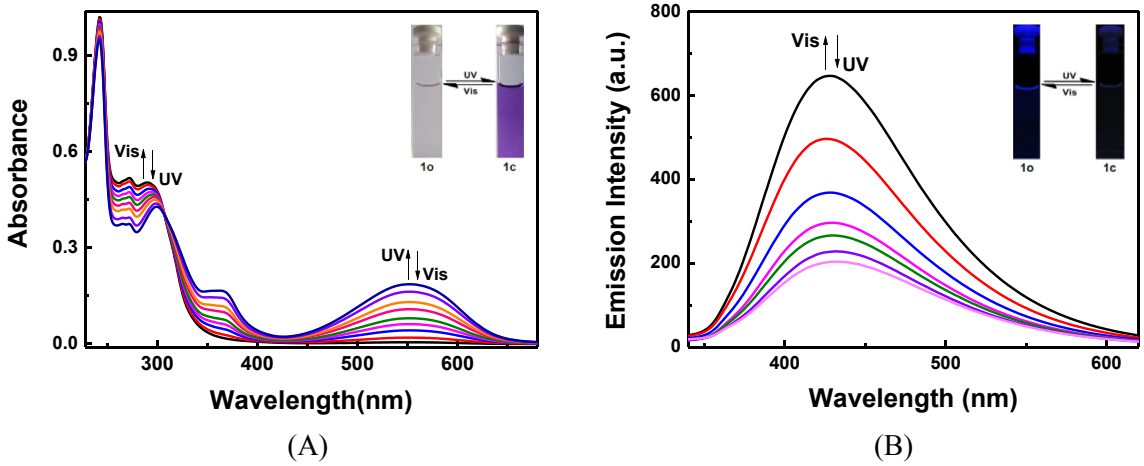


Fig. 1. Changes in the absorption spectrum and fluorescence of **1o** (2.0×10^{-5} mol L^{-1}, in methanol) upon alternating irradiation with UV and visible light: (A) absorption spectral change; (B) fluorescence change, excited at 324 nm.