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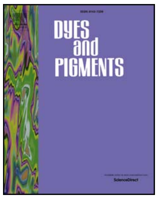

Highly sensitive and selective turn-on fluorescent sensor for dual recognition of Cu^{2+} and CN^- based on a methylquinoline derivative

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ABSTRACT

In this work, we successfully introduced a novel strategy for the rational design of a fluorescence turn-on probe based on diarylethene for copper ion and cyanide ion recognition. The probe was designed by conjugating diarylethene bromide with 2-(methylquinoline-8-yloxy) acetohydrazide and exhibited a 45-fold and 15-fold fluorescent enhancement in the presence of 5 equiv. of Cu^{2+} and 34 equiv. of CN^- respectively. This probe is more stable than chemosensors with Schiff base structure and has multicolor changes with the stimuli of lights, CN^-, and Cu^{2+}. This probe can be used to distinguish Cu^{2+} from CN^- *in vitro*. Furthermore, a logic circuit was designed based on the fluorescent properties of this probe.

1. Introduction

Copper is the third abundant element in human bodies and it plays a critical role in various physiological processes. It functions as a cofactor of many important enzymes and is related to the generation of reactive oxygen species *in vivo.* [1] Alterations of its cellular homeostasis is connected to serious neurodegenerative diseases, such as Menkes and Wilson's disease, familial amyotrophic lateral sclerosis, Alzheimer's disease and prion diseases [2]. Deficiency of Cu^{2+} can lead to the loss of Cu-dependent enzymes which are related to the development of brain, causing Menkes disease. Disorder of copper transport can lead to the accumulation of Cu^{2+} in the liver and brain, causing Wilson's disease [3]. Anion recognition is now an area of growing interest in chemistry due to its importance in a wide range of environmental, clinical, chemical, and biological applications [4]. Among various anions, cyanide is extremely toxic to living organisms. It has been widely used in synthetic fibers, resins, herbicides, and the gold extraction processes [5,6]. CN^- is one of the most toxic anions to human beings, which interacts with the active site of cytochrome a_3 and inhibits the cellular respiration, causing vomiting, convulsion, loss of consciousness and even death [7–10]. In recent years, copper and cyanide become important environmental pollutants due to widespread use and it is necessary to detect copper and cyanide ions in environment and in biological samples.

Among several sensing strategies, fluorescence sensing is a valuable technique which has advantages such as high sensitivity, rapid response and ease of application [11]. In particular, fluorescence "turn-on" type probes are highly desirable [12]. To date, various fluorescent probes based on coumarin [13–16], naphthalimides [17,18], qulioline [19–21], and rhodamine [22,23] for the detection of Cu^{2+} have been reported. However, most of these sensors for the detection of Cu^{2+} work in a "turn-off" mode because of its paramagnetic nature [24]. The Cu^{2+} selectivity of some of the probes are interfered by Hg^{2+} with a fluorescence quenching phenomenon [25]. In addition, few of the reported sensors function with a fluorescence "turn-on" mode for the detection of Cu^{2+} or the fluorescence enhancement ratio is small [26]. Meanwhile, different kinds of fluorescent probes for CN^- detection were investigated in the past few years [27–30]. Using copper ensembles to identify CN^- through a Cu^{2+} displacement approach is a popular way to design CN^- detectors [31–33]. Nonetheless, some probes show poor selectivity with other anionic interference [30,34], and some probes are difficult to synthesis for its complex structure [10,35]. So far, people are still working on developing new chemosensors for the detection of CN^-.

Photochromism is the ability of organic compounds to change its structure and properties by irradiation with different wavelengths of light [36,37]. Different kinds of photochromic compounds like azobenzenes diarylethenes or spiropyrans have been applied to various fields [38,39]. Among these, diarylethene derivatives are the most promising compounds due to their outstanding fatigue resistance, fast response, and excellent thermal stability [40]. To date, many diarylethene derivatives have been reported as fluorescence sensors, such as diarylethene with thieno-imidazole [41], aminoquinoline [42], 2-alkynylbenzaldoxime [43] and antipyrine [44]. Most of these derivatives

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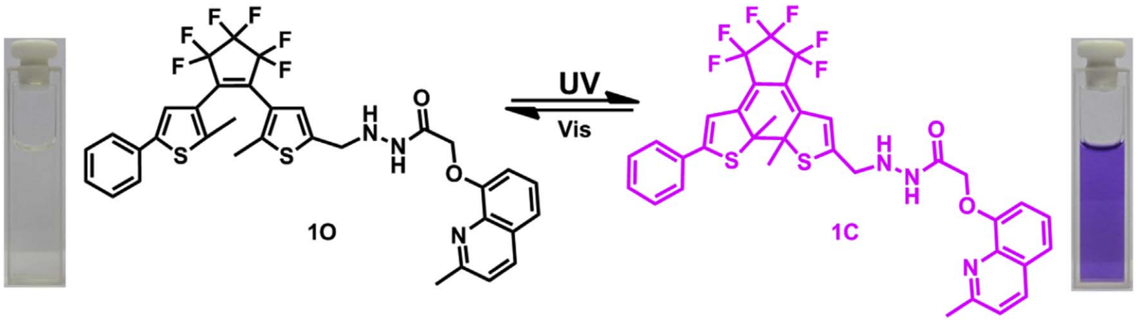
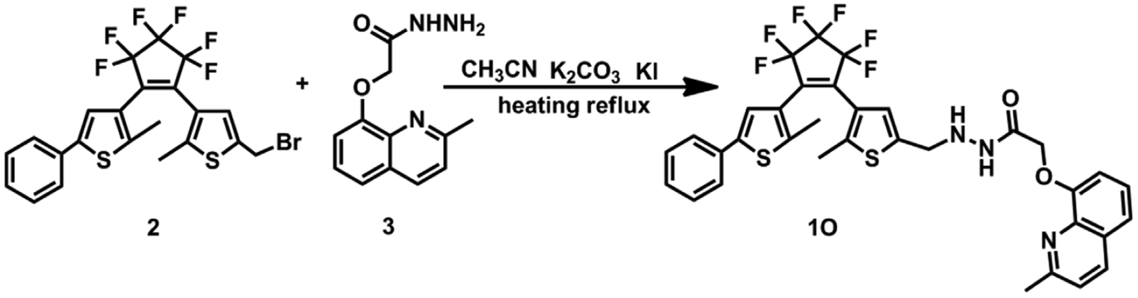


Scheme 1. Photochromism of diarylethene **1O**.



Scheme 2. Synthesis route to diarylethene **1O**.

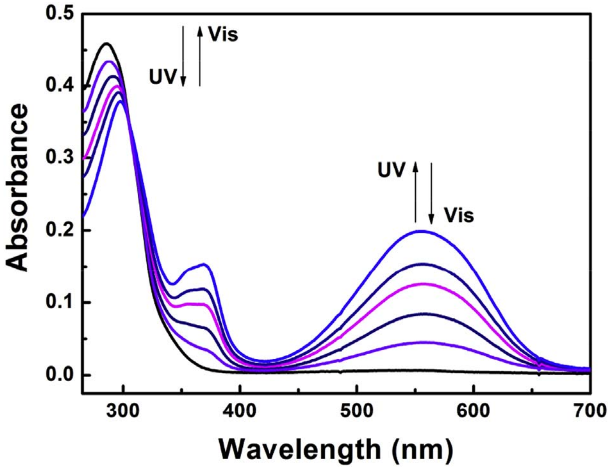


Fig. 1. Changes in the absorption spectra of **1O** upon alternating irradiation with UV and visible light in acetonitrile (2.0×10^{-5} mol L^{-1}).

were designed for the detection of Al^{3+}, Zn^{2+} or Cr^{3+}. Developing diarylethene derivatives for Cu^{2+} and CN^{-} recognition with fluorescent switch property was still desirable.

Here, we designed a novel fluorescence “turn-on” probe of a diarylethene derivative with a methylquinoline moiety, which can detect both Cu^{2+} and CN^{-} with high selectivity and specificity. We previously synthesized a chemosensor for Zn^{2+} and F^{-} recognition with Schiff base structure [45], but as known to us, the Schiff base is unstable. In order to solve this problem, we used benzyl bromide and ammonia for the synthesis of the detector here to avoid the unstable characteristics of Schiff base. The properties of our chemosensor and its selectivities towards cations and anions were investigated. It exhibited a 45-fold and 15-fold fluorescence enhancement in the presence of 5 equiv. of Cu^{2+} and 34 equiv. of CN^{-} respectively. The selectivity of this probe for copper in metal ions and cyanide in anions are both very good. In addition, the chemosensor can be used for naked eye detection of CN^{-}. The chemosensor reported here can be used as a real-time detector for Cu^{2+} and CN^{-}. The photochromic process of the diarylethene was shown in Scheme 1.

2. Material and method

2.1. General methods

Unless otherwise mentioned, all reagents for the synthesis of the target compound were obtained from commercial suppliers and were used without further purification. Mass spectra were measured with a Bruker amazon SL Ion Trap Mass spectrometer (ESI). Infrared spectra (IR) were collected on a Bruker Vertex-70 FT-IR spectrometer. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as solvents and tetramethylsilane (TMS) as an internal standard. Lights of appropriate wave-lengths were isolated by using different light filters. UV/vis absorption spectra were measured on an Agilent 8453 UV/vis spectrometer. Photoirradiation was carried out using an MUL-165 UV lamp and an MVL-210 visible lamp. Fluorescent spectra were recorded with a Hitachi F4600 fluorescence spectrophotometer. The fluorescent quantum yield was measured with an Absolute PL Quantum Yield Spectrometer QYC11347-11. All the cations were added in the form of metal nitrates except for K^{+}, Ba^{2+}, Mn^{2+}, and Hg^{2+}, (all of their counter ions were chloride ions). The solutions of metal ions (0.1 M) were prepared by the dissolution of their respective metal salts in distilled water. Necessary dilutions were made according to each experimental set up. All of the measurements were conducted at room temperature unless otherwise stated.

2.2. Synthesis of **1O**

The synthetic route of the target diarylethene, [1-(2-methyl-5-phenyl-3-thienyl)-2-{2-methyl-5-[4-methylene-2-(methylquinoline-8-methoxyl) acethlhydrazino]-3-Thienyl} perfluorocyclopentene (**1O**) is shown in Scheme 2. Compounds **2**[46,47] and **3**[48–50] were facilely synthesized in high yield by the procedures published before. Compounds **2** (0.01 g, 0.20 mmol) and **3** (0.04 g, 0.20 mmol) were dissolved in anhydrous CH_3CN (60 mL). Then K_2CO_3 (0.13 g, 0.80 mmol) and KI (0.03 g, 0.20 mmol) were added, and the resulting mixture was heated at 353 K for 6 h. Subsequently, the reaction mixture was cooled to room