

A Novel Ratiometric Fluorescent Chemosensor for Cd²⁺

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Abstract Novel ratiometric fluorescent chemosensor C7 was synthesized and characterized by UV–vis and fluorescence spectroscopy. C7 showed high sensitivity for Cd²⁺ among Na⁺, Mg²⁺, Cu²⁺, Pb²⁺, Ni²⁺, Fe³⁺, Zn²⁺, Ag⁺, Hg²⁺ and Cd²⁺ in ethanol.

Keywords Ratiometric · Fluorescent chemosensor · Cadmium ion

Introduction

In the past decades the development of fluorescent chemosensor for sensing heavy transition metal ions has been receiving a great attention [1–5]. Fluorescent sensors are powerful tools to detect heavy metal ions because of the simplicity, high sensitivity, high selectivity and instantaneous response. Most reported fluorescent sensors are based on the fluorescence increase (turn-on) or decrease (turn-off) upon binding to metal ions [6, 7]. However, fluorescence signal is readily perturbed by environmental factors, such as pH, temperature, and solvent polarity [8]. Ratiometric measurements have attracted important attention because of the features that permit signal rationing when receptors interact with analytes; a dual emission system can minimize the measurement errors because of factors such as phototransformation, receptor concentrations, and environmental effects [8].

Cadmium is a naturally occurring minor element, and due to the widely used in industrial application, such as coating steel, nickel cadmium battery, human exposed to cadmium is significantly increased [9, 10]. Cadmium is known to be extremely toxic in natural environments and is listed by the U.S. Environmental Protection Agency as one of 126 priority pollutants. There have

been many reports on the toxicity of Cd²⁺ to procreation, bones, kidneys, nerve system, and tissues, consequently resulting in renal dysfunction, calcium metabolism disorders, and an increased incidence of certain forms of cancers [11, 12]. So it is important to find a method to monitor the concentration of cadmium in drinking water or in living cells. Recently, some cadmium selective fluorescent chemosensors was reported [13–20], as a part of work to search high sensitive and high selective fluorescent chemosensor, we reported a novel Cd²⁺ fluorescent sensor based on the iminocoumarin in this paper.

Experiment

All reagents were used as purchased without any purification. NMR experiments were performed with a JEOL AL-300 spectrometer and the chemical shifts were recorded with respect to TMS as an internal reference. HR-MS was recorded on JMS-700 apparatus. UV–vis and fluorescence experiments were carried out by Shimadzu UV-3100 and Hitachi FL-4500, respectively.

Compound 1 [21] and compound 2 [22] was synthesized according to the reference, C7 as shown in Scheme 1 was synthesized as following: A mixture of compound 1 (0.30 g, 0.80 mmol) and compound 2 (0.30 g, 1.6 mmol) was dissolved in 40 mL ethanol in a 100 mL 3-neck flask and then was added acetic acid (0.46 mL, 8 mmol). The resulted mixture was stirred at refluxed for 5 h under argon, cooled and the solvent was evaporated under the reduced pressure, the residue was diluted with 100 mL of 2 M sodium carbonate and extracted with dichloromethane. The collected organic phase was washed with brine, dried over sodium sulfate, and evaporated to dryness. The residue was chromatographed on silica gel to afford C7 (0.25 g, 41 %).

¹H-NMR (300 MHz, CDCl₃): δ 8.45 (s, 1H), 8.11 (d, *J*=8.25 Hz, 2H), 7.98(d, *J*=8.13 Hz, 1H), 7.81 (d, *J*=8.07 Hz, 1H), 7.65 (d, *J*=8.04 Hz, 1H), 7.45–7.36 (m, 4H), 6.92 (s, 1H),

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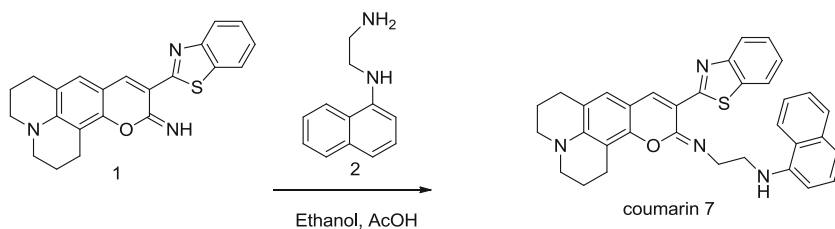
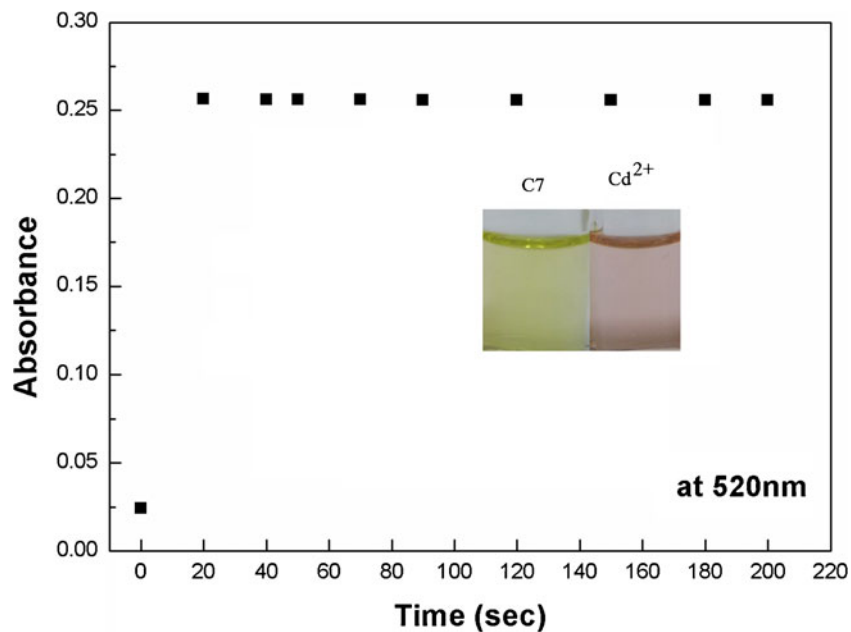
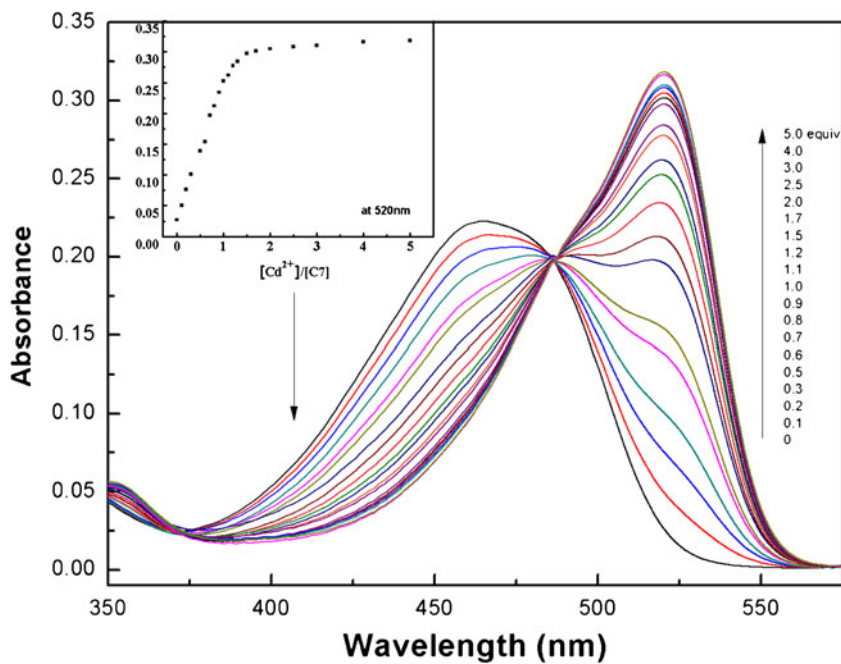
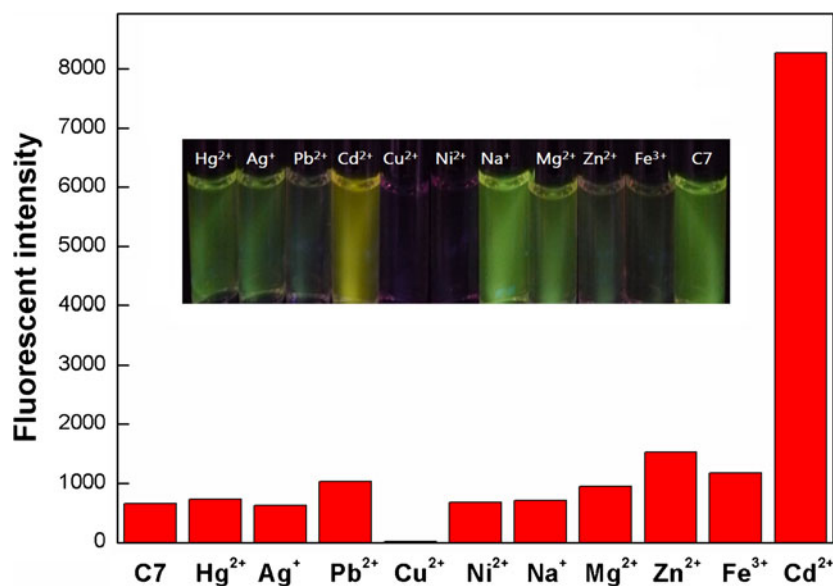
Scheme 1 Synthesis route for C7**Fig. 1** Time-dependent absorption changes of C7 in the present of Cd^{2+} in ethanol. Insert figures: color changes of C7 without (*left*) and with (*right*) the addition of Cd^{2+} **Fig. 2** Absorption spectra of C7 10 μM in ethanol obtained by adding CdCl_2 (0–5 eq) solution. The insert indicating the absorption spectra change with the ratio of $[\text{Cd}^{2+}]/[\text{C7}]$ 

Fig. 3 Fluorescence spectra of C7 (10 μ M) in the absence and presence of various metal ions in ethanol (Ex=520 nm). Insert: Color changes of C7 in the absence and presence of various metal ions



6.77(d, $J=7.5$ Hz, 1H), 5.67 (s, 1H), 4.08–4.06(m, 2H), 3.64 (s, 2H), 3.28 (s, 4H), 2.90–2.88 (m, 4H), 2.00 (s, 4H).

¹³CNMR (75 MHz, CDCl₃) δ : 162.3, 153.1, 144.5, 144.3, 135.0, 128.4, 127.9, 126.7, 125.7, 124.5, 123.9, 121.8, 121.2, 120.7, 117.1, 106.2, 106.1, 50.1, 49.5, 44.9, 44.6, 27.3, 21.4, 20.6, 13.8.

HR-MS (ESI⁺): m/z calcd for M⁺: 542.2140, found 542.2140.

Result and Discussion

The absorption spectroscopy of C7 in ethanol in the present of various metal ions including Na⁺, Mg²⁺, Cu²⁺, Pb²⁺, Ni²⁺,

Fe³⁺, Zn²⁺, Ag⁺, Hg²⁺ and Cd²⁺ was investigated at first. Free C7 exhibits an absorption maximum at 464 nm and a yellow color, upon addition of Cd²⁺, as shown in Fig. 1 the color was changed to light pink in 20 s and the absorption has a 54 nm red shift from 464 nm to 520 nm which meaning a complexes was formed between Cd²⁺ and C7. Figure 2 depicted the titration spectrum of absorption, the intensity of absorption kept as a constant when 2 equivalent of Cd²⁺ was added to the solution of C7.

To examine the sensing behavior of C7 in ethanol further, the response of fluorescence spectra to various metal ions was investigated (Fig. 3). From Fig. 3, it could be seen that the ethanol solution of C7 (10 μ M) exhibited green

Fig. 4 Fluorescence titration spectra of C7 (10 μ M) in ethanol in the presence of (0–5 equiv) of Cd²⁺. (Ex=500 nm)

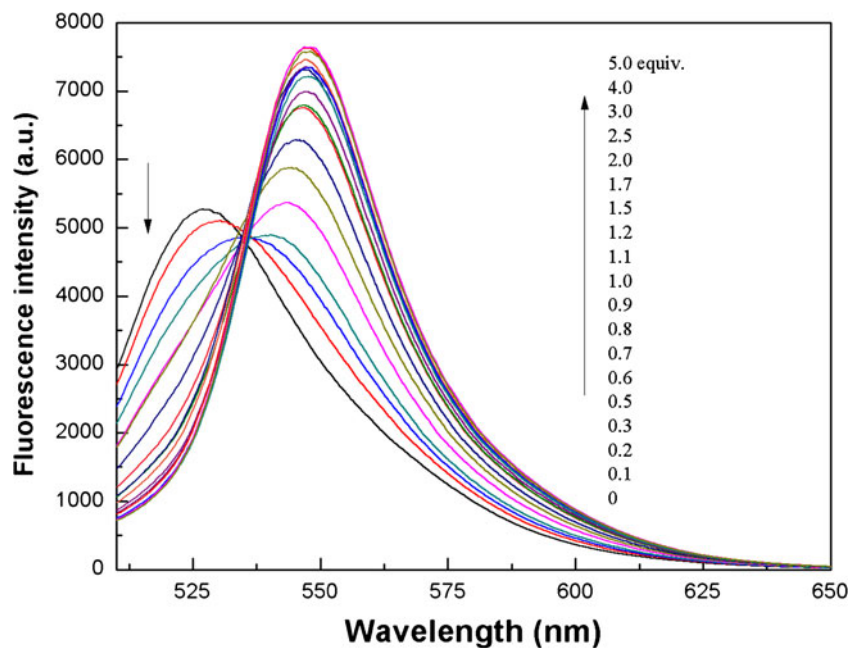
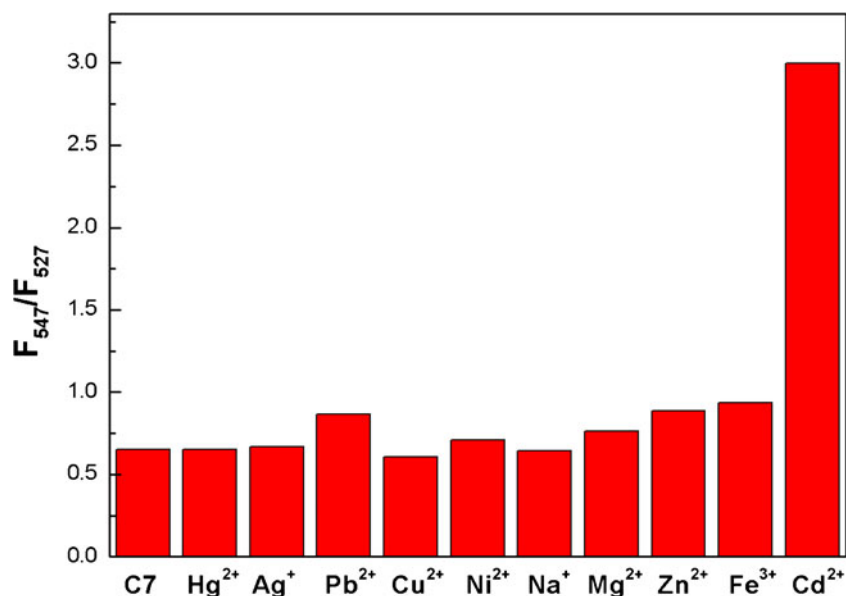


Fig. 5 The fluorescent responses (F_{547}/F_{527}) of C7 with various metal ions (10 eq) in ethanol. The concentration of C7 was 10 μM , and EX=520 nm



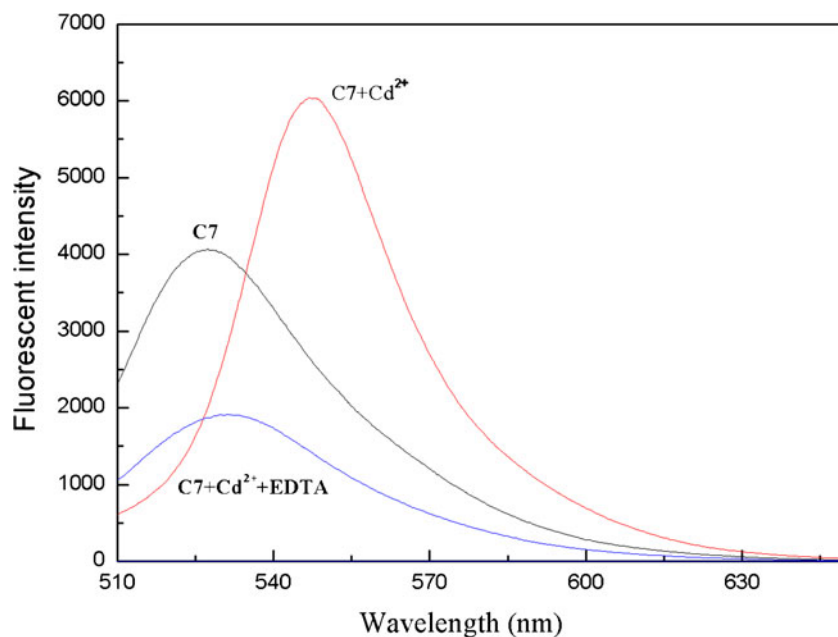
fluorescence. Upon the injection of Na⁺, Mg²⁺, Cu²⁺, Pb²⁺, Ni²⁺, Fe³⁺, Zn²⁺, Ag⁺, Hg²⁺ and Cd²⁺ (10 μM), only Cd²⁺ caused an outstanding yellow fluorescence enhancement, other metal ions no obvious fluorescence change except Cu²⁺, which quenched the fluorescence.

As depicted in Fig. 4, the fluorescence emission spectra of C7 display an emission band centered at 527 nm when excited at 500 nm. Upon addition of various concentrations of cadmium ions, the emission band centered at 525 nm decreases and a new emission peak gradually appears at longer wavelength 547 nm. The fluorescence emission spectrum of C7 demonstrates that

only cadmium ions cause a red shift with slight fluorescence intensity enhancements as shown in figure. Moreover, the presence of all the above mentioned cations do not alter the Cd²⁺-induced F_{547}/F_{527} distinctly (Fig. 5). Treatment with the metal ion chelator EDTA (Fig. 6) for 1 min at room temperature reduces the emission distinctly, implying coumarin7 can be monitor Cd²⁺ in ethanol reversibly.

In conclusion, novel fluorescent sensor C7 was synthesized and characterized by absorbance and fluorescence spectrum. C7 can be used as a sensitive fluorescent sensor monitor Cd²⁺ in ethanol.

Fig. 6 The reversibility of C7 when treat with EDTA



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