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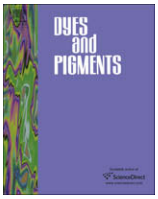

Fluorescence enhancement of coumarin–quinoline by transition metal ions: Detection of paramagnetic Ni^{2+} and Co^{2+}

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ABSTRACT

A readily available coumarin–quinoline was employed as a novel fluorescent probe for paramagnetic Co^{2+} and Ni^{2+} ions, which are well-known fluorescence quenchers. NMR and IR indicated that the enhanced fluorescence response was attributable to coordination of the paramagnetic Ni^{2+} or Co^{2+} ions with the coumarin–quinoline compound. Given the difficulty of designing enhanced fluorescent probes for paramagnetic Co^{2+} and Ni^{2+} ions, the coumarin–quinoline compound may inspire the further development of more sophisticated sensing constructs for the fluorescence detection of these transition metal ions.

1. Introduction

Recently, the development of molecular sensing systems for transition metal ions has gained intense attraction [1–7]. Although great success has been made in this field, the majority of fluorescence probes exhibits a fluorescence quenching response upon binding with paramagnetic transition metal ions [8–12]. As fluorescence quenching probes' response often results in low signal-to-noise ratio [13,14], it is desirable to detect transition metal ions using an enhanced fluorescence signal.

Although many fluorescent probes that display fluorescence amplification for transition metal ions such as Cu^{2+} [15,16], Zn^{2+} [17,18], Fe^{3+} [19,20], Hg^{2+} [21,22] have been reported, fluorescence molecules suitable for use with typical transition metal fluorescence quenchers namely, Ni^{2+} and Co^{2+}, are scarce. To circumvent the fluorescence quenching problem, paramagnetic Co^{2+} ions have to be oxidized to non-fluorescence-quenching diamagnetic Co^{3+} ions before fluorescence testing [23–25]. Bharadwaj [26] and Qian [27] reported two probes that provided an enhanced fluorescence response toward Ni^{2+} and Co^{2+} in the absence of oxidizing agents. However, caution must be exercised in the interpretation of the enhanced fluorescence observed with these probes, as suggested by de Silva et al. [28], as the onset of fluorescence is most likely attributable to the protonation of the amino receptor by the acidic hydration shells of the transition metal salts in moist organic solvents [29]. *Newport Green* (Molecular Probes Inc.) is a fluorescent indicator for Ni^{2+} and Co^{2+} ions [30,31] that is highly expensive as its synthesis is very complex. Hence, there is a need to develop readily available fluorescent probes which display an enhanced fluorescence due to coordination with Ni^{2+} or Co^{2+} ions. Clearly, this is a very challenging task because of the marked quenching effect of these two paramagnetic metal ions.

This paper describes coumarin–quinoline **1** (Fig. 1) as a novel prototype of a fluorescent probe for paramagnetic Ni^{2+} and Co^{2+}. Fluorescence enhancement is more likely due to the binding of the metal ions than due to the protonation of the quinoline receptor by the coordinated acidic water molecules. Compound **1** is composed of a typical coumarin dye and an 8-alkoxylquinoline moiety. Our hypothesis is that the fluorescence emission of the coumarin dye may be diminished by the 8-alkoxylquinoline moiety by the photo-induced electron transfer (PET), which is consistent with the redox potentials of 7-methoxycoumarin and quinoline moieties [32,33]. However, upon binding of the transition metal ions to the putative cation-binding site in the 8-alkoxylquinoline moiety [34–36], the PET process is inhibited, which will lead to a fluorescence

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enhancement. Notably, for this hypothesis to be working, it is critical that the transition metal ions should not interact with the dye in the complex [37], otherwise the fluorescence quenching instead of enhancement may occur.

2. Experimental section

2.1. Materials and instruments

All reagents and solvents were obtained commercially and were used without further purification. NMR spectra were measured on an INOVA-400 or BRUKER-500 spectrometer using TMS as an internal standard. MS (ESI) analyses were performed using a Waters Micromass ZQ-4000 spectrometer. Electronic absorption spectra were recorded with a SHIMADZU UV-2450 spectrometer. The emission spectra were recorded on a HITACHI F4500 fluorescence spectrophotometer. Infrared (IR) absorption spectroscopic analysis was performed with a TENSOR27 spectrometer. TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from Qingdao Ocean Chemicals.

*2.2. Synthesis of 3-(bromomethyl)-7-methoxycoumarin (**3**)*

To a solution of compound **2** (450.0 mg, 2.36 mmol) in 25 ml of CCl_4 were added NBS (463.0 mg, 2.60 mmol) and a trace amount of AIBN, and the mixture was then heated to reflux. After reaction for 8 h, the solvent was removed under reduced pressure and the residue was then purified by chromatography on silica gel (CH_2Cl_2:petroleum ether = 1:1) to afford compound **3** as a colorless powder. Yield: 523.2 mg (83.1%). M.p.: 106–110 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 3.89$ (s, 3H, CH_3), 4.43 (s, 2H, CH_2), 6.82 (d, $J = 2.0$ Hz, 1H, CH), 6.82–6.89 (m, 2H, CH), 7.39–7.46 (m, 1H, CH), 7.79 (s, 1H, CH). MS (ESI): m/z: 269.0 $[M+H^+]$. $C_{11}H_9BrO_3$ (269.09): Calcd. C 49.10, H 3.37; Found C 49.42, H 3.16.

*2.3. Synthesis of 7-methoxy-3-((quinolin-8-yloxy)methyl)-2H-chromen-2-one (**1**)*

3-(Bromomethyl)-7-methoxycoumarin (30.0 mg, 0.11 mmol), 8-hydroxyquinoline (16.2 mg, 0.11 mmol), and K_2CO_3 (20.2 mg, 0.15 mmol) were added to a dry DMF solution (3 ml), and the reaction mixture was heated to 80–85 °C. After reaction for 9 h, the solvent was removed under reduced pressure and the residue was then purified by chromatography on silica gel (CH_2Cl_2:petroleum ether = 2:1) twice to afford **1** as a colorless powder. Yield: 18.7 mg (49.9%). M.p.: 136–138 °C. ^1H NMR (500 MHz, CD_3Cl, ppm): $\delta = 3.88$ (s, 3H, CH_3), 5.35 (s, 2H, CH_2), 6.83–6.86 (m, 2H, CH), 7.16 (q, 1H, CH), 7.41 (d, 1H, $J = 8.5$ Hz, CH), 7.46 (q, 2H, CH), 7.50 (q, 1H, CH), 8.09 (s, 1 H, CH), 8.20 (dd, 1H, $J = 8.0$ Hz, CH), 9.03 (dd, 1H, $J = 4.5$ Hz, CH); ^{13}C NMR (125 MHz, CD_3Cl, ppm): $\delta = 162.59$, 160.80, 155.02, 153.64, 149.47, 140.17, 139.78, 136.18, 129.60, 129.05, 126.80, 121.79, 120.49, 120.45, 112.76, 112.73, 109.75, 100.58, 65.30, 55.78. MS (ESI): m/z: 334.1 $[M+H^+]$. $C_{20}H_{15}NO_4$ (333.34): Calcd. C 72.06, H 4.54, N 4.20; Found C 72.39, H 4.15, N 4.01.

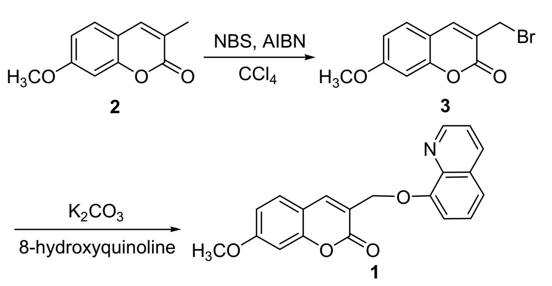

Fig. 1. Synthesis of compound **1**.

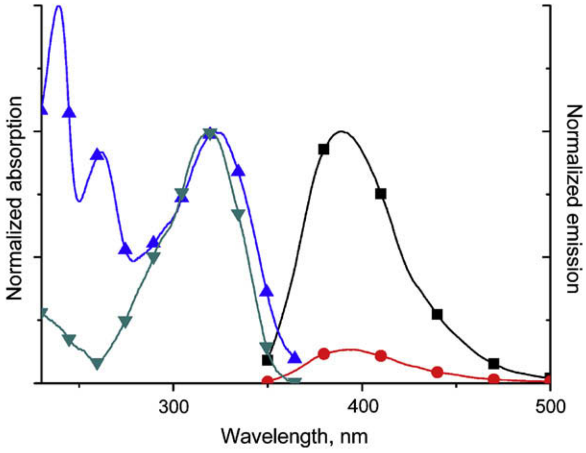

Fig. 2. Left: the normalized absorption of **2** (▼) and **1** (▲). Right: the normalized emission spectra of **2** (■) and **1** (●) while keeping the peak ratio between **2** and **1** unchanged.

2.4. Absorption and fluorescence spectroscopy

All titration experiments were carried out at ambient temperature, unless otherwise mentioned. UV–vis spectra were measured using an UV–vis SHIMADZU UV-2450 spectrophotometer. Quartz cuvettes with a 1 cm path length and 3 ml volume were used for all measurements. Metal chlorate (Hg^{2+}, Ni^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Na^+, K^+), nitrate (Ag^+, Fe^{3+}) or sulfate (Mn^{2+}) stock solutions were prepared in methanol. Compound **1** was dissolved in methanol at room temperature to afford the probe stock solution (500 μM). Test solutions were prepared by placing 0.1 ml or 0.5 ml of the probe stock solution and an appropriate aliquot of each metal stock into a 5 ml volumetric flask, and diluting the solution to 5 ml with methanol or water. The resulting solution was shaken well before recording the absorption and emission spectra. Unless otherwise noted, for all measurements, the excitation wavelength was 338 nm, and both the excitation and the emission

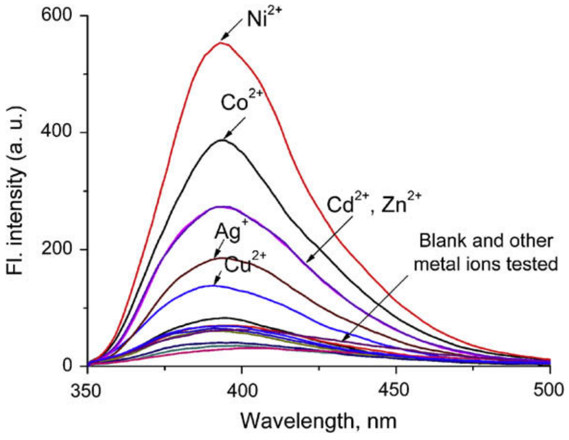

Fig. 3. The emission spectra of **1** (10 μM) in the presence of various metal ions (20 equiv.). Excited at 338 nm.