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

Weiying Lin*, Lin Yuan, Zengmei Cao, Jianbo Feng, Yanming Feng

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, Hunan 410082, PR China

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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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* Corresponding author. Tel./fax: +86 731 8821464.
E-mail address: weiyinglin@hnu.cn (W. Lin).

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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. ^{1}H 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. ^{1}H 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.

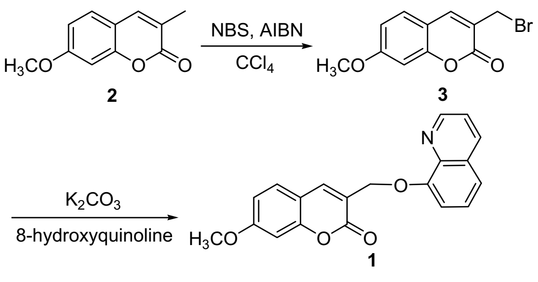

Fig. 1. Synthesis of compound **1**.

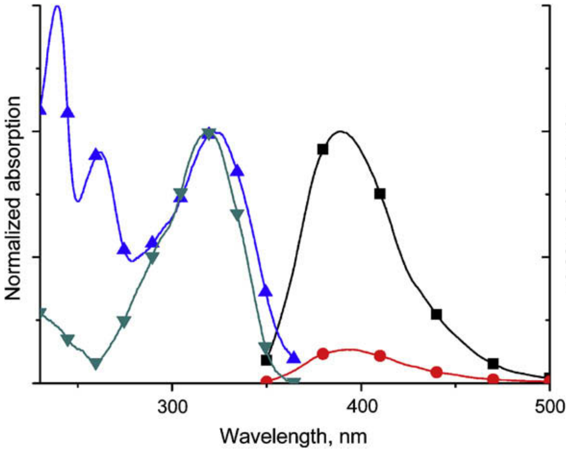

Fig. 2. Left: the normalized absorption of **2** (▼) and **1** (▲). Right: the normalized emission spectra of **2** (■) and **1** (●) while keeping the peak ratio between **2** and **1** unchanged.

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

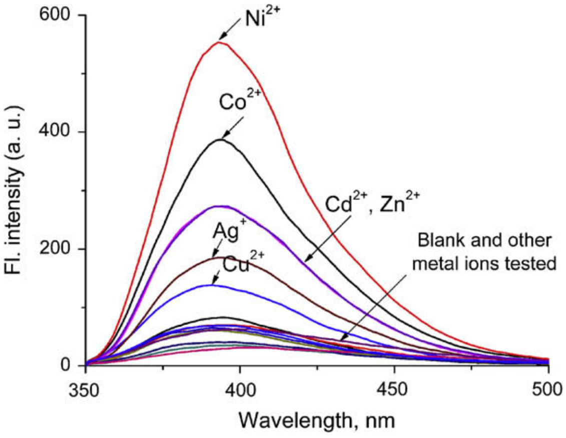

Fig. 3. The emission spectra of **1** (10 μM) in the presence of various metal ions (20 equiv.). Excited at 338 nm.

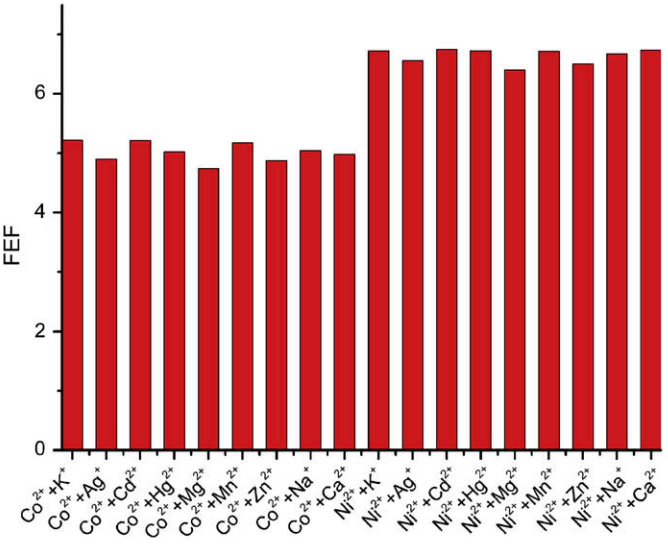

Fig. 4. The fluorescence enhancement factor (FEF) of compound **1** (10 μM) upon addition of Co^{2+}/Ni^{2+} ions in the presence of various metal ions (10 equiv.). Excited at 338 nm and emission collected at 392 nm.

slit widths were 2.5 nm. Fluorescence quantum yield was determined in spectroscopic grade CH_3OH at room temperature using quinine sulfate ($\Phi_r = 0.546$ in 1 N H_2SO_4) as standard and it was calculated by equation (1) as reported [36,37].

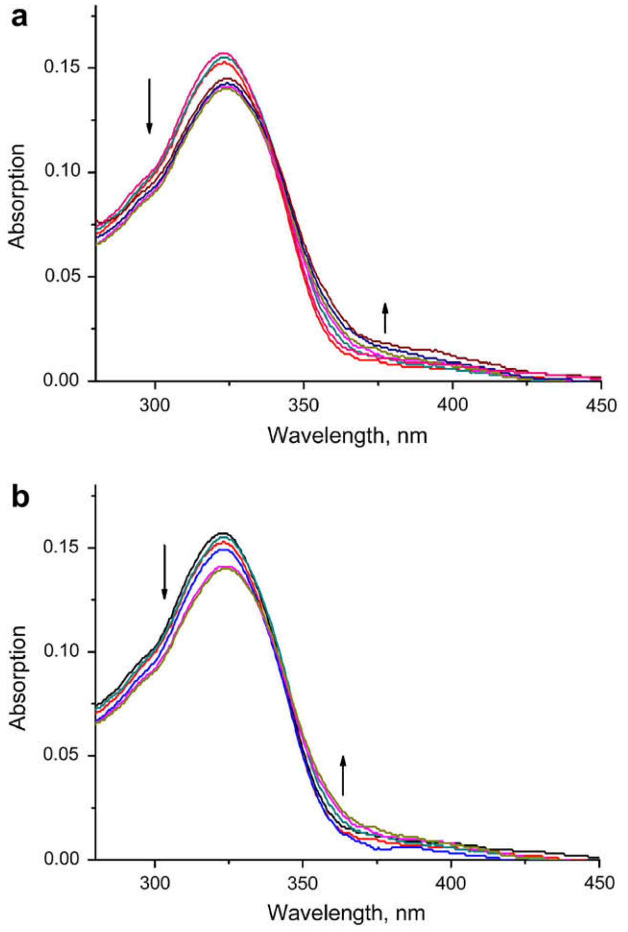

Fig. 5. The absorption spectra of compound **1** (10 μM) with the addition of (a) Ni^{2+} and (b) Co^{2+} ions (0–20 equiv.).

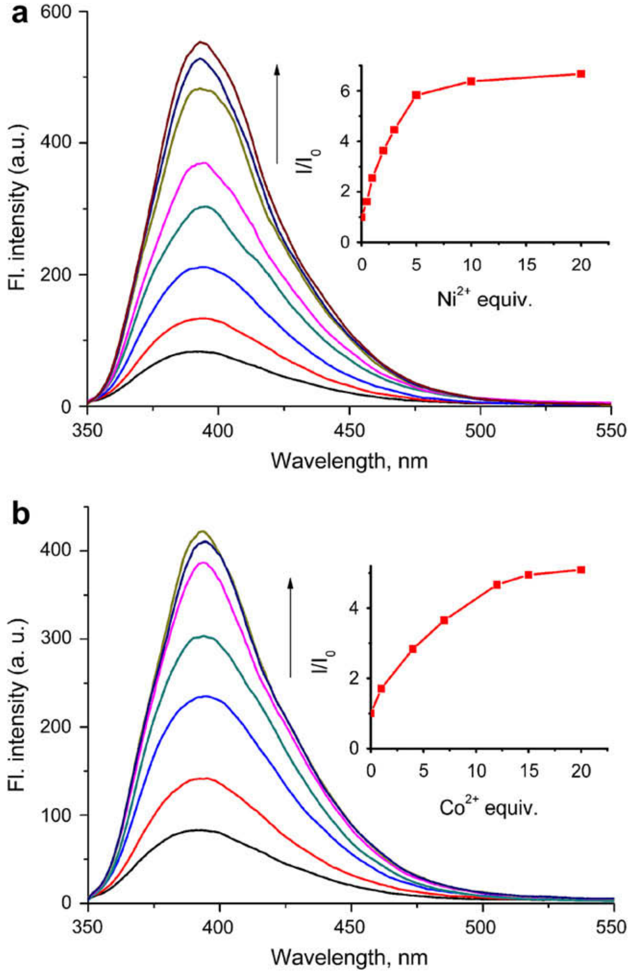

Fig. 6. The emission spectra of **1** (10 μM) with the addition of (a) Ni^{2+} and (b) Co^{2+} (0–20 equiv.) on excitation at 338 nm. Inset: The relative fluorescence change of **1** against Ni^{2+} or Co^{2+} ($\lambda_{ex} = 338$ nm, $\lambda_{em} = 392$ nm).

$$\Phi_s = \Phi_r(A_rF_s/A_sF_r)\left(\eta_s^2/\eta_r^2\right) \tag{1}$$

where s and r denote the sample and reference, respectively, A is the absorbance, F is the relative integrated fluorescence intensity, and η is the refractive index of the solvent.

3. Results and discussion

3.1. Synthesis of compound *1*

One of the favorable features of compound **1** is its ease synthesis. It was readily prepared in two steps using straightforward chemistry (Fig. 1). A standard procedure was used to make the intermediate **3**, 3-(bromomethyl)-7-methoxycoumarin, which was then reacted with 8-hydroxyquinoline (1 equiv.) in dry DMF solution at 80–85 °C to afford the target compound **1** in modest yield. The structures of the intermediate and the final product were fully characterized by NMR, ESI-MS, and elementary analysis.

3.2. Spectroscopic properties of compound *1*

The absorption and emission spectra of compound **1** and the reference compound **2** in methanol are shown in Fig. 2. The absorption spectrum of compound **1** displayed the characteristic transitions of the coumarin dye around 328 nm and the typical

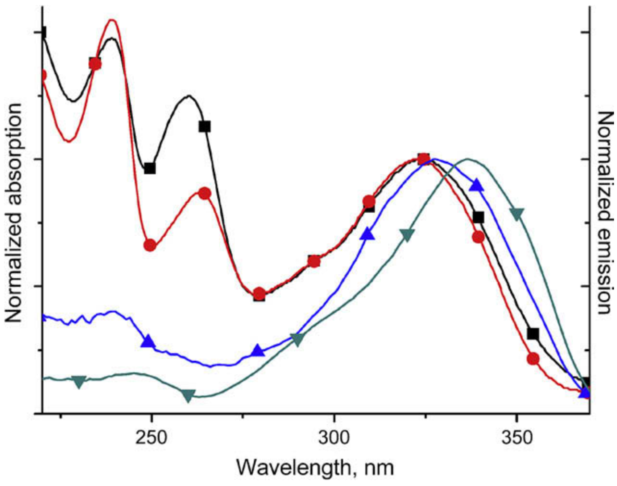

Fig. 7. Excitation spectra of compound **1** (▲), **1** + (20 equiv.) Ni^{2+} (▼) recorded at 392 nm, and the absorption spectra of **1** (●), **1** + (20 equiv.) Ni^{2+} (■).

transitions of the alkoxylquinoline around 239 and 262 nm, indicating that these two moieties have no significant electronic interactions in the ground state. Furthermore, compound **1** showed a comparatively slight emission at 392 nm, with a quantum yield (Φ) of 0.04 with reference to quinine sulfate [38,39]. This low fluorescence nature of free **1** compared to the reference compound **2** ($\Phi = 0.34$) could be attributed to the quenching of the coumarin dye by the quinoline moiety via PET [40].

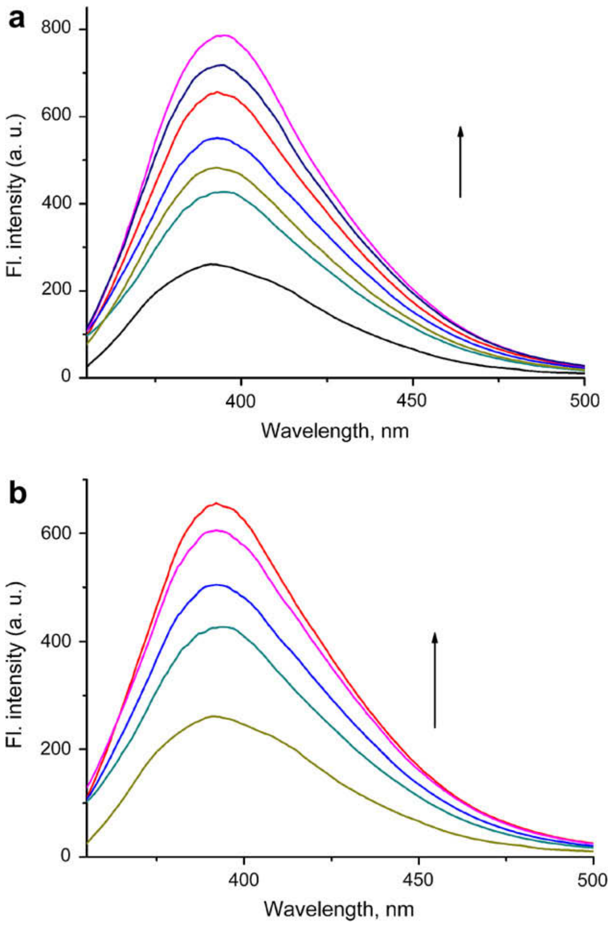

Fig. 8. The emission spectra of compound **1** (50 μM) with the addition of (a) Ni^{2+} and (b) Co^{2+} (0–10 equiv.) in MeOH/H_2O (9:1) on excitation at 338 nm.

3.3. Selectivity studies

To evaluate the selectivity, compound **1** was treated with various metal ions including Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Mn^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Co^{2+} or Ni^{2+}. Representative alkali metals and alkaline-earth metal ions such as Na^+, K^+, Ca^{2+}, Mg^{2+} only induced minimum perturbation in the fluorescence spectra of compound **1** (Fig. 3) when excited at 338 nm (the maximal excitation wavelength of the coumarin dye), while some transition metal ions such as Fe^{3+}, Pb^{2+}, Hg^{2+}, and Mn^{2+} elicited fluorescence quenching to a different extent. However, in the presence of Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, in particular for Co^{2+} and Ni^{2+}, compound **1** exhibited a significant fluorescence enhancement in methanol. Thus, readily available compound **1** showed a fluorescent turn-on response to Co^{2+}/Ni^{2+}. Notably, all the known fluorescent Co^{2+}/Ni^{2+} sensing systems exhibited a relatively modest selectivity for Co^{2+}/Ni^{2+} over other metal ions [26,27,31]. Thus, compound **1** developed herein showed a selectivity that is superior or at least comparable to that of the known fluorescent Co^{2+}/Ni^{2+} sensing systems.

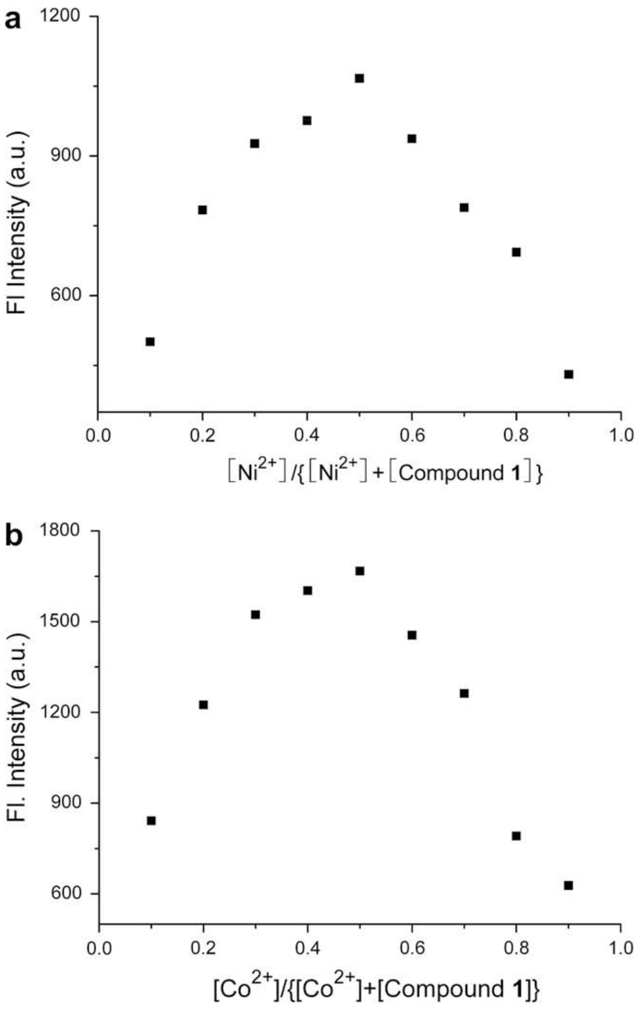

Fig. 9. Job plots for the determination of the stoichiometry of compound **1** to Ni^{2+} (a) and Co^{2+} (b). The total concentrations of **1** and metal ions were kept constant (50 μM). Excitation and emission were at 338 and 392 nm, respectively.

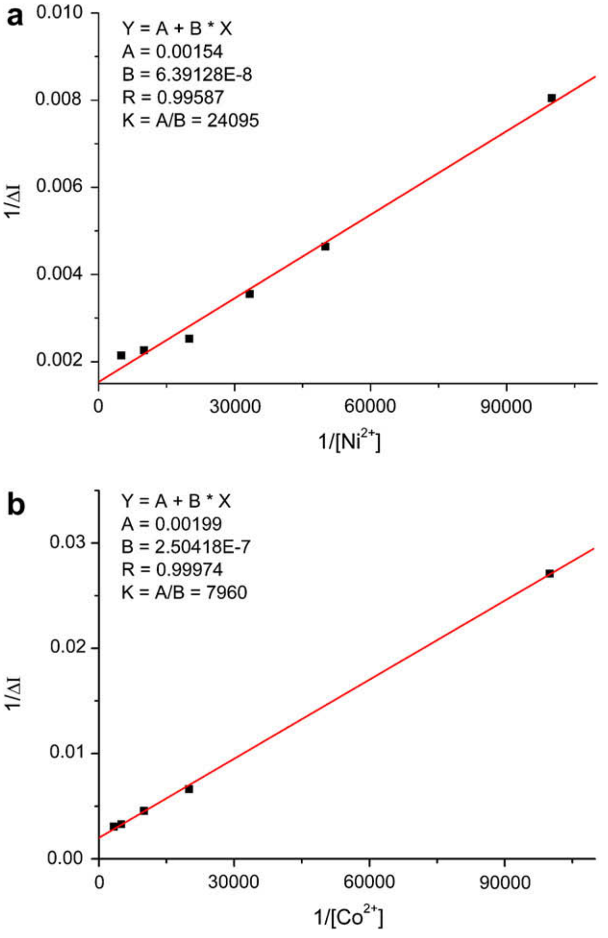

Fig. 10. Benesi–Hildebrand plots for Ni^{2+}-bound **1** (a) and Co^{2+}-bound **1** (b).

To further test the potential applications of compound **1** as a fluorescence turn-on probe for Co^{2+}/Ni^{2+}, the fluorescence response of compound **1** to Co^{2+}/Ni^{2+} in the presence of representative competing ions was studied. As shown in Fig. 4, most of the competing ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Hg^{2+}, Mn^{2+}, Cd^{2+}, Ag^+, Zn^{2+} exhibited minimum interference in the detection of Co^{2+}/Ni^{2+}, indicating that compound **1** could be used for selective detection of Co^{2+}/Ni^{2+} even under competition from these competing ions.

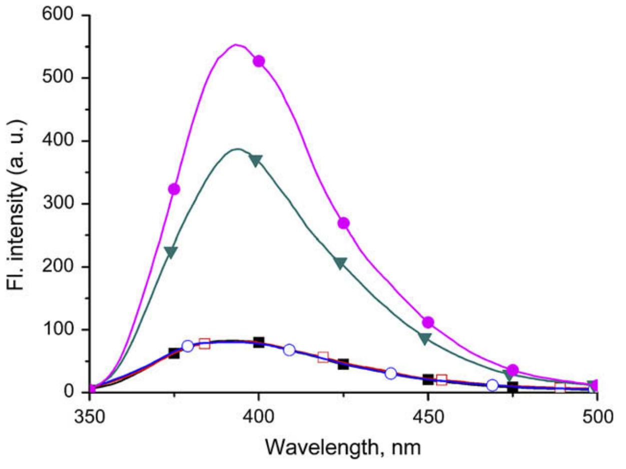

Fig. 11. The fluorescence spectra of compound **1** (■), compound **1** + Ni^{2+} (●), **1** + Co^{2+} (◄), compound **1** + Ni^{2+} + ethylenediamine (○), and compound **1** + Co^{2+} + ethylenediamine (□). Excitation at 338 nm.

3.4. *Sensing response of compound* ***1*** *to* Ni^{2+} *and* Co^{2+} *ions*

The absorption spectra of compound **1** in the presence of different concentrations of Ni^{2+} ions are displayed in Fig. 5a. Upon introduction of Ni^{2+} ions, the absorption spectra of **1** only exhibited minor variations, which is consistent with the hypothesized PET signaling mechanism [41]. When increasing concentrations of Ni^{2+} ions were added, compound **1** displayed a gradual increase of the fluorescence around 392 nm (Fig. 6a), suggesting that the PET process is inhibited. The quantum yield (Φ) of the Ni^{2+}-bound complex reached 0.27. Furthermore, the excitation spectrum of Ni^{2+}-bound complex indicates that the fluorescence emission peak around 392 nm originates from the coumarin dye (Fig. 7). The similar absorption spectra change and fluorescence enhancement behavior was also observed for Co^{2+} ions (Figs. 5b and 6b). The quantum yield (Φ) of the Co^{2+}-bound complex was measured as 0.20. Furthermore, compound **1** also exhibited a fluorescence turn-on behavior toward Ni^{2+} and Co^{2+} ions in $MeOH/H_2O$ (9:1) (Fig. 8). Thus, compound **1** represents a rare example of fluorescence turn-on probes for paramagnetic Ni^{2+} and Co^{2+} ions in the absence of oxidizing agents.

3.5. *Stoichiometry and binding constant studies*

To determine the stoichiometry of compound **1** and transition metal ions in the complex, Job's method [42–45] was employed by using the emission changes at 392 nm as a function of molar fraction of Ni^{2+} or Co^{2+}. A maximum emission was observed when the molar fraction of Ni^{2+} reached 0.5 (Fig. 9a), indicating that Ni^{2+} ions form a 1:1 complex with the sensing compound (the same stoichiometry value was obtained by using the emission changes at 392 nm for Co^{2+} ions, Fig. 9b). The stability constant of the complex

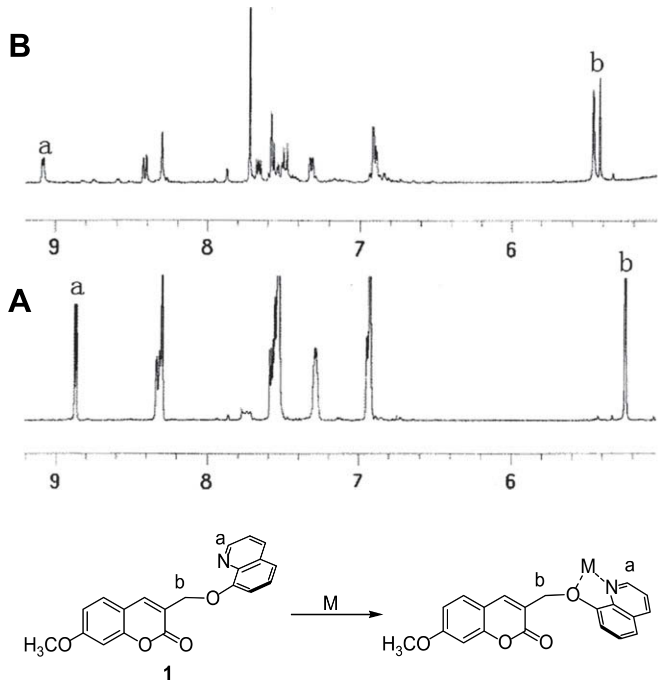

Fig. 12. Partial ^1H NMR (400 MHz) spectra of compound **1** in the absence (A) or presence (B) of Cd^{2+} ions in CD_3OD at room temperature.

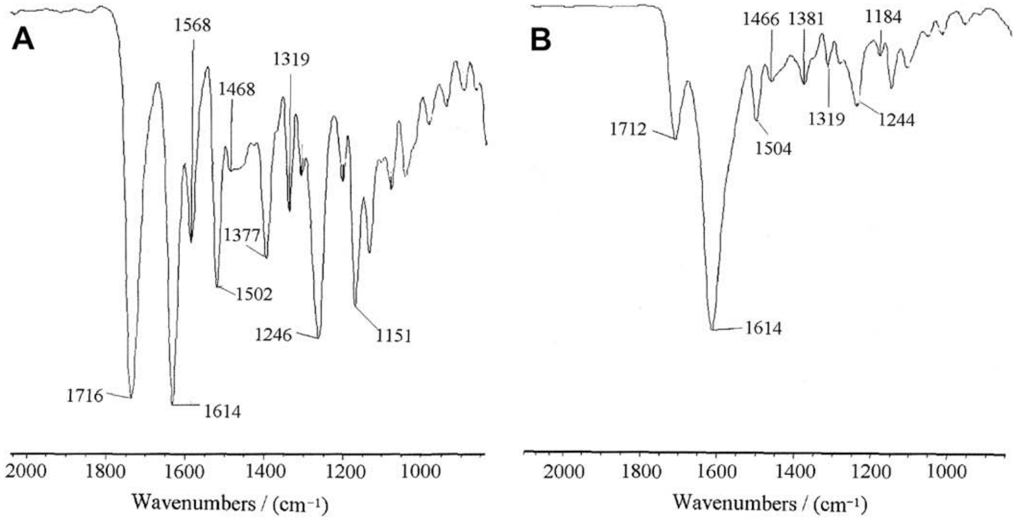

Fig. 13. Partial infrared spectra (KBr) of free **1** (A) and **1** with Ni^{2+} (B) at room temperature.

was then calculated to be $2.41 \times 10^4\ M^{-1}$ and $7.96 \times 10^3\ M^{-1}$ for Ni^{2+} and Co^{2+}, respectively, with a good linear relationship by a 1:1 binding mode (Fig. 10) [46,47]. As expected, the coordination of Ni^{2+} or Co^{2+} to compound **1** is reversible as evidenced by the complete reversal of the fluorescence signal to free **1** when excess ethylenediamine was added to Ni^{2+} or Co^{2+}-bound complex **1** (Fig. 11). This demonstrates the reversible binding of **1** with metal ions and excludes the occurrence of an irreversible redox reaction.

3.6. Binding mode studies

Because Co^{2+} and Ni^{2+} have paramagnetic character and Cd^{2+} could also elicit a marked fluorescence enhancement (Fig. 3), for clarity, diamagnetic Cd^{2+} instead of paramagnetic Co^{2+} or Ni^{2+} was chosen in the ^1H NMR study of the metal ion complexation. Changes in the ^1H NMR spectra of compound **1** before and after the addition of Cd^{2+} are shown in Fig. 12. In general, Cd^{2+} induced the well-resolved resonance signals of the probe molecule to become broad and shifted. For example, upon the addition of Cd^{2+}, the resonance signals corresponding to H_a on the pyridine shift downfield from 8.87 to 9.08 ppm, and the resonance signals corresponding to H_b on the methylene is split into a double peak. The marked shift in the ^1H NMR resonance signals of the 8-alkoxylquinoline moiety indicates that indeed the transition metal ions coordinate with the 8-alkoxylquinoline receptor of compound **1**. However, the coumarin dye of the probe does not participate in the coordination as evidenced by the IR spectroscopy studies. For the free compound **1**, the carbonyl group of the lactone on the coumarin moiety showed a characteristic IR peak at 1716 cm^{-1} (Fig. 13). Upon addition of metal ions, this carbonyl group IR peak displayed no distinct shift. Additionally, the fact that the maximal emission wavelength (392 nm) of the metal ion-bound complex is identical with that (392 nm) of the reference coumarin **2** further supports that the transition metal ions do not bind with the coumarin dye in the complex, otherwise an apparent shift in the emission should be observed [17]. We believe that no interactions of the transition metal ions with the coumarin dye coupled with the inhibition of the PET in the complex could account for the fluorescence enhanced response for paramagnetic Ni^{2+} and Co^{2+} ions.

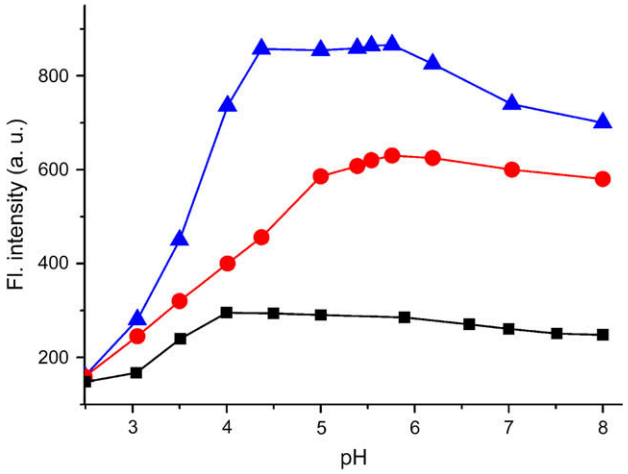

Fig. 14. Changes in the fluorescence intensity of free compound **1** (50 μM) (■) and compound **1** (50 μM) upon the addition of Ni^{2+} (20 equiv.) (▲) or Co^{2+} (●) as pH varied in $MeOH/H_2O$ (9:1) ($\lambda_{ex} = 338$ nm, $\lambda_{em} = 392$ nm).

Importantly, the finding that Fe^{3+} ions, which are much more acidic than Ni^{2+} and Co^{2+} ions, do not elicit any fluorescence enhanced response (Fig. 3) suggests that the fluorescence turn-on is not likely due to the protonation of the quinoline receptor by the coordinated acidic water molecules. Moreover, H^+ only caused slightly fluorescence enhancement in $MeOH/H_2O$ (9:1) (pH 3.0–8.0) (Fig. 14), which is much smaller than that induced by Ni^{2+}/Co^{2+} ions in the same pH. This provides further evidence that the fluorescence enhanced response is probable in light of the coordination of the transition metal ions to compound **1**.

4. Conclusions

In summary, we have developed readily available compound **1** as a novel prototype of fluorescence turn-on probes for paramagnetic Co^{2+}/Ni^{2+} with a selectivity for Co^{2+}/Ni^{2+} over other metal ions comparable to the known sensing systems. The NMR and IR spectroscopic studies indicate that the metal ions coordinate with the quinoline receptor but not with the coumarin dye, which is vital to the fluorescence amplified probes for paramagnetic metal ions based on the PET signaling mechanism. In addition, the control experiments indicate that the fluorescence enhanced response is due to the coordination of the transition metal ions to compound **1**.

Given the great difficulty in design of fluorescence enhanced probes for paramagnetic Co^{2+} and Ni^{2+}, compound **1** could inspire the further development of more sophisticated sensing constructs for the fluorescence turn-on detection of these transition metal ions with high sensitivity and selectivity.

Acknowledgments

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References

[1] Lakowicz JR. Topics in fluorescence spectroscopy. In: Probe design and chemical sensing. 3rd ed., vol. 4. New York: Kluwer Academic Publishers; 2002.

[2] de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, et al. Signaling recognition events with fluorescent sensors and switches. Chemical Reviews 1997;97:1515.

[3] Valeur B, Leray I. Design principles of fluorescent molecular sensors for cation recognition. Coordination Chemistry Reviews 2000;205:3.

[4] Keefe MH, Benkstein KD, Hupp JT. Luminescent sensor molecules based on coordinated metals: a review of recent developments. Coordination Chemistry Reviews 2000;205:201.

[5] de Silva AP, Fox DB, Huxley AJM, Moody TS. Combining luminescence, coordination and electron transfer for signalling purposes. Coordination Chemistry Reviews 2000;205:41.

[6] Gokel GW, Leevy WM, Weber ME. Crown ethers: sensors for ions and molecular scaffolds for materials and biological models. Chemical Reviews 2004;104:2723.

[7] McQuade DT, Pullen AE, Swager TM. Conjugated polymer-based chemical sensors. Chemical Reviews 2000;100:2537.

[8] Weng YQ, Yue F, Zhong YR, Ye BH. A copper(II) ion-selective on–off-type fluoroionophore based on zinc porphyrin-dipyridylamino. Inorganic Chemistry 2007;46:7749.

[9] Ma Y, Luo W, Quinn PJ, Liu Z, Hider RC. Design, synthesis, physicochemical properties, and evaluation of novel iron chelators with fluorescent sensors. Journal of Medicinal Chemistry 2004;47:6349.

[10] Ouchetto H, Dias M, Mornet R, Lesuissec E, Camadro JM. A new route to trihydroxamate-containing artificial siderophores and synthesis of a new fluorescent probe. Bioorganic and Medicinal Chemistry 2005;13:1799.

[11] Murphy CB, Zhang Y, Troxler T, Ferry V, Martin JJ, Jones WE. Probing Forster and Dexter energy-transfer mechanisms in fluorescent conjugated polymer chemosensors. The Journal of Physical Chemistry B 2004;108:1537.

[12] Montalti M, Prodi L, Zaccheroni N. Fluorescence quenching amplification in silica nanosensors for metal ions. Journal of Materials Chemistry 2005;15: 2810.

[13] Rurack K, Resch-Genger U. Rigidization, preorientation and electronic decoupling—the 'magic triangle' for the design of highly efficient fluorescent sensors and switches. Chemical Society Reviews 2002;31:116.

[14] Rurack K. Flipping the light switch 'ON' – the design of sensor molecules that show cation-induced fluorescence enhancement with heavy and transition metal ions. Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy 2001;7:2161.

[15] Kim HJ, Hong J, Hong A, Ham S, Lee JH, Kim JS. Cu^{2+}-induced intermolecular static excimer formation of pyrenealkylamine. Organic Letters 2008;10:1963.

[16] Martinez R, Zapata F, Caballero A, Espinosa A, Tarraga A, Molina P. 2-Aza-1,3-butadiene derivatives featuring an anthracene or pyrene unit: highly selective colorimetric and fluorescent signaling of Cu^{2+} cation. Organic Letters 2006;8:3235.

[17] Lim NC, Atilgan S, Ozdemir T, Akkaya EU. A sensitive and selective ratiometric near IR fluorescent probe for zinc ions based on the distyryl-bodipy fluorophore. Organic Letters 2008;10:4065.

[18] Teolato P, Rampazzo E, Arduini M, Mancin F. Silica nanoparticles for fluorescence sensing of Zn^{II}: exploring the covalent strategy. Chemistry – A European Journal 2007;13:2238.

[19] Lim NC, Pavlova SV, Brückner C. Squaramide hydroxamate-based chemidosimeter responding to iron(III) with a fluorescence intensity increase. Inorganic Chemistry 2008;48:1173.

[20] Bricks JL, Kovalchuk A, Trieflinger C, Nofz M, Buschel M, Tolmachev AI, et al. On the development of sensor molecules that display Fe^{III}-amplified fluorescence. Journal of the American Chemical Society 2005;127:13522.

[21] Yoon S, Miller EW, He Q, Do PH, Chang CJ. A bright and specific fluorescent sensor for mercury in water, cells, and tissue. Angewandte Chemie International Edition 2007;46:6658.

[22] Nolan EM, Lippard SJ. Turn-on and ratiometric mercury sensing in water with a red-emitting probe. Journal of the American Chemical Society 2007;129:5910.

[23] Zeng Z, Jewsbury RA. The synthesis and applications of a new chromogenic and fluorescence reagent for cobalt(II). Analyst 1998;123:2845.

[24] Mori I, Takasaki K, Fujita Y, Matsuo T. Selective and sensitive fluorometric determinations of cobalt(II) and hydrogen peroxide with fluorescein-hydrazide. Talanta 1998;47:631.

[25] Ma Q, Cao QE, Zhao Y, Wu S, Hu Z, Xu Q. Two sensitive fluorescence methods for the determination of cobaltous in food and hair samples. Food Chemistry 2000;71:123.

[26] Gosh P, Bharadwaj PK. Ni(II), Cu(II), and Zn(II) cryptate-enhanced fluorescence of a trianthrylcryptand: a potential molecular photonic OR operator. Journal of the American Chemical Society 1996;118:1553.

[27] Xiao Y, Qian X. Novel highly efficient fluoroionophores with a peri-effect and strong electron-donating receptors: TICT-promoted PET and signaling response to transition metal cations with low background emission. Tetrahedron Letters 2003;44:2087.

[28] Callan JF, de Silva AP, Magri DC. Luminescent sensors and switches in the early 21st century. Tetrahedron 2005;61:8551.

[29] The highly acidic Fe^{3+} leaded to the largest fluorescence enhancement further supports the belief that the fluorescence turn-on is more likely due to the protonation of the amino receptor by acidic hydration shells of transition metal salts in moist organic solvents than due to the transition metal ion binding.

[30] Haugland RP. Handbook of fluorescent probes and research chemicals. 6th ed. Eugene, OR: Molecular Probes, Inc.; 1996.

[31] Prestel H, Gahr A, Niessner R. Detection of heavy metals in water by fluorescence spectroscopy: on the way to a suitable sensor system. Fresenius' Journal of Analytical Chemistry 2000;368:82.

[32] Seidel CAM, Schulz A, Sauer MHM. Nucleobase-specific quenching of fluorescent dyes. 1. Nucleobase one-electron redox potentials and their correlation with static and dynamic quenching efficiencies. Journal of Physical Chemistry 1996;100:5541.

[33] de Sousa ER, Marques EP, Fernandes EN, Zhang J, Marques ALB. Graphite electrodes modified by 8-hydroxyquinolines and its application for the determination of copper in trace levels. Journal of the Brazilian Chemical Society 2006;17:177.

[34] Huang K, Yang H, Zhou Z, Yu M, Li F, Gao X, et al. Multisignal chemosensor for Cr^{3+} and its application in bioimaging. Organic Letters 2008;10:2557.

[35] Zhou Z, Yu M, Yang H, Huang K, Li F, Yi T, et al. FRET-based sensor for imaging chromium(III) in living cells. Chemical Communication 2008:3387.

[36] Yang H, Zhou Z, Huang K, Yu M, Li F, Yi T, et al. Multisignaling optical-electrochemical sensor for Hg^{2+} based on a rhodamine derivative with a ferrocene unit. Organic Letters 2007;9:4729.

[37] Schwarze T, Muller H, Dosche C, Klamroth T, Mickler W, Kelling A, et al. Luminescence detection of open-shell transition-metal ions by photoinduced electron transfer controlled by internal charge transfer of a receptor. Angewandte Chemie International Edition 2007;46:1671.

[38] Berlman IB. Handbook of fluorescence spectra of aromatic molecules. New York: Academic Press; 1971.

[39] Ajayaghosh A, Carol P, Sreejith S. A ratiometric fluorescence probe for selective visual sensing of Zn^{2+}. Journal of the American Chemical Society 2005;127: 14962.

[40] An energy transfer mechanism can be excluded, because there are no spectral overlap between the coumarin emission and the quinoline absorption.

[41] Gunnlaugsson T, Ali HDP, Glynn M, Kruger PE, Hussey GM, Pfeffer FM, et al. Fluorescent photoinduced electron transfer (PET) sensors for anions: from design to potential application. Journal of Fluorescence 2005;15:287.

[42] Vosburgh WC, Cooper GR. Complex ions. I. The identification of complex ions in solution by spectrophotometric measurements. Journal of the American Chemical Society 1941;63:437.

[43] Avirah RR, Jyothish K, Ramaiah D. Dual-mode semisquaraine-based sensor for selective detection of Hg^{2+} in a micellar medium. Organic Letters 2007;9:121.

[44] Huang X, Guo Z, Zhu W, Xie Y, Tian H. A colorimetric and fluorescent turn-on sensor for pyrophosphate anion based on a dicyanomethylene-4*H*-chromene framework. Chemical Communications 2008:5143.

[45] Guo Z, Zhu W, Xie Y, Shen L, Tian H. A fluorophore capable of crossword puzzles and logic memory. Angewandte Chemie International Edition 2007;46:5549.

[46] Benesi HA, Hildebrand Jh. A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons. Journal of the American Chemical Society 1949;71:2703.

[47] Ho IT, Lee GH, Chung WS. Synthesis of upper-rim allyl- and *p*-methoxyphenylazocalix[4]arenes and their efficiencies in chromogenic sensing of Hg^{2+} ion. Journal of Organic Chemistry 2007;72:2434.