A Novel Optochemical Sensor for Fe^{3+} by an Intramolecular Charge-transfer Fluorescence Probe: 4-Dimethylamino-2′,5′-dihydroxychalcone

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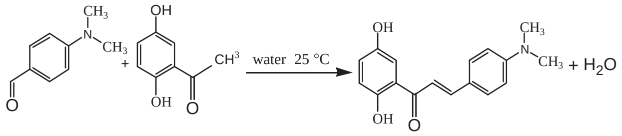
4-Dimethylamino-2′,5′-dihydroxychalcone (DMADHC), a typical compound that exhibits excited-state intramolecular charge-transfer (ICT) characteristics and possesses good photophysical properties, is synthesized and used as fluoroionophore for a Fe^{3+} sensitive optochemical sensor. The sensor shows a linear response toward Fe^{3+} in the concentration range of 3.984×10^{-7}–1.135×10^{-5} M with a limit of detection of 8.223×10^{-9} M. It exhibits excellent selectivity for Fe^{3+} over a large number of cations such as alkali, alkaline earth, and transitional-metal ions.

Iron is widely distributed in nature and is one of the most important elements in biological systems. It plays a crucial role in many biochemical processes at the cellular level and it is an essential element for the formation of hemoglobin of red cells and plays an important role in the storage and transport of oxygen to tissues.[1] The development of reliable sensing methods for iron ions is therefore of considerable importance for environment and human health. Among chemosensory systems, fluorescent for the sensing and reporting of chemical species are currently of significant importance for chemistry, biology, and environmental science, due to simple instrumentation, high selectivity, and direct visual perception even in very dilute solutions.[2] The design and synthesis of a sensitively and selectively fluorescent sensor is a most versatile and widespread approach for chemists and a number of fluorescent receptors have been reported to have a pronounced selectivity for a particular metal ion. However, only a few have reported on fluorescent chemosensors for Fe^{3+} ion.[3,4] As the reported sensors are fairly complex molecules and their syntheses are often expensive and cumbersome, it is still desirable to look for new ionophores for preparing Fe^{3+} sensors. In the present study, 4-dimethylamino-2′,5′-dihydroxychalcone (DMADHC), a typical compound that exhibits excited-state intramolecular charge-transfer (ICT) characteristics and possesses good photophysical properties, is synthesized and used as fluoroionophore for a Fe^{3+} sensitive optochemical sensor. The synthesis route (only one step, Scheme 1) was simple and the yield was high. In a previous study, we have investigated its spectral characteristics.[5] Herein, we try to use chalcone derivative: 4-Dimethylamino-2′,5′-dihydroxychalcone (DMADHC) as fluoroionophores for optochemical sensors for metal ions.



Scheme 1. Synetheis of DMADHC.

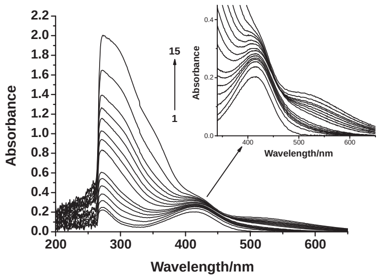


Figure 1. Absorption spectra of DMADHC (1×10^{-5} M) in DMF in the presence of Fe^{III}. The concentration of Fe^{III} (from 1 to 15) is in the range of 1.996×10^{-5}–5.660×10^{-4} M. The experiment was carried out at 20 ± 1 °C.

DMADHC was synthesized according to a reported method.[6] The compound was identified by MS, ^{1}H NMR and IR spectra. The UV–vis absorption spectrum of DMADHC (DMF, 1×10^{-5} M) is shown in Figure 1 and it has two absorption bands in the UV–vis region with maxima at 270 and 420 nm that result from n–π^* and π–π^* transitions, respectively. Fe^{3+} has absorption at 296 nm, which cannot affect the investigation of DMADHC. A gradual increase in the absorption of DMADHC is obtained with the addition of Fe^{3+}, and a faint bathochromic shift from 270 to 274 nm, while the peak at 420 nm has a marked blue-shift from 420 to 403 nm. In addition, the absorption extent at 270 nm is significantly higher than that at 420 nm, which implies that Fe^{3+} has significant effect on the n–π^* transition. The lone pair transit from the N atom to the 3d orbital of Fe^{3+} on the one hand decreases solvation of the lone pair of DMADHC molecule, which heightens the energy level of the n orbital and the energy difference between n and π^* decreases. On the other hand, the attractive polarisation forces between the Fe^{3+} ion and the DMADHC heighten the energy levels of both the excited (π^*) and unexcited states (n). This effect is greater for the unexcited state, and so the energy difference between the excited and unexcited states is slightly reduced. These two factors result in the red shift of absorption spectra. The obvious absorption extent increasing at 270 nm implies that a stable complex between Fe^{3+} and DMADHC is combined and the noncovalent bond is the main force not the electrostatic attraction. In addition, a new absorption peak appears at 523 nm, which also proves a new coordination compound is formed between Fe^{3+} and DMADHC.

DMADHC can emit strong fluorescence in DMF at 540 nm with excitation at 419 nm, which can be quenched by Fe^{3+} ion but the maximum wavelength did not change (Figure 2). These results arise from the lone pair transit from the N atom to the 3d orbital of Fe^{3+} and the ICT is restrained after combining with Fe^{3+} ion. To interpret the data from fluorescence quenching studies, it is important to understand what kind of interaction

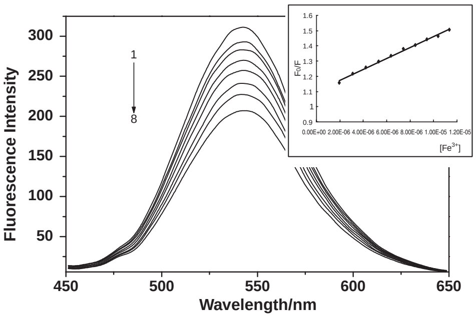


Figure 2. The fluorescence spectra of DMADHC (1×10^{-5} M, DMF) in the presence of Fe^{3+} with the excitation at 419 nm, the concentration of Fe^{3+} (from 1 to 8): 0, 0.4, 3.1, 5.3, 6.4, 8.4, 10.39, and 11.35 μM. The insert is the Stern–Volmer regression curve. The experiment was carried out at 20 ± 1 °C.

takes place between the fluorophore (DMADHC) and the quencher (Fe^{3+}). If it is assumed that the fluorescence quenching of DMADHC induced by Fe^{3+} is a dynamic quenching process, fluorescence quenching is described by the Stern–Volmer equation:

$$F_0/F = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \qquad (1)$$

where F_0 and F are the fluorescence intensities of DMADHC before and after the addition of Fe^{3+}, respectively, k_q the bimolecular quenching constant, τ_0 the lifetime of the fluorophore in the absence of quencher (for DMADHC, the lifetime of the fluorophore is approximately 2.05 ns[7]), [Q] is the concentration of Fe^{3+}, and K_{SV} is the Stern–Volmer quenching constant. Hence, eq 1 is applied to determine K_{SV} by linear regression of a plot of F_0/F against [Q]. A linear Stern–Volmer plot is generally indicative of a single class of fluorophores, all equally accessible to the quencher. In the linear range of the Stern–Volmer regression curve (Figure 2) the average quenching constants for Fe^{3+} (having the lowest quenching effect) is calculated to be $4.09 \times 10^4\,M^{-1}$, thus k_q is $1.99 \times 10^{13}\,M^{-1}\,s^{-1}$. The value is 10^3-fold higher than the maximum value possible for diffusion limited quenching ($\approx 10^{10}\,M^{-1}\,s^{-1}$), which suggests that the quenching is not initiated by dynamic collision but a specific interaction occurring between DMADHC and Fe^{3+}. That is to say a stable complex between DMADHC and Fe^{3+} is formed.

Various metal ions including $Cu^{2+}(Cl^-)$, $Zn^{2+}(CH_3COO^-)$, $Mg^{2+}(Cl^-)$, $Co^{2+}(Cl^-)$, $Pb^{2+}(CH_3COO^-)$, $Ca^{2+}(Cl^-)$, $Fe^{3+}(Cl^-)$, $Al^{3+}(SO_4{}^{2-})$, $Fe^{2+}(SO_4{}^{2-})$, $K^+(SO_4{}^{2-})$, $Sn^{2+}(Cl^-)$, $Na^+(SO_4{}^{2-})$ have been investigated[8] and the results show that DMADHC exhibits the highest selectivity to Fe^{3+} based on the fluorescence quenching factor as the judgement standard. The fluorescence quenching factor k ($(F_0 - F)/F_0$) of Fe^{3+} is calculated to be 0.2432, which is much larger than those of other metal ions. This obvious selectivity of DMADHC for Fe^{3+} and their fluorescence characteristics in complexation towards metal ions indicate that DMADHC possess a concerted coordination behavior and it can be utilized selectively to determine Fe^{3+} by fluorescence emission spectra in a non-aqueous system. The change in the electron density of the terminal nitrogen atom affects the fluorescence because a significant decrease in the intensity is observed; for instance, the fluorescence decreases when the nitrogen atoms are protonated by the microenvironment. Accordingly, there is the possibility for DMADHC to recognize metal cations.

Under the best experimental conditions, the analytical characteristics of Fe^{3+} based on the fluorescence quenching of DMADHC have been exploited. The results show that the fluorescence intensity changes of ΔF as a function of the Fe^{3+} concentration is linear in the range of 3.984×10^{-7}–1.135×10^{-5} M, and the linear regression equation is $\Delta F = 6 \times 10^6[Fe^{3+}] + 40.893$ ($r = 0.9972$). The limit of detection is 8.85×10^{-9} M, which is calculated as three times the standard deviation of the blank and the RSD is 0.18% ($n = 11$).

Various common cations including Sn^{2+}, Cu^{2+}, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Co^{2+}, and Pb^{2+}, which might coexist with Fe^{3+}, are investigated for their effect on the determination of Fe^{3+} and the results reveal that most alkali and alkaline earth metal cations, and some transition-metal cations including Mg^{2+} and Al^{3+} at a concentration of 1.0×10^{-3} M do not show significant interfering effect on the Fe^{3+} assay with relative error less than ±5%. Many other transition-metal cations such as Co^{2+}, presenting in a concentration less than 1.0×10^{-4} M do not show appreciable interfering effect on the Fe^{3+} assay.

The accuracy and the reliability of the method are further evaluated by recovery experiment with high, medium, and low concentration of Fe^{3+} in the liner range and the results show the recoveries are in the range of 97.50–99.03%, which indicate that the proposed method is suitable for real samples. The content of Fe^{3+} in a multivitamin tablet was determination based on the proposed method. Note that in the sample iron is in the form of Fe^{2+}, and it needs to be oxidized to Fe^{3+} at first. Results show that the concentration of Fe^{3+} found by the proposed optochemical sensor is 7.89 ± 0.06 μM, which matches the marker of 8 μM. It can be seen that the content of iron ions as determined by the present sensor is in good agreement with the stated content in multivitamin tablet with a relative error less than 2%. It can be concluded that the present sensor seems useful for the determination of iron ions in real samples. The proposed method is suitable for the determination of Fe^{3+} in multi-vitamin tablets with satisfactory results. It provides a basis theory for ICT as the fluorescence sensor for the determination of metal ions.

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7 The fluorophore lifetime of DMADHC was determined on a FLS-920 Combined fluorescence lifetime and steady state spectrometer (Edinburgh, UK). A Picosecond diode laser of 405 nm was chosen as the source for the fluorescence lifetime determination. Both the excitation and emission slit widths were 1.20 nm. The average fluorophore lifetime of DMADHC was 2.05 ± 0.01 ns by repeatedly measuring six times.
8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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