



Selective fluorescent sensor for mercury ions in aqueous media using a 1,4-dihydropyridine derivative



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ABSTRACT

Novel 1,4-dihydropyridine (DHP) derivatives containing 3 carboxylic acid units are synthesized via cyclotrimerization of *N*-substituted β -aminoacrylates followed by basic hydrolysis of the triester. These DHP derivatives are readily soluble in aqueous media buffered at pH 8.0 and the solutions give blue fluorescent signals with quantum yields of 7–23%. One of these compounds, bearing a *p*-methoxyphenyl *N*-substituted group, shows specific fluorescent quenching with the mercuric ion (Hg^{2+}). The fluorescent signal of the DHP derivative decays over a period of minutes to hours depending on the Hg^{2+} concentration, which implies that the sensing mechanism involves chemical reaction between the Hg^{2+} ion and the DHP compound. The ^1H NMR and MS data suggest that Hg^{2+} mediates the oxidation of the DHP ring into a pyridinium ring. The event is useful for fluorescent detection of Hg^{2+} at the micromolar level within 30 min, with a detection limit of 0.2 μM in aqueous medium.

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1. Introduction

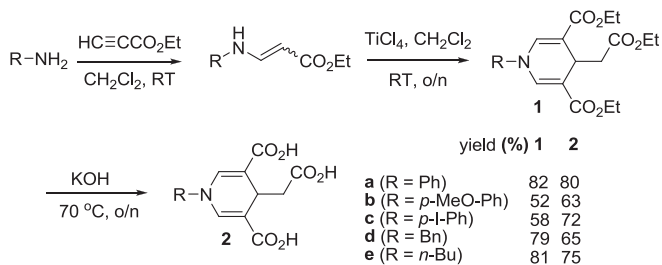
The design and synthesis of new fluorescent chemosensors for the efficient detection of toxic heavy metal ions are one of the most important research topics in environmental chemistry and biology.^{1–11} Among heavy metals, mercury is considered as one of the most highly toxic metals and is widely present as a contaminant in both ionic and molecular compounds in all environmental spheres. It can cause severe damage to the nervous system of human beings¹² and long term accumulation of this metal in the body leads to a permanent deterioration of the brain, kidneys, and developing fetus.^{13–16}

Presently, ICP-MS is a gold standard for quantitative analysis of mercury(II) because of its high sensitivity.^{17–20} However, this technique requires expensive instruments and a skilled operator, which are not readily possible for onsite analysis. Sensing systems or sensor kits for the detection of mercury(II) are thus attractive for onsite applications. Due to their sensitivities and simple detection procedures, fluorescent chemosensors have attracted much attention during the past two decades. Generally, there are two different design approaches of fluorescent chemosensors for mercury(II) detection, which are based on reversible weak interactions^{21–28} and

non-reversible reactions.^{29–38} Several reaction-based Hg^{2+} probes, so called chemodosimeters, can provide high selectivity, sensitivity, and reliable record.²⁶ The irreversible chemical reactions between the fluorescent molecules and mercury(II) usually change both absorption and fluorescence spectra of the fluorophore that may lead to high sensitivity and dual modes of detection. Among reported fluorescent mercury(II) chemosensors, only a few systems can be used in aqueous media without any presence of organic solvents.^{30–34} In this contribution, we would like to report the synthesis of novel 1,4-dihydropyridine (DHP) derivatives containing three carboxylic acid units using our recently reported cyclotrimerization reaction as the key step.³⁹ These DHP derivatives are readily soluble in aqueous media and the solutions give blue fluorescent signals, which were found to be useful as a fluorescent chemosensor of mercury(II) ion.

The synthesis of 1,4-dihydropyridine (DHP) derivatives was performed according to our recently reported method based on the cyclotrimerization of β -amino acrylates in the presence of TiCl_4 Lewis acid (Scheme 1).³⁹ The triester derivatives of DHP (**1**) were obtained in 52–82%, which were readily hydrolyzed under basic conditions to give the corresponding DHP tricarboxylic acids (**2**) in satisfactory yields (63–80%). The structures of **1** and **2** were confirmed by ^1H NMR, ^{13}C NMR and MS (Figs. S7–S21). The tricarboxylic acids **2** showed good water solubility in a pH 8.0 phosphate buffer (PB) solution and gave strong blue light emission under black light.

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Scheme 1. Synthesis of fluorescent sensor 2.

2. Results and discussion

Electronic absorption and emission spectra of **2** were collected in pH 8.0 PB solution. The absorption maxima were observed in a range of 347–358 nm (Table 1) corresponding to the characteristic $\pi-\pi^*$ transition of the DHP ring.^{40–42} The molar extinction coefficients of this transition for **2a–d** were in a range of 4.67×10^3 – 6.74×10^3 M⁻¹ cm⁻¹, but only 4.11×10^2 M⁻¹ cm⁻¹ for **2e**. The difference in the molar extinction coefficients suggests that the presence of a phenyl substituent can facilitate the electronic transition within the DHP ring. In the case of **2a**, **2b**, and **2c**, another strong band of the *N*-substituted aryl moiety around 280–300 nm was also observed. All of these compounds exhibited an emission peak in a range of 432–445 nm with fluorescence quantum efficiencies (ϕ_f) of 0.07–0.23. The similarity of the absorption and emission peaks indicates that the DHP units in these compounds have similar HOMO and LUMO levels. Again, the lower quantum yield of **2a–d** compared to **2e** confirms that the benzene ring can stabilize the DHP excited state. Hence, the lower stability of **2e** excited state can lead to a faster radiative decay process, which in turn gives the higher quantum efficiency. Due to its high extinction coefficient and quantum efficiency, **2b** showed the highest blue emission appearance (Table 1), and it was therefore selected for further investigation in sensing applications.

Table 1
Photophysical properties of tricarboxylic DHP (**2a–e**) in pH 8.0 PB solution

DHP	R	Absorption		Emission		Appearance (1 mM) under black light
		λ_{\max} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{\max} (nm)	ϕ_f^a	
2a	Ph	288 347	1.85×10^4 6.03×10^3	435	0.08	
2b	<i>p</i> -MeO-Ph	281 352	2.24×10^4 6.74×10^3	443	0.14	
2c	<i>p</i> -I-Ph	300 353	1.73×10^4 4.67×10^3	432	0.07	
2d	Bn	357	6.36×10^3	439	0.09	
2e	<i>n</i> -Bu	358	4.11×10^2	445	0.23	

^a Ref. = Quinine sulfate in 0.1 M H₂SO₄ ($\phi_f = 0.54$) was the reference.

The fluorescent responses of **2b** (1 μ M) toward 14 metal ions (Na⁺, Ca²⁺, Zn²⁺, Hg²⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Fe²⁺, Fe³⁺, Cd²⁺, Al³⁺, Mn²⁺, and Pb²⁺) were evaluated in aqueous PB solutions. Upon the addition of the metal ion (50 equiv) into a solution of **2b**, only Hg²⁺ caused a significant fluorescence quenching effect after 30 min (Fig. 1). This highly selective fluorescence quenching was also observable by the naked-eye (Fig. 2a). In the presence of interfering metal ions at the concentration of $5 \times$ [Hg²⁺], the fluorescence

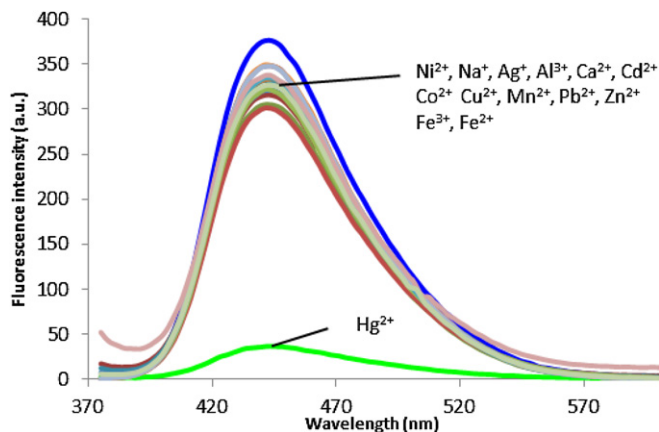


Fig. 1. Fluorescence quenching profile of **2b** (1 μ M), 30 min after addition of each metal ion (50 μ M) in pH 8.0 PB solution ($\lambda_{\text{ex}}=352$ nm). Acetate salts were used except for CdSO₄, FeSO₄, and Fe(NO₃)₃.

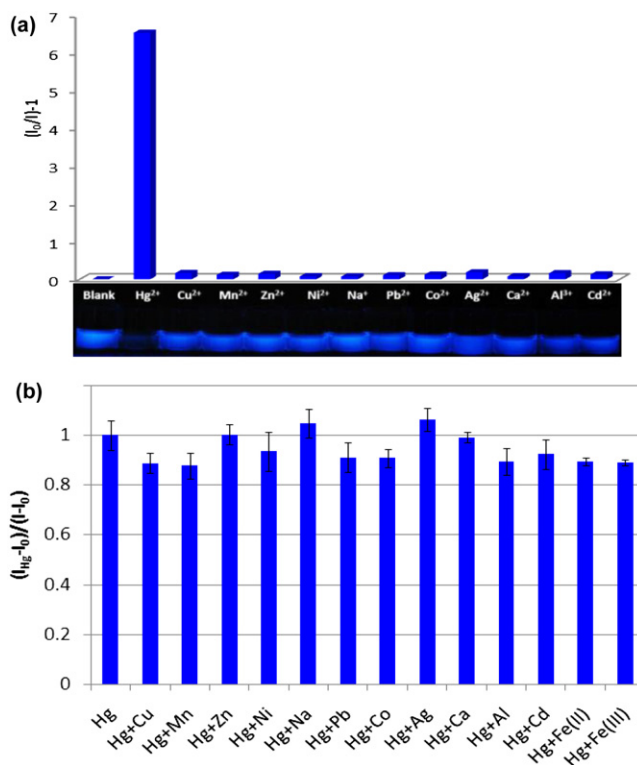


Fig. 2. a) Fluorescence response (I_0/I)-1 of **2b** (1 μ M) and the photograph under black light of **2b** (0.1 mM) 30 min after addition of metal ion (50 μ M and 1 mM, respectively), b) inference study in the [**2b**]:[Hg²⁺] ([1 μ M]:[10 μ M]) system with the interfering metal ion [M^{n+}]=50 μ M in pH 8.0 PB solution ($\lambda_{\text{ex}}=352$ nm).

quenching responses were within 90–105% of the original quenching by only Hg²⁺ (Fig. 2b). However, with higher concentration of the interfering metal ions (10 \times), extra quenching responses were observed for Fe²⁺ and Fe³⁺.

During the preliminary sensing study, we found that the fluorescence quenching by Hg²⁺ proceeded gradually, therefore, the fluorescence intensity was monitored for 60 min (Fig. S2). The kinetic results showed that the intensity decreased and reached the minimum after 30 min. Since the quenching process was relatively slow, we hypothesized that it was a result of a chemical reaction rather than the fast dynamic or static quenching mechanism. Furthermore, the addition of a strong chelating reagent, such as EDTA, did not regain the fluorescence signal (Fig. S3). The result confirmed that the quenching was not caused by the complexation between

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