



A highly sensitive and selective ratiometric fluorescent probe based on conjugated donor–acceptor–donor constitution of 1,8-naphthyridine for Hg²⁺

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ABSTRACT

A new 1,8-naphthyridine based di-olefinic chemosensor was designed, synthesized and its sensing behavior towards metal ions was investigated by UV–vis, fluorescence and ¹H NMR spectroscopic methods. A highly Hg²⁺-selective fluorescence enhancing property (>1.5-fold) in conjunction with a visible colorimetric change from yellow to purple has been observed, leading to a potential fabrication of both “naked-eye” and fluorescence detection of Hg²⁺. Our designed sensor of the donor–acceptor–donor system shows high selectivity towards mercury(II) ion over other competing metal ions.

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1. Introduction

The design and synthesis of fluorescent probes with desirable properties are of considerable importance in supramolecular chemistry due to their fundamental role in medical, environmental, and biological applications [1–3]. The highly toxic metal ion Hg²⁺ causes serious health and environmental problems [4]. The soluble inorganic Hg²⁺ ion, which provides a pathway for contaminating large amounts of water, is a caustic and carcinogenic material with a high cellular toxicity [5]. Methyl mercury is usually generated through microbial methylation in aquatic sediments from Hg²⁺ ions, and the subsequent accumulation of methyl mercury by humans through the food chain may lead to serious and permanent damage to the brain. Therefore, it is very important for the routine detection of Hg²⁺ ion in the environmental monitoring of rivers and larger bodies of water, and in the evaluation of the safety of aquatically derived food supplies. Many kinds of chemical and physical sensors have been developed for the detection of Hg²⁺, among which the fluorescence based sensors represent a simple, but sensitive technique providing detection limits of as low as ppb [6–9]. So far, the development of practical fluorescent chemosen-

sors for many heavy transition metal [10–12] (HTM) ions is still a challenge [13–17]. Hg²⁺ belongs to the so-called “silent ions” since, unlike some biological metal ions (such as Fe²⁺, Mn²⁺ or Cu²⁺), it does not have an intrinsic spectroscopic or magnetic signal because of its 5d¹⁰ 6s⁰ electronic configuration. The fluorometric detection of such ions is based in the use of small-molecule fluorescent sensors that consist of an ionophore–chromophore system. There are some examples of fluorescence quenching chemosensors for Hg²⁺ in organic or aqueous solutions [18–21]. However, there are few chemosensors with fluorescence enhancement (FE) for Hg²⁺ in organic solutions [22–27], and few in aqueous solutions. Most of the fluoroionophores for Hg²⁺ consist of fluorophores and macrocycle receptors (e.g., aza-crown ether) or the receptors containing sulfur atoms [28–33], and there are some fluorescent probes for Hg²⁺ designed on the basis of chemical reaction, redox, and the photodynamic principle [34–37]. Therefore, novel selective chemosensors with FE for Hg²⁺ in aqueous–organic system become our target.

This work is aimed at the design and construction of a new class of colorimetric and fluorometric dual-channel assay to specifically detect the presence of Hg²⁺ over a wide range of other cations. The 1,8-naphthyridine (napy) moiety is one of the most useful fluorophores for the construction of fluorogenic chemosensors for a variety of important chemical species. Particularly, the 1,8-naphthyridine (napy) and its derivatives have been widely used as a guanine recognition reagents and bidentate ligands. However, there are very few reports about the derivatives of 1,8-naphthyridine as fluorescent sensors for transition metals [38–41].

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In order to shift the emission bands to a blue or red region, a conjugated donor (D)–acceptor (A)–donor (D) molecule incorporating a central moiety of naphthyridine and two terminal moieties of dimethylaniline connected by ethenyl bridges (R1) was selected. In this report, we describe the synthesis and designed the molecule R1 of D–A–D assembly for UV–vis and fluorescence spectral studies of Hg^{2+} ion.

The naphthyridine moiety acts as the acceptor site, whereas the dimethylaniline moiety functions as the donor site (Scheme 1). The acceptor and donor moieties are connected by ethenyl bridges to form a conjugated scaffold. In general, several binding states may exist in equilibrium. At the early stage, the binding of the D–A–D molecule with a metal ion at the acceptor site, forming D–AM–D (1:1), would enhance the acceptor strength to facilitate ICT (Intramolecular Charge Transfer). When a metal ion binds at one of the donor sites, the resulting D–A–DM (1:1) may also facilitate ICT due to the resulting A–DM unit function as an enhanced electron-withdrawing group. When the D–A–D molecule is saturated with metal ions at the late stage, all the acceptor and donor sites are bound to metal ions to form a 1:3 complex (MD–AM–DM) (Scheme 1). A hypsochromic spectral shift thus occurs to account for the great decrease of dipole at this stage [42].

2. Experimental

2.1. General

2-Methyl-6-pycolin and N,N-dimethyl aniline were purchased and used without further purification. ^1H NMR spectra were obtained using 300 MHz NMR spectrometer and ^{13}C NMR spectra were obtained using 75 MHz or 125 MHz NMR spectrometers. Column chromatography was performed with silica gel (100–200 mesh). Fluorescence spectra were measured using spectroscopic grade solvents. The fluorescence measurements were performed at room temperature (temperature controlled at $18 \pm 2^\circ\text{C}$) and within 1 h after the sample preparation.

2.2. Synthetic procedures of R1

2,7-Bis [2-(N,N-dimethyl-4-aminophenyl)-vinyl]-[1,8]naphthyridine (R1): Synthesis of R1 was accomplished by modification of an established procedure. N,N-dimethyl-4-aminobenzaldehyde was synthesized according to reported methods [43–45]. Equivalent moles of 2,7-dimethyl naphthyridine (100 mg, 0.238 mmol) and p-dimethylaminobenzaldehyde (71 mg, 0.4765 mmol) were dissolved in 5 ml of fresh and dry DMF. The solution was stirred in a round bottom flask attached to a drying tube. Sodium hydride (0.330 g, 12.5 equiv.) and potassium t-butoxide (0.886 g, 6.25 equiv.) were added to the flask one after another, making sure that the drying tube remains attached after each addition. This reaction mixture was stirred for 24 h. About 15 g of ice was taken in a large beaker to which 10 ml of saturated ammonium chloride (NH_4Cl) was added. The stirred reaction mixture was then poured into the beaker of ice, and 5 ml of saturated ammonium chloride was added to it to dissolve any remaining product in the flask. The mixture in the beaker was stirred for about 15 min, and the resulting solid was collected using a vacuum filter. The solid product was washed with cold water while the vacuum was on, and left in the vacuum to air dry the product overnight. The yield of this product was 78%. The product was characterized by ^1H NMR, ^{13}C NMR, X-ray crystallography, mass spectroscopy. Mp $290\text{--}292^\circ\text{C}$; ^1H NMR (CDCl_3 , 300 MHz): δ 7.90–8.02 (m, 2H), 7.59 (s, 2H), 7.52–7.56 (m, 2H), 7.2812–7.2838 (d, $J=0.78$ Hz, 4H), 7.21 (s, 2H), 6.74–6.77 (d, $J=8.46$ Hz, 4H), 3.04 (s, $J=7.5$ Hz, 12H); ^{13}C NMR (75 MHz, CDCl_3): δ 164.5, 155.8, 141.8, 140.9, 133.6, 128.9,

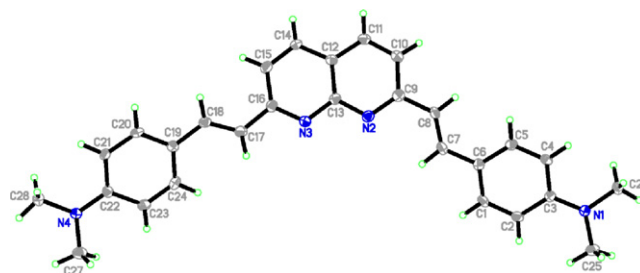


Fig. 1. Ortep diagram of receptor R1.

128.2, 124.8, 117.1, 115.9, 38.9, 36.5, 29.6, 27.3; IR: $\gamma(\text{cm}^{-1})$: 3440, 2915, 2848, 1616, 1578, 1521, 1502, 1368, 1301, 1197, 1145, 977, 814, 748. TOF MS ES(+); m/z calcd for $\text{C}_{28}\text{H}_{28}\text{N}_4(\text{M})^+$: 420.1314. Found $(\text{M}+\text{H})^+$: 421.1245.

The synthetic route is shown in Scheme 2.

2.3. X-ray crystallography

The structure of R1 is further confirmed by single crystal X-ray diffraction and is shown in Fig. 1.

3. Results and discussion

3.1. UV–vis titration

The absorption spectra of sensor R1 in the presence of different concentrations of Hg^{2+} ions are displayed in Fig. 2. When increasing concentrations of Hg^{2+} ions are introduced in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1), the absorbance peak is centered at 441 nm and gradually decreased with concomitant appearance of a red shifted peak around 579 nm. This red shift is assigned at the early stage (D–AM–D species in Scheme 1) to an efficient ICT process from the dual-armed electron-donor dimethylaniline groups. A double bond is inserted between the napy ring and the dimethylaniline moiety to elongates the π conjugation, so that the absorption could further extend into the visible region.

Thereby, upon binding to a metal ion at the acceptor naphthyridine site, the electron-donating capability of the dimethylaniline moiety should increase, which leads to stronger ICT. A bathochromic shift in the absorption spectra upon addition of metal ions is thus expected. The titrations were carried out by using var-

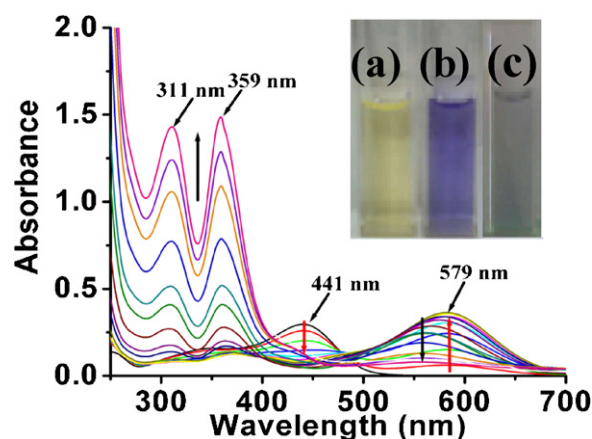
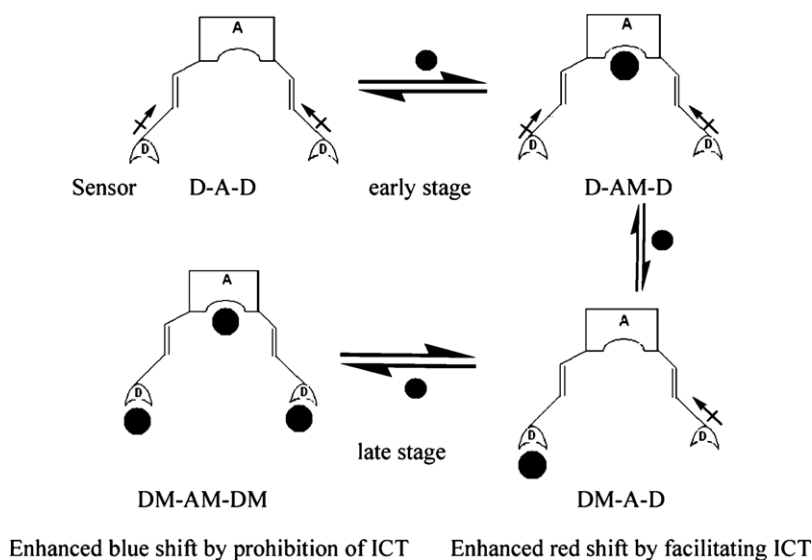


Fig. 2. Absorbance spectra of compound R1 in the presence of increasing Hg^{2+} concentrations (0, 2, 4, 6, 8, 10, 14, 20, 24, 30, 35, 40, 50, 60, 70, and $80\ \mu\text{M}$) in a CH_3CN –water solution (50:50, v/v). The concentration of the R1 was $c = 1.0 \times 10^{-5}$ M. Inset: (a) only receptor R1, (b) R1 + 10 equiv. of Hg^{2+} , and (c) R1 + more than 10 equiv. of Hg^{2+} .



Scheme 1. Design of metal ion sensor with conjugated D–A–D assemblies. A: acceptor; D: donor. Metal ion (M): ●; dipolar vector: \rightarrow .

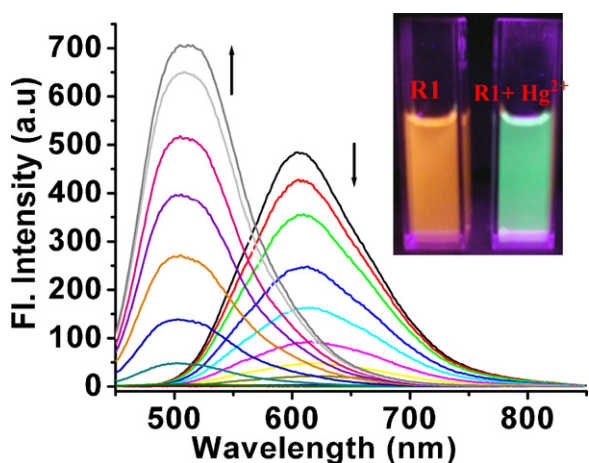
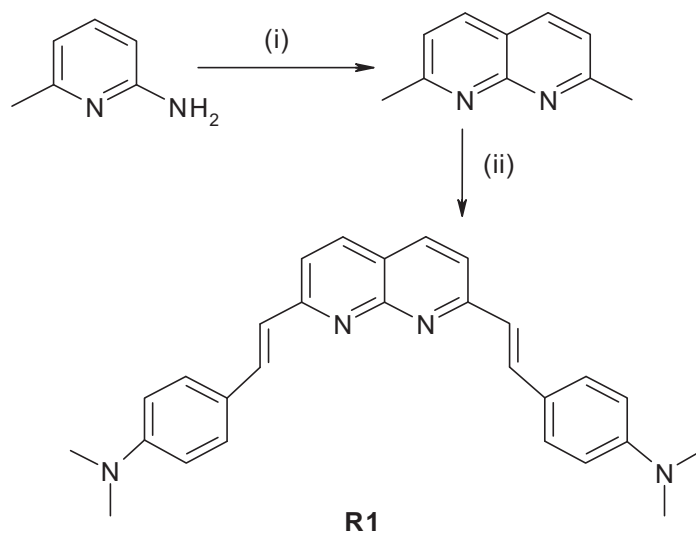


Fig. 3. Emission spectra of R1 in the presence of increasing Hg^{2+} concentration (0, 2, 4, 6, 8, 10, 14, 20, 24, 30, 35, 40, 50, 60, 70, and 80 μM) in a $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solution (50:50, v/v). Excitation wavelength was 441 nm with 5 nm slit widths. The concentration of the chemosensor was $c = 1.0 \times 10^{-6}$ M.

ious amounts of Hg^{2+} ion as the aqueous solution of perchlorate salt. Furthermore, a well-defined isosbestic point was observed at 486 nm, which suggests a new complex formation (R1 with Hg^{2+} produces a single component). The 138 nm red shift should result in a significant change in the absorption ratios. Indeed, sensor R1 displays a remarkable enhancement in absorption ratios (A_{579}/A_{441}) from 0.021 to 6.18 upon Hg^{2+} treatment. More importantly, the absorption changes are clearly visible to the naked eye. The pale yellow solution of R1 immediately changed to purple in accordance with this large red-shift ($\Delta\lambda = 138$ nm). The purple color of the mixture solution faded when more than 10 equiv. of Hg^{2+} ions were added (Fig. 2, inset). Accordingly, an extraordinarily large hypsochromic shift ($\Delta\lambda = 220$ and 286 nm) from 579 nm to 359 and 311 nm respectively were observed. By addition of more than 10 equiv. of Hg^{2+} ions, all the acceptor and donor sites in molecule R1 were likely saturated to reach a late stage of complexation (DM–AM–DM species in Scheme 1), in which the saturated complex would only possess the least ICT property. The prohibition of π conjugation thus results in a great hypsochromic shift of the absorption band.



Scheme 2. Synthesis of R1. Reagents and conditions: (i) crotonaldehyde, H_3PO_4 , 120 $^\circ\text{C}$, 12 h and (ii) N,N-dimethyl p-amino benzaldehyde, NaH, dry DMF, N_2 , rt, 24 h.

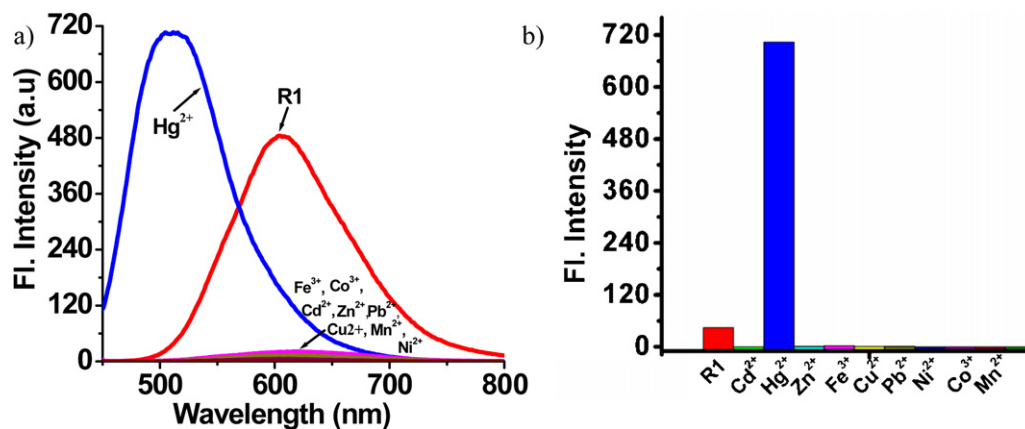


Fig. 4. (a) Fluorescence response of R1 (1×10^{-6} M) with various metal ions (100 equiv.) except Hg^{2+} in a CH_3CN -water solution (50:50, v/v) at 298 K. $\lambda_{\text{ex}} = 441$ nm. (b) The relative fluorescence intensities of R1 (1×10^{-6} M) at 514 nm with various metal ions (100 equiv.) except Hg^{2+} in CH_3CN -water solution (50:50, v/v) at 298 K. $\lambda_{\text{ex}} = 441$ nm.

3.2. Fluorescence titration

The fluorescence properties of R1-Hg^{2+} are surveyed in typical aqueous-organic solvent systems. R1 exhibits relative strong fluorescence emission at 608 nm ($\Phi_f = 0.07$) [46,47] in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1) upon excitation at 441 nm.

During titration of Hg^{2+} , a new fluorescence emission peak appears at about 514 nm and the intensity is dramatically enhanced with initial emission intensity at 608 nm which is decreased indicating an Hg^{2+} -selective dual-emissive-type (on-off-on) signaling behavior (Fig. 3). Upon gradual addition of Hg^{2+} ion, the fluorescence intensity of R1 increases by over 1.5-fold accompanied by a large blue shift ($\Delta\lambda = 94$ nm) in the emission spectrum. The dramatic change in visual fluorescence color from orange to green of R1 in the absence and presence of Hg^{2+} further supported the blue shift emission response (inset in Fig. 3).

However, when other cations are added, the fluorescence of R1 is significantly quenched (Fig. 4a and b), indicating an efficient Hg^{2+} -selective (on-off-on) behavior. How could we explain these phenomena? On the basis of the above fact, the hypsochromic shift or blue shift in the emission spectra upon addition of Hg^{2+} ion can be rationalized by ICT in the excited state of the napy moiety by the lone pair of electrons on the nitrogen atoms in the electron-donor dimethylaniline groups [48,49]. We speculate that the fluorescence change could contribute to two points. First, in the early stage the system is expected to follow the PET (Photoinduced Electron Transfer) mechanism where, upon excitation of the free probe, an electron would be transferred from the dimethylaniline groups to the fluorophore and hence diminishing fluorescence. Second, coordination of the Hg^{2+} to all the acceptor and donor sites in molecule R1 were likely saturated to reach a late stage of complexation (DM-AM-DM species in Scheme 1) and hence suppressed the ICT process and this process also contributes to the turn-on fluorescence enhancement [50]. ICT, instead of PET, is responsible for the large wavelength shift. Upon titration of $\text{Hg}(\text{II})$, more and more molecules undergo complexation and hence suppressed the ICT, leading the stronger fluorescence at the ICT emission wavelength (514 nm).

3.3. ^1H NMR titration

To look further into the nature of the interaction between R1 and the Hg^{2+} ion, ^1H NMR experiments are carried out in CDCl_3 (Fig. 5). Thus, the aliphatic protons of the NMe_2 units experience more downfield shifts of 0.25 ppm upon addition of Hg^{2+} , whereas an aromatic and ethylenic protons show relatively small downfield shifts (0.056–0.15 ppm). The downfield shift of the NMe_2 protons

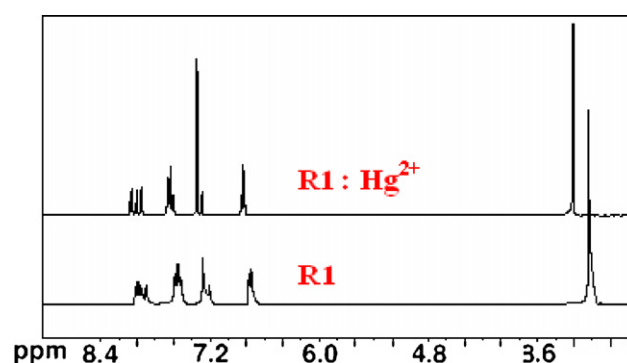


Fig. 5. ^1H NMR spectra of R1 (bottom) and in the presence of Hg^{2+} (top) in CDCl_3 .

is due to the decrease in electron density of the NMe_2 moieties by Hg^{2+} co-ordination at the donor sites. The complexation of R1- Hg^{2+} results in shifts of an aromatic and ethylenic protons to downfield, which indicates that D-A-D molecule is saturated with metal ions, all the acceptor and donor sites are bound to metal ions to form a 1:3 complex (DM-AM-DM).

4. Conclusion

In conclusion, the 1,8-naphthyridine based dual-armed D-A-D molecule R1 exhibits a new class of colorimetric and fluorimetric probe for Hg^{2+} ion detection with high selectivity and sensitivity on the basis of the PET and ICT. A highly Hg^{2+} -selective fluorescence enhancing property (>1.5 -fold) in conjunction with a more convenient “naked-eye” colorimetric detection of the Hg^{2+} ion. The two stage colorimetric property of R1 was unique in the detection of Hg^{2+} ion in aqueous media, e.g., $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1). It represents one of the few acyclic fluorescent probes that allow a selective detection of Hg^{2+} in aqueous-organic solvent instead of the commonly used macrocycles for metal ion detection. The D-A-D constitution demonstrated in this study can serve as a protocol for the future design of metal ions and other possible analytes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.04.031.

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