

A 2-Styryl-1,8-naphthyridine derivative as a versatile fluorescent probe for the selective recognition of Hg²⁺, Ag⁺ and F⁻ ions by tuning the solvent

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A novel fluorescent probe **1** has been synthesized by a microwave reaction, and its ion-binding and fluorescence-sensing properties have been investigated under different solvent conditions. The analysis results indicated that probe **1** can act as a multiple analysis probe by simply tuning the solvent. Probe **1** exhibited high selectivity toward Hg²⁺ through fluorescence quenching in H₂O/DMF. In H₂O/1,4-dioxane solution, probe **1** selectively recognized and discriminated between Ag⁺ and Hg²⁺ displaying ratiometric behaviour. Moreover, probe **1** readily recognized the anion F⁻ via the ratiometric fluorescent mode in CH₃CN. Furthermore, distinct colour changes were observed under UV light, which can be seen by the naked eye and thus used for distinguishing Hg²⁺, Ag⁺ and F⁻ from the other ions screened herein using probe **1**. Interestingly, almost pure white light emission was evident by simply tuning the F⁻ anion-concentration, which makes this system a potential candidate for smart and tunable luminescent materials.

Keywords: Fluorescent probe; Solvent effect; White light emission; Ratiometric; Hg²⁺ / Ag⁺ / F⁻

Introduction

Numerous cations and anions play vital roles in biological and environmental processes. However, beyond an optimum limit, each of these ions could potentially become dangerous to human life. The detection and estimation of such analytes has become very important.[1] Fluorescent probes are well known candidates for detecting ions and molecules owing to their high sensitivity, selectivity, rapid response rates and ease of manipulation.[2-5] Together with their capacity for real-time imaging, these attributes have led to their wide adoption in the detection of biologically relevant ions.[6-10] It is noteworthy that the contamination of an analysis matrix usually results from the synergistic contribution of two or more infectants, and often makes the single-analyte analysis platform less useful. Hence, it is essentially to develop a single molecule having different responses toward multi-analytes, which would simplify routine analysis in a cost-effective manner.

Among the various heavy and transition metals, Hg^{2+} is one of the most highly toxic, and can easily pass through biological membranes, and accumulate in organisms to cause serious threat to human health.[11] Along with the widespread use of mercury in industry, mercury contamination (especially Hg^{2+}) of the natural environment has attracted increasing concern.[12] It is very important to be able to routinely detect Hg^{2+} ion in terms of environmental monitoring, and in the evaluation of the safety of aquatically derived food supplies.

With the rapid development of human society, Ag^+ has been extensively utilized in the electronic, photographic, imaging and pharmaceutical industries. Despite the sterilization function of Ag^+ , it can cause severe damage to both the environment and human beings.[13, 14] Besides its physical appearance, silver possesses some unique chemical properties, which has led to its use in various chemical and biological applications. The widespread use of gold and silver, however, can cause adverse effects to the environment as well as in biological systems. Accordingly, suitable detection methods are required for evaluation of the adverse effects as well as for investigating their beneficial biological effects.[15]

Anions also play fundamental and functional roles in many biological processes, and thus, in healthcare. Some small ions that induce biological dysfunctions are of paramount research importance. Among the anions, F^- is of particular interest owing to its established role in dental care and clinical treatment for osteoporosis.[16] Therefore, it is important to develop optical probes exhibiting high selectivity, good sensitivity, and rapid response rates toward the F^- ion. Moreover, for an ideal F^- probe, possessing an optical response with a ratiometric value, exhibiting signal changes which allow for naked-eye detection, having optical signals in the near-infrared region, and been able to operate under practical situations are prerequisites.[17] Some F^- probes are based on molecular interactions of F^- -induced via H-bonding. Nevertheless, most of these H-bonding-based F^- chemosensors exhibit extremely poor selectivity since they are susceptible to interference from alkaline anions such as AcO^- . [18, 19] We thus note that there have been few reported examples fulfilling all the aforementioned criteria.

Therefore, the development of a single probe for trace level determination of these three ions, namely Hg^{2+} , Ag^+ and F^- , is very challenging. Recently, a few probes have been explored for the selective sensing of various cations as well as anions, for example $\text{Zn}^{2+}/\text{AcO}^-$, [20] $\text{Hg}^{2+}/\text{Au}^{3+}$, [21] $\text{Hg}^{2+}/\text{Cu}^{2+}$, [22] $\text{CN}^-/\text{SO}_3^{2-}/\text{Fe}^{3+}$, [23] $\text{CN}^-/\text{HSO}_3^-/\text{pH}$, [24] $\text{Hg}^{2+}/\text{F}^-$, [25] $\text{Zn}^{2+}/\text{Al}^{3+}/\text{Cu}^{2+}/\text{F}^-$, [26]

Hg²⁺[27] and Hg²⁺/F⁻[28]. Our group also has reported multifunctional probes for Zn²⁺/Mg²⁺/F⁻[29] and Al³⁺/F⁻[30]. However, the highly efficient detection of multiple analytes using a single chemosensor remains a challenging task.

In our constant pursuit to develop novel sensing probes for various biological and environmentally relevant analytes, we report herein a single versatile multiple target intramolecular charge transfer (ICT) probe, namely 2-{2-(1,8-naphthyridin-2-yl)vinyl}phenol (probe **1**). [31] Probe **1** consists of naphthyridine and phenolic moieties which are connected through a π -conjugated vinyl spacer. The naphthyridine acts as an electron acceptor unit and the hydroxyl group acts as an electron donor unit. Probe **1** not only possesses a fluorometric ability to recognize Hg²⁺ in DMF/H₂O (19/1, v/v), but also exhibits ratiometric behaviour toward Hg²⁺ and Ag⁺ in 1,4-Dioxane/H₂O (19/1, v/v). Additionally, probe **1** also demonstrates selective ratiometric behaviour towards F⁻ in CH₃CN. Interestingly, an unexpected tunable white light emission was also observed by simply tuning the F⁻ anion-concentration.

Results and discussion

Synthesis of probe **1**

Microwave irradiation possesses several advantages over conventional heating, for example, homogeneous and rapid heating (deep internal heating), spectacular accelerations in reactions as a result of the heating rate and selective heating. Consequently, microwave-assisted organic reactions can produce high yields and lower quantities of by-products, which can make purification of target products easier. [32-35] Indeed, new reactions are possible that cannot be achieved by conventional heating. Herein, a microwave reaction was employed as an efficient method to synthesize probe **1**. The synthetic route was carried out as outlined in Scheme 1. The structure of probe **1** was unambiguously confirmed by ¹H/¹³C NMR, IR and MS spectra (Fig. S1 ~ S4).

Scheme 1. The synthetic route of probe **1**.

Chromogenic sensing of Hg²⁺ and Ag⁺ in aqueous solution

The recognition properties of probe **1** toward various metal ions (Li⁺, Na⁺, K⁺, Ag⁺, Hg²⁺, Mg²⁺, Ca²⁺, Ba²⁺, Sr²⁺, Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Pb²⁺, Cd²⁺, Al³⁺ and La³⁺) were investigated by fluorescence spectroscopy in different media. In a DMF/H₂O (19/1, v/v) solution, probe **1** (10 μ M) exhibited a strong fluorescence emission at 475 nm upon excitation at 375 nm ($\Phi_f = 0.21$, versus quinine sulfate $\Phi_f = 0.55$ as a reference). Upon addition of 20 equiv. of various metal cations (see above), there were no obvious fluorescent intensity changes except for Hg²⁺. The addition of 20 equiv. Hg²⁺ resulted in acute fluorescence quenching and the fluorescence quantum yield was reduced to $\Phi_f = 0.035$ (Fig. 1a). It strongly suggested that probe **1** was highly selective towards Hg²⁺ in DMF/H₂O (19/1, v/v) solution. Furthermore, a fluorescence titration experiment of probe **1** with Hg²⁺ was carried out to give more information about this process (Fig. 1b). On gradually increasing the amounts of Hg²⁺, the fluorescence intensity of probe **1** significantly decreased indicating efficient Hg²⁺-selective ON-OFF behaviour. [36] The formation of a **1**-Hg²⁺ complex induced almost total fluorescence quenching, which is ascribed to the highly efficient and

thermodynamically favourable electron or energy transfer from the naphthyridine fluorophore to the metal center in this medium.[37] The stoichiometry of the interaction between probe **1** and Hg^{2+} was confirmed to be a 1:1 ratio according to the molar ratio method (Fig. 1b, inset). Mass spectral analysis further confirmed the formation of a 1:1 ratio for the **1**- Hg^{2+} complex with the generation of molecular ion peaks at $m/z = 449.058$ ($[\text{1+Hg-H}]^+$, Fig. S5). The association constant for probe **1** with Hg^{2+} was calculated to be $1.3 \times 10^5 \text{ M}^{-1}$ by using a Benesi-Hildebrand plot assuming a 1:1 stoichiometry (Fig. S6). Based on the fluorescence titration experiments, the limits of detection ($\text{LOD} = 3\sigma/\text{slope}$) for probe **1** towards Hg^{2+} was calculated to be $3.5 \times 10^{-8} \text{ M}$. A non-linear curve was obtained which suggested the fluorescence quenching process of probe **1** on addition of Hg^{2+} is both a static and dynamic quenching process. (Fig. S7).

Figure 1. (a) Fluorescence spectra of probe **1** (10 μM) alone and in the presence of 20 equiv. of various metal ions in DMF/ H_2O (19/1, v/v). Inset: the colour change of probe **1** in the absence and the presence of Hg^{2+} under 365 nm UV light; (b) Fluorescence spectral titration of Hg^{2+} in DMF/ H_2O (19/1, v/v). Inset: intensity at 475 nm versus the number of equivalents of Hg^{2+} added. Metal ions: Li^+ , Na^+ , K^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Al^{3+} , La^{3+} and Hg^{2+} . $\lambda_{\text{ex}}/\lambda_{\text{em}} = 375/475 \text{ nm}$.

Interestingly, an entirely different fluorescence recognition behaviour for probe **1** was observed when the solvent was switched from DMF to 1,4-dioxane (Fig. 2). Free probe **1** (10 μM) displayed a relatively strong fluorescence emission at 430 nm ($\Phi_f = 0.13$) upon excitation at 368 nm in 1,4-dioxane/ H_2O (19/1, v/v) solution. The selectivity/recognition experiment revealed that the presence of Ag^+ or Hg^{2+} resulted in obvious red-shifts, viz from 430 nm to 480 nm (the addition of Ag^+) or from 430 nm to 530 nm (the addition of Hg^{2+}), whilst no significant changes were observed in the presence of any of the other tested metal cations. Discernable colour changes for the solution of probe **1** from blue to blue-green (Ag^+) or to yellow-green (Hg^{2+}) were observed under the UV-lamp, which were attributed to the differing red-shift wavelengths (Fig. 2, inset). These observations indicate that probe **1** is not only highly selective for the recognition of Hg^{2+} and Ag^+ , but can also further distinguish each of them by their different colours (i.e. “naked-eye” detection). The different recognition behaviour in different solvents system indicates that the fluorescence recognition capability of probe **1** is solvent-dependent.

Figure 2. Fluorescence spectra of probe **1** (10 μM) and in the presence of 20 equiv. of various metal ions in 1,4-dioxane/ H_2O (19/1, v/v). Inset: the colour change of probe **1** in the absence and the presence of Ag^+ , Hg^{2+} under 365 nm UV light; Metal ions: Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Al^{3+} , La^{3+} , Ag^+ and Hg^{2+} . $\lambda_{\text{ex}}/\lambda_{\text{em}} = 368 \text{ nm}/430, 480 \text{ and } 530 \text{ nm}$.

In order to obtain more detail about the complexation of probe **1** with Ag^+ and Hg^{2+} in 1,4-dioxane/ H_2O (19/1, v/v), fluorescence titration experiments of probe **1** (10 μM) with Ag^+ or Hg^{2+} were carried out. Upon addition of Ag^+ , the fluorescent intensity of probe **1** exhibited a gradually decrease in the 430 nm emission band, which was accompanied by a new red shifted (50 nm) emission band (480 nm, $\Phi_f = 0.50$) with an isoemission point at 465 nm (Fig. 3a). Under the same conditions, on addition of Hg^{2+} , the emission of probe **1** at 430 nm decreased, whilst a new red shifted (100 nm) emission band centered at 530 nm appeared with a distinct isoemission point

at 500 nm (Fig. 3b). These observations indicated that probe **1** exhibited a ratiometric fluorescent response toward Ag^+ and Hg^{2+} ions in 1,4-dioxane/ H_2O (19/1, v/v). It is well-known that ratiometric probes are better than any of other type of probes given their built-in correction for environmental effects and self-correcting capability.[38, 39] The ratiometric fluorescence spectra in the presence of Ag^+ and Hg^{2+} is most likely an intramolecular charge transfer (ICT) based optical response.[40] This suggested that the **1**- Ag^+ and **1**- Hg^{2+} complexes strongly promoted the ICT from the donor hydroxyl group to the acceptor naphthyridine moieties, resulting in a red-shift of the fluorescence spectra. However, when both the acceptor and donor sites are bound to metal ions, according to the preference of binding states in equilibrium, a larger bathochromic shift might be attributed to the stronger ICT, and a smaller bathochromic shift attributed to the weaker ICT.[41]

The fluorescence intensity ratio (Ag^+ : $F_{480\text{ nm}}/F_{430\text{ nm}}$ and Hg^{2+} : $F_{530\text{ nm}}/F_{430\text{ nm}}$) of probe **1** when treated with Ag^+ or Hg^{2+} was obtained from the relationship of intensity ratio *versus* ion concentration, and the stoichiometry of the interaction revealed a 1:1 ratio for the **1**- Ag^+ and **1**- Hg^{2+} complexes (Fig. 3a, inset and Fig. 3b, inset). Mass spectrum analysis further confirmed the formation of a 1:1 **1**- Hg^{2+} complex (Fig. S5) as well as a 1:1 **1**- Ag^+ complex (Fig. S8) with the generation of molecular ion peaks at $m/z = 449.058$ [**1**+ Hg -H] $^+$ and $m/z = 355.372$ [**1**+ Ag] $^+$, respectively. The association constants for complex **1**- Ag^+ and **1**- Hg^{2+} were estimated to be $6.1 \times 10^4 \text{ M}^{-1}$ and $4.4 \times 10^4 \text{ M}^{-1}$ by using a Benesi-Hildebrand plot assuming a 1:1 stoichiometry, respectively (Fig. S9 and Fig. S10). The limits of detection (LOD) for probe **1** towards Ag^+ or Hg^{2+} were calculated to be $5.0 \times 10^{-8} \text{ M}$ and $3.1 \times 10^{-8} \text{ M}$, respectively (Fig. S11 and Fig. S12). All of these data also indicated that probe **1** not only possesses high selectivity but also high sensitivity toward Ag^+ and Hg^{2+} ions in 1,4-dioxane/ H_2O (19/1, v/v).

Figure 3. (a) Fluorescence spectral titration of probe **1** (10 μM) with Ag^+ in 1,4-dioxane/ H_2O (19/1, v/v). Inset: intensity ($F_{480\text{ nm}}/F_{430\text{ nm}}$) *versus* the number of equivalents of Ag^+ added. (b) Fluorescence spectral titration of probe **1** (10 μM) with Hg^{2+} in 1,4-dioxane/ H_2O (19/1, v/v). Inset: intensity ($F_{530\text{ nm}}/F_{430\text{ nm}}$) *versus* the number of equivalents of Hg^{2+} added. $\lambda_{\text{ex}} = 368 \text{ nm}$.

To further investigate the practical applicability of the probe **1** as a Ag^+ or Hg^{2+} ion selective fluorescent sensor, competitive experiments were carried out in the presence of Ag^+ or Hg^{2+} ions (0.2 mM) mixed with Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , La^{3+} , Al^{3+} , Hg^{2+} and Ag^+ at 0.2 mM in DMF/ H_2O (19/1, v/v) or 1,4-dioxane/ H_2O (19/1, v/v) solution. As shown in Fig. S13 ~ S15, no obvious interference to the selective response of probe **1** toward Ag^+ or Hg^{2+} in the presence of any of the other metal cations occurred. Furthermore, a practical application of probe **1** was evaluated, namely the standard addition method to detect Ag^+ and Hg^{2+} in lake water samples under the optimized conditions (probe **1**, 10 μM , 1,4-dioxane/ H_2O , 19/1, v/v). The experimental result revealed that the Ag^+ concentration of lake water was 0.7038 μM and the Hg^{2+} concentration was 1.496 μM . All the measurements were performed three times. The results showed satisfactory recovery and R.S.D. values for all of the samples (Fig. S16 and Table S1~S2). These results demonstrated that probe **1** meets the monitoring sensitivity as well as selectivity requirements necessary for the screening of environmental water samples. Accordingly, these observations suggested that probe **1** can be used as a practical selective fluorescent probe for

Ag⁺ or Hg²⁺ ions.

Optical response of probe 1 to F⁻

We have explored the ability of probe 1 as a chromogenic and fluorogenic indicator for basic anions. However, it is well-known that hydrogen bonding interactions of anions with host molecule generally diminish in protic solvents. Hence, most of the anion recognition processes were observed in non-aqueous and aprotic solvents.

Thus, we investigated the effect of anions on the emission properties of probe 1 (20 μM) in acetonitrile solution (Fig. 4). Free probe 1 displayed a strong fluorescence emission at 465 nm upon excitation at 355 nm, and its fluorescence quantum yield was calculated to be 0.12 *versus* quinine sulfate as a reference material. Interestingly, upon addition of F⁻ (10 equiv.), the intense emission band at 465 nm was acutely quenched ($\Phi_f = 0.044$) and an accompanying new weak fluorescent emission peak at ~ 605 nm appeared. No significant change was observed on addition of other anions (AcO⁻, HSO₄⁻, H₂PO₄⁻, PF₆⁻, ClO₄⁻, Cl⁻, Br⁻, I⁻, NO₃⁻), which indicated a high selectivity for the F⁻ anion. There was a remarkable fluorescence response associated with an obvious colour change from blue to light pink under a UV-lamp (Fig. 4, inset). This suggested that probe 1 can further function as a fluorescence sensor via naked eye detection and act as a probe for the F⁻ anion in acetonitrile. Furthermore, the coexisting anion experiments using the probe 1-F⁻ complex revealed that the other competing anions did not interfere with the detection of F⁻ (Fig. S17). Thus, all of the results suggested that probe 1 is an excellent probe for F⁻ ion in acetonitrile.

Figure 4. Fluorescence spectra of probe 1 (20 μM) and in the presence of 10 equiv. of various anions in CH₃CN. Inset: the colour change of probe 1 in the absence and the presence of F⁻ under 365 nm light. Inset: intensity ($F_{650\text{ nm}}/F_{460\text{ nm}}$) *versus* the number of equivalents of F⁻ added. Anions: AcO⁻, HSO₄⁻, H₂PO₄⁻, PF₆⁻, ClO₄⁻, Cl⁻, Br⁻, I⁻, NO₃⁻ and F⁻. $\lambda_{\text{ex}} = 355\text{ nm}$.

The fluorescent emission titration experiments revealed a ratiometric behaviour in which the fluorescence intensity of probe 1 (50 μM, $\lambda_{\text{em}} = 465\text{ nm}$) gradually diminished and a new emission band gradually appeared at about 605 nm (Fig. 5b). The appearance of isoemissive points at 560 nm, clearly supported the existence of more than one species in the medium. The observed significant red shift of probe 1 upon interaction with F⁻ was attributed to enhancement of the ICT due to deprotonation of the -OH fragments. A 2:1 stoichiometry for a probe-fluoride interaction was determined by obtaining the ¹H NMR titration spectra as a function of F⁻ concentration (Fig. 9b). The binding constant was estimated using the Benesi-Hildebrand method and was found to be $K_a = 1.2 \times 10^4\text{ M}^{-1}$ (Fig. S18). The limit of detection (LOD) of probe 1 for F⁻ has been estimated as $2.8 \times 10^{-7}\text{ M}$ (Fig. S19). The above observations clearly demonstrated that the visible colour changes were probably due to hydrogen bonding interactions and in particular further deprotonation processes between the two phenolic OH groups of the sensors with F⁻. The formation of negative oxygen ions further strengthens the polarity and electron-donating ability of the -OH group and leads to a dramatic red shift (140 nm) of the emission band.

More interestingly, upon increasing the concentration of F⁻, dramatically tunable colour changes from deep blue to white and pink-orange were obtained (Fig. 5a). Furthermore, the CIE chromaticity diagram (Fig. 5c) revealed that the coordinates for the white-light emission are (0.33, 0.32), which are close to those of the emission for pure white light (0.33, 0.33). As we know, the

study of organic molecules for white light emission has attracted significant attention due to their tunable emission properties, which makes them potential candidates for smart and tunable luminescent materials.[42] Several approaches have been reported regarding the generation of white light from organic molecules.[43-48] However, white light emission in response to an anion-recognition event is, to the best of our knowledge, hitherto only reported in one case, even though this would be a closer mimic to biological light production that is triggered by ions.[49]

Figure 5. (a) Photographs of the solution of probe **1** (50 μM) upon addition of increasing concentrations of F^- anion (0 ~ 50 equiv) in CH_3CN under UV light at 365 nm; (b) Fluorescence spectral titration of probe **1** (50 μM) with F^- in CH_3CN ; (c) The 1931 CIE chromaticity coordinate changes from blue (0.17, 0.19) to white (0.33, 0.32), and pink-yellow (0.36, 0.31) with the addition of 0, 25, and 50 equiv. of F^- anions to the probe **1** (50 μM) CH_3CN solution with $\lambda_{\text{ex}} = 365$ nm, where X is the chromaticity coordinate that represents the proportion of red primary and Y is the chromaticity coordinate that represents the proportion of green primary.

The recognition mechanism of probe **1** towards ions

In order to find out the reasons for the different binding behaviour of probe **1** toward Hg^{2+} , Ag^+ and F^- , ^1H NMR titration experiments using probe **1** were conducted under the same conditions as for the fluorescent experiments.

For the **1**- Hg^{2+} complex in $\text{DMF-}d_7/\text{D}_2\text{O}$ (19/1, v/v) solution (Fig. 6): on increasing the amount of Hg^{2+} from 0 ~ 1 equiv., the protons of the naphthyridine moiety (H1 ~ H5) gradually shifted downfield (0.30 - 0.71ppm). In contrast, the protons of the vinyl group (H6 ~ H7) and benzene ring (H8 ~ H11) exhibited relatively smaller upfield shifts (0.06 - 0.42ppm). The proton of hydroxyl group (H12) was also shifted upfield, which was confirmed by the use of D_2O (only $\text{DMF-}d_7$) in the ^1H NMR titration spectra (Fig. S20). These results are ascribed to the formation of a **1**- Hg^{2+} complex through the lone-pair of the nitrogens on the naphthyridine and oxygen on the phenolic moiety. The decreasing electron-cloud was transferred from the naphthyridine fluorophore to the metal center and resulted in a de-shielding effect and a downfield shift. On the other hand, the increasing electron-cloud was transferred from the oxygen on the hydroxyl group to the benzene ring, which resulted in a shielding effect and an upfield shift. Hence, we propose a plausible binding model for the probe **1** with Hg^{2+} ion as shown in Fig. S21.

Figure 6. Partial ^1H NMR spectra of probe **1** (5 mM) and increasing concentrations of Hg^{2+} in $\text{DMF-}d_7/\text{D}_2\text{O}$ (19/1, v/v) solution at 298K.

Interestingly, a different mechanism was found for the **1**- Hg^{2+} complex when the solvent was switched to dioxane. Upon increasing the Hg^{2+} concentration from 0 ~ 1 equiv. in probe **1** dioxane- $d_8/\text{D}_2\text{O}$ (19/1, v/v) solution, the protons of the naphthyridine moiety (H1 ~ H5) were shifted downfield, which resulted from the reduction of the electron-cloud density of the naphthyridine by the coordination of metal ions. The protons of the vinyl group (H6 ~ H7) and benzene ring (H8 ~ H11) and were shifted upfield (Fig. 7a). Compared with the $\text{DMF-}d_7/\text{D}_2\text{O}$ (19/1, v/v) system, similar phenomena were observed except that the dioxane- $d_8/\text{D}_2\text{O}$ (19/1, v/v)

system exhibited a larger chemical shift. However, the proton of the hydroxyl group (H12) disappeared upon the addition of Hg^{2+} which may be attributed to deprotonation and the formation of the $\mathbf{1}\text{-Hg}^{2+}$ complex in the absence of D_2O (conducted in dioxane- d_8 , Fig. S22). In other words, the deprotonated oxygen also participated in the complex process. The deprotonated oxygen strongly promoted the ICT process from the donor phenolic group to the acceptor naphthyridine moieties, resulting in a red-shift of the fluorescence spectra. The upfield shift might be due to a through-bond effect. [52, 53] Consequently, we propose the plausible binding model for the probe **1** with Hg^{2+} ion as shown in Fig. 7b.

Figure 7. (a) Partial ^1H NMR spectra of probe **1** (5 mM) and increasing concentrations of Hg^{2+} in dioxane- d_8 / D_2O (19/1, v/v) solution at 298K; (b) Plausible binding model of the probe **1** with Hg^{2+} ion complexes. + denotes downfield and - denotes an upfield shift.

For the $\mathbf{1}\text{-Ag}^+$ complex, we selected $\text{DMSO-}d_6$ as a solvent given the poor solubility of Ag^+ in dioxane- d_8 for the ^1H NMR titration experiments. Upon addition of Ag^+ from 0 ~ 1 equiv. to the probe **1**/ $\text{DMSO-}d_6$ solution, when compared with the $\mathbf{1}\text{-Hg}^{2+}$ complexation, the protons of the naphthyridine moiety (H1 ~ H5), hydroxyl group (H12) as well as the protons of the vinyl group all slightly shifted downfield ($\Delta\delta = 0.04 - 0.23$ ppm), and no detectable chemical shifts were observed for the protons of the benzene ring (H8 ~ H11) (Fig. 8a). The downfield shift was attributed to the interaction between the metal Ag^+ and the nitrogen atoms and oxygen atom of the hydrogen group. The ^1H NMR titration results for the $\mathbf{1}\text{-Ag}^+$ complex were consistent with the smaller red shift value observed in the fluorescence spectra (Fig. 2). Thus, we propose the plausible binding model of the probe **1** with Ag^+ ion as shown in Fig. 8b.

Figure 8. (a) Partial ^1H NMR spectra of probe **1** (5 mM) and increasing concentrations of Ag^+ in $\text{DMSO-}d_6$ solution at 298K; (b) Plausible binding model of the probe **1** with Ag^+ ion complexes. + denotes downfield and - denotes an upfield shift.

^1H NMR titration experiments were also carried out in order to study the $\mathbf{1}\text{-F}^-$ complexation. The ^1H NMR chemical shift of the phenolic hydroxyl (-OH) proton appeared at δ 10.10 ppm in the absence of F^- ; upon addition of 0.25 equiv. of F^- , the signal for the OH proton completely disappeared; on continued addition of 0.5 equiv. of F^- , a new peak appeared at ~ 16 ppm, which further developed into a typical triplet (Fig. 9a). These results indicated that the phenolic -OH was initially involved in H-bonding with the fluoride ion and then a deprotonation occurred, attributed to the bi-fluoride ions FHF^- and FDF^- . [50, 51] At the same time, the protons of the naphthyridine moiety and the benzene ring underwent upfield shifts (through-bond effect).[52, 53] All of these observations, especially the deprotonation of the hydroxyl groups, indicated that hydrogen-bonding was present. It was thought to strengthen the polarity and electron-donating ability of the -OH group and lead to an increase of electron density upon complexation with the anion. The proton NMR studies clearly favoured the H-bonding interaction between the -OH fragments of **1** and F^- followed by deprotonation. Consequently, the ICT increased due to charge propagation from the hydroxyl groups to the naphthyridine units. The reaction stoichiometry between the probe **1** and F^- has been realized by obtaining the ^1H NMR titration spectra as a

function of the F^- concentration. Upon addition of 2.0 equiv. of F^- , a clear inflection point was observed and an equilibrium reached according to the chemical shift changes of H8~ H11 *versus* F^- concentration, which suggested a 2:1 stoichiometry for a probe-fluoride interaction (Fig. 9b). Thus, we propose the plausible binding model of the probe **1** with F^- ions as shown in Fig. 9c.

Figure 9. (a) Partial 1H NMR spectra of probe **1** (5 mM) and increasing concentrations of F^- in DMSO- d_6 solution at 298K; (b) Chemical shift changes of probe **1** *versus* F^- concentration in 1H NMR titration spectra; (c) Plausible binding model of the probe **1** with F^- ion complexes.

Conclusions

In conclusion, we report the facile preparation using microwaves of a naphthyridine derived fluorescent probe **1**. The behaviour of probe **1** is solvent-dependent and it acts as a sensitive multifunctional cation/anion probe. Probe **1** exhibited good selectivity towards Hg^{2+} over other competitive ions in DMF/ H_2O (19/1, v/v) in fluorescence quenching mode. Probe **1** also exhibited good selectivity toward Hg^{2+} and Ag^+ over other competitive ions in 1,4-dioxane/ H_2O (19/1, v/v) in the ratiometric fluorescence mode. Additionally, probe **1** possessed excellent selective recognition towards the anion F^- in CH_3CN in ratiometric fluorescence mode. Furthermore, distinct colour changes were observed under UV light, which can be visualized by the naked eye for distinguishing Hg^{2+} , Ag^+ and F^- from the other ions screened herein using probe **1**. Another notable feature of the probe is that almost pure white light emission was realized by tuning the F^- anion-concentration, which makes it a potential candidate for use in smart and tunable luminescent materials. The fluorescent spectral titrations, 1H NMR spectroscopic titrations and mass spectrometry revealed that different recognition mechanisms were in operation, which resulted in the different recognition ability. This work provides a promising cheap strategy for the simultaneous detection of metal ions and anionic species by one probe in environmentally relevant systems.

Experimental

Materials and equipments

Salicylaldehyde and acetic anhydride were purchased commercially (Aldrich and Alfa Aesar Chemical Co., Ltd.). The solutions of the metal ions were prepared from their perchlorates. All the anions were prepared from their tetra-*n*-butylammonium salts (Sigma-Aldrich Chemical Co. Ltd.). 2-Methyl naphthyridine was prepared according to the reported procedure.[54] Other chemicals used in this work were of analytical grade and were used without further purification. Double distilled water was used throughout.

Fluorescence spectra were recorded on a Cary Eclipse Fluorescence Spectrometer (Varian). Absorption spectra were recorded on a UV-vis TU-1900 spectrophotometer (Beijing General Instrument Co., China). 1H NMR spectra were measured on a WNMRI-500 MHz NMR (Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences) spectrometer at room temperature using TMS as an internal standard. MALDI-TOF mass spectra was collected on a BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometer

(Bruker) with cyano-4-hydroxycinnamic acid as matrix. IR spectra were recorded on a Vertex 70 FT-IR spectrometer (Bruker). The microwave reaction was using a Discover microwave reactor (CEM).

Synthesis of probe 1

0.50 g of 2-methyl naphthyridine (3.47 mmol), 0.51 g of salicylaldehyde (4.16 mmol) and 10 mL acetic anhydride were added in a 25 mL microwave reaction tube. The mixture was kept in a microwave reactor under 50 W microwave irradiation power at 130 °C for 40 min. The solvent was removed by reduced pressure to give an oily liquid. The crude product was dissolved in hot ethanol, and then acetone was added with stirring to give a precipitate, which was collected by filtration to afford the target probe **1** (0.30 g, 35 %) as a yellow solid. m.p. 163 - 164 °C (crystallization from acetone); ¹H NMR (500 MHz, DMSO-*d*₆, 2.50 ppm) δ : 10.10 (s, 1 H, -OH), 9.04 - 9.05 (m, 1 H, ArH), 8.40 - 8.43 (m, 2 H, ArH), 8.18 (d, 1 H, *J* = 15.0 Hz, -CH=CH-), 7.86 (d, 1 H, *J* = 8.5 Hz, ArH), 7.72 (d, 1 H, *J* = 7.0 Hz, ArH), 7.54 - 7.57 (m, 1 H, ArH), 7.52 (d, 1 H, *J* = 15.0 Hz, -CH=CH-), 7.20 (t, 1 H, *J* = 7.0 Hz, ArH), 6.94 (d, 1 H, *J* = 8.0 Hz, ArH) and 6.88 (t, 1 H, *J* = 7.5 Hz, ArH) ppm; ¹³C NMR (500 MHz, DMSO-*d*₆, 39.5 ppm) δ : 159.6, 156.6, 156.1, 154.2, 138.4, 137.6, 131.6, 130.6, 128.0, 127.8, 123.2, 122.1, 122.0, 121.8, 119.9 and 116.6 ppm; IR (KBr, cm⁻¹) ν : 3453, 1636, 1468, 1380, 1088, 982, 859 and 542; HRMS (MALDI-TOF) *m/z*: [M+H]⁺ Calculated for C₁₆H₁₃N₂O: 249.1028; Found: 249.1078 [M + H]⁺.

Spectral measurements

To a 10 mL volumetric flask containing different amounts of metal ion (20 mM), the requisite amount of probe **1** (0.1 mM, 1.0 mL) was added directly via micropipette. For Hg²⁺, diluted with DMF/H₂O (19/1, v/v) mixed solvent or diluted with 1,4-dioxane/H₂O (19/1, v/v) mixed solvent to 10 mL for fluorescence spectra measurement; For Ag⁺, diluted with 1,4-dioxane/H₂O (19/1, v/v) mixed solvent to 10 mL. To a 10 mL volumetric flask containing different amounts of anion (2 mM), the requisite amount of probe **1** (0.1 mM, 1.0 mL) was added directly via micropipette. For fluorescence spectra measurements, the solutions were diluted with CH₃CN solvent to 10 mL. Fluorescence spectra were measured after addition of the ions at room temperature to equilibrium. Fluorescence measurements were carried out with excitation and emission slit width of 10 nm and 10 nm.

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