

A Fluorescent Hypochlorite Probe Built on 1,10-Phenanthroline Scaffold and its Ion Recognition Features

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Abstract In this study, the synthesis of 7-((Hydroxyimino)methyl)-1,10-phenanthroline-4-carbaldehyde oxime (**1**) in two steps starting from 4,7-dimethyl-1,10-phenanthroline (**2**) is reported. It is found that compound **1** can be used as a fluorogenic probe for the detection of hypochlorite ion in aqueous solution. NMR and mass spectral analysis indicate that probe **1** undergoes a chemical transformation through its oxime units upon treatment with hypochlorite, which results in a remarkable enhancement of the emission intensity. Also, metal ion recognition properties of probe **1** is investigated. It is noted that compound **1** is responsive to Zn²⁺, Cd²⁺, Ni²⁺ and Cu²⁺ metal ions, which reduced the emission intensity under identical conditions.

Keywords Fluorescence · Probe · Hypochlorite · 1,10-phenanthroline

Introduction

Reactive oxygen species (ROS) represent an important class of intermediates, which play crucial roles in many biological and/or pathological process in living organisms [1]. It is well known that they are mainly produced from oxygen during the electron transport chain in order to eliminate undesired xenobiotics [2]. However, it should be noted that over production of ROS increases the oxidative stress, which may lead to some

neurodegenerative diseases such as Alzheimer's and neuron degeneration along with cancer, cardiovascular diseases, and arthritis etc. Among the ROS, hypochlorite is a significant ion for the immune system. It is generated from the reaction of chloride ions with H₂O₂ in the presence of myeloperoxidase enzyme [3, 4]. Moreover, hypochlorite is indispensable for our daily life, which is frequently used in disinfection of drinking water, household bleach, cooling-water and/or cyanide treatment in a concentration range of 10⁻⁵-10⁻² M [4, 5]. Consequently, the design and synthesis of novel and sensitive compounds, which can selectively detect hypochlorite ion become an important topic [2-4, 6-18].

In this context, fluorescent compounds that consist of a signaling unit attached with a suitable recognition unit offer a powerful tool for the selective and sensitive detection of target ions as analytes, which play essential roles in many biological, chemical and environmental processes. To date, many excellent examples of fluorescent probes for the detection of a variety of ions and molecules have been reported [19-35].

1,10-phenanthroline skeleton [36], which bears an integrated signaling and recognition moiety, is a good candidate for intensity-based optical probes. For example, Kaur and Alreja reported the differential absorption changes of a simple tailor-made amidic functionality based on 1,10-phenanthroline unit with Cd²⁺, Zn²⁺ and Cu²⁺ metal ions [37]. Yang et al. reported a three-arm phenanthroline derivative as a colorimetric and fluorescent sensor for fluoride [38]. Algi et al. reported that 1,10-phenanthroline with orthogonal BODIPY units can be used as turn-off fluorescent Cd²⁺ probe [39]. Chemical modification of this 1,10-phenanthroline derivative also allowed tailoring the selectivity from one ion (Cd²⁺) to another (Zn²⁺) [40]. Also, they have reported that chromogenic Fe²⁺ and fluorogenic Zn²⁺ detection was possible with an imidazo-phenanthroline scaffold [41].

In this paper, the design, synthesis and properties of a new compound, viz. 7-((Hydroxyimino)methyl)-1,10-phenanthroline-4-carbaldehyde oxime (**1**), is described. It

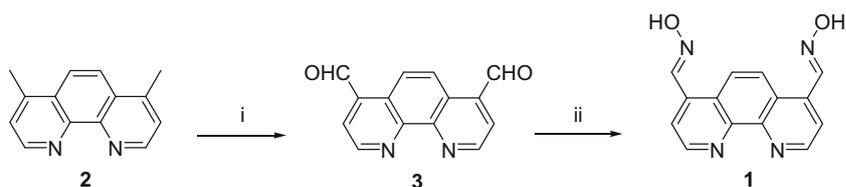
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Scheme 1 Synthesis of probe **1**.

Conditions: i- SeO_2 , 1,4-dioxane-water (4 %, v/v), 100°C , 60 %; ii- $\text{NH}_2\text{OH}\cdot\text{HCl}$, NEt_3 , $\text{C}_2\text{H}_5\text{OH}$, 78°C , 85 %



should be noted that this novel compound **1** is rationalized on the basis of a chemodosimeter approach [42–44], which would allow fluorescence detection of hypochlorite ion via deoximation reaction in aqueous solution. Furthermore, 1, 10-phenanthroline scaffold in **1** would be used for the detection of some certain metal ions in aqueous solution. It is found that probe **1** immediately undergoes an oxidation reaction with NaClO through its oxime units in 0.1 M Na_2CO_3 - NaHCO_3 buffer containing DMF (pH = 9.0, 30:1 v/v) at room temperature (rt). NMR and mass spectral data indicated that **1** undergoes a chemical transformation, which resulted in a remarkable enhancement of the emission intensity. Importantly, this paves the way of detection of NaClO with **1** in aqueous solution. It is noteworthy that this novel probe **1** is highly selective to hypochlorite ion when compared to some other ROS and anions (vide infra). On the other hand, probe **1** also induces turn-off fluorogenic responses to metal ions such as Zn^{2+} , Cd^{2+} , Ni^{2+} and Cu^{2+} ions under identical conditions.

FTIR spectra were recorded on Perkin Elmer Spectrum 100 model FTIR with an attenuated total reflectance (ATR). ^1H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded on a Bruker DPX-400 or Ultrashield 300 NMR Spectrometers. Combustion analyses were carried out by using a LECO CHNS-932 analyzer. LC MS spectra were recorded on a Thermo Scientific TSQ Quantum Acces Max spectrometer. UV-vis and fluorescence measurements were recorded on Varian Cary 50 and Varian Cary Eclipse spectrophotometers, respectively. Melting points were determined on a Schorrp MPM-H2 model apparatus and are uncorrected. The synthesis of **3** [39, 40] was carried out according to a published procedure. Hypochlorite solutions, which was obtained from a local supplier (Migros A.Ş.), were prepared from commercial bleach (5 % NaClO solution). Metal solutions were freshly prepared from the corresponding perchlorate salts.

Synthesis of 7-((Hydroxyimino)methyl)-1,10-Phenanthroline-4-Carbaldehyde oxime (**1**)

To a solution of **3** (118 mg, 0.5 mmol) and NEt_3 (0.21 mL, 1.5 mmol) in ethanol (60 mL) was added $\text{NH}_2\text{OH HCl}$ (104 mg, 1.5 mmol). The mixture was heated under reflux overnight and the solid part was filtered while the solution was hot: grey solid, 113 mg, yield 85 %, mp. $282\text{--}284^\circ\text{C}$. ^1H NMR (300 MHz, DMSO-d_6) δ /ppm: 12.11 (s, 2 H, OH),

Experimental Section

General

All chemicals were purchased from Sigma Aldrich Chemicals or Merck Company and used as received unless otherwise

Fig. 1 Emission intensity changes of compound **1** (3.3×10^{-5} M) depending on the pH

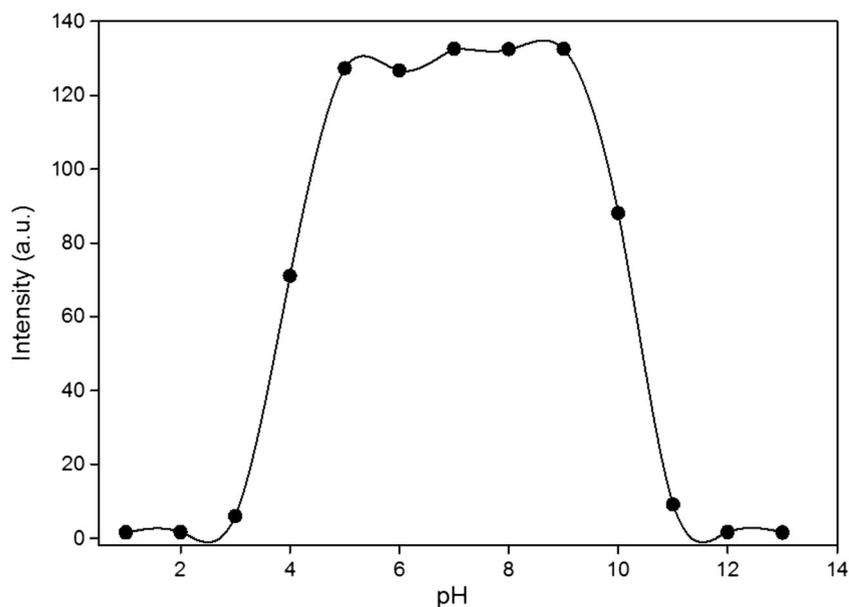
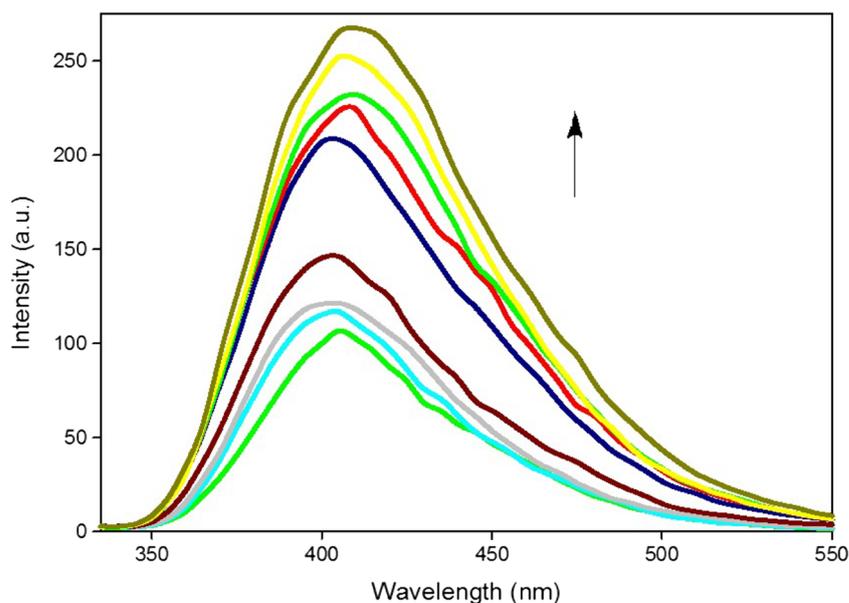


Fig. 2 Emission spectra of **1** (3.3×10^{-5} M) upon addition of NaClO (0; 0.67×10^{-4} ; 1.0×10^{-4} ; 1.67×10^{-4} ; 3.0×10^{-4} ; 3.33×10^{-4} ; 3.67×10^{-4} ; 4.0×10^{-4} ; 5.67×10^{-4} M) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)



9.13 (d, $J = 4.6$, 2 H), 8.99 (s, 2 H), 8.64 (s, 2 H), 8.00 (d, $J = 4.6$ Hz, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm : 150.3, 146.8, 146.5, 137.4, 125.3, 123.9, 121.2; FTIR-ATR (cm^{-1}): 3280, 2990, 1790, 1732, 1698, 1651, 1608, 1583, 1566, 1513, 1435, 1389, 1353, 1307, 1291, 1234, 1224, 1184, 1164, 1102, 1050, 988, 963, 945, 931, 883, 854, 842, 826, 753, 730, 704, 663. Anal Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_2$: C, 63.15; H, 3.79; N, 21.04; Found: C, 63.13; H, 3.82; N, 21.07; LCMS (m/z) Calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_2$: 266.08 [M^+]; Found: 265.32 [M-H^+].

1 + Zn^{2+} Complex

^1H NMR (300 MHz, DMSO-d_6) δ/ppm : 12.60 (s, 2 H, OH), 9.17 (s, 2 H), 9.16 (bs, 2 H), 8.87 (bs, 2 H), 8.37 (d, $J = 5.0$ Hz,

2 H). LCMS (m/z) Calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_2\text{Zn}$: 330.01 [M^+]; Found: 344.98 [$\text{M} + \text{H}_2\text{O} - 4\text{H}^+$].

Results and Discussion

The target compound **1** was synthesized via a two-step reaction sequence, which was started from **2** (Scheme 1). In the first step, compound **2** was readily oxidized with SeO_2 in dioxane-water mixture (4 %, v/v) to give dialdehyde **3** in 60 % yield [39, 40]. In the next step, dialdehyde **3** was treated with hydroxylamine HCl salt in the presence of NEt_3 in refluxing ethanol. Compound **1** was characterized by ^1H and ^{13}C NMR, mass spectral data and elemental analysis, which were proved the structure (see Supporting Information Fig. S1-S3).

Fig. 3 Emission spectra of **1** (3.3×10^{-5} M) in the presence of a variety of ROS and anions (NaClO , H_2O_2 , OH, tBuO, O_2^- , NO_2^- , ClO_4^- , CN^- , Cl^- , Br^- , I^- , F^- , AcO^- , PF_6^- , BF_4^- , H_2PO_4^- , OH^- , IO_3^- , PO_4^{3-} and SO_4^{2-} , 5.67×10^{-4} M) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)

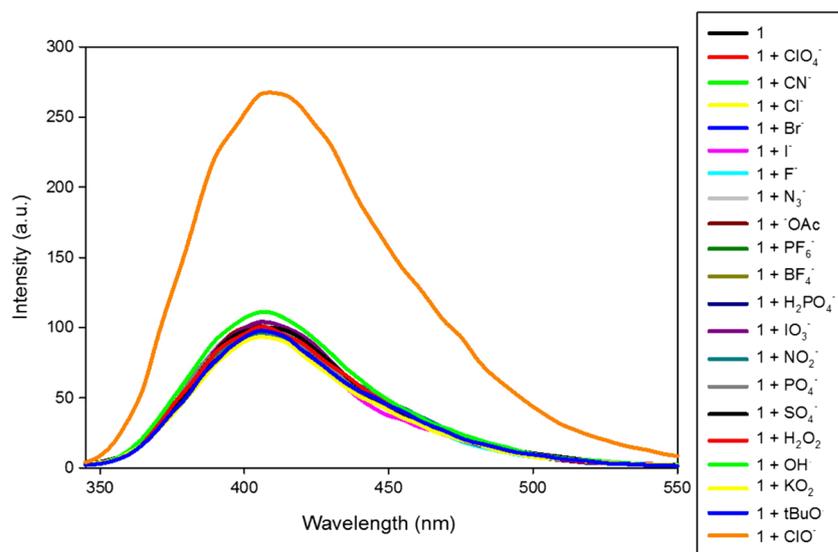


Fig. 4 Relative fluorescence spectral changes for **1** (3.3×10^{-5} M) in the presence of a variety of ROS and anions (NaClO , H_2O_2 , OH^- , tBuO^\cdot , O_2^- , NO_2^- , ClO_4^- , CN^- , Cl^- , Br^- , I^- , F^- , AcO^- , PF_6^- , BF_4^- , H_2PO_4^- , OH^- , IO_3^- , PO_4^{3-} and SO_4^{2-} , 5.67×10^{-4} M) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)

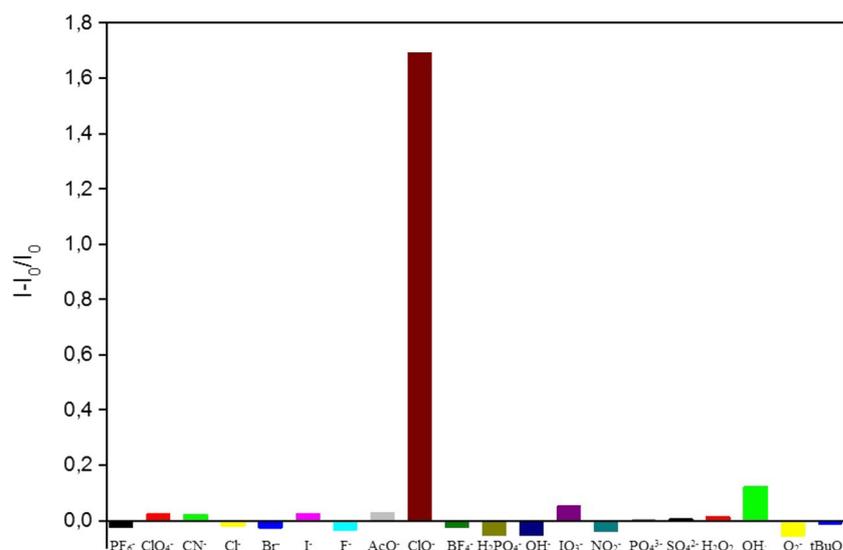
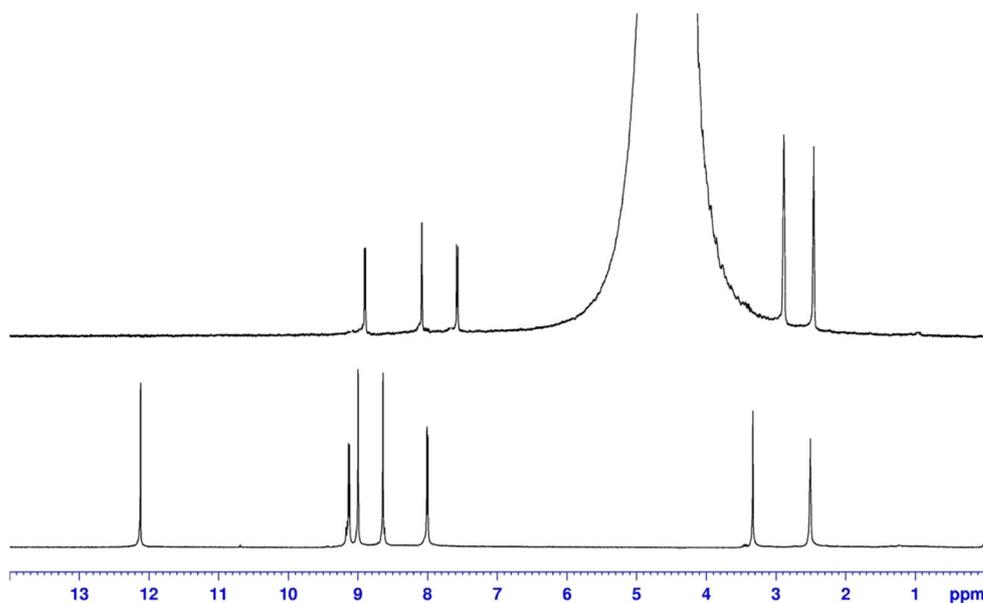
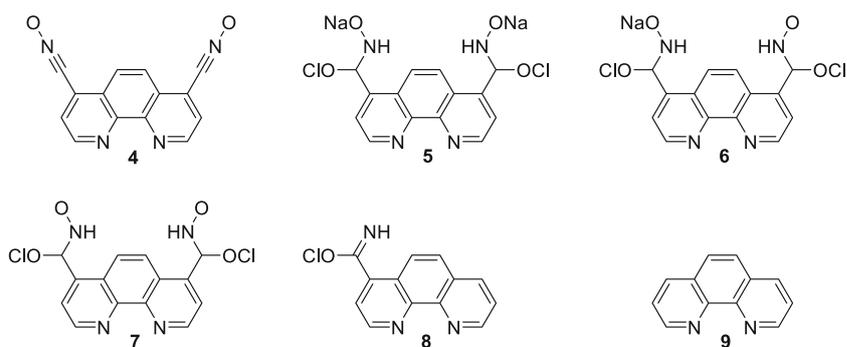


Fig. 5 ^1H NMR spectrum of probe **1** before (down) and after (up) the addition of NaClO in DMSO-d_6 (300 MHz)



Scheme 2 Plausible reaction intermediates **4-9** from mass spectral analysis



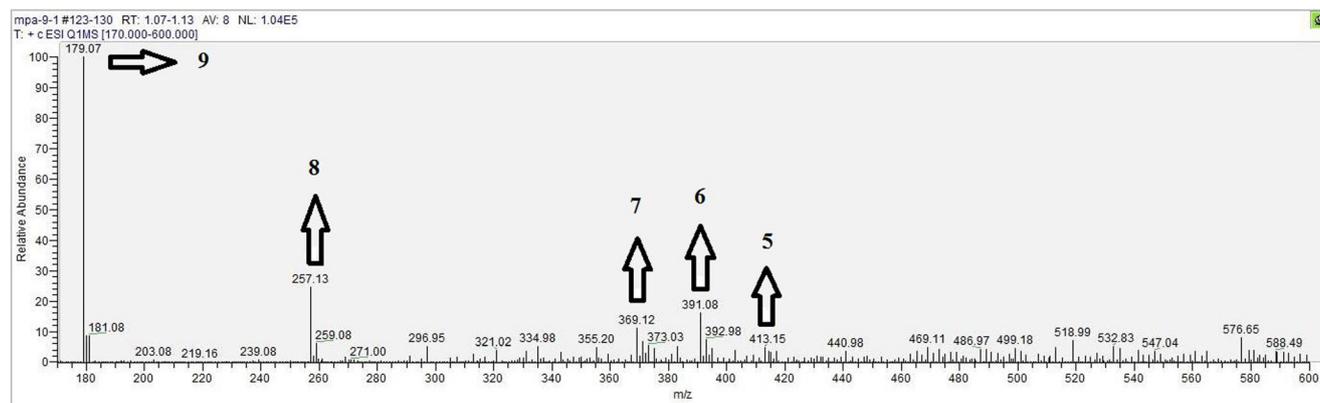
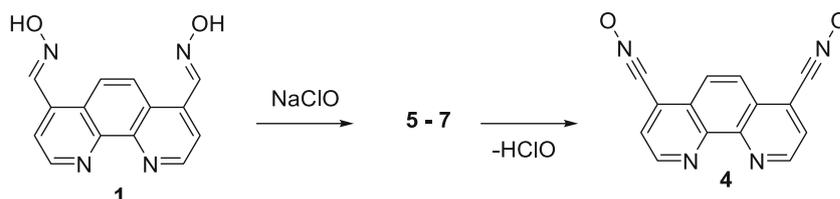


Fig. 6 Mass spectrum (LC MS) of the reaction mixture

Scheme 3 Suggested mechanism of the reaction between compound **1** and sodium hypochlorite



Optical properties of compound **1** (3.3×10^{-5} M) were investigated in 0.1 M Na_2CO_3 - NaHCO_3 buffer containing DMF (pH = 9.0, 30:1 v/v) at room temperature (rt). UV-vis absorption spectrum of **1** consists of a broad band between 250 and 350 nm with a λ_{max} of 290 nm (Fig. S4). pH dependent emission spectral changes of compound **1** were also recorded. It was found that compound **1** was highly stable over a range of pH values from 5 to 9 and the emission intensity of compound **1** is independent of pH between pH 5 and pH 9 (Fig. 1). However, the emission intensity diminished below pH 5 and above pH 9 probably due to protonation and

deprotonation of the compound under acidic and basic conditions, respectively. Figure 1 suggests that compound **1** mainly preserves its structure between pH 5 and pH 9. The emission intensity of compound **1** diminishes below pH 5 probably due to the protonation of the nitrogen atoms of 1,10 phenanthroline ring [36] and/or the hydroxyl group of oxime units. However, deprotonation of the oxime units [45] might take place above pH 9, which also decreases the emission intensity of compound **1**.

Considering the pH dependent emission intensity changes of compound **1** and the pK_a of HOCl, spectrophotometric

Fig. 7 Emission spectrum of probe **1** (3.3×10^{-5} M) in the presence of a variety of metal ions (Al^{3+} , Cu^{2+} , Cd^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+}) (1.0 equiv.) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)

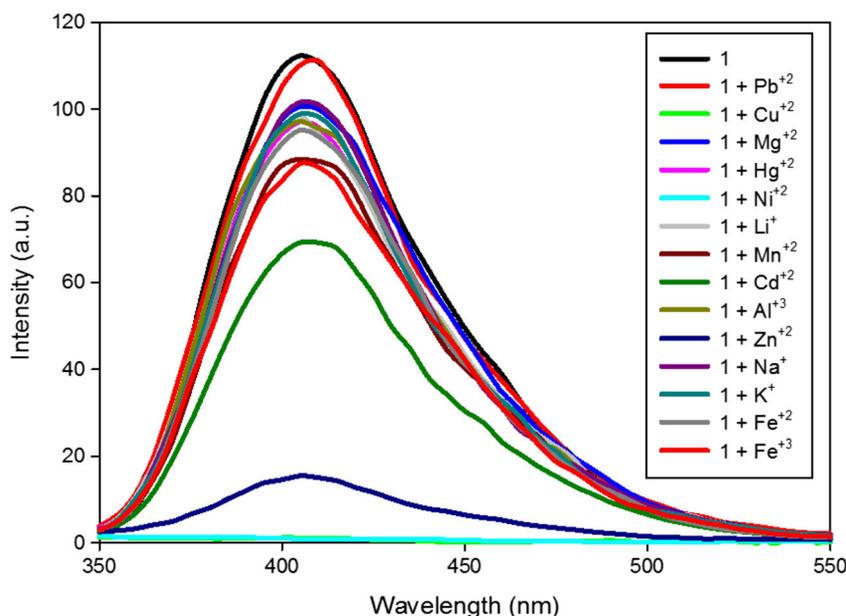
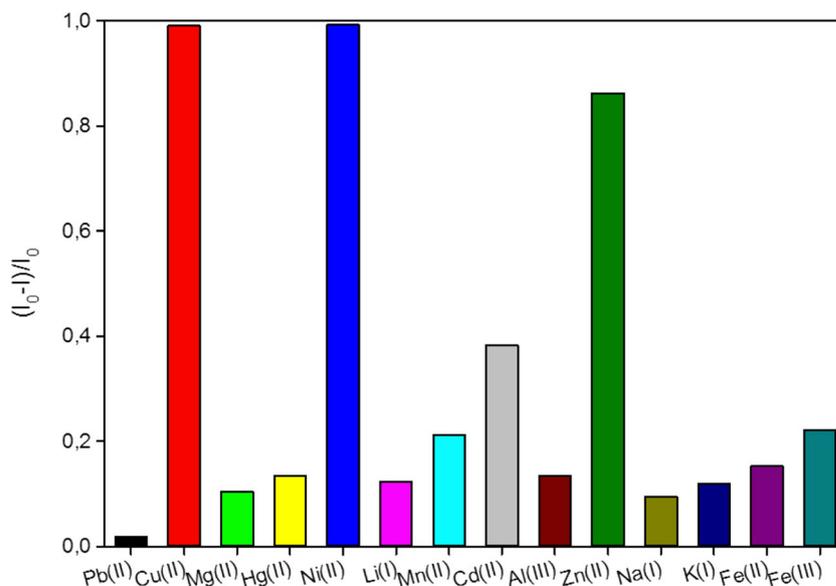


Fig. 8 Relative emission intensity changes for **1** (3.3×10^{-5} M) in the presence of a variety of metal ions (Al^{3+} , Cu^{2+} , Cd^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+}) (1.0 equiv.) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)



titrations of **1** with hypochlorite were carried out in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, rt) at pH = 9.0. It was noted that the addition of NaClO to a solution of **1** resulted a hypsochromic shift of the absorption band around 18 nm (Fig. S4). On the other hand, spectrophotometric titrations of **1** with NaClO resulted in a remarkable enhancement of the emission intensity up to 2.5-fold (Fig. 2).

It was noteworthy that compound **1** (3.3×10^{-5} M) was silent to the presence of the other ROS and anions such as H_2O_2 , OH^- , tBuO^- , O_2^- , NO_2^- , ClO_4^- , CN^- , Cl^- , Br^- , I^- , F^- , AcO^- , PF_6^- , BF_4^- , H_2PO_4^- , OH^- , IO_3^- , PO_4^{3-} and SO_4^{2-} as depicted in Fig. 3 and 4. These results clearly indicated that the fluorogenic response of compound **1** was both highly

selective and sensitive to hypochlorite ions under the given conditions. Importantly, this paves the way of compound **1** as a highly sensitive and selective probe for the detection of hypochlorite ions among the others under the given conditions. The high selectivity and sensitivity of compound **1** to hypochlorite ions can be explained by the selective reaction taking place between oxime and hypochlorite ions. Oximes can be destroyed by a specific reaction promoted by hypochlorite ions under mild conditions [4]. It is reasonable to assume that hypochlorite ions reacts selectively with compound **1** whereas other species do not give any reaction with **1** under the given conditions. The distinct reaction conditions required for deoximation could account for the high selectivity of **1** to hypochlorite ions over other species.

Fig. 9 Emission spectral changes of **1** (3.0×10^{-5} M) in the presence of various amounts of Cd^{2+} ions (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 equiv) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)

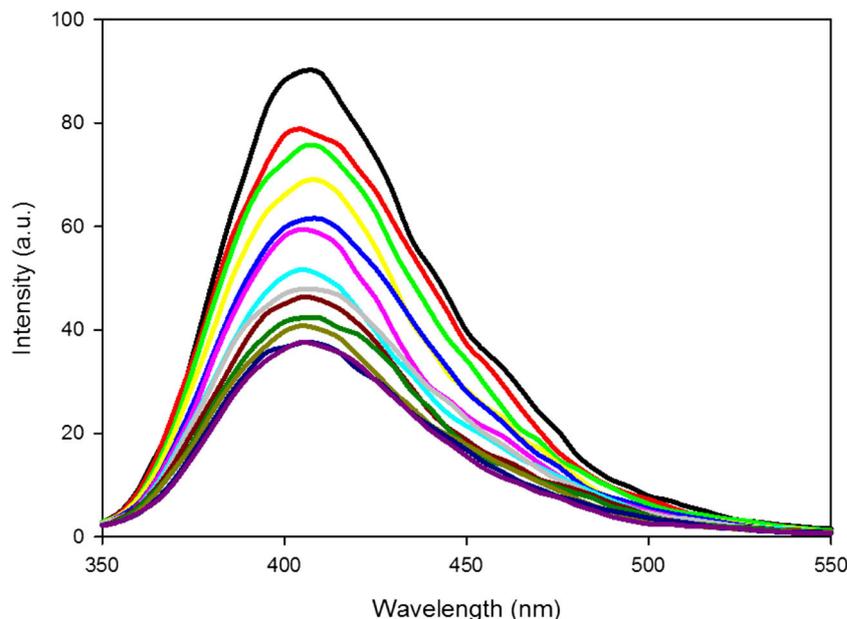
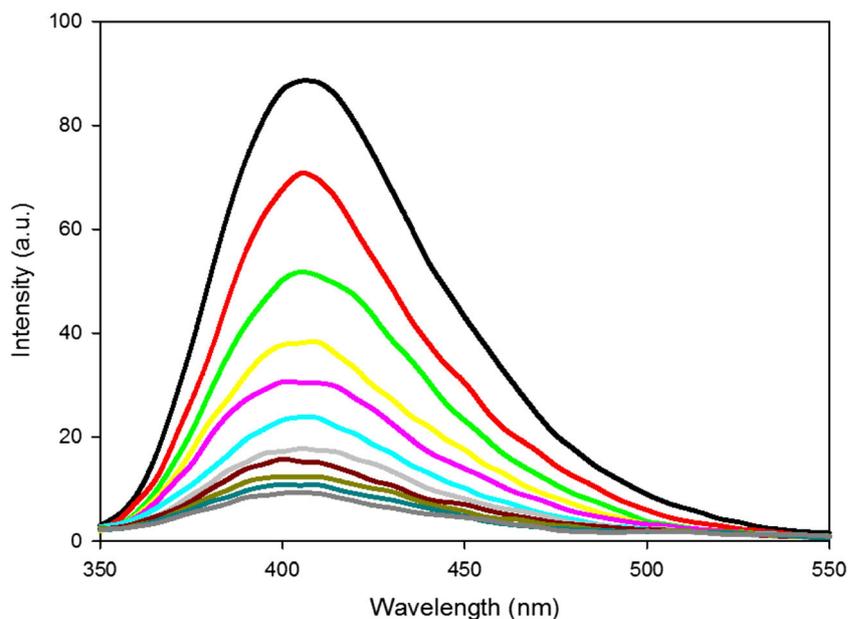


Fig. 10 Emission spectral changes of **1** (3.0×10^{-5} M) in the presence of various amounts of Zn^{2+} ions (0, 0.1, 0.2, 0.3, 0.5, 0.6, 0.7, 0.8, 1.0, 1.5 and 2.0 equiv) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)



The detection limit of probe **1** towards NaClO was calculated to be 5.0×10^{-5} M under these conditions (Fig. S5). Considering the fact that the physiological concentration [2] of NaClO is around 5–200 μM , this novel compound **1** is a promising candidate as a fluorescent probe for the detection of NaClO in aqueous solution.

On the basis of these results, it is reasonable to assume that compound **1** undergoes a chemical transformation in the presence of NaClO through the oxime units in the structure [42–44]. In order to get a deeper understanding of this chemical transformation, ^1H NMR and mass spectral analysis were carried out. ^1H NMR (Fig. 5) analysis of the reaction mixture suggested the formation of nitrile oxide **4** as a plausible

intermediate in this oxidation reaction (Scheme 2). In contrast, mass spectral (Fig. 6) analysis of the reaction mixture did not elicit the presence of **4** under the analysis conditions of LC MS. However, mass spectra (Fig. 6) clearly elucidated the presence of **5–9** as plausible intermediates in the reaction (Scheme 2).

This observation indicated that hypochlorite promoted reaction of compound **1** started with the addition of hypochlorite ions into the double bond of oxime units to give intermediates **5–7**, which probably furnished compound **4** after elimination of HClO (Scheme 3) [44].

Considering the fact that the probe **1** was built on a 1,10-phenanthroline scaffold, metal ion recognition features of **1**

Fig. 11 Emission spectral changes of **1** (3.0×10^{-5} M) in the presence of various amounts of Cu^{2+} ions (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 equiv) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)

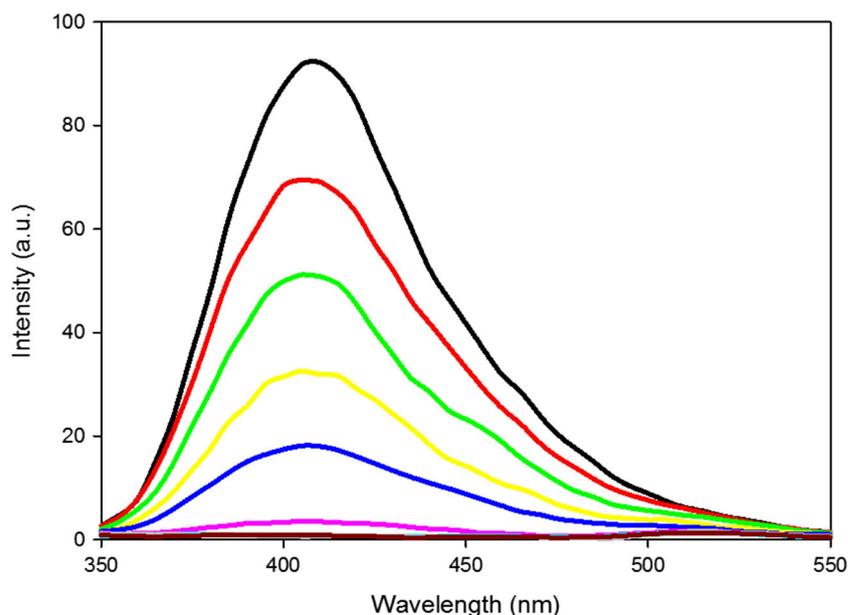
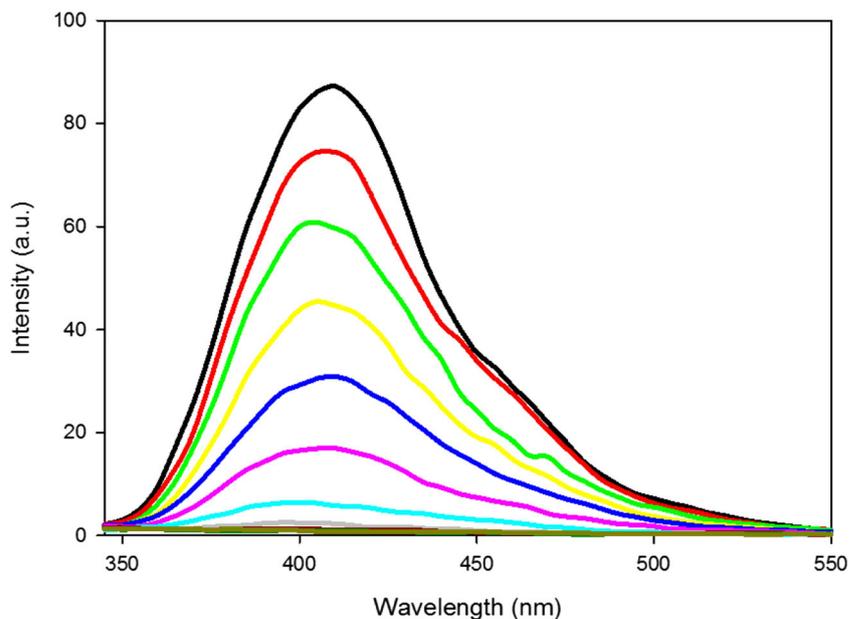


Fig. 12 Emission spectral changes of **1** (3.0×10^{-5} M) in the presence of various amounts of Ni^{2+} ions (0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50 equiv) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt., $\lambda_{\text{exc}} = 290$ nm)



were also investigated. It was found that UV-vis absorption spectra of **1** (3.3×10^{-5} M) induced nominal changes upon addition of various metal ions (Al^{3+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ and Pb^{2+}) (1 equiv) (Fig. S6) in 0.1 M Na_2CO_3 - NaHCO_3 buffer-DMF solution (30:1 v/v, pH = 9.0, rt), albeit Cd^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+} ions caused the formation of new shoulders and/or bands at 358 nm (Fig. S7), 360 nm (Fig. S10), 357 nm (Fig. S13) and 352 nm (Fig. S16) in the absorption, respectively. On the basis of these changes in the absorption spectra, it can be safely concluded that these metal ions are bound to probe **1** probably through the nitrogen atoms of the phenanthroline scaffold. Moreover, such changes in the absorption spectra of probe **1** were allied with the changes observed in the emission intensity as discussed below. The addition of metal ions such as Al^{3+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ and Pb^{2+} did not cause any significant change in the emission spectrum of probe **1** (Fig. 7). However, Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} ions elicit dramatic changes in the emission intensity of probe **1** (Fig. 8). It is well known that 1, 10-phenanthroline scaffold is a good chelating candidate, which can give coordination compounds through the nitrogen ring atoms [36, 46]. It is possible that probe **1** might also interact with the metal ions through the nitrogen atoms. The dramatic changes in the emission profile of probe **1** could easily be realized when the ionic radius of Ni^{2+} (0.69 Å), Cu^{2+} (0.73 Å), Zn^{2+} (0.74 Å) and Cd^{2+} (0.78 Å) were considered. The spectrophotometric results suggested that the interaction of metal ions with **1** mainly dependent on the ionic radius of metal ions [46, 47]. The metal ions that have smaller and/or bigger ionic radius did not cause any significant change in the emission spectrum of probe **1** since they did not interact efficiently with probe **1**.

Spectrophotometric titrations of compound **1** with Cd^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+} ions were given in Fig. 9, 10, 11 and 12, respectively. These results suggested that probe **1** was also responsive to the given metal ions (Cd^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+}). The detection limits [31, 33–35, 39–41] of probe **1** for Cd^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+} metal ions were calculated on the basis of the spectrophotometric titrations, and they were found to be 2.56×10^{-6} M (Fig. S8), 1.09×10^{-6} M (Fig. S11), 1.88×10^{-6} M (Fig. S14) and 1.38×10^{-6} M (Fig. S17), respectively. Moreover, the binding constants (K_a) of probe

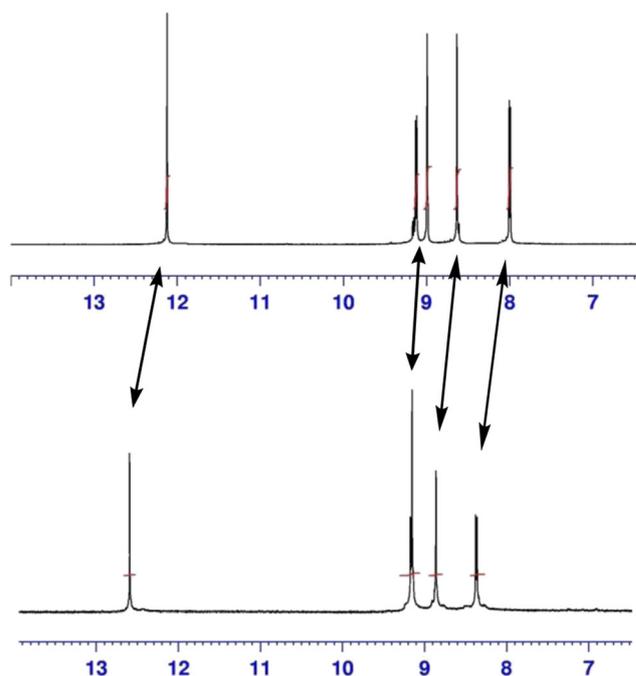


Fig. 13 Partial ^1H NMR spectra of **1** (up) and **1** + Zn^{2+} complex in (DMSO-d_6)

1 with Cd^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+} ions were determined from the emission intensity data following the steady-state fluorometric method in which I_0 referred to the fluorescence intensities of solutions of **1** [31, 33–35, 39–41]. When $I_0/(I - I_0)$ vs. $[\text{M}]^{-1}$ were plotted, K_a values for Cd^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+} metal ions were calculated to be $5.13 \times 10^4 \text{ M}^{-1}$ (Fig. S9), $5.30 \times 10^4 \text{ M}^{-1}$ (Fig. S12), $3.33 \times 10^4 \text{ M}^{-1}$ (Fig. S15), and $1.10 \times 10^4 \text{ M}^{-1}$ (Fig. S18), respectively.

^1H NMR (300 MHz, DMSO-d_6) spectra of probe **1** in the absence and presence of Zn^{2+} ion were depicted in Fig. 13. It can be seen that the proton signals of probe **1** experienced down field shifts around 0.05 ppm and 0.49 ppm in the presence of the metal ion. These result demonstrate that the metal ions are bound to probe **1** probably through the nitrogen atoms of 1,10-phenanthroline scaffold. Furthermore, mass spectral analysis clearly revealed the formation of the complexes between probe **1** and Zn^{2+} , Cd^{2+} , Cu^{2+} and Ni^{2+} ions (Fig. S19–S22).

Conclusions

In summary, a novel compound **1**, which is based on 1,10-phenanthroline scaffold with oxime units, is devised in order to be used as a fluorescent ion probe. It is found that compound **1** undergoes an oxidation reaction with NaClO through its oxime units, which results in a remarkable enhancement of the emission intensity up to 2.5-fold in 0.1 M Na_2CO_3 - NaHCO_3 buffer containing DMF (pH = 9.0, 30:1 v/v, rt). It is noteworthy that the response of probe **1** is highly selective and sensitive to hypochlorite ion. Importantly, this paves the way of selective detection of NaClO with **1** among some other ROS and anions in aqueous solution. In addition to this, probe **1** induces turn-off fluorogenic responses to metal ions such as Zn^{2+} , Cd^{2+} , Ni^{2+} and Cu^{2+} ions under identical conditions. The binding constants (K_a) for Zn^{2+} , Cd^{2+} , Ni^{2+} and Cu^{2+} ions were calculated to be in the order of $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$.

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