Experimental and Theoretical Studies on a Simple S–S-Bridged Dimeric Schiff Base: Selective Chromo-Fluorogenic Chemosensor for Nanomolar Detection of Fe$^{2+}$ & Al$^{3+}$ Ions and Its Varied Applications

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**ABSTRACT:** A simple S–S (disulfide)-bridged dimeric Schiff base probe, L, has been designed, synthesized, and successfully characterized for the specific recognition of Al$^{3+}$ and Fe$^{2+}$ ions as fluorometric and colorimetric “turn-on” responses in a dimethylformamide (DMF)-H$_2$O solvent mixture, respectively. The probe L and each metal ion bind through a 1:1 complex stoichiometry, and the plausible sensing mechanism is proposed based on the inhibition of the photoinduced electron transfer process (PET). The reversible chemosensor L showed high sensitivity toward Al$^{3+}$ and Fe$^{2+}$ ions, which was analyzed by fluorescence and UV–vis spectroscopy techniques up to nanomolar detection limits, 3.826 × 10$^{-9}$ and 1.754 × 10$^{-9}$ M, respectively. These experimental details were advocated by density functional theory (DFT) calculations. The practical utility of the chemosensor L was further demonstrated in electrochemical sensing, in vitro antimicrobial activity, molecular logic gate function, and quantification of the trace amount of Al$^{3+}$ and Fe$^{2+}$ ions in real water samples.

**INTRODUCTION**

The rapid advancement of fluorescent chemosensors for the recognition of cations has captivated notable attention of researchers because of their great selectivity, high responsivity, low detection limit, and naked eye recognition. In addition to their fascinating sensing toward any type of analyte species, they are still the preferable techniques utilized in medical, environmental, and biological applications. Although various scientific methods are available explicitly for the detection of cations, the colorimetric/fluorescent methods are observed as better ones. Besides, the potential of evaluating samples for different targets using a solitary sensor results in quicker analytical performance and probable cost reduction. After oxygen and silicon, the third most abundant metallic element (by weight 8.3%) in the geosphere of the earth is aluminum. Additionally, it exists in many animals, natural waters, and plants as an Al$^{3+}$ ion. As such, the Al$^{3+}$ ion is extensively utilized in different fields, including pharmaceuticals, food packaging, manufacturing industry, and water cleansing. As a consequence, it could enter the human body without much of a stretch through food and water because of the wide usage in different platforms. The World Health Organization (WHO) outlined that the average day-by-day intake of aluminum in human body is roughly 3–10 mg and the bearable admission is assessed to be 7 mg/kg of body weight. The extreme exposure of human body to Al$^{3+}$ ions also causes numerous risky diseases such as the progression of bone disease in children, encephalopathy, Alzheimer’s disease, Meknes disorder, and Parkinson’s disease. Until now, not very many fluorescent chemosensors have been investigated for selective detection of Al$^{3+}$ ions. The poor coordination ability, strong hydration capacity, and lack of spectroscopic characteristics of the Al$^{3+}$ ion have made its screening and detection difficult. Therefore, the advancement of profoundly selective and sensitive fluorescent Al$^{3+}$ sensors having turn-on sort of fluorescence changes is of critical interest for fast and careful discrimination of Al$^{3+}$ ions from other potentially competing metal ions at a very low concentration (nanomolar level) in biological and environmental systems.

Similarly, iron is the most imperative bioactive transition metal involved in living systems and also the most essential trace element for human sustenance. The World Health Organization has reported that every day need of Fe$^{2+}$ for a human body is around 10–50 mg/day. In addition, it plays a critical role in biochemical processes like oxygen transportation, cellular metabolism, and DNA synthesis and is...
also involved in electron transfer.46–49 Accordingly, it is broadly dispersed in environmental and biological materials.50–53 Be that as it may, Fe\textsuperscript{2+} ion deficiency or over-consumption causes various diseases such as low blood pressure, heart diseases, kidney damages, hemochromatosis, anemia, cellular damage, atherosclerosis, cancer, and neurological disorders.54,55 In view of the above reasons, the development of a reliable recognition method for concentration level of Fe\textsuperscript{2+} ion has consistently attracted a lot of consideration in environmental and scientific fields are important yet additionally opportune.56

Conventional signaling mechanisms such as photoinduced electron transfer (PET), CT, ET, and excimer/exciplex, etc. have been evolved/used for the optical recognition of various analytes based on the principal photophysical properties of fluorescent chemosensors.56–59 The photoinduced electron transfer (PET) mechanism has been involved most extensively in fluorescent chemosensors among other conventional mechanisms.56–71 When photoinduced electron transfer (PET) takes place from lone pairs of electronnegative atoms (N, O, and S) of a sensor molecule to highest occupied molecular orbital (HOMO) of excited fluorophore, turn-on fluorescence occurs. This PET process causes the quenching of fluorophore and reviving via the inhibition of PET by guest species.72–74 In continuation of our work toward developing small-molecule-based colorimetric/fluorometric chemosensors, we herein report a simple naphthalene-based Schiff base fluorometric and colorimetric chemosensor for post-transition (Al\textsuperscript{3+}) and transition (Fe\textsuperscript{3+}) metal ions through the photoinduced electron transfer (PET) mechanism. To the best of our knowledge, L is the first naphthalene-based probe having the quality of recognizing both Al\textsuperscript{3+} and Fe\textsuperscript{2+} ions via two different detection modes.

**RESULTS AND DISCUSSION**

**Synthetic Design of Probe L.** Probe L was obtained by a simple single-step Schiff base reaction between cystamine dihydrochloride and 2-hydroxy naphthaldehyde in methanol with good yield (Scheme 1). The probe L was characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR and liquid chromatography–mass spectrometry (LC-MS) analyses (Figures S2–S4). For an effective chemosensor, signaling (fluorophore) and ion-binding (ionophore) units linked with a suitable spacer are highly essential. In our work, we have chosen naphthalene as a fluorophore because of its excellent photophysical properties, high fluorescence quantum yield, better coordination ability, and competitive stability. Disulfide-containing cystamine dihydrochloride was selected as an ionophore as it is an important constituent in numerous metalloproteins and bioenzymes that plays a vital role in their thermal stability and biocatalytic activities. In this context, our work focus on the development of the typical naphthalene-based probe L for selective detection of Al\textsuperscript{3+} and Fe\textsuperscript{2+} by dual mode of detection, fluorogenic and chromogenic, respectively.

**Colorimetric Recognition of Fe\textsuperscript{2+}. Response of L toward Fe\textsuperscript{2+} Ions.** The UV–vis absorption spectrum of probe L in dimethylformamide (DMF)-H\textsubscript{2}O HEPES (1:1 (v/v), 50 mM, pH = 7.4) shows two intense bands with \(\lambda_{\text{max}}\) at 400 and 422 nm (Figure S5). The selective absorption response of probe L (2 × 10\textsuperscript{-5} M) to Fe\textsuperscript{2+} was investigated over various metal ions of environmental and biological significance such as Ag\textsuperscript{+}, Al\textsuperscript{3+}, Ba\textsuperscript{2+}, Bi\textsuperscript{3+}, Ca\textsuperscript{2+}, Cd\textsuperscript{2+}, Ce\textsuperscript{3+}, Co\textsuperscript{2+}, Cr\textsuperscript{3+}, Cu\textsuperscript{2+}, Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Hg\textsuperscript{2+}, K\textsuperscript{+}, La\textsuperscript{3+}, Li\textsuperscript{+}, Mg\textsuperscript{2+}, Mn\textsuperscript{2+}, Na\textsuperscript{+}, Ni\textsuperscript{2+}, Pb\textsuperscript{2+}, Sr\textsuperscript{2+}, Zn\textsuperscript{2+}, and Zr\textsuperscript{4+} in DMF-H\textsubscript{2}O HEPES (1:1 (v/v), 50 mM, pH = 7.4) at \(\lambda_{\text{ex}} = 340\) nm. During the absorption spectral analysis, a distinguishable change in the spectra was observed at 418 nm upon addition of Fe\textsuperscript{2+}. Interestingly, other metal ions produced little or no changes in the absorbance spectra with probe L (Figures 1 and S6). The counter anionic effect of probe L was analyzed with FeSO\textsubscript{4}, Fe(C\textsubscript{6}H\textsubscript{5}O\textsubscript{2})\textsubscript{2}, and Fe(OH)\textsubscript{2} metal salts to discriminate Fe\textsuperscript{2+} ions (Figure S7). Therefore, this result proves that probe L could serve as a potential colorimetric sensor for Fe\textsuperscript{2+} and the enhancement is due to the inhibition of the photoinduced electron transfer process (PET).

**Interference of Other Metal Ions.** To study the realistic utility of probe L, the dual metal cross tainting test was executed, as shown in Figure 2. The competition experiments were carried out by monitoring the changes in the emission intensity before and after adding Fe\textsuperscript{3+} into the L solution with interferants (100 equiv, DMF-H\textsubscript{2}O HEPES solution (1:1 (v/v), 50 mM, pH = 7.4)) at \(\lambda_{\text{ex}} = 340\) nm. During the absorption spectral analysis, a distinguishable change in the spectra was observed at 418 nm upon addition of Fe\textsuperscript{2+}. Interestingly, other metal ions produced little or no changes in the absorbance spectra with probe L (Figures 1 and S6). The counter anionic effect of probe L was analyzed with FeSO\textsubscript{4}, Fe(C\textsubscript{6}H\textsubscript{5}O\textsubscript{2})\textsubscript{2}, and Fe(OH)\textsubscript{2} metal salts to discriminate Fe\textsuperscript{2+} ions (Figure S7). Therefore, this result proves that probe L could serve as a potential colorimetric sensor for Fe\textsuperscript{2+} and the enhancement is due to the inhibition of the photoinduced electron transfer process (PET).

**Effect of pH and Time Response.** To study the practical applicability of probe L as an effective colorimetric sensor, we
examined the effect of pH on response of the absorption spectral bands of probe L to Fe²⁺ at different pH values from 1 to 12 (Figures S8 and S9). For this, the solution was prepared by mixing NaOH and HCl in DMF-H₂O (1:1 v/v). The result shows that there is no significant change in probe L at acidic and basic conditions. However, at neutral conditions, L + Fe²⁺ is quite stable and there is a slight enhancement of absorption above pH 9 and below pH 4. This clearly uncovers the optimal condition of probe L to behave as a better sensor for the analytes under the physiological pH of 7.4. Additionally, a study on the effect of time response was likewise performed to determine the time involved in the binding between probe L and Fe²⁺ by monitoring the changes in the absorption spectrum (DMF-H₂O HEPES (1:1 (v/v), 50 mM, pH = 7.4)). The UV−vis absorbance spectra increased, showed the maximum limit until 2 min, and then remained stable for more than 10 min (Figures S10 and S11). Hence, in a short time, probe L favorably recognizes Fe²⁺ ions and perhaps it can be utilized for sensing of Fe²⁺ ions in biological and environmental real sample analysis.

**Stoichiometry and Binding Mode Studies.** To understand the binding mode between probe L and Fe²⁺, we carried out UV−vis titrations of probe L by continuous addition of various concentrations of Fe²⁺ ions in DMF-H₂O HEPES (1:1 (v/v), 50 mM, pH = 7.4). The free probe L showed no significant changes in absorbance at 418 nm, but the absorbance gradually enhanced with an increase in the concentration of Fe²⁺ ions (0−55 equiv) at 418 nm and got saturated during the addition of 55 equiv of Fe²⁺ ions (Figure 3). This result shows that L/Fe²⁺ has 1:1 binding stoichiometry. The notable peak at m/z S14.04 for the complex [L + Fe²⁺] in the mass spectra further advocates the strong binding between probe L and Fe²⁺ (Figure S20).

To further validate the stoichiometry of L and Fe²⁺, the absorbance changes were used as a function of mole fraction of Fe²⁺ in Job’s plot method and the maximum absorbance was observed at 0.5, as shown in Figure 4, which eventually predicts a 1:1 binding stoichiometry between probe L and Fe²⁺. The detection limit of probe L was determined as 17.54 × 10⁻⁹ M using the formula \(\delta S/S\), where \(\delta\) denotes the standard deviation of the blank signal and \(S\) denotes the slope of the linear calibration plot. Furthermore, the Benesi–Hildebrand nonlinear curve fitting method confirms the above binding stoichiometry (Figure 5). The association constant \((K_a)\) of the L + Fe²⁺ complex is determined by eq 1:

\[
\frac{1}{A - A_0} = \frac{1}{A' - A_0} + \frac{1}{K_a[A' - A_0][Fe²⁺]} \tag{1}
\]

![Figure 2. UV−vis absorption changes of probe L with a mixture of dual metal ions (Fe²⁺ and other stated metal ions) in DMF-H₂O HEPES (1:1 (v/v), 50 mM, pH = 7.4). Error bars indicate the standard deviation among three samples, and the average is taken from them.](image)

![Figure 3. UV−vis absorption spectrum of probe L (2 × 10⁻⁵ M) in DMF-H₂O HEPES solution (1:1 v/v, 50 mM, pH = 7.4) with different concentrations (0−55 equiv, \(\lambda_{ex} = 340\) nm) of Fe²⁺.](image)

![Figure 4. Job’s plot for the complexation of the [L + Fe²⁺] system in DMF-H₂O HEPES solution (1:1 v/v, 50 mM, pH = 7.4). Error bars indicate the standard deviation among three samples, and the average is taken from them.](image)

![Figure 5. Benesi–Hildebrand nonlinear curve fitting plot (absorbance at 418 nm) of probe L assuming 1:1 binding stoichiometry with Fe²⁺. Error bars indicate the standard deviation among three samples, and the average is taken from them.](image)
where $A$ is the UV–vis absorbance in the presence of Fe$^{2+}$ and $A_0$ is the UV–vis absorbance in the absence of Fe$^{2+}$ at 418 nm, respectively. $A'$ is the maximum absorbance of probe $L$ in the presence of excess amount of Fe$^{2+}$. Plotting of $1/A - A_0$ versus $1/[Fe^{2+}]$ showed a linear relationship (Figure 5), which also confirms the 1:1 binding stoichiometry of $L + Fe^{2+}$. The association constant was calculated as $K_a = 2.15 \times 10^2$ M$^{-1}$ for the $L + Fe^{2+}$ complex.

**Reversibility of the Probe $L$.** The chemical reversibility of the molecular recognition process of probe $L$ was performed, which is an important requirement for the detection of specific analytes (Figure 6). Accordingly, by adding ethylenediaminetetraacetic acid (EDTA; 100 equiv) to a mixture of the $L + Fe^{2+}$ complex, the original absorption spectra evolved at 418 nm. Hence, the free probe $L$ can again participate in another $Fe^{2+}$ binding process. This reversible response of probe $L$ with this sort of chelating ability toward $Fe^{2+}$ meant that the probe $L$ in buffered solution is chemically reversible and can be used for selective recognition of $Fe^{2+}$ in biological and environmental real samples up to 10 cycles, as shown in Figures 6b and S12.

**Fluorescent Recognition of Al$^{3+}$. Response of $L$ toward Al$^{3+}$ Ions.** Fluorescence emission highly depends upon the nature of the solvent system. In our present work, the maximum fluorescence emission is observed in DMF as compared to any other solvents including methanol, ethanol, acetonitrile, dimethyl sulfoxide, and tetrahydrofuran. The outcomes showed that probe $L$ could be used to detect the Al$^{3+}$ through fluorescent emission in DMF. The $\lambda_{ex}$ was fixed at 400 nm for cation binding studies based on the absorption spectrum of $L$ and showed $\lambda_{em}$ around 453 nm in DMF-H$_2$O HEPES (1:1 (v/v), 50 mM, pH = 7.4). Afterward, the binding property of probe $L$ with various cations was analyzed by fluorescence spectroscopy upon addition of several cations such as Ag$^+$, Al$^{3+}$, Ba$^{2+}$, Bi$^{3+}$, Ca$^{2+}$, Cd$^{2+}$, Ce$^{3+}$, Co$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Hg$^{2+}$, K$^+$, La$^{3+}$, Li$^{+}$, Mg$^{2+}$, Mn$^{2+}$, Na$^+$, Ni$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, and Zr$^{2+}$ in DMF-H$_2$O HEPES (1:1 (v/v), 50 mM, pH = 7.4) solution. The free probe $L$ showed a weak fluorescence emission at 453 nm. However, upon addition of various metal ions to the solution of $L$, there were no prominent changes in the fluorescence intensity except in the case of Al$^{3+}$ (Figures 7 and S13). The counter anionic effect of probe $L$ was studied with AlCl$_3$ and Al$_2$(SO$_4$)$_3$ metal salts to discriminate Al$^{3+}$ ions (Figure S14). Therefore, the high fluorescence intensity of probe $L$ during the addition of Al$^{3+}$ exhibits a selective recognition over the other cations by a fluorescence turn-on mechanism.

**Interference of Other Cations.** To investigate the effect of interfering cations such as Ag$^+$, Ba$^{2+}$, Bi$^{3+}$, Ca$^{2+}$, Cd$^{2+}$, Ce$^{3+}$, Co$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, K$^+$, La$^{3+}$, Li$^{+}$, Mg$^{2+}$, Mn$^{2+}$, Na$^+$, Ni$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, and Zr$^{2+}$; 100 equiv, $\lambda_{ex} = 400$ nm) in DMF-H$_2$O HEPES solution (1:1 (v/v), 50 mM, pH = 7.4) solution were performed, as shown in Figure 8. The results show that relatively low interference or no interference was observed for the recognition of Al$^{3+}$ in the presence of other potentially competing cations. Therefore, the $L + Al^{3+}$ system shows no changes upon addition of other competitive cations.
cations. Thus, probe L can be used for the specific recognition of Al$^{3+}$ ions in real-sample sensing analysis.

**Effect of pH and Time Response.** To comprehend the practical applicability of probe L, a correlation study has been performed between L and L + Al$^{3+}$ at various pH ranges to fix a particular pH to investigate the photophysical properties in DMF-H$_2$O (1:1 (v/v)) (Figures S15 and S16). Experimental outcomes demonstrate that there is a slight quenching of fluorescence intensity in probe L at both high acidic and basic conditions. Conversely, for L + Al$^{3+}$, at acidic conditions (beneath pH 5), the fluorescence intensity increases with the decreasing pH values, and in the pH range of 6–8 pH, it shows very steady enhancement. Again, it decreases with increasing pH values at basic conditions (above pH 8). These results demonstrate that probe L shows good fluorescence response toward Al$^{3+}$ under the physiological and neutral pH conditions. Therefore, a pH of 7.4 was fixed as the ideal working condition throughout the spectroscopic analyses. Besides, the fluorescence response of probe L to Al$^{3+}$ in DMF-H$_2$O HEPES (1:1 (v/v), 50 mM, pH = 7.4) versus time (in minutes) was additionally analyzed (Figures S17 and S18). The fluorescence emission intensity increased and achieved the maximum level of saturation in 4 min and kept unaltering for further 10 min. From this study, plainly the probe L can recognize the Al$^{3+}$ in a short time frame of 4 min, which could be of potential value for biological and environmental Al$^{3+}$ detection.

**Stoichiometry and Binding Mode Studies.** To get further insight into the limit of detection and binding interaction between Al$^{3+}$ with L, we performed fluorescence titrations of the probe L in the solution containing different concentrations of Al$^{3+}$ ions (DMF-H$_2$O HEPES (1:1 (v/v), 50 mM, pH = 7.4)). The fluorescence intensity increased with the increasing concentration of Al$^{3+}$ (0–80 equiv) with notable changes. The probe L showed no obvious changes in fluorescence emission intensity at 453 nm when it is excited at 400 nm. Stepwise, progressive additions of Al$^{3+}$ to probe L showed a strong emission, increasing the fluorescence enhancement at 453 nm (Figure 9). Furthermore, the spectral changes arrested when 80 equiv of Al$^{3+}$ was added. We proposed that this phenomenon could be ascribed to the formation of a ligand–metal complex inhibiting the photoinduced electron transfer (PET) process. The coordination between probe L and Al$^{3+}$ obstructs the PET mechanism. Nevertheless, it introduces rigidity and consequently reduces the flexibility in probe L. Along these lines, the complexation of Al$^{3+}$ with probe L recovers emission of naphthol and results in a strong fluorescence emission.

The Job plot technique was utilized to find out the stoichiometry between Al$^{3+}$ and probe L. The emission intensity of L + Al$^{3+}$ at 453 nm was plotted as a function of its molar fraction under a constant total concentration. The maximum emission point appeared at a molar fraction of 0.5, which is demonstrative of the 1:1 complexing stoichiometry between probe L and Al$^{3+}$ (Figure 10). The detection limit of probe L was determined as 38.26 × 10$^{-9}$ M. Moreover, the complexing stoichiometry between probe L with Al$^{3+}$ ion was also confirmed using the Benesi–Hildebrand nonlinear curve fitting method. The association constant ($K_a$) of the L + Al$^{3+}$ complex is determined by eq 2 as follows:

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{K_a[I' - I_0]}{[\text{Al}^{3+}]}$$

(2)

Here, I and I$_0$ are the fluorescence intensities at 453 nm in the presence and absence of Al$^{3+}$, respectively; I' is the saturated intensity of probe L in the presence of excess amount of Al$^{3+}$; and [Al$^{3+}$] is the concentration of Al$^{3+}$ ions added. Plotting of 1/($I - I_0$) versus 1/([Al$^{3+}$]) showed a linear relationship (Figure 11), which also strongly supports the 1:1 complexing stoichiometry of L + Al$^{3+}$, and the association constant $K_a$ was calculated to be 3.81 × 10$^3$ M$^{-1}$.

The coordination modes of probe L with Al$^{3+}$ were further studied by the $^1$H NMR titration experiment. Figure 12 shows the spectral changes in chemical shifts of probe L with and without Al$^{3+}$ (0–2 equiv). There is a slight upfield shift in the "–OH proton and "C═N" proton on addition of 1 equiv of Al$^{3+}$. This clearly indicates that the O atom of the phenolic –OH group and the N atom of the C═N (amine) group are coordinated strongly to the Al$^{3+}$ ion. At this point, on increasing the addition of Al$^{3+}$, there was no reasonable spectral change, which confirms the 1:1 binding of L to Al$^{3+}$.

**Reversibility of the Probe L.** For a few useful applications, the recognition and reversibility of the probe L toward Al$^{3+}$ is a vital necessity. The reversibility process was inspected during the addition of EDTA (100 equiv) to the complex mixture of L and Al$^{3+}$ in DMF-H$_2$O HEPES (1:1 (v/v), 50 mM, pH = 7.4). The fluorescence intensity at 453 nm disappeared, as shown in Figure 13a. However, addition of Al$^{3+}$ again to the mixture of L + Al$^{3+}$ containing EDTA attained a considerably enhanced...

![Figure 9. Fluorescence titration spectra of probe L (4 × 10$^{-6}$ M) upon incremental addition of Al$^{3+}$ ions (0–80 equiv, $\lambda_{ex} = 400$ nm) in DMF-H$_2$O HEPES solution (1:1 v/v, 50 mM, pH = 7.4).](https://dx.doi.org/10.1021/acsomega.9b04294)

![Figure 10. Job’s plot for determining the stoichiometry of probe L and Al$^{3+}$ ions in DMF-H$_2$O HEPES solution (1:1 v/v, 50 mM, pH = 7.4; $\lambda_{em} = 400$ nm). Error bars indicate the standard deviation among three samples, and the average is taken from them.](https://dx.doi.org/10.1021/acsomega.9b04294)
fluorescence intensity. As an outcome, the fluorescence intensity changes were recyclable simply through the addition of EDTA. These results showed that EDTA could be a proper chelating reagent, which could completely regenerate the probe $L$ for further repeated usage toward Al$^{3+}$ as an off–on switch chemosensor. The regenerated probe $L$ can be used up to 10 cycles, as shown in Figures 13b and S19. The comparative examination of probe $L$ with recently reported sensors is outlined in Table 1.

Based on the above results, the proposed binding mechanism is illustrated in Scheme 2. The probe $L$ exhibits weak absorbance and low fluorescence emission as a result of the intramolecular photoinduced electron transfer process. Both emission and absorption show strong enhancement upon addition of Al$^{3+}$ and Fe$^{2+}$ ions to the probe $L$, respectively. The high enhancement may be due to the suppression of the photoinduced electron transfer process of the probe $L$ and the rigidity of the complex after binding with respective ions. Job’s plot study, Benesi–Hildebrand nonlinear curve fitting analysis, and the mass spectra confirm the binding stoichiometry of [H]/[G] (1:1) of $L + Al^{3+}$ and $L + Fe^{2+}$.

**Microscopic Studies.** Furthermore, to acquire a better comprehension of the surface topography changes, scanning electron microscopy (SEM) images of $L$, $L + Al^{3+}$, and $L + Fe^{2+}$ were examined, which are displayed in Figure 14a–c. Before and after complexation, there are differences in SEM images, showing a crystal-like structure in probe $L$, which agglomerated upon addition of Al$^{3+}$ and became plain and giving plate-like structure due to the complexation of $L + Fe^{2+}$. The chemical compositions of $L + Al^{3+}$ and $L + Fe^{2+}$ were estimated by energy dispersive X-ray analysis (EDAX) analysis (Figure 14d,e), which directly indicates the existence of carbon (C), oxygen (O), nitrogen (N), sulfur (S), aluminum (Al), and Iron (Fe) elements in the synthesized $L + Al^{3+}$ and $L + Fe^{2+}$ complexes.

**FT-IR Analysis.** FT-IR analysis was performed to get insight into the structure and binding mode of the complexes. In the FT-IR spectra of probe $L$, the characteristic absorption bands at 3002, 1570, and 650 cm$^{-1}$ are due to the OH, C≡N, and S−S stretching groups, respectively. There is a notable shift in the absorption bands of probe $L$ on addition of Al$^{3+}$ ions from 3002, 1570 and 650 to 3010, 1576, and 652 cm$^{-1}$, respectively. In the IR spectra of $L + Fe^{2+}$, stretching bands are shifted to 3043, 1574, and 652 cm$^{-1}$ from the bands of free probe $L$, respectively. These shifts indicate the possible binding of Al$^{3+}$ ions and Fe$^{2+}$ ions with the OH and C≡N groups of probe $L$, respectively (Figure 15).

**Density functional theory (DFT) Studies.** To understand the structure of $L$ and its complexation with Al$^{3+}$ and Fe$^{2+}$, density functional theory and ab initio calculations at the B3LYP/6-311++G** and HF/6-31G* levels of theory were performed, respectively. The optimized geometries of $L + Al^{3+}$ and $L + Fe^{2+}$ complexes at the B3LYP/6-311+G** level of theory are shown in Figure 16a–c. From Figure 16b, it is observed that $L + Al^{3+}$ forms a pentadentate complex, wherein Al$^{3+}$ interacts with nitrogen (Al–N(1), Al–N(2)), oxygen (Al–O(1), Al–O(2)), and sulfur (Al–S(2)) having bond lengths of 1.939, 1.938, 1.942, 1.961, and 2.437 Å, respectively, as shown in Table 2. Similarly, in the case of $L + Fe^{2+}$, the structure forms a pentadentate complex, on interacting with
two nitrogen atoms, two oxygen atoms, and one sulfur atom (Figure 16c). On comparing the bond lengths of the L + Fe^{2+} complex, it was observed that Al−N1, Al−N2, Al−O1, and Al−O2 bond lengths are shorter, indicating that Al^{3+} could have more profound interaction with the probe L than Fe^{2+}. Overall, the interaction of Fe^{2+} and Al^{3+} has a significant effect on the geometry of the probe, as observed from Figure 16. The optimized energy of the probe L is −2061.91 hartrees and that of its complexes L + Al^{3+} and L + Fe^{2+} are −2303.56 and −3325.20 hartrees, respectively. The interaction energies of L + Al^{3+} and L + Fe^{2+} complexes are found to be −33.85 and −19.86 eV, respectively. The results clearly indicate that though Fe^{2+} forms more covalent bonds with the probe L, Al^{3+} seems to have stronger interaction and hence could be the most suitable metal ion to complex with the probe L.

Figure 17 shows the FT-IR spectra of L, L + Al^{3+}, and L + Fe^{2+} structures calculated at the B3LYP/6-311++G** level of theory. The calculated frequencies at the HF/6-31G* and B3LYP/6-311++G** levels of theory are listed in Table 3. For receptor L, three distinctive absorption bands are observed at 472, 1711, and 3788 cm\(^{-1}\) frequencies, which correspond to S−S, C=N, and O−H vibrations, respectively. Upon interaction of Al^{3+}, the bands undergo significant reduction in the frequency, thereby showing a shift toward the red region. Similarly, in the L + Fe^{2+} complex, the absorption band is obtained at 498 cm\(^{-1}\) for the S−S vibration, which is a blue shift from the probe, while C=N and O−H vibrations are red-shifted. The frequency calculated at HF/6-31G* for all of the structures matches well with the B3LYP, as seen from Table 3.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are calculated for the complexes and depicted in Figure 18. For the receptor L, the HOMO and LUMO energies are −6.042 and −1.703 eV, respectively, and the calculated energy gap value is 4.339 eV. Upon complexation of Al^{3+} and Fe^{2+} with the probe L, the energy gap values are found to be 0.101 and 0.100 eV, respectively.
respectively. Comparatively, \(L + \text{Al}^{3+}\) and \(L + \text{Fe}^{2+}\) complexes have an almost smaller energy gap, justifying that they are easily polarizable and more reactive.\(^{85,86}\)

The ionization potential \((I)\) and electron affinity \((A)\) along with various other chemical reactivity descriptors for the probe \(L\) and its complexes are calculated and listed in Table 4. The chemical potentials of \(L\), \(L + \text{Al}^{3+}\), and \(L + \text{Fe}^{2+}\) structures are found to be \(-3.873\), \(-0.479\), and \(-0.370\) eV, respectively. A significantly large value for the \(L + \text{Fe}^{2+}\) complex clearly indicates that it is more stable and hence does not decompose spontaneously.\(^{87}\) The global softness value of the \(L + \text{Fe}^{2+}\) complex is high compared to the \(L + \text{Al}^{3+}\) complex, identifying the former to be more polarized than its counterpart. Other reactivity descriptors further justify the result, making \(L + \text{Fe}^{2+}\) as the more suitable complex than \(L + \text{Al}^{3+}\). The graphical representation of Mulliken atomic charges for the structures is depicted in Figure 19. From the Mulliken data, it is observed that all of the hydrogen atoms have negative charges and most of the carbon atoms have positive charges.

The experimental and theoretical \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of the probe \(L\) are shown in Figure 20. The corresponding chemical shift values are presented in Table 5. The NMR spectra of the probe \(L\) are theoretically calculated by gauge-independent atomic orbitals (GIAOs) with respect to tetramethylsilane (TMS) at the B3LYP/6-311++G** level of theory.
The aromatic proton peaks in the benzene rings are usually observed between 7 and 8 ppm. In this study, the chemical shifts for the benzene ring of protons are experimentally observed to be in the range of 7.21–8.08 ppm. The theoretically calculated chemical shift for the same is found to be between 7.49 and 7.93 ppm and matches well with our experimental result. Experimentally, the chemical shift values of H21 and H19 atoms that belong to the methylene group are 3.98 and 3.17 ppm, respectively. The calculated chemical shifts of C25 and C23 are found to be 54.14 and 49.16 ppm, respectively, and they match well with our experimental results.

The correlation graph between the experimental and theoretical 1H and 13C NMR chemical shifts of the probe L is depicted in Figure 21. The correlation coefficients of 1H and 13C NMR were calculated to be 0.993 and 0.991, and they are in good agreement.

Further time-dependent density functional theory (TD-DFT) calculations using the B3LYP/6-311++G** level were performed for L and L + Fe2+ structures to study their UV absorption characteristics. The simulated absorption spectra of L and L + Fe2+ structures are shown in Figure 22, and the calculated results are listed in Table 6. The UV–visible spectra for the probe L exhibit the maximum absorption peak at 320.06 nm in the UV region \((E = 3.874 \text{ eV and } f = 0.158 \text{ au})\) along with two absorption peaks located at 316.20 and 310.71 nm \((E = 3.921 \text{ eV, } f = 0.088 \text{ au and } E = 3.990 \text{ eV, } f = 0.001 \text{ au})\), respectively. In the case of the L + Fe2+ complex, the strongest absorption peak is featured at 1639.50 nm \(E = 0.756 \text{ eV, } f = 0.001 \text{ au}\), which is red-shifted from the corresponding strongest absorption peak of the probe L. Two additional small peaks are identified at 1274.76 and 863.28 nm \(E = 0.973 \text{ eV, } f = 0.001 \text{ au and } E = 1.436 \text{ eV, } f = 0.001 \text{ au}\) for the complex.

Application Studies. Determination of Al3+ & Fe2+ Ions in Real Water Samples. To demonstrate the practical utility of probe L, we have estimated the most abundant Al3+ and Fe2+ ions in different water samples to find the feasibility of probe L via fluorescence and UV–vis absorption techniques. The samples were carefully filtered using a 0.5 μL membrane and utilized for the sensing studies. Through atomic absorption spectroscopy (AAS analysis), the reading of 0.5–6 ppm was registered for Al3+ and Fe2+ ion concentrations. Two different

![Figure 17. FT-IR spectra of L, L + Al3+, and L + Fe2+ calculated at the B3LYP/6-311++G** level of theory.](https://dx.doi.org/10.1021/acsomega.9b04294)
commercially available water samples were analyzed by this method, all within the Port Blair, Andaman, region (Table 7). The spiked samples were analyzed and confirmed with known standard Al$^{3+}$ and Fe$^{2+}$ ion solutions added to probe L (4 μM). The result indicates that the probe L could be potentially utilized for the recognition of the selected metal ions in real water samples without any interferences of other coexisting metal ions.

Electrochemical Behavior of Probe L with Al$^{3+}$ and Fe$^{2+}$ Ions. Electrochemical sensing execution of probe L toward Al$^{3+}$ and Fe$^{2+}$ ions has been investigated. The cyclic voltammogram (CV) of probe L was estimated in the presence and absence of various cations such as Al$^{3+}$, Fe$^{3+}$, Ni$^{2+}$, and Hg$^{2+}$, respectively. Here, probe L exhibited some incredible changes upon addition of Al$^{3+}$ metal ions in DMF solution. Also, electrochemical oxidation of the first peak of probe L was observed,
which corresponds to the reversible behavior.\textsuperscript{90–93} It might be due to the oxidation of the imine group in which the first oxidation potential observed is $-0.96$ V. As seen in Figure 23a, probe L alone demonstrated the reduction potential ($E_{\text{red}}$) of $-0.96$ V. Conversely, on addition of Al$^{3+}$, the oxidation potential of L + Al$^{3+}$ shifted to $-0.62$ V. Interestingly, on simultaneous addition of Al$^{3+}$ and Fe$^{2+}$, the peak potential again shifted to $-0.57$ V. This notable potential shift ($E_{\text{ox}}$) reveals the bonding attraction between the probe L and Al$^{3+}$ ions. Figure 23b shows that the addition of Ni$^{2+}$ and Hg$^{2+}$ could not cause any shift in the potential of probe L. Meanwhile, under comparative conditions, probe L on investigation with the previously described cations such as Fe$^{2+}$, Ni$^{2+}$, and Hg$^{2+}$ did not show any significant potential shift or changes in the oxidation peak (Figure 23a,b). All of the above outcomes showed that the probe L is highly sensitive

Table 5. Experimental and Theoretical $^1$H and $^{13}$C NMR Isotropic Chemical Shifts (with Respect to TMS) of Probe L

| atoms | theoretical | experimental |
|-------|-------------|--------------|
| H14   | 9.22        | 9.15         |
| H4    | 8.29        | 7.64         |
| H6    | 7.93        | 8.08         |
| H1    | 7.85        | 7.75         |
| H3    | 7.76        | 7.43         |
| H2    | 7.49        | 7.21         |
| H21   | 3.84        | 3.98         |
| H19   | 2.68        | 3.17         |
| C21   | 163.24      | 160.10       |
| C7    | 136.40      | 137.55       |
| C6    | 134.05      | 134.64       |
| C4    | 129.72      | 129.35       |
| C2    | 128.71      | 128.37       |
| C13   | 128.11      | 125.82       |
| C11   | 126.03      | 122.77       |
| C10   | 120.51      | 119.07       |
| C8    | 117.74      | 106.45       |
| C23   | 49.16       | 50.38        |
| C25   | 54.14       | 38.46        |
| S1    | 314.02      | –            |
| N1    | 392.89      | –            |

Figure 20. Theoretical and experimental $^1$H and $^{13}$C NMR isotropic chemical shifts of probe L.

Figure 21. Correlation graph between the experimental and theoretical (B3LYP) $^1$H and $^{13}$C NMR chemical shifts of probe L.

Figure 22. UV–vis absorption spectra of the probe L and complex L + Fe$^{2+}$ in the gas phase.
and selective to Al³⁺ ions than other aggressive cations. From these investigations, the overall order of selectivity is Al³⁺ > Fe²⁺ > Ni²⁺ > Hg²⁺ (Table S1). Finally, the results provide useful information about the electrochemical sensing nature of probe L toward Al³⁺.

**Antimicrobial Activity of Probe L with Al³⁺ and Fe²⁺ Ions.**

The in vitro biological screening effects of the probe L and its complexes L + Al³⁺ and L + Fe²⁺ were examined against potential pathogens including both bacteria and fungi such as *Staphylococcus aureus*, *Escherichia coli*, and *Aspergillus flavus* by the disc diffusion method. Empty sterile discs added with the probe L and complexes L + Al³⁺ and L + Fe²⁺ were incubated carefully. The test solution was spread out, and the growth of the inoculated pathogen was found to be affected during this period. The inhibition zone developed in the plates was measured (Figure S21). The results show that both the complexes have moderate activity against bacterial and fungal species (Table 8). L + Al³⁺ was found to be more active than probe L and probe L + Fe²⁺ in the bacterial species *S. aureus* and *E. coli*. The results on antifungal activity of probe L + Al³⁺ show moderate activity in *A. flavus*, whereas probe L and L + Fe²⁺ show less activity comparatively.

**Molecular Logic Gate Function.** A molecular Boolean logic function was designed based on the reversible fluorescence behavior of the probe L in the presence of Al³⁺/Fe²⁺ and EDTA (Figure 24). The emission intensity (λ<sub>max</sub> = 453 nm) and absorbance (λ<sub>max</sub> = 418 nm) of the probe L were taken as the two outputs of the logic gate function, which were obtained by the addition of Al³⁺/Fe²⁺ and EDTA as the two inputs. In this system, strong fluorescence or absorption was considered as the ON mode (output = 1), while weak fluorescence or absorption was considered as the OFF mode (output = 0). In stage 1, the free probe L was taken as the base constituent and it showed no obvious change in the emission intensity and absorbance with the addition of EDTA (input 2) alone as well as with the addition of equal proportion of Al³⁺/Fe²⁺ and EDTA (inputs 1 and 2). However, the fluorescent emission and absorbance were switched “ON” by the treatment of Al³⁺/Fe²⁺ (input 1) alone. Thus, the presence of Al³⁺/Fe²⁺ was represented through a NOT gate to realize the logic function. Since the simultaneous presence of Al³⁺/Fe²⁺ and EDTA did not produce any significant change in the output of probe L, this combination (L + Al³⁺/Fe²⁺ + EDTA) was taken as the base constituents in stage 2. The results obtained in this stage were found to be identical to those of stage 1. Figure 25b shows the truth table formulated on the basis of the obtained emission intensity and absorbance changes in both the above stages. The input–output relationships clearly show that the molecular interactions of each stage mimic a NOR gate function (with inverted input 1) outlined in Figure 25a.

**CONCLUSIONS**

In conclusion, we have developed an elegant, effective, and economic naphthalene-based probe L as a chemosensor for the detection of Al³⁺ and Fe²⁺ ions by two different spectroscopic systems. Probe L exhibits selective detection of Al³⁺ ions by fluorimetry with a detection limit of 38.26 × 10⁻⁹ M and of Fe²⁺ ions by colorimetry with a detection limit of 17.54 × 10⁻⁹ M. The recognition of Al³⁺ and Fe²⁺ by probe L is free from the interference of Fe²⁺ and Al³⁺ ions, respectively, and also from other potentially competing cations. The probe L can be regenerated from its complexes with a suitable chelating agent such as EDTA and thus showing its reversible nature. The potential applications of probe L are demonstrated in real-water sample analysis, electrochemical sensing, in vitro antimicrobial studies, and molecular logic function. Therefore, probe L might serve toward the development of cation-targeting chemosensors in biological, environmental, and medical monitoring systems. Further tuning of the spacer and fluorophore toward the novel construction of chemosensors is currently underway in our laboratory.

**EXPERIMENTAL SECTION**

**Materials and Instruments.** All chemicals and solvents (of analytical reagent grade and spectroscopic grade) used for synthesis were purchased from a commercial source (Sigma-Aldrich) and used without any purification. The 1H NMR and 13C NMR spectra of the ligand and complex were recorded on Bruker 400 and 100 MHz spectrometers (DMSO-d₆), respectively, with tetramethylsilane (SiMe₄) as an internal standard. The chemical shifts (δ) were expressed in ppm. LC-MS was performed on a LC/MS TOF mass spectrometer. Fourier transform infrared spectrum was recorded on a Shimadzu IRPrestige-21 spectrophotometer. A Jasco V-730 spectrophotometer was used for recording UV–vis absorption spectra at 24 ± 1 °C. JEOL model JSM-6390 was used for examining electron microscope (SEM) studies.

**Table 6. Values of Excitation Energy (E), Oscillator Strength (f), and Wavelength (λ<sub>max</sub>) of L and the L + Fe²⁺ Complex**

| structures | excitation energy E (eV) | oscillator strength f (au) | λ<sub>max</sub> (nm) |
|------------|--------------------------|---------------------------|----------------------|
| L          | 3.8737                   | 0.1575                    | 320.06               |
|            | 3.9211                   | 0.0875                    | 316.20               |
|            | 3.9903                   | 0.0014                    | 310.71               |
| L + Fe²⁺   | 0.7562                   | 0.0007                    | 1639.50              |
|            | 0.9726                   | 0.0014                    | 1274.76              |
|            | 1.4362                   | 0.0005                    | 863.28               |

**Table 7. Detection of Al³⁺ and Fe²⁺ Ions in Water Samples**

| test sample  | concentration of Al³⁺ present in blank (ppm) (AAS) | Al³⁺ ion spiked (ppm) | Al³⁺ ion found (fluorescence) (ppm ± SD) | Concentration of Fe²⁺ present in blank (ppm) | Fe²⁺ ion spiked (ppm) | Fe²⁺ ion found (ppm) (colorimetry) (mean ± SD) |
|--------------|----------------------------------------------------|-----------------------|-----------------------------------------|------------------------------------------|-----------------------|-----------------------------------------------|
| Delanipur    | 0.934                                               | 2                     | 1.98 ± 0.21                             | 1.058                                    | 2                     | 2.06 ± 0.10                                  |
| ground water |                                                    | 4                     | 4.01 ± 0.12                             | 4                                        | 4                     | 4.14 ± 0.14                                  |
|              |                                                    | 6                     | 6.10 ± 0.15                             | 6                                        | 6                     | 5.97 ± 0.14                                  |
| Chakargaon   | 0.861                                               | 2                     | 2.03 ± 0.11                             | 0.536                                    | 2                     | 2.02 ± 0.12                                  |
| ground water |                                                    | 4                     | 3.88 ± 0.17                             | 4                                        | 4                     | 4.0 ± 0.10                                   |
|              |                                                    | 6                     | 5.97 ± 0.14                             | 6                                        | 6                     | 6.03 ± 0.15                                  |

*The results are the mean ± SD (n = 3).*
Fluorescence emission spectral measurements were carried out using a Jasco FP-8200 spectrophotometer at 24 ± 1 °C. A stock solution of probe L (2 × 10⁻³ M) was prepared freshly in the system of DMF–H₂O (1:1 (v/v), 50 mM, pH = 7.4, HEPES buffer) before the experiments for all spectroscopic analyses. The stock solutions of cations for binding studies were prepared using high-purity chloride and nitrate salts of different metals of Ag⁺, Al³⁺, Ba²⁺, Bi³⁺, Ca²⁺, Cd²⁺, Ce³⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, K⁺, La³⁺, Li²⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺, Sr²⁺, Zn²⁺, and Zr²⁺ by dissolving in DMF–H₂O HEPES buffer solution (1:1 (v/v), 50 mM, pH = 7.4). The fluorescence titration of probe L (4 × 10⁻⁶ M) was performed with a series of solutions containing various equivalents of Al³⁺ ions. The colorimetric titration of probe L (2 × 10⁻⁵ M) was carried out with a series of solutions containing various equivalents of Fe²⁺ ions. The electrochemical measurements were performed with a glassy carbon (Alfa Aesar with a purity

Table 8. Antimicrobial Activity of Probe L alone and with Al³⁺ and Fe²⁺ Ions by the Disc Diffusion Method
d

| sample        | S. aureus (mean ± SD) | E. coli (mean ± SD) | A. flavus (mean ± SD) |
|---------------|-----------------------|---------------------|-----------------------|
| control       | 25 ± 0.2              | 22 ± 0.1            | –                     |
| L             | 5 ± 0.4               | 5 ± 0.3             | 25 ± 0.3              |
| L + Al³⁺      | 15 ± 0.1              | 10 ± 0.3            | 36 ± 0.4              |
| L + Fe²⁺      | 2 ± 0.1               | 4 ± 0.2             | 32 ± 0.1              |

“*The results are the mean ± SD (n = 3)."

Fluorescence emission spectral measurements were carried out using a Jasco FP-8200 spectrophotometer at 24 ± 1 °C. A stock solution of probe L (2 × 10⁻³ M) was prepared freshly in the system of DMF–H₂O (1:1 (v/v), 50 mM, pH = 7.4, HEPES buffer) before the experiments for all spectroscopic analyses. The stock solutions of cations for binding studies were prepared using high-purity chloride and nitrate salts of different metals of Ag⁺, Al³⁺, Ba²⁺, Bi³⁺, Ca²⁺, Cd²⁺, Ce³⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, K⁺, La³⁺, Li²⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺, Sr²⁺, Zn²⁺, and Zr²⁺ by dissolving in DMF–H₂O HEPES buffer solution (1:1 (v/v), 50 mM, pH = 7.4). The fluorescence titration of probe L (4 × 10⁻⁶ M) was performed with a series of solutions containing various equivalents of Al³⁺ ions. The colorimetric titration of probe L (2 × 10⁻⁵ M) was carried out with a series of solutions containing various equivalents of Fe²⁺ ions. The electrochemical measurements were performed with a glassy carbon (Alfa Aesar with a purity

Figure 23. Cyclic voltammograms obtained on (a) probe L through Al³⁺, Fe²⁺, and both of Al³⁺ and Fe²⁺ and (b) various metal ions Ni²⁺ and Hg²⁺ (100 equiv) with the 0.1 M TBAP supporting electrolyte in DMF solution.

Figure 24. Fluorescence emission and absorption spectra of probe L and L + Al³⁺/Fe²⁺ (stage 1) and fluorescence emission and absorption spectra of L + Al³⁺/Fe²⁺ with the simultaneous addition of EDTA and Al³⁺/Fe²⁺ (stage 2).
of 99.99% and with an exposed surface area of 0.07 cm²) electrode used as a working electrode and Pt wire as a counter electrode, in which Ag/AgCl with 3.0 M KCl assisted as the reference electrode.

**Synthesis of the Chemosensor (L).** Probe L was obtained by stirring a mixture of cystamine dihydrochloride (0.5 g, 4.40 mmol) and 2-hydroxy naphthaldehyde (1.52 g, 8.80 mmol) in methanol (30 mL). A catalytic amount (5 drops) of TEA was added dropwise into the above mixture and stirred at 70 °C for 2 h. The precipitate formed was filtered, washed with methanol thoroughly, dried at room temperature, and recrystallized in ethanol to give 1-(((E)-(2-(2-(2-((E)-(2-hydroxynaphthalen-1-yl) methylene amino)ethyl)disulfanyl)-ethylimino)methyl)naphthalen-2-ol L as a brown microcrystalline solid. Yield: 85% mp: 89 °C. 1H NMR (400 MHz, DMSO, ppm): δ 14.11−14.09 (d, J = 8.8 Hz, 1H), δ 9.15−9.13 (d, J = 9.6 Hz, 1H), δ 8.08−8.06 (d, J = 8.4 Hz, 1H), δ 7.75−7.72 (d, J = 9.6 Hz, 1H), δ 7.64−7.63 (d, J = 7.6 Hz, 1H), δ 3.98−3.97 (d, J = 4.8 Hz, 2H), δ 3.17−3.14 (t, J = 13.2 Hz, 2H). 13C NMR (100 MHz, DMSO, ppm): δ177.03, 160.10, 137.55, 134.64, 129.35, 128.37, 125.82, 122.77, 119.07, 106.45, 50.38, 38.46. Elemental analysis: C26H24N2O2S2; calcd.: C, 67.80; H, 5.25; N, 6.08; found: C, 67.76; H, 5.24; N, 6.02. LC-MS calcd. for C26H24N2O2S2: [M+] 460; found: [M+ +H]+ 461.

**Computational Details.** The geometries of L, L + Al³⁺, and L + Fe²⁺ structures were fully optimized by density functional theory (DFT) and ab initio using Becke’s three-level parameter Lee−Yang−Parr (B3LYP)75,76 and Hartee Fock (HF)77 levels along with 6-311++G** and 6-31G* basis sets, respectively. Vibrational frequency analysis was performed for all of the structures, confirming them to occupy the local minima. The interaction energies of all of the complexes were calculated as the difference between the total energy of the complex and the sum of isolated fragments, and their results were corrected for the basis set superposition error (BSSE) by the counterpoise correction method of Boys and Bernardi, in eq 3, as follows.78

\[
\Delta E = E_{AB} - (E_A + E_B) + \text{BSSE}
\]

where \(E_{AB}\) is the total energy of the complex and \(E_A\) and \(E_B\) are the energies of their constituent monomers or fragments. HOMO−LUMO energies and molecular electrostatic potential (MEP) analysis were performed at the B3LYP/6-311++G** level of theory to find the reactive sites of electrophilic and nucleophilic reactions.79 All of the theoretical calculations and the molecular representations are done using the Gaussian 09 program package80 and chemcraft software,81 respectively.

**Electrochemical Studies.** BioLogic SP-150 potentiostats, (France) were employed for the electrochemical investigation. All examinations were completed in an electrochemical cell (10 mL) with the conventional three-electrode setup at room temperature. In the electrochemical measurements, the GC electrode used as a working electrode and Pt wire as a counter electrode, in which Ag/AgCl with 3.0 M KCl assisted as a...
reference electrode. Likewise, all of the electrochemical experiments were done in 2 × 10⁻⁵ M probe L with a 0.1 M "TBAP supporting electrolyte. In addition, all of the electrochemical studies were carried out in a N₂ atmosphere. The cyclic voltammogram was obtained in the potential range from −1.5 to 0.5 V at a sweep rate of 0.05 V s⁻¹. Before each estimation, the electrode was polished with emery paper.

**In Vitro Antimicrobial Activity.** The antibacterial activities of probe L and its complexes were performed against the bacterial species *S. aureus* and *E. coli* by the disc diffusion method. The standard antibacterial agents used in this study were kanamycin and chloramphenicol. Nutrient agar medium was used for the growth of test organisms in Petri plates. The compounds were dissolved in DMSO and soaked in Whatman’s no. 3 filter paper disc of 5 mm diameter and 1 mm thickness. Each sterile disc was incorporated individually with prepared compounds. Precautions were taken to prevent the flow of the compounds from the discs to the outer surface. The prepared compounds were applied in small quantities on discs, the lids were kept in a laminar suspension. To allow any excess surface moisture to be equally with a swab dipped in the standard inoculum for fungal growth. Subsequently, the zone of inhibition was recorded in mm.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04294.

- UV-vis, pH, time response, NMR, mass spectrum, antimicrobial activity, and electrochemical sensing studies of probe L and complexes L + Al³⁺ and L + Fe³⁺, including colorimetric metal selectivity bar graph; counter anion effect on colorimetric metal selectivity; colorimetric graphs of pH effect, time effect, and EDTA effect; and fluorometric graphs (PDF)

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**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

EDTA, ethylenediaminetetraacetic acid; DFT, density functional theory; DMF, dimethylformamide; EDAX, energy dispersive analysis of X-rays; HEPES, 4-(2-hydroxyethyl)-1-piperazinethanesulfonic acid; DMSO, dimethyl sulfoxide; NMR, nuclear magnetic resonance; DNA, deoxyribonucleic acid

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