Research Article

Schiff-Based Fluorescent-ON Sensor L Synthesis and Its Application for Selective Determination of Cerium in Aqueous Media

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Received 29 December 2019; Revised 15 March 2020; Accepted 28 March 2020; Published 24 April 2020

Academic Editor: Giuseppe Quero

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In the present study, a fluorescent sensor L for sensing of Ce^{3+} ion was designed and characterized by XRD, ¹HNMR, and FTIR. Its fluorescence behavior towards metal ion was examined by fluorescence spectroscopy. Chelation-enhanced fluorescence was shown by the sensor L upon interaction with Ce^{3+} ion. This fluorescent sensor exhibits high sensitivity and selectivity towards Ce^{3+} ion in acetonitrile solution, forming 2 : 1 (L : M) complex as determined by Job's plot. Association constant was found to be $1 \times 10^7 M^{-1}$ estimated from the Benesi-Hildebrand plot. No significant interference was observed in the presence of other studied alkali, alkaline, and transition metal ions. A rapid response was observed when employed for the determination of Ce^{3+} ion in spiked water samples with a limit of detection equal to $3.4 \times 10^{-8} M$.

1. Introduction

Heavy metal contamination of water bodies is a severe concern of the modern era as it badly affects the natural environment and living beings [1, 2]. Even at a relatively low level of exposures, they are neurotoxic and carcinogenic [3]. Heavy metals are added to water sources due to industrial and anthropogenic activities [4]. Among the rare earth metal cations, cerium (being a heavy metal) is widely distributed in the earth crust. It has a variety of industrial applications in metallurgy, luminescence, microelectronics, agriculture, magnetism, nuclear energy, glass, and ceramics [5]. Cerium can also be found in fluorescent lamps, coloured televisions, arc lamps, and energy-saving lamps. Due to this wide range of usage, cerium concentration is gradually increasing in soils and water bodies. Cerium can cause severe systemic disorders in aquatic animal bodies including damage to the nervous system, reproduction system, and cell membranes.

It also causes health problems in human especially in a working environment, e.g., lung embolisms, damage to the liver during long-term exposure, endomyocardial fibrosis, and dendriform pulmonary ossification [6, 7]. It also affects human metabolism, blood pressure, appetite, lowering cholesterol level, and risk of blood coagulation [8, 9]. Liu et al. developed thiophene-containing bis-pyridyl-bis-amide complexes having a good coordination ability for heavy metal ions, high stability in acids, and bases [10].

A number of techniques are in use to determine cerium in water samples like electrothermal atomization atomic absorption spectroscopy [11], inductively coupled plasma mass spectroscopy [12], and high-performance liquid chromatography. However, applicability of all these methods is a question mark due to expensive instrumentation, slow response time, lack of sensitivity/selectivity, and having limited portability [11]. In recent years, fluorescence technology for probing various environmental and biologically

FIGURE 1: Chemical structure and synthesis of sensor L [1-((pyrimidine-4-ylimino)methyl)naphthalene-2-ol].

important analytes has become a powerful tool because of its rapid response, low cost, real-time monitoring, easy operation, high sensitivity, simplicity, potential for portability, and noninvasive properties [13].

Schiff base containing an azomethine group is the compound synthesized by condensation of carbonyl compounds with primary amines. Due to their structure flexibility and strong coordination capabilities, they are extensively used in the field of coordination chemistry. They coordinate through the nitrogen atom of the azomethine group and the oxygen atom of the deprotonated phenolic group [14]. Due to their multiple biological activities such as antibacterial, antitumor, insecticidal, anticancer, anticonvulsant, anti-inflammatory, and cytotoxicity, as prodrugs, in the strengthening of immune response against cancer, in HIV, and in leukemia, Schiff bases have been studied intensively over the past few decades [15]. They are also widely used in electrochemical and optical sensors [16]. The design of fluorescent sensors for the detection of heavy metal cations is a hot research subject that is under investigation these days. Only few sensors have been reported for the detection of lanthanide metal ions.

In the present research work, a Schiff base fluorescent material: [1-((pyrimidine-4-ylimino)methyl)-naphthalene-2-ol] (sensor L), has been designed for the selective determination of cerium in water. Sensor L has naphthalene entity as the signalling site while imine and hydroxyl as the binding moieties. Sensor L was fluorescently silent in the absence of cerium but upon coordination with target analyte exhibited a significant chelation-enhanced fluorescence effect at λ_{em} 351 nm.

2. Experimental

All experiments were performed in open air using analytical grade reagents, CH_3CN solvent, and distilled water. The chemical reagents (HCl, NaOH, CH_3CN , CH_3COOH , and DMSO) and other solvents (like ethyl acetate, n-hexane, and nitrate salt of lead, barium, cadmium, potassium, cerium, and mercury; sulphate salts of copper, magnesium, zinc, and manganese; and chloride salts of sodium, nickel, and arsenic, 2-hydroxy-1-naphthaldehyde, and 2-aminopyrimidine) were from Sigma-Aldrich, Germany. For the determination of melting point, Stuart-SMP 10 was used. FTIR spectrum of sensor L was obtained using Prestige 21 Shimadzu Japan spectrophotometer. X-ray diffraction data was collected on

a Bruker kappa APEXIICCD diffractometer. Refinements were carried out using full-matrix least squares techniques on F2 using the program SHELXL-97. UV-vis spectra were taken using a UV-vis 1800 spectrophotometer (Shimadzu, Japan). The $^1\text{H-NMR}$ of the sensor molecule was measured with the help of a JEOL 400 MHz spectrometer using deuterated DMSO as the solvent. The chemical shift of protons is given with reference to residual protons of the deuterated solvents (ppm) = $2.50 \pm .01$. Fluorescence measurements were carried out using an RF-5301PC Spectrophotofluorometer (Shimadzu, Japan).

3. Synthesis of [1-((Pyrimidine-4-ylimino)methyl)-naphthalene-2-ol]

The [1-((pyrimidine-4-ylimino)methyl)-naphthalene-2-ol] referred as sensor L was synthesized by adopting the literature procedure [17]. To a methanolic solution of 2-hydroxy-1-naphthaldehyde (10 mmol, 0.95 g) 3 drops of acetic acid were added to deprotonate it. An equimolar amount of 2-aminopyrimidine (10 mmol, 1.72 g) was then added dropwise over a period of 10 min followed by reflux at 80°C with vigorous stirring for a period of 14 h. Upon completion of the reaction, a light yellow product was formed. Reaction was continuously monitored by thin layer chromatographic (TLC) technique, using an appropriate solvent system, n-hexane : ethyl acetate (6 : 4), and the spots were recognized with the help of iodine chamber. After reaction completion, the product obtained was filtered, washed with excess of ethanol, dried, and recrystallized from hexane with 82% yield, having a melting point of $94\text{--}96^\circ\text{C}$ (uncorrected). The IR (KBr, cm^{-1}): $\nu_{\text{C-OH}}$ 1298, 1207; $\nu_{\text{C=N}}$, 1616, ν aromatic C=C, 1494, 1436; ν aromatic-C-H, 3036. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ ppm = 14.53 (br, 1H, HO), 10.81 (s, 1H, N=CH), 9.56, 9.53, 8.94, 8.92-6.52 (m, 9H, Aromatic without assignment). The structure and synthesis of sensor L are given in Figure 1.

4. Solution Preparation for Spectroscopic Measurement

Sensor L stock solution was prepared in acetonitrile as it was not soluble in water. Metal ion stock solutions were prepared in distilled water using nitrate salt of lead, barium, cadmium, potassium, cerium, and mercury; sulphate salts of copper,

TABLE 1: FTIR frequencies for sensor L.

IR band (C=N) (cm^{-1})	IR band (C-OH) (cm^{-1})	IR band Ar C-H (cm^{-1})	IR band Ar C=C (cm^{-1})	IR band aliphatic C-O (cm^{-1})
1612	1294,1210	3036	1491,1436	1136,1035

magnesium, zinc, and manganese; and chloride salts of sodium, nickel, and arsenic. Working solutions were prepared from stock solution by appropriate dilution. UV-visible and fluorescence spectra of sensor L were recorded in acetonitrile/water mixture (2 : 8). For spectroscopic analysis each time a fresh test sample was prepared by taking 7 mL of sensor L and 3 mL of metal ions in a beaker, equilibrated at room temperature. The pH of the test sample was adjusted using NaOH and HCl. Fluorescence analysis was performed with a slit width of 10 nm using quartz cuvettes of 1 cm path length.

5. UV-Visible Analysis

Owing to the weak water solubility of sensor L ($5\ \mu\text{M}$), the spectra were taken in acetonitrile/water (2 : 8) mixture. The solution of cerium was prepared in the range 2-20 μM . Test solution containing a fixed amount of sensor L while increasing concentration of cerium was prepared, and spectra were recorded in the range 200-800 nm.

6. Metal Ion Binding Study by Fluorescence Titration

Sensor L ($5\ \mu\text{M}$) was added with varied metal ion concentrations (up to 200 μM), and fluorescence spectra were recorded in the range 200-800 nm at λ_{em} 351 nm. Among the examined metal ions, only cerium was able to enhance the fluorescence of sensor L. Job's plot experiment was conducted by plotting the fluorescence intensity at the y -axis to determine the binding stoichiometry between sensor L and cerium. Association constants of sensor L-cerium complex were determined by the Benesi-Hildebrand equation.

7. Results and Discussions

7.1. IR Data. For the identification of functional groups present in the synthesized sensor L, FTIR spectroscopic analysis was performed. The peak details are presented in Table 1. The characteristic bands assigned to different functional groups were based on comparison with the available literature. The appearance of characteristic stretching band (C=N) in sensor L at $1612\ \text{cm}^{-1}$ and disappearance of aldehyde carbonyl (C=O) peak in the region of $1700\ \text{cm}^{-1}$ confirm the formation of sensor L (Figure 1S). Strong bands at $3,036\ \text{cm}^{-1}$ were assigned to the aromatic C-H group. The spectrum displayed absorption bands at 1491 and $1436\ \text{cm}^{-1}$ corresponding to the aromatic C=C group while at 1294 and $1210\ \text{cm}^{-1}$ representing phenolic (-OH) stretching vibration. In addition to the abovementioned IR band, it also exhibited bands at 1136 and $1035\ \text{cm}^{-1}$ for the aliphatic -C-O group [18].

FIGURE 2: Molecular structure of sensor L with partial numbering scheme; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level.

7.2. Characterization by $^1\text{H-NMR}$. The $^1\text{H-NMR}$ spectrum of sensor L shows a number of characteristic peaks as expected for the proposed structure of the compound, sensor L. There are two characteristic peaks to elucidate the structure: one is azomethine (HC=N-) group which appears at 10.81 and the other one is proton at δ 14.53 as a result of zwitterion formation between OH protons with imine nitrogen which is a clear indication of the product formation (Figure 2S). Aromatic protons of other moieties appear as overlapping multiplets and cannot be precisely assigned. The data set obtained for sensor L is well comparable with the reported data for structurally analogous compounds [19, 20].

7.3. Characterization by X-Ray Diffraction. A single crystal of sensor L was grown from slow evaporation of its mother liquor. Single crystal X-ray diffraction analysis was used for the confirmation of solid-state structure of sensor L (CCDC No. 1987815). For data collection, ω scan and multiscan corrections were applied. Crystallographic analyses were carried out with the Bruker kappa APEXII CCD diffractometer, with a graphite monochromator (Mo-K α radiation) ($\lambda = 0.71073\ \text{\AA}$) at ambient temperature. The crystal solution and refinements of sensor L were handled with SHELXL-97 [21] and publ CIF [22]. Full-matrix least squares techniques were used for final refinement on F 2 . Sensor L crystallizes in an orthorhombic system with the space group $P2_12_12_1$. The molecular view of sensor L with a partial numbering scheme is shown in Figure 2. The crystallographic data pertaining to crystal structure solution and refinement are given in Table 2. In the molecule, the naphthalene ring is regarded as the principal ring system. All atoms and ring system of the molecule are coplanar with negligible deviation. The characteristic bond lengths are C10-C11 1.381, C11-N11.340,

TABLE 2: Crystal parameters and structure refinement of sensor L.

Crystal parameter	Values
Chemical formula	C ₁₅ H ₁₁ N ₃ O
Formula weight	249.27
Space group	P2 ₁ 2 ₁ 2 ₁
Theta (max)	0.639
Crystal system	Orthorhombic
a (Å)	5.9125 (4)
b, c (Å)	12.5465 (9), 7.4635 (18)
μ (mm ⁻¹)	0.09
Z	4
$R[F^2 > 2\sigma(F^2)]$	0.043
$wR(F^2)$	0.120
Temperature (K)	296
Volume (Å ³)	1224.20
c (Å)	16.5028 (13)
No. of reflection	3560
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	13509, 3560, 1502
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.056, 0.161, 0.93
No. of restraints	2
Crystal size (mm)	(0.43 × 0.32 × 0.27)
$\Delta\rho$ max, $\Delta\rho$ min (e Å ⁻³)	0.24, -0.26
Radiation type	Mo-K α
Crystal colour	Yellow

N1-C12 1.397, and C1-O1 1.266 Å. Bond angles C12-N1-C11 124.51, N1-C11-C10 124.40, and O1-C1-C10 122.44° are well comparable with literature reports for structurally similar molecules [23]. The structure of sensor L indicates intramolecular hydrogen bonding as shown in Figure 3, since the molecule (L) contains electron-rich centres such as N, O, and π -bonds, which are involved in stabilizing the supramolecular structure of the compound. The O1 of each molecule interacts with CH function of neighbouring naphthalene moiety (separation distance is O1-C5 3.419 Å). C1 of the molecule is considerably polar, and it interacts with N3 of the neighbouring pyrimidine moiety with a separation distance of 3.247 Å. Similarly, pi-pi interaction between C2 and C11 can also be observed with a distance of 3.357 Å. These interactions collectively extend the structure in a 3D fashion (Figure 3).

7.4. UV-vis Absorption Spectroscopic Analysis. The UV-visible spectrum of sensor L showed characteristic main absorption band in the range 250–390 nm with a $\lambda_{\max}$ of 320 nm (Figure 3S). Upon addition of Ce³⁺ to sensor L, $\lambda_{\max}$ was shifted to 330 nm. The red shift of $\lambda_{\max}$ is an indication of coordination involving the hydroxyl and imine as a receptor and Ce³⁺ as an analyte. Upon addition of different concentrations of Ce³⁺ to sensor L solution, a marked enhancement in absorbance at 330 nm was noted. For absorbance analysis, test samples of sensor L, 5 μ M, and different concentrations of Ce³⁺ ions were prepared.

All the operations were performed at room temperature. The correlation coefficient value ($R^2 = 0.989$; Figure 4S) obtained was in good agreement with that reported in the literature [24].

7.5. Fluorescence Studies. The fluorescence spectrum of sensor L was taken in the range of 200–800 nm with varying excitation wavelengths from 220 to 400 nm. The maximum fluorescence intensity for sensor L was observed at 351 nm as excitation wavelength as shown in Figure 5S.

7.6. Preliminary Study. The response of sensor L to fluorescence and UV radiation were evaluated through a titration method, and a good linear response has been observed (Figures 6S and 7S). Fluorescence response of sensor L (5 μ M) was examined in CH₃CN/H₂O mixture (2:8) towards different metal ions (200 μ M). First, the fluorescence emission of sensor L was studied in the range 250–800 nm with an excitation at 290 nm and an emission at 351 nm. Due to internal charge transfer phenomenon, very weak emission intensity was displayed at 351 nm by the free sensor L. To investigate metal ions sensing ability of sensor L, metal ions were separately added to the sensor L solution. The mixtures were equilibrated for 3 min at room temperature and transferred separately into cuvette, and the fluorescence of each test solution was monitored at 351 nm. Among the metal ions studied, only Ce³⁺ was able to enhance the fluorescence of sensor L (Figure 8S) which was due to combined effects of chelation, C=N isomerization, and intramolecular charge transfer mechanism [24].

7.7. Effect of Time. For fluorescent sensor, response time is one of the most important parameters to be measured. For this purpose, kinetic studies of fluorescent sensor L (10 μ M) separately and in the presence of Ce³⁺ (3 μ M) were studied from fluorescence spectra by measuring fluorescence emission intensities at different time intervals. The time range for this study was from 1 to 10 min. At 351 nm in the absence of Ce³⁺, no change in the fluorescence intensity occurred showing the stability of subject sensor L in the given conditions. In fluoremetric analysis, longer response time is undesired. The sensor L displayed instantaneous enhancement at 351 nm upon the addition of Ce³⁺ solution, indicating fast response of sensor L with Ce³⁺ (Figure 9S). The response time was less than 40 seconds even for high concentration of Ce³⁺. These results show that the determination of Ce³⁺ can be done immediately without any delay upon Ce³⁺ addition and sensor L is highly detectable in real samples with fast response (in terms of time).

7.8. Effect of Solvents. Changes in the fluorescence emission intensities of sensor L upon formation of complex with Ce³⁺ were investigated in a number of solvents including dimethyl sulfoxide (DMSO), methanol/water (2/8 v/v), N,N-dimethylformamide (DMF), acetone, chloroform, hexane, toluene, ethanol/water (2/8 v/v), and dichloromethane (Figure 10S). No solvent, other than the mixture of acetonitrile/water (2/8 v/v), showed good results in terms of fluorescence emission intensity [25].

FIGURE 3: Part of 3D network of sensor L possessing intramolecular hydrogen bonding.

SCHEME 1: Proposed structure of Ce complex formed after uptake of twofold molar amount of ligand under the given conditions of pH and temperature.

7.9. Determination of Detection Limit. Free sensor L ($5\ \mu\text{M}$) quenches fluorescence due to internal charge transfer phenomenon at λ_{em} 351 nm. Upon the addition of an equivalent of Ce^{3+} to sensor L solution (Figure 11S), enhancement at 351 nm occurred gradually by increasing Ce^{3+} concentration in the tested range ($10\text{--}100\ \mu\text{M}$) which was due to the inhibition of internal charge transfer phenomenon. A best sensor is one which can detect even low concentration of metals. In the current study, the limit of detection of sensor L was found to be $3.4 \times 10^{-8}\ \text{M}$, determined from fluorescence spectra, which is much lower as compared to those of other reported sensors in the literature [26]. The limit of detection was calculated according to the formula:

$$\text{Detection limit} = \frac{3\sigma}{K}, \quad (1)$$

where σ is the standard deviation of blank measurements and K is the slope of the plot of the fluorescence intensity versus sample concentration [27]. The mechanism of interaction can be explained as follows.

7.10. Association Constant and Binding Stoichiometry. For association constant and binding stoichiometric ratio deter-

mination, equimolar solutions ($10\ \mu\text{M}$) of both sensor L and Ce^{3+} were used (Figure 12S). Job's plot analysis was performed by continuous increase of one part and decrease of another part while keeping total concentration of both sensor L and Ce^{3+} constant at $10\ \mu\text{M}$ (Figure 13S). Binding ratio was determined from their respective fluorescence emission intensities. Maximum fluorescence intensity was achieved at a molar fraction of 0.7 at 351 nm indicating 1:2 binding stoichiometry between sensor L and Ce^{3+} ion. It means that one Ce^{3+} ion binds to two units of sensor L.

There are four potential coordination sites in the ligand, including three N of guanidyl moiety and an oxygen of the hydroxyl group attached to the naphthyl group. The proposed structure of complex formed by mixing the ligand solution and $\text{Ce}(\text{NO}_3)_3$ salt is given in Scheme 1. The ligand is expected to act as bidentate and can also act as tridentate. In either case, the proposed structure as given in the Scheme 1 will be afforded. The coordination sphere of f-block elements like Ce can easily be expanded to 8 [28]. In several cases, the coordination number 6 [29] has also been reported. Since the bulk of our ligand is moderate and the bonding is expectedly strong, therefore, we expect that the proposed structure 2 in the scheme would be a probable complex with extra stability under the provided conditions of pH 7, at 60°C in methanol.

FIGURE 4: Selectivity of sensor L (15 μM) in the presence of interfering metal ions (300 μM) and cerium (15 μM) at λ_{em} 351 nm.

The selectivity of the ligand regarding Ce was found to be excellent under these conditions while other metal ions were sensed up to negligible limit. Our investigations with respect to sensing of other metal ions as stated above are in progress, and it is hoped that conditions will be optimized soon to carry out the same with the given ligand.

Association constant was measured from the Benesi-Hildebrand plot from the increase in fluorescence intensities of sensor L as a function of Ce^{3+} ion concentration (Figure 14S). Based on equation (2), the association constant value was calculated.

$$\frac{F_{\text{max}} - F_0}{F - F_0} = 1 + \frac{1}{K} [\text{Ce}^{3+}]^2. \quad (2)$$

In the given equation, K (M^{-2}) is the association constant, F_0 is the fluorescence emission intensity of sensor L in the absence of Ce^{3+} ion, F_{max} being the fluorescence intensity of sensor-L in excess of Ce^{3+} ion, and F is the intensity noted at different concentrations of Ce^{3+} ion at 351 nm. The association constant K was calculated graphically by plotting $F_{\text{max}} - F_0 / F - F_0$ versus $1/[\text{Ce}^{3+}]^2$. A good linear relationship with slope (7×10^{-11}) and intercept (1.399), respectively, were observed, confirming 2:1 binding stoichiometric ratio. The association constant (K_a) value was determined from the slope and intercept of the line as cited above and was found to be $3 \times 10^{11} \text{ M}^{-2}$ [30].

7.11. Effect of pH. In order to find out an appropriate pH for complexation of sensor L (5 μM) with Ce^{3+} (10 μM) pH analysis were conducted using NaOH and HCl solutions for pH adjustment (Figure 15S). Fluorescence intensity was monitored at 351 nm in the absence and presence of Ce^{3+} ion (10 μM) in the pH range 1-12. Upon change in pH of the test solution, change in fluorescence emission intensity of the complex was observed due to the presence of lone pairs of electrons on nitrogen and OH groups in sensor L. The fluorescence intensity of sensor L remained unaffected by varying the pH. On the other hand, the sensor L cerium complex showed a significant effect on its fluorescence emission intensity with change in pH. At low pH, the complex was found to be unstable and have low fluorescence

emission intensity due to protonation of hydroxyl and amine moiety that acts as binding sites. With gradual increase of pH, drastic change in fluorescence emission intensity was observed. At pH 7, the complex was highly stable and maximum fluorescence emission intensity was observed. While at pH >7, a decrease in fluorescence emission intensity was observed due to $\text{Ce}(\text{OH})_3$ formation thereby reducing the Ce^{3+} complex concentration. From these results, it can be deduced that sensor L can be employed at physiological pH range. The results obtained are in good agreement with respect to a comparative study performed on free sensor L [31].

7.12. Metal Ion Competition Study. Selectivity is one of the most important characteristics of a sensor, which is the relative response for the metal ion of interest over other competitive metal ions present in the samples. Therefore, to determine selectivity of sensor L toward Ce^{3+} , 15 μM of sensor L and Ce^{3+} and 300 μM of other competitive metal ions were prepared in a acetonitrile/water mixture (2:8) and distilled water, respectively, and its fluorescence emission intensities at 351 nm were monitored. The result (Figure 4) shows that none of these metal ions interfere with Ce^{3+} ions showing high sensitivity and selectivity of sensor L with Ce^{3+} ions and can be successfully applied for Ce^{3+} ion determination in different water samples containing these competing metal ions [32].

7.13. Stability of Sensor L Solution. The stability of sensor L solution and its complex with cerium was determined up to 2 months by checking the fluorescence intensity at different intervals of time. The sensor L solution was stable up to 2 months as no change in fluorescence intensity was observed indicated in Figure 16S. The same stability was also observed for sensor L complex with cerium.

7.14. Comparison of Sensor L with Previous Works. Specific properties of the synthesized sensor L towards Ce^{3+} were compared with those of some previously reported sensors for Ce^{3+} determination (Table 3). Most of these sensors required arduous testing media that quenched fluorescence upon interaction with Ce^{3+} . On the other hand, sensor L

TABLE 3: Comparison of sensor L with previous results in the literature.

Structure of sensor	Fluorophore	Analyte detection mode	Analyte	Limit of detection	Optimal pH	Testing media	Ref.
3-Amino-5-(4,5,6,7-tetrahydro-1H-indol-2-yl)isoxazole-4-carboxamide	Selective chelation enhanced fluorescence	Ce ³⁺	8.91×10^{-6}	6-8	(CH ₃ CN/H ₂ O) (9/1: v/v)	Wang et al., [35]
Pyrrole-isoxazole derivative	Enhancement in fluorescence intensity	Ce ³⁺	7.9×10^{-5}	3.0–7.5	Protic media	Esteves et al., [36]
Multivalent rhodamine ligands	Quenching in fluorescence intensity	Ce ³⁺ As ³⁺	8.2×10^{-6}	NA	Nonproteinogenic amino acids	Lizhu et al., [37]
7-Nitrobenz-2-oxa-1,3-diazole	Enhancement in fluorescence intensity	Ce ³⁺	6.4×10^{-6}	3-6	Salicylaldehyde	Elshehy et al., [38]
1-[(4-Hydroxyanilino)methylidene]-naphthalen-2(1H)-one	Quenching in fluorescence intensity	Ce ³⁺	7.1×10^{-6}	NA	Azatriphenylenes	Chahmana et al., [34]
[N,N0-di(Quinoline-2-methylene)-1,2-phenylenedimine]	Enhancement in fluorescence intensity	Ce ³⁺	6.8×10^{-5}	7-9	Roform	Gupta et al., [12]
[1-((Pyrimidine-4-ylimino)methyl)naphthalene-2-ol]	Enhancement in fluorescence intensity	Ce ³⁺	3.4×10^{-8}	2-10	(CH ₃ CN/H ₂ O) (8/2: v/v)	Present work
non fluorescent

FIGURE 5: Reversibility of binding interaction between sensor L ($15 \mu\text{M}$) and cerium ($15 \mu\text{M}$) with the addition of EDTA ($15 \mu\text{M}$).

FIGURE 6: Real spiked water sample analysis, Ce^{3+} ($10\text{--}50 \mu\text{M}$) at λ_{em} 351 nm.

shows a number of attractive analytical features such as one-step easy synthesis, enhancement in fluorescence emission intensity, wide pH range, and its applications for rapid determination of Ce^{3+} in real water samples. The results obtained from the current study give ultra-high selectivity and sensitivity for the trace amount of Ce^{3+} ion determination as compared to other developed sensors [33].

7.15. Reversibility of Sensor L. The reversibility of sensor L was investigated using a common chelating agent ethylene diamine tetra acetic acid (EDTA). One equivalent of EDTA solution was added to a solution containing sensor L- Ce^{3+} complex. The fluorescence intensity was measured at 351 nm after EDTA interaction. The fluorescence emission signal was restored at 351 nm with the addition of EDTA thus showing that the process of chelation of sensor L with cerium is reversible as indicated in Figure 5.

7.16. Determination of Cerium in Different Water Samples. Application of the newly synthesized sensor L was assayed

by analysing real water samples by collecting water samples from the outlet of our analytical Lab, Batkhela and Thana (areas located in Khyber Pakhtunkhwa, Pakistan). With a known concentration of Ce^{3+} ($10\text{--}50 \mu\text{M}$), all these samples were spiked, and its fluorescence emission intensity was noted at λ_{em} 351 nm as shown in Figure 6. The results showed that change in fluorescence intensity of L was directly proportional to Ce^{3+} ion concentration. Therefore, the sensor L could be applied for the determination of trace amount of Ce^{3+} ions in real water highlighting the applicability of sensor L in the control of environmental pollution with high sensitivity and selectivity [34].

8. Conclusion

In this study, a new fluorescent, sensor L for rapid, sensitive, and selective determination of Ce^{3+} in aqueous samples has been developed. The sensor was characterized by a number of instrumental techniques that confirmed the synthesis of sensor L and their sensing behavior toward Ce^{3+} . The 2:1

stoichiometry of sensor L to Ce^{3+} was determined from Job's plot based on UV-vis absorption and fluorescence analysis. Sensor L showed coordination with Ce^{3+} through the deprotonated phenolic group, azomethine nitrogen, and oxygen. Sensor L demonstrated high selectivity and ultrahigh sensitivity for Ce^{3+} among alkali, alkaline, and heavy and transition metals analysed, with 3.4×10^{-8} M limit of detection and $1 \times 10^7 \text{ M}^{-1}$ association constant.

Data Availability

All the data associated with this research has been presented in this paper.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding this work through research group no. RG-1440-009.

Supplementary Materials

CCDC No. 1987815 contains the supplementary crystallographic data for complex 1. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. (*Supplementary Materials*)

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