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RESEARCH ARTICLE

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Fluorescence modulation of naphthalene containing salicyl hydrazide-based receptor through aggregation-induced emission enhancement approach: Dual detection of lanthanum and cyanide ions in semi-aqueous medium

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Abstract

The sensing activity of naphthalene containing salicyl hydrazide-based fluorescence receptor has been improved through aggregation-induced enhanced emission mechanism approach in semi-aqueous medium. The receptor has been found to be selective toward La^{3+} with approximately 70-fold fluorescence enhancement due to a combined effect of keto-enol tautomerism inhibition and chelation enhanced fluorescence with a detection limit of 3.91×10^{-6} M. In addition, the receptor is also able to sense CN^- with a detection limit of 3.55×10^{-6} M via deprotonation effect, justifying its multiple analyte sensing behaviour. Hence, the current analytical methodology improves the sensing activity of the probe and also provides a greener alternative for La^{3+} and CN^- detection.

KEYWORDS
Aggregation induced emission enhancement (AIEE), Cyanide, Fluorescence, Lanthanum, Naphthalene

1 | INTRODUCTION

Development of highly sensitive chemosensors for quantitative and qualitative analysis of both cationic and anionic moieties is of considerable importance, as they play an important role in various industrial, environmental, and biological processes.[1–5] Among the cationic moieties, lanthanides have been extensively used in lasers, fiber optics, superconductors, refractive index lenses, and so forth.[6] Lanthanides exhibit intrinsic luminescence properties due to f–f electron transition,[7–10] and therefore the resultant materials show luminescence with long lifetime, large Stokes shifts, and narrow emission bands.[11–14] This property would reduce the probability of interferences from auto-fluorescence and scattering light, thus giving the effective luminescence measurement. Some of the lanthanide ions for example Eu^{3+} and Tb^{3+} are used to develop luminescent probes for the detection of different analytes in the biological system with high sensitivity indicated by the variable emission intensities.[15–19] However, the toxic nature of lanthanides in animals as revealed by various

Abbreviations used: ADP, adenosine di-phosphate; AIEE, aggregation-induced enhanced emission mechanism; AMP, adenosine monophosphate; ATP, adenosine triphosphate; CHEF, chelation-enhanced fluorescence; DMF, dimethylformamide; DMSO, dimethylsulfoxide; ESI, electronic supplementary information; ESIPT, excited state intramolecular proton transfer; HRMS-MS, high-resolution mass spectrometry; ICT, intramolecular charge transfer; IR, infrared spectroscopy; NMR, nuclear magnetic resonance; TBA, tetrabutylammonium; TBACN, tetrabutylammonium cyanide; TBAOH, tetrabutylammonium hydroxide; THF, tetrahydrofuran; TMAOH, tetramethylammonium hydroxide; UV–vis, ultraviolet–visible.

[Correction added on 27 April 2021, after first online publication: Address of corresponding author Vimal K. Bhardwaj has been corrected.]

studies cannot be ignored. These rare earth particles get settled in the lungs when inhaled and are gradually absorbed into the body.[20]

In this class of lanthanides, the lanthanum compound are relevant in different biological processes, namely hydrolysis of phosphodiester, lipid peroxidation, diagnosis of hyperphosphatemia, ATPase activity, and as antitumor agents.[21–23] Although the toxicity of these rare earth elements has been less reported in humans, it is known that strong binding of phosphate ester with lanthanum ions can lead to the destruction of phosphate diester in DNA due to fast hydrolysis.[20] These features of lanthanum ions can be a potential threat for micro and higher organisms, thus making lanthanum to be categorized among the class of highly toxic metal ions. Therefore, the increased utility of lanthanum compounds in industries and its subsequent discharge into the environment can pose greater life hazards. Keeping in view these harmful effects of lanthanum ions, the design and development of certain luminescent molecular probes to identify the contamination of the environmental samples with high sensitivity and selectivity has become inevitable for the chemists.[24] Among various lanthanides, La^{3+} ions are considered as non-luminous due to their $3d^{10}4f^{0}$ electronic configuration and therefore the literature cover very rare reports on investigation on luminescent complexes based on La^{3+} ions.[25] Cyanide, on the other hand, is another toxic anion that produces adverse health effects. It is known to inhibit the electron transport chain in the mitochondria even in traces (0.5–3.5 mg/kg of bodyweight) and can lead to the death of human beings.[26,27] The wider use of cyanide at industrial level can be a cause of the severe contamination of ground and/or drinking water due to accidental spillage.[28,29]

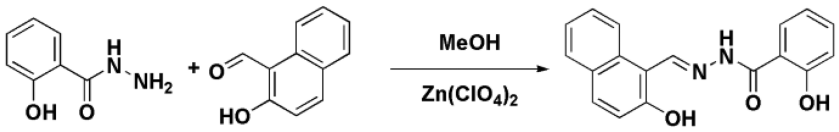
Consequently, to monitor such type of contaminations several chromatographic, voltammetric, and electrometric techniques have been developed for qualitative and quantitative analysis of various cationic or anionic species.[30–32] However, in comparison to the above-mentioned techniques, optical sensing is more appreciated as it is simple, inexpensive, fast, and more sensitive. Moreover, optical sensing has also the advantage of visual detection of analytes that can be used for preliminary screening of contaminated samples.[33–35] In the published work, a number of ligands with N, O/S donor as binding sites have been used for efficient sensing of several transition metal ions.[3,36–40] On the other hand, different types of ligands such as urea, thiourea, amide, and imidazole functionalities have been reported for anion sensing through hydrogen bonding.[41–46] Although a number of bifunctional chemosensors have been reported for the detection of cations and anions,[47–52] the multiple sensing of both La^{3+} and CN^{-} ions by a single receptor is still rare.

Konstantlanos and co-workers have developed acylhydrazone Schiff base, namely 2-hydroxy-1-naphthaldehyde salicyloyl hydrazone-based receptor probe **HL**.[53] This probe is used to examine its sensing behavior towards metal ion and found its selective detection ability for Mg^{2+} over other metal in ethanol as the medium. Later, Liu and co-workers also used this probe for the recognition of Y^{3+} in volatile organic solvent like THF. However, this probe showed very weak fluorescence emission toward La^{3+} in THF.[54] Consequently, with an aim to improve the activity of this probe for La^{3+} recognition, we have synthesized fluorescent aggregates of the receptors. The fluorescent aggregates show more efficient recognition of analytes based upon AIEE.[55–58] The synthesis of fluorescent aggregates also provides an advantage to use this probe in aqueous media over volatile organic solvent like THF. In addition to La^{3+} sensing the "single sensor for multiple analytes" concept has also been explored for the receptor. The fluorescent aggregates of the same receptor were also tested for different anion recognition studies and are found to be highly active for cyanide sensing.

2 | RESULTS AND DISCUSSION

Compound **HL** was synthesized by modification of an already reported method (Scheme 1).[53,54] A condensation reaction of 2-hydroxy-naphthaldehyde with salicyl hydrazide in methanol (1:1) provided the imine-linked receptor **HL** in 89.8% yield. The structures of compound **HL** was confirmed from its spectroscopic and analytical data (Supporting Information). The imine linkage of the compound was characterized by a singlet at 9.55 ppm in ^{1}H NMR spectra (Figure S1, ESI). A band at 1598 cm^{-1} in IR spectrum also supported the formation of imine linkages (Figure S2, ESI). High-resolution mass spectrum of the compound showed a parent ion peak at 307 $[(M + 1)]^{+}$ in positive ion mode (Figure S3, ESI). The purity of compounds was established from the elemental analysis.

Initially the fluorescence spectrum of the receptor was recorded. The dilute solution of compound **HL** in DMF exhibits a weak emission band at 482 nm when excited at 328 nm (Figure 1). Further fluorescent aggregates of **HL** were prepared using re-precipitation method.[59–61] This method involves injection of **HL** (stock solution of **HL** in pure DMF) to deionized water. The differential solubility of **HL** in DMF (good solubility) and water (highly insoluble) and mutual miscibility of the two solvents is the governing feature of re-precipitation method (Figure S4, ESI). A significant change in fluorescence emission intensity was observed by the variation in DMF–H_2O (v/v) mixture. Incremental addition of water fraction to DMF solution of ligand leads to enhancement of emission intensity. The emission intensity of ligand reaches maximum in approximately 20–25% (v/v) water fraction along with small red shift in the emission band from 482 to 493 nm (Figure S5, ESI). This change in fluorescence behavior can be explained on the basis of aggregate formation with change in solvent system.



SCHEME 1 Synthesis of compound **HL**

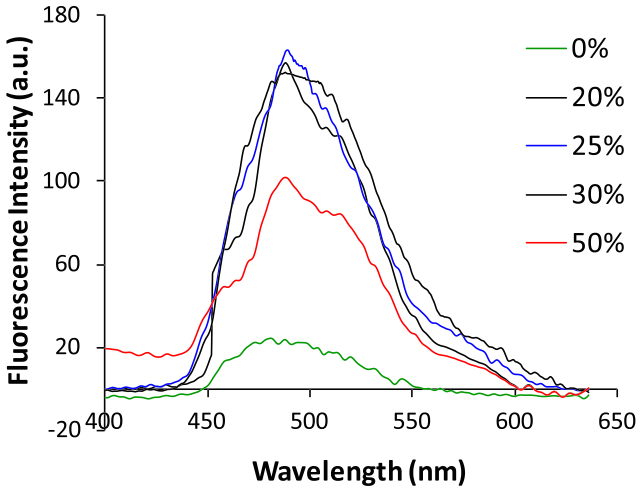


FIGURE 1 Fluorescence spectra of compound **HL** (5×10^{-6} M) showing the variation of fluorescence intensity in DMF–H_2O at 0–50% water fraction (λ_{ex} = 323 nm)

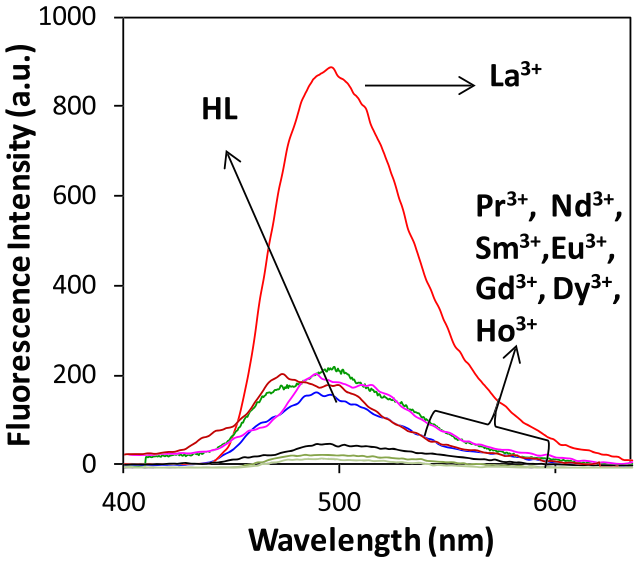


FIGURE 2 Fluorescence spectral changes of **HL** aggregates (5×10^{-6} M) in the presence of different metal ions (10.0 equiv.) such as La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, and Ho^{3+} with an excitation of 328 nm in DMF:H_2O (3:1, v/v) solution

The aggregation leads to the restricted intramolecular rotations that prevent non-radiative decay for fluorescence quenching causing fluorescence enhancement, namely AIEE.[55–57] Hence, high fluorescence intensity with bathochromic shift was observed in the presence of water fraction. Further addition of water to DMF solution of receptor **HL** results in the quenching of emission intensity. This quenching in intensity is observed as a result of increased aggregation. As the aggregation increased, only the molecules on the surface of aggregates emitted light upon excitation and contributed to the fluorescent intensity that leads to a decrease in overall emission intensity. Hence, a solution of **HL** in 25% H_2O–DMF composition has been used for all studies. Representative Figure 1 shows the variation in fluorescence intensity of **HL** in H_2O–DMF at 0%, 20%, 25%, 30%, and 50% water fraction. The formation of aggregates further confirmed by emergence of a level-off tail in the absorption spectrum (in 25% H_2O–DMF solution) at higher wavelength (Figure S6, ESI). The level-off tail is characteristic of Mie scattering[62–64] due to the aggregation of receptor molecules.

2.1 | Cation recognition studies of HL

To evaluate the chemosensory response of **HL** toward lanthanum ion (La^{3+}), an aqueous solution of La $(NO_3)_3 \cdot 6H_2O$ was added to a stock solution of **HL** aggregates. Free receptor **HL** (5×10^{-6} M) exhibits a weak fluorescence emission at 493 nm when excited at 328 nm. Upon addition of La^{3+}, the receptor **HL** shows strong fluorescent enhancement in the emission band at 493 nm. The ion recognition properties of **HL** aggregates were also explored for some other lanthanides (such as Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, and Ho^{3+}); however, none of these metal ions show any significant change in the fluorescence spectra (Figure 2).

The free receptor **HL** is a weak emitter, due to ESIPT mechanism through keto-enol tautomerism involving the phenolic protons of 2-hydroxy-naphthalene moiety and sp^2 nitrogen of imine linkage.[65]

The observed fluorescence enhancement for La^{3+} can be explained due to the formation of a chelate complex (rigid system) between **HL** and the La^{3+} ion, leading to the CHEF effect.[66] Fluorescent recognition studies support the high selectivity of the receptor for La^{3+} over other lanthanides. The Job plot[67] showed a 2:1 stoichiometry of the complex formed between **HL** and La^{3+} (Figure S7, ESI). To further confirm the stoichiometry between the host and guest ion species, HRMS–MS analysis was performed (Figure S8, ESI). The positive ion mass spectrum peak at *m/z* 749.019 corresponding to $[2\ L + M]^+$ supported the formation of a 2:1 complex. Based on Job plot and mass analysis, the structure of the **2 L**–La^{3+} complex has been proposed as shown in Scheme 2.

To further investigate the chemo-sensing properties of **HL**, a fluorometric titration was performed with incremental addition of La^{3+} ions (Figure 3a). The fluorescence intensity of receptor increases with the increase in La^{3+} concentration until 7.0 equivalents and further increase of La^{3+} concentration resulted in the saturation of fluorescence intensity. Thus, receptor **HL** exhibits approximately 70-fold fluorescence enhancement upon binding of La^{3+}.

The photophysical properties of **HL** were also examined using UV–vis spectroscopy (Figure S9, ESI). The UV–vis spectrum of receptor **HL** (1×10^{-5} M) exhibited absorbance bands at 314, 328, 365, 380, 444, and 472 nm. Upon gradual addition of La^{3+} solution (0–7.0 equiv.) to the receptor, new sharp complex bands at 274 and 419 nm were observed. Meanwhile, appearance of isosbestic points at 264, 300, 340, 395, and 458 nm further supports the complex formation between receptor **HL** and La^{3+} (Figure 3b). Assuming a 2:1

SCHEME 2 Proposed structure and fluorescence enhancement mechanism of the **2 L**–La^{3+} complex

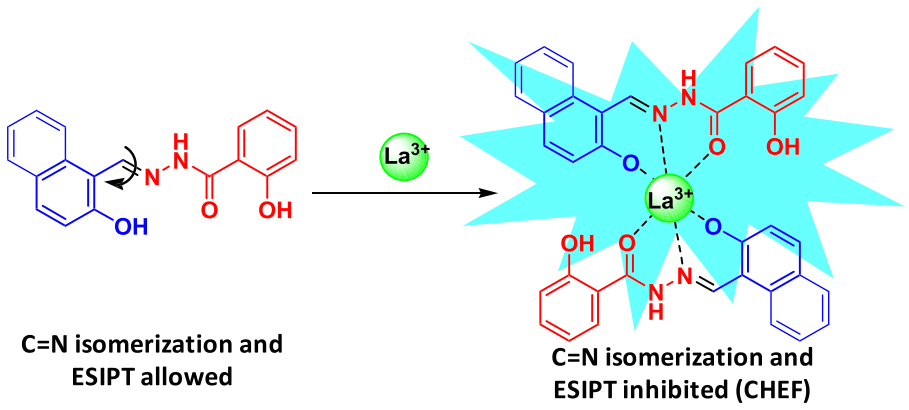
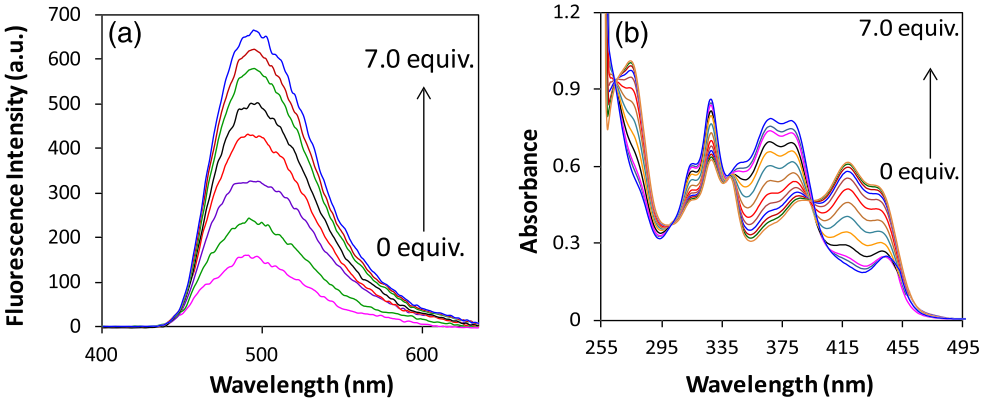


FIGURE 3 (a) Fluorescence spectral changes of receptor HL (5×10^{-6} M) with increasing concentrations of La^{3+} (0–7.0 equiv.) in DMF:H_2O (3:1, v/v) solution (λ_{ex} = 328 nm). (b) Changes in UV–vis spectrum of HL (1×10^{-5} M) upon gradual addition of La^{3+} (0–7.0 equiv.) in DMF:H_2O (3:1, v/v) solution



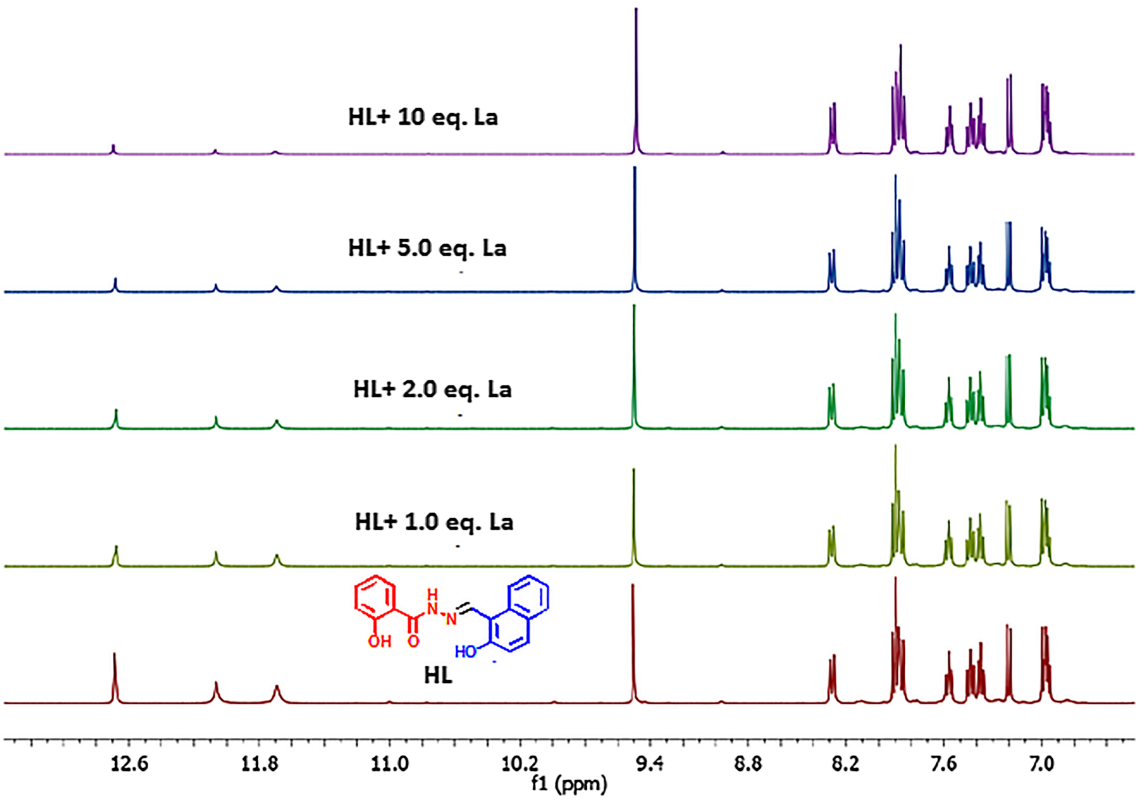


FIGURE 4 ^1H NMR titration spectra of **HL** with La^{3+} (0–10.0 equiv.) in DMSO-d_6/D_2O

stoichiometry, the association constant (K_a) was calculated using fluorescence titration data of the receptor **HL** with La^{3+} from Benesi–Hildebrand plot, namely $(F_{max} - F_0)/(F - F_0)$ versus $1/[La^{3+}]$[2] [68] A good linear relationship was found, corresponding to 2:1 stoichiometric ratio (Figure S10, ESI). The association constant (K_a) value was determined from the slope and intercept of the line and was found to be 8.70×10^9 M^{-2}. Further, the detection limit of **HL** as a sensor for La^{3+} ions was found to be 3.91×10^{-6} M by linear fitting graph (Figure S11, ESI), which is significantly low to allow the fluorogenic detection of micromolar concentrations of La^{3+}.[69]

In order to check the potential interference in **HL**–La^{3+} binding over the other lanthanide ions, competitive titrations were carried out with solutions containing equimolar amounts of La^{3+} and 10 equivalents of interfering cations (Figure S12, ESI). The results show that the solutions exhibit significant fluorescence in all these cases and no quenching of fluorescence intensity is observed, suggesting no interference of other lanthanide ions in La^{3+} binding.

Further, the binding mode of **HL** with La^{3+} was confirmed by ^1H NMR titration of the receptor with La^{3+} salt ($LaNO_3$) in DMSO-d_6/D_2O (Figure 4). On incremental addition of La^{3+} to **HL**, the signals corresponding to hydroxyl and amide groups at 12.73, 12.11, and 11.73 ppm, respectively, showed significant downfield shift (Δδ of 0.08, 0.04, and 0.06 ppm, respectively). At low concentrations (0.5–2.0 equiv.), all the hydroxyl and amide signals broadened and finally disappeared at higher concentration (10.0 equiv.), which is similar to the observations reported by Liu and co-workers with yttrium and terbium complexes of acylhydrazone Schiff base.[54] These results support the deprotonation of phenolic hydrogen during complexation. Deprotonation mechanism has been further confirmed by the ^1H NMR spectrum of **HL** in basic conditions, namely upon addition of 3.0 equiv. of TMAOH, complete disappearance of hydroxyl protons was observed (Figure S13, ESI).

2.2 | Anion and biomolecule recognition studies of HL

In addition to the metal-ion sensing properties, the fluorescence behavior of **HL** toward different anions and biomolecules (AMP, ADP, ATP) have also been investigated. Fluorescent aggregates of **HL** were used for the recognition of different anions (F^-, Cl^-, Br^-, I^-, N_3^-, NO_3^-, ClO_4^-, $H_2PO_4^-$, SO_4^-, AcO^-, CN^-) in the respective TBA salts and different biomolecules (AMP, ADP, ATP).

To evaluate the chemosensory response of **HL** an aqueous solution of anions and biomolecules was added to a stock solution of **HL** aggregates. As previously mentioned, free receptor **HL** (5×10^{-6} M) exhibits a weak fluorescence emission at 493 nm when excited at 328 nm. The addition of CN^- ion solution induced a perceptible bathochromic shift of fluorescence emission with one major band at 482 nm and one shoulder band at 460 nm. However, none of the other anion and biomolecules showed any significant change in the fluorescence spectra (Figure 5a). This observation showed that **HL** behaves as a "turn-on" fluorescence sensor for CN^- over the other

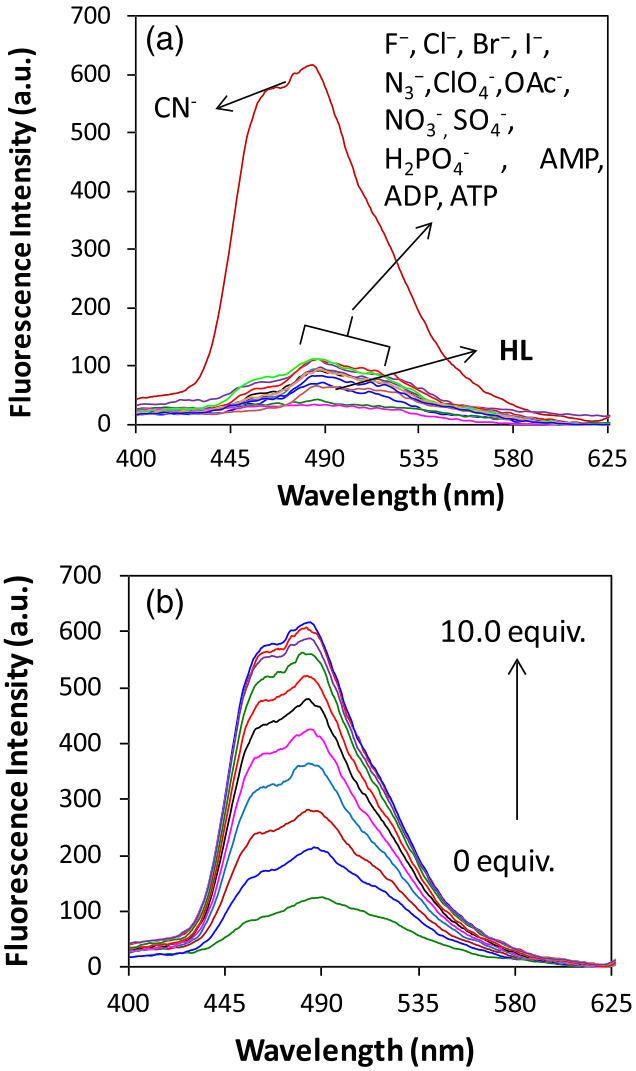


FIGURE 5 (a) Fluorescence emission spectra (λ_{exc} = 328 nm) of receptor HL (5×10^{-6} M) in the presence of 10 equiv. of various anions and biomolecules in DMF:H_2O (3:1, v/v). (b) Fluorescence emission spectra (λ_{exc} = 328 nm) of receptor HL (5×10^{-6} M) in the presence of (0–10.0 equiv. of CN^- in DMF:H_2O (3:1, v/v)

anion and biomolecules.[59] To understand the interaction between **HL** and CN^- ion, emission titrations were monitored (Figure 5b). Upon the addition of CN^- from 0 to 10.0 equiv., a gradual increase in emission intensity of **HL** at 460 and 482 nm, with a visible color change was observed.

The photophysical properties of **HL** were further investigated using UV–vis spectroscopy. UV–vis spectrum of **HL** (5×10^{-5} M) exhibited absorption band characteristic peaks at 314, 327, 365, 380, 444, and 472 nm (Figure S14, ESI). Upon the small successive addition of CN^- solution (1.2×10^{-5} M, 1.8×10^{-5} M, and 2.4×10^{-5} M) a new peak arises at 387 nm with the appearance of four isosbestic points centered at 297, 334, 344, and 385 nm in the absorbance spectra (Figure 6).

In order to confirm whether the color change originated from the transition of ICT through a deprotonation mechanism, the interaction

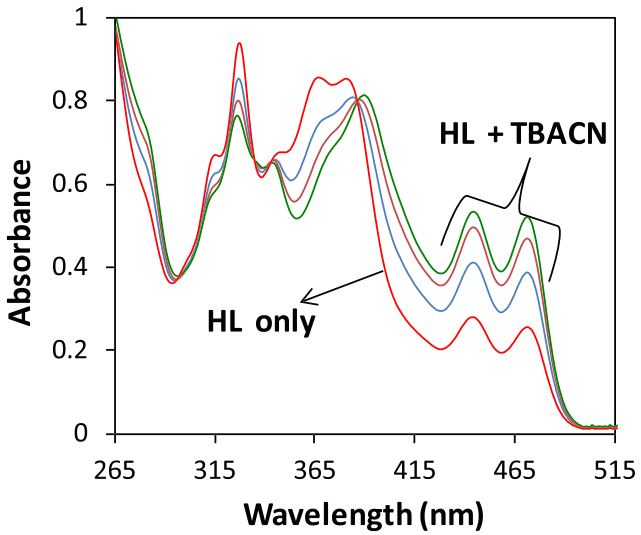


FIGURE 6 Absorbance spectra showing changes in **HL** (1.2×10^{-5} M) with incremental addition (1.2×10^{-5} M, 1.8×10^{-5} M, and 2.4×10^{-5} M) of TBACN

between **HL** and TBAOH was performed. UV–vis spectral change of **HL** upon addition of TBAOH was almost identical to that of **HL** upon addition of TBACN as shown in Figure S15 (ESI. Based on these observations, the deprotonation of HL by CN^- ion has been proposed (Scheme 3). The Job's plot analysis showed that **HL** and CN^- interact in 1:1 ratio (Figure S16, ESI).[67] To further confirm the stoichiometry between the **HL** and CN^- ion species, HRMS–MS analysis was performed that showed a peak at *m/z* 852.4691 in negative ion mode corresponding to [2(**HL**-H) + TEA]$^-$ (Figure S17, ESI). Consequently, Job's plot and ESI mass observations have supported the deprotonation mechanism of HL in a 1:1 (HL: CN^-) fashion as shown in Scheme 3.[70]

Based on the mass spectrometry analysis and Job's plot analysis, the association constant (K_a) of complexation was determined as $8.1 \times 1\ 0^4\ M^{-1}$ from Benesi–Hildebrand plot (Figure S18, ESI).[68] The detection limit of **HL** as a fluorescence sensor for CN^- analysis was found to be 3.55×10^{-6} M (Figure S19, ESI).[69] The selectivity of **HL** as a fluorescent sensor for the detection of cyanide ions was studied in the presence of other interfering anions. Competitive titrations of receptor **HL** in the presence of 100 equiv. of interfering anions were performed (Figure S20, ESI). There was no interference for CN^- detection in the presence F^-, Cl^-, Br^-, I^-, N_3^-, NO_3^-, ClO_4^-, $H_2PO_4^-$, SO_4^-, and AcO^-. Hence, receptor **HL** could be used as a selective fluorescence sensor for CN^- in the presence of most of the competing anions.

We performed the ^{1}H NMR in DMSO-d6 of HL (Figure 7) to further elucidate its binding interaction with CN^-. Upon the addition of 3.0 equiv. of TBACN the signals corresponding to hydrogens of –OH and –NH disappeared. The signals due to protons belonging to the aromatic zone were broadened and shifted slightly upfield, probably due to delocalization of negative charge generated from the deprotonation of receptor HL by CN^-.[71] These results of TBACN were compared with ^{1}H NMR of **HL** in the presence of TMAOH (as previously discussed in Figure S13, ESI) and were found to be identical, further supporting the deprotonation mechanism in DMSO-d_6.

2.3 | Simultaneous cation and anion recognition studies

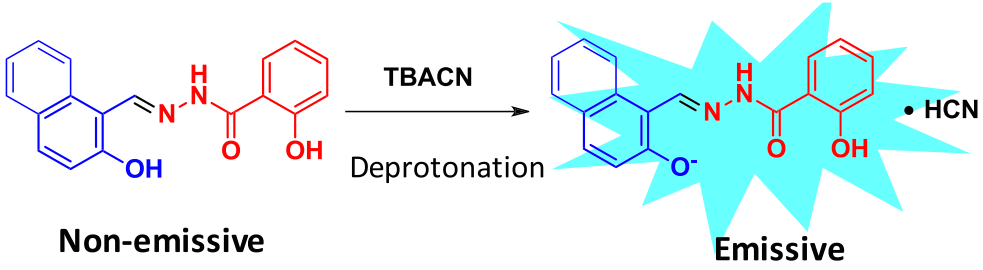
Further, the probe has been investigated to study the simultaneous effects of CN^- addition in HL–La^{3+} solution and La^{3+} addition in the HL–N^- complex solution using UV–vis spectroscopy. There was no significant spectral change in HL–La^{3+} solution upon the addition of CN^- (10.0 equiv.) in DMF:H2O (3:1, v/v). However, upon addition of La^{3+} (10.0 equiv.) in the HL–CN^- complex solution, the receptor showed a significant shift in the band, similar to HL–La^{3+} complex (Figure S21, ESI). Based upon these observations, it is further confirmed that the binding of La^{3+} is followed by the deprotonation of receptor as previously mentioned. The presence of CN^- ion facilitates the formation **2 L–La^{3+}** complex by assisting in the deprotonation of the receptor.

3 | EXPERIMENTAL

3.1 | General information

All chemicals were obtained from commercial suppliers and used without further purification. All solvents were dried by standard methods. Methanol was distilled from magnesium methoxide. Acetonitrile was dried by distillation from P_2O_5. ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECS 400- MHz spectrometer. FT-IR spectra were recorded as neat with ATR on BRUKER TENSOR-27, with zinc selenide window spectrometer in the range of 600–4,000 cm^{-1}. The absorption spectra were recorded on a

SCHEME 3 Proposed sensing of **HL** for the detection of CN^-



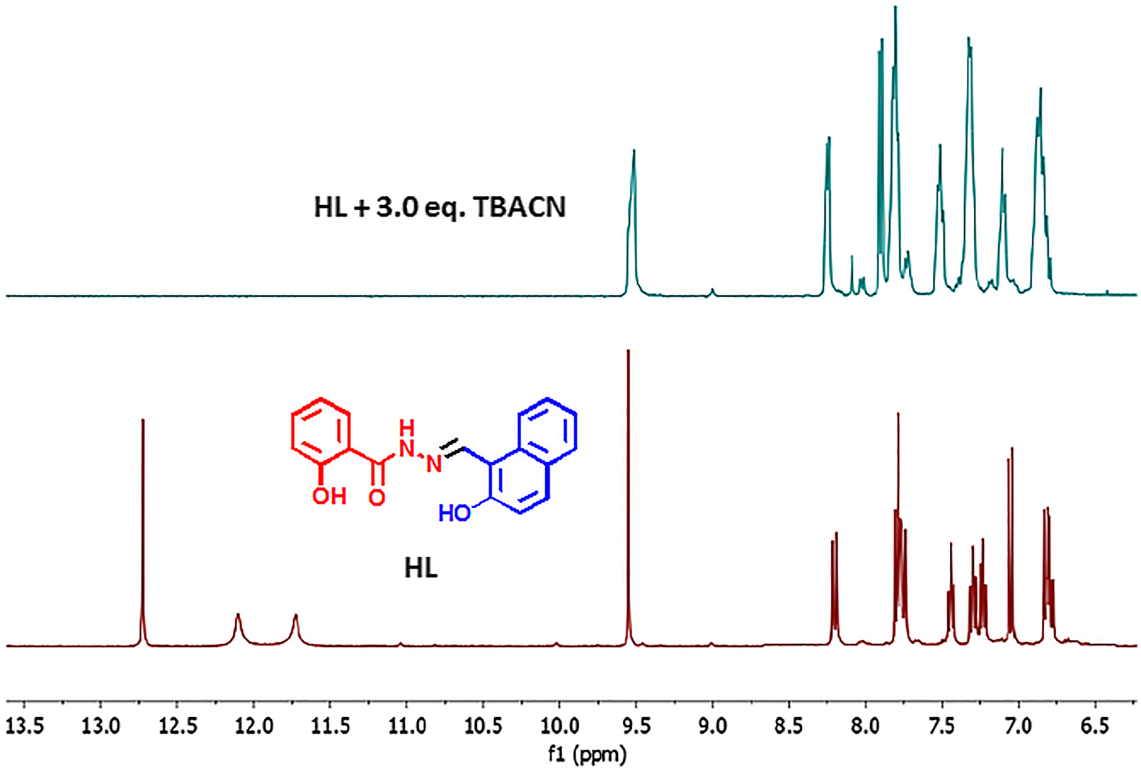


FIGURE 7 ^{1}H NMR spectra of **HL** in absence and presence of TBACN (3.0 equiv.) in DMSO-d_6

Shimadzu 1800 UV–vis spectrophotometer. Photoluminescence spectra were recorded on a PerkinElmer LS55 fluorescence spectrophotometer. Mass spectra were recorded on waters XEVO G2-XS QT (HRMS) and SYNAPT G2-S mass spectrometer (ESI).

3.2 | Preparation of compound HL

Compound **HL** was prepared by mixing the respective methanolic solutions of salicyl hydrazide (152.2 mg, 1.0 mmol) and 2-hydroxy-naphthaldehyde (172.18 mg, 1×10^{-3} M) with the constant stirring at room temperature for 3 h. The color of the solution changed to yellow and precipitates separated out in quantitative yield. Yield = 89.8%, 275 mg. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.73 (s, 1H), 12.11 (s, 1H), 11.73 (s, 1H), 9.55 (s, 1H), 8.34 (d, 1H), 7.94 (m, 3H), 7.62 (t, 1H), 7.48 (t, 2H), 7.42 (d, 1H), 7.14 (m, 2H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.72, 158.51, 157.89, 147.44, 133.78, 132.68, 131.44, 128.69, 128.55, 127.57, 127.50, 123.33, 120.73, 118.92, 118.65, 117.05, 115.48, 108.36. Selected ATR-FTIR (cm^{-1}): 3435 (–OH), 3,230 (–NH), 3,030 (Ar-C-H), 2,822 (alph-C-H), 1,624 (C=O), 1,598 (C=N). HRMS (ES^{+}): (m/z) = 307 [**HL**+1]$^{+}$.

3.3 | UV–vis/fluorescence ion recognition studies

All of the recognition studies were performed at room temperature and before recording any spectrum adequate time was given to ensure the uniformity of the solution. The ion recognition behavior of compound **HL** was evaluated from the changes in UV–Vis absorption/fluorescence spectra upon addition of particular salt in an aqueous medium. For titrations, volumetric flasks were taken, each containing standard solution of receptor along with incremental amounts of a particular ion in HEPES buffered aqueous solution.

3.4 | Stoichiometry determination

Job's analysis was conducted to obtain the stoichiometry of host-guest complex of receptors **HL**. Receptors with appropriate concentration were dissolved in suitable solvent medium. Solutions of receptors of 12.0, 10.8, 9.6, 8.4, 7.2, 6.0, 4.8, 3.6, 2.4, 1.2, and 0 μL were prepared and transferred to vials. Each vial was diluted with reference solvent to make a total volume of 2.98 mL. Cation/anion solutions of 0, 1.2, 2.4, 3.6, 4.8, 6.0, 7.2, 8.4, 9.6, 10.8, and 12.0 μL were added to each diluted solution of receptors. Each vial had a total volume of 3.0 mL. After shaking the vials for 2–3 min, absorbance spectra were recorded at room temperature. The fluorescence spectra were recorded for the complex formed. The plot of [HG] versus mole fraction was used to determine the stoichiometry of the host–guest complex formation.[67]

3.5 | Association constant (K_a) calculation

The association constant was calculated on the basis of the titration curves of the receptor **HL** with La^{3+}.The association constant was calculated according to the Benesi–Hildebrand equation:

$$\frac{F_{max}-F_0}{F-F_0} = \frac{1}{Ka}\left[La^{3+}\right]^{n.}$$

where K_a is association constant, F_0 is the emission intensity of receptor in the absence of host, F is the emission intensity in the presence of guest (added metal ion), F_{max} is the maximum emission intensity in the presence of guest, and n is the binding stoichiometry ratio between host and guest. The K_a value was calculated from the slope and intercept by plating $(F_{max} - F_0)/(F - F_0)$ versus $1/[La^{3+}]$[2] (with 2:1 complex stoichiometry) using Benesi–Hildebrand equation.[68] Similarly, the association constant has been calculated for anion recognition studies.

3.6 | Detection limit calculation

Detection limits were determined from change in the fluorescence titration data of receptor in the presence of La^{3+} or CN^-. The fluorescence intensity at different concentrations of metal ion was normalized from lowest and highest intensity value. Further, by fitting the linear regression curve with respect to normalized titration data (plotting of normalized intensity vs. Log $[La^{3+}]$ or Log $[CN^-]$) detection limits were calculated at the crossing point along x-axis.[69]

4 | CONCLUSIONS

Salicyl hydrazide-based naphthalene containing fluorescence receptor has been synthesized by a modified procedure. The fluorescent aggregates of the receptor have been used with an aim to improve the activity of this probe for La^{3+} recognition based upon AIEE. The receptor exhibited an approximately 70-fold fluorescence enhancement upon binding to La^{3+} in DMF:H_2O (3:1, v/v) solution due to a combined effect of keto-enol tautomerism inhibition and CHEF. Furthermore, **HL** behaves as a "turn-on" fluorescence sensor for CN^- among various anions via a fluorescence enhancement through deprotonation mechanism. Thus, the strategy developed can be used for the useful sensing of multiple analytes with a single chemosensor.

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