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A Novel Phenolate-Thiadiazolyl Based Carbonate Sensor: Design, Synthesis and Characterization

CHANDANA PRAMANIK

Department of Chemistry, Dinabandhu Andrews College, 54 Raja S.C. Mallick Road, Kolkata-700084, India

Corresponding author: E-mail: pramanikc23@gmail.com

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A highly selective and sensitive phenolate-thiadiazolyl based colorimetric as well as fluorometric chemosensor (*E*)-2-(((5-(2-chlorophenyl)-1,3,4-thiadiazol-2-yl)imino)methyl)-6-ethoxy phenol (HL) has been designed and synthesized by Schiff base reaction. This probe has been characterized by spectroscopic techniques such as NMR (^{1}H), ESI-MS and IR spectroscopy. This probe, HL can detect selectively carbonate anion in *tris*-HCl buffer solution (10 mM, pH 7.2, 1:1 v/v) medium by colorimetric and fluorometric method. The limit of detection of the probe towards carbonate is 0.435 μM. The 1:1 stoichiometry of binding of HL and carbonate was supported by ESI-MS spectra, TGA and Job's plot analysis.

Keywords: Phenolate, Thiadiazolyl, Schiff base, Carbonate, Spectroscopy, Chemosensor.

INTRODUCTION

Certain anions serve as ion channels and counter ions to sodium and potassium; for instance, chlorides are vital components of the extracellular environment for the regulation of acid-base fluid balance and the maintenance of gastric juice pH [1-9]. Among other anions, carbonate ions are significant minerals due to their practical applications in a range of settings, especially in geological and industrial applications [10-12]. The primary source of carbonate in the universe is the hydrolysis of carbon dioxide into carbonic acid, which is then converted into carbonates and bicarbonates. Carbonate compounds are used in many products such as glass, rayon, rubber, plastic, paper, printing ink, toothpaste, cosmetics and food. Calcium carbonate, a substance necessary for geological and marine processes, is used by nature to perform a variety of tasks in marine animals including cell growth and skeleton formation. Biomineralization is a common mechanism that produces calcium carbonate and it is a good candidate for power [13-17]. Carbonate is a medically necessary anion in humans due to its vital role as a blood buffer [18,19]. Developed countries have therefore authorized the use of metal carbonate forms as food additives [20]. Furthermore, carbonate anions are essential in many situations including hydrology, medical uses and agricultural planting [21-23]. Carbonates have several positive impacts including preventing soil acidification, improving soil fertility and carbon sequestration and preventing the transfer of heavy metals from soil to plants. The oxyanion of carbonates is essential for preserving blood pH and avoiding metabolic or respiratory acidosis [24-26].

Carbonate salts are necessary component in the pharmaceutical industry too [27,28]. Finding a method to identify carbonate anion in physiological and biological environments is therefore necessary. Several analytical methods including spectroscopic [29], chromatographic [30], electrochemical [31], acoustic emission methods [32], continuous-flow [33], pH ion-SFET [34,35] and carbonate-selective electrodes [36]. Nonetheless, these procedures are costly, time-consuming, require careful sample preparation, and exhibit no notable impact on human vision. Furthermore, there is an urgent need to design simple, inexpensive and easily manufactured chemosensors for carbonate detection that can identify real samples without interference from endogenous substrates. Fluorescent sensors with excellent selectivity, enhanced sensitivity, non-destructive nature, fast response times and real-time monitoring have been developed with a lot of effort and have become a strong substitute for current sensing techniques in recent years [37]. Chemosensors that can detect the presence of anions, are important for both ecology and physiology using optical responses and the human eye [38-48]. The development of sensitive and selective sensor

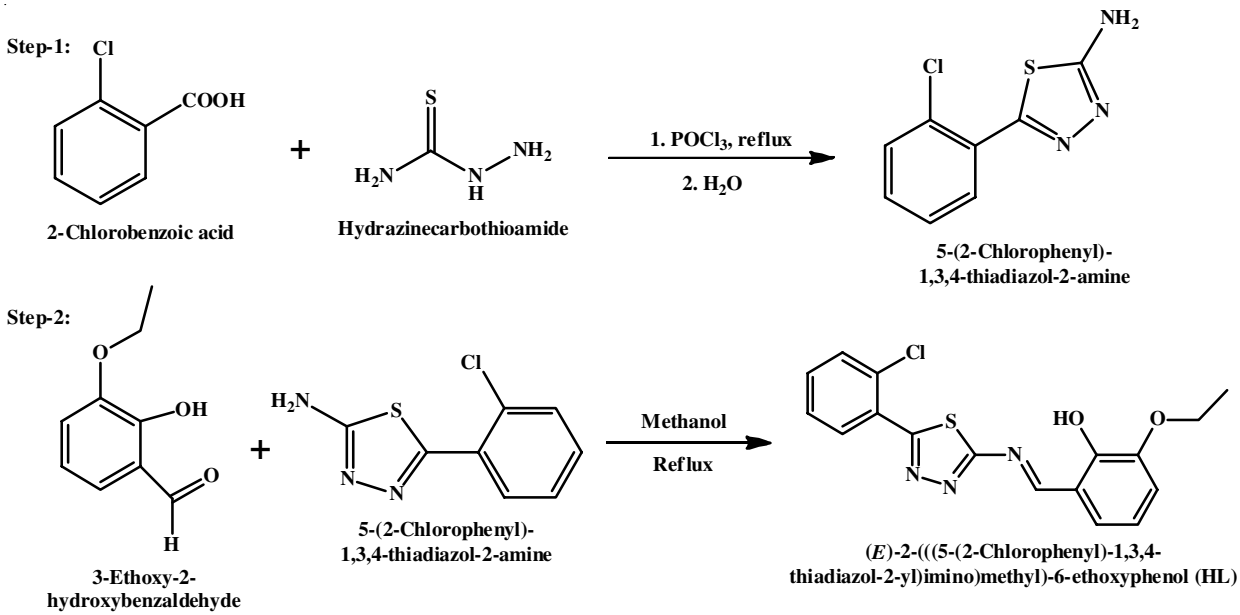
systems to detect carbonate anion species has received a lot of attention. Recently, few researchers [37,46] have reported different heterocylic moeity based chemosensor for the carbonate ion detection. Several compounds containing phenolic group has also been extensively used in earlier studies to specifically detect different anions [47-53]. In this study, a newly phenolate-thiadiazole based chemosensor is reported which can selectively recognize carbonate anion in *tris*-HCl buffer solution (10 mM, pH 7.2, 1:1 v/v) medium. Here, electron-donating ethoxy group has been utilized to generate strong ligand field environment. Consequently, in this study (*E*)-2-(((5-(2-chlorophenyl)-1,3,4-thiadiazol-2-yl)imino)methyl)-6-ethoxyphenol has been synthesized by Schiff base reaction between 3-ethoxy-2-hydroxy benzaldehyde and 5-(2-chlorophenyl)-1,3,4-thiadiazol-2-amine. The proposed chemosensor can detect CO_3^{2-} ions in an aqueous medium colorimetrically and fluorometrically with enhanced sensitivity and selectivity.

EXPERIMENTAL

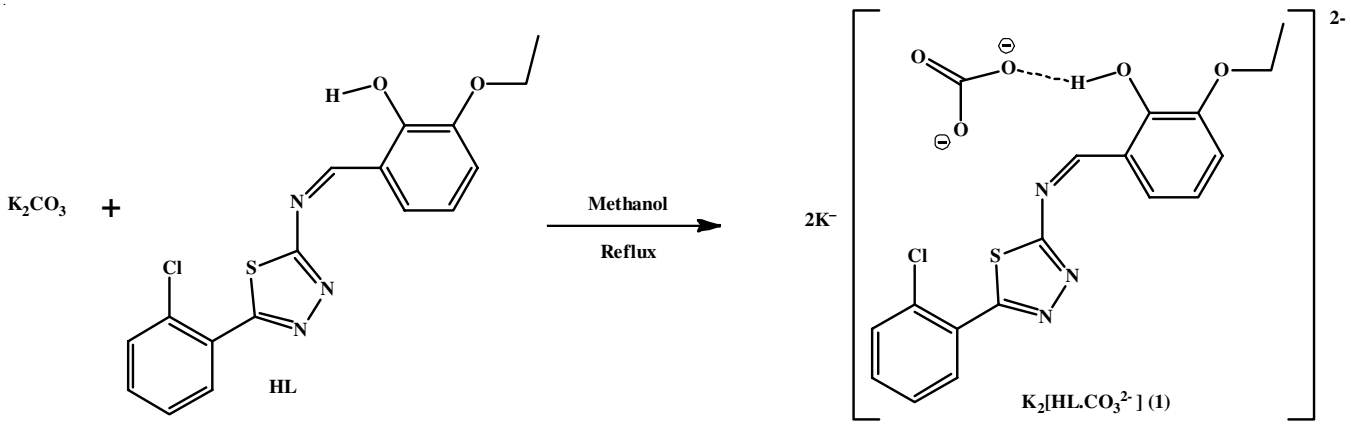
Solvent and salts used for the synthesis and spectrophotometric studies were purchased from Sigma-Aldrich, USA. The starting chemicals required for the synthesis of probe *viz*. 2-chlorobenzoic acid, thiosemicarbazide, 3-ethoxy-2-hydroxybenzaldehyde and phosphorus oxychloride were also procured from Sigma-Aldrich, USA. The UV-visible absorption spectra were obtained using a Perkin-Elmer Lambda 35 spectrophotometer in the wavelength range of 200-800 nm. Fluorescence spectrophotometer LS45 (wavelength range of 200-1000 nm) was used to evaluate the fluorescence properties of ligand in tris-HCl buffer solution (10 mM, pH 7.2, 1:1 v/v) solution. Infrared spectra of the KBr plated sampled were recorded in the range 4000–500 cm^{-1} using a Perkin-Elmer Spectrophotometer. The ^1H NMR spectra of the ligands and other compounds were recorded in DMSO-d_6 using Jeol JNM-ECZ400S/L1 NMR spectrometer (400 MHz). Thermal studies were performed using a Perkin-Elmer Thermal Analyzer TGA4000 instrument at a heating rate of 20 ºC/min under a nitrogen atmosphere. In deionized water, stock solutions of different ions (1×10^{-3} M) were prepared. The chemosensor stock solution (1×10^{-3} M) was prepared in aqueous methanolic tris-HCl buffer at pH 7.2. As required, the ligand solution gets diluted to 1×10^{-5} M. Aqueous methanolic tris-HCl buffer at pH 7.2 was used for the competitive assay of various anions and cations. Titration studies involve addition of ion (1×10^{-3} M) stock solution dropwise to a 30 µL solution of HL (1×10^{-3} M) that has been prefilled in a quartz optical cell with an optical path length of 1.0 cm. The final solution was kept at a concentration of 1×10^{-5} M [54].

Synthesis of 5-(2-chlorophenyl)-1,3,4-thiadiazol-2-amine: To a mixture of 2-chlorobenzoic acid (0.005 mol) and thiosemicarbazide (0.005 mol), 10 mL $POCl_3$ was added. After stirring for 10 min, the reaction mixture was refluxed for 1-2 h and excess $POCl_3$ were discarded under vacuum. Then, the residue was poured in to ice-water and the formed solid was filtered off, washed with water after air dried solid product was recrystallized from ethanol [55].

Synthesis of (*E*)-2-(((5-(2-chlorophenyl)-1,3,4-thiadiazol-2-yl)imino)methyl)-6-ethoxyphenol (HL): A 20 mL of dehydrated methanol was used to dissolve 1.055 g (5 mmol) of 5-(2-chlorophenyl)-1,3,4-thiadiazol-2-amine. Then 5 mL of 3-ethoxy-2-hydroxybenzaldehyde (0.83 g) was added dropwise with continuously stirred. After that, the reaction mixture was refluxed for 12 h in dry reflux condition. After refluxation, the reaction mixture was allowed to evaporate in air. A yellow solid was separated out and collected (**Scheme-I**). Yield 1.26 g, 82.35%; m.p. > 200 ºC. Elemental anal. of $C_{17}H_{14}ClN_3O_2S$: calcd. (found) %: C, 56.75 (56.56); H, 3.92 (3.98); N, 11.68 (11.79). ESI-MS: *m/z* 360.07 (HL,100%). FTIR (KBr, ν_{max}, cm^{-1}): 3436 (-OH), 3079 (sp^2 C-H), 2973 (sp^3 C-H), 1597 (vs, C=N), 12.54, 1186 (vs, C-O), 1459 (vs, C=C), 776 (m, C-Cl); ^1H NMR (500 MHz, DMSO-d_6, δ ppm): 8.47 (s, 1H), 8.04 (s, 1H), 7.70-7.68 (m, 3H), 7.59-7.47 (m, 1H), 7.21-7.19 (m, 1H),



Scheme-I: Synthetic route of chemo-sensor HL



Scheme-II: Synthesis of adduct HL-CO_3^{2-} (**1**)

6.91-6.94 (m, 1H), 4.31 (s, 1H, OH), 4.11 (q, 2H, *J* = 6.5 Hz), 1.06 (t, 3H, *J* = 6.5Hz).

Synthesis of L-CO_3^{2-} adduct (1): To a 20 mL methanolic solution of HL (1 mmol, 0.36g), a methanolic solution of K_2CO_3 was added dropwise. The colour of the solution changed from yellow to red and then blackish brown after refluxing for 4 h. After then reaction mixture was filtered blackish brown solid product was obtained by evaporation of mixture (**Scheme-II**). Yield: 0.398 g (79% based on metal salt). Elemental anal. calcd. (found) % for $C_{18}H_{14}ClK_2N_3O_5S$: C, 43.41 (43.23); H, 2.83 (2.93); N, 8.44 (8.61). ESI-MS: *m/z* 497; FTIR (KBr, ν_{max}, cm^{-1}): 3428.86 (O-H), 3139 (sp^2 C-H), 2925 (sp^3 C-H), 1591 (C=N), 1530 (C=C), 1384, 1351(C-O), 748(C-Cl).

RESULTS AND DISCUSSION

The proposed chemosensor HL, one of the majority of N, O-based Schiff base receptors for CO_3^{2-} anion, has been developed using a simple and affordable process with a high yield (< 80%) by a 1:1 condensation reaction of 5-(2-chlorophenyl)-1,3,4-thiadiazol-2-amine and 3-ethoxy-2 hydroxybenzaldehyde (**Scheme-I**). Since water pollution was typically the primary cause of different ions bioaccumulation, the organic sensor should be extremely water-soluble and able to identify analytical substances in an aqueous media. Because of the hydrophobic aromatic side-chain, the probe HL is not entirely soluble in pure water in this case; therefore, methanol can be utilized to increase water solubility. Because of its stability over 5 days, the stock solution of HL has been made in a 1:1 v/v solution of methanol-tris HCl buffer (10 mM, pH 7.2). The HL is more precisely suitable for anion sensing due to its obstinate behaviour against metal ions. The strong intramolecular hydrogen bondings (O–H …N) of ligand may be due to the non-affinity towards metal ions since they prevented the development of M–N bonds. It is important to observed that the generated probe HL can only form an adduct with carbonate ions. Under refluxed conditions, the probe HL combines with K_2CO_3 in methanol to generate a high-yield blackish brown product (**Scheme-II**).

Spectroscopic analysis: The chemosensor was subjected to ^{1}H NMR in a DMSO-d_6 solvent. At δ 8.47 ppm, a distinct peak of imine (H-C = N) protons is visible. The peaks maxima for each aromatic proton were found in the δ 6.91–8.04 ppm range and aliphatic proton are at δ 4.11 (two proton) and δ 1.06 (three proton). One -OH proton is present at δ 4.31ppm. In the ESI mass spectrum of probe HL, the base peaks are found at *m/z* 360.08 and 362.06 corresponding to HL and $[HL + 2H]^+$. The experimental mass spectrum of the carbonate adduct is well matched at *m/z* value at 497 corresponding to $[L + 2K^+ + CO_3^{2-}]$. The deprotonation of HL prior to the formation of the adduct is strongly supported by the result. Furthermore, the ν(O–H) stretching vibration (3436 cm^{-1}) in HL during adduct formation further confirmed the deprotonation occurrence. The downfield shift of about 8 cm^{-1} confirms the structurally bound carbonate O–H peak at 3428 cm^{-1} in the adduct.

Photophysical study (UV-vis spectroscopy): The probe HL was also subjected to a UV–Vis titration investigation by adding varying concentrations of CO_3^{2-} (1.1 equivalent) (Fig. 1a). When the amount of CO_3^{2-} is increased, the probe HL displays two well defined isosbestic spots at 265 and 329 nm, as shown in Fig. 1a. The absorbance of the newly formed red-shifted band at 472 nm, which was induced by CO_3^{2-} continuously enhanced with the addition of CO_3^{2-} (1.1 equiv.), declined while the blue-shifted band around 287 nm decreased (Fig. 1a). Since, the addition of CO_3^{2-} caused the well-known bathochromic shift of about 56 nm (Δλ = 343 nm – 287 nm), the π-conjugate structure of probe HL experiences an intramolecular charge transfer (ICT) mechanism from the thiadiazole moiety to the imine moiety of the probe HL-CO_3^{2-} system. As a result, the probe HL may be effectively employed as a "naked-eye" carbonate sensor for real-world uses and on-site examination. This suggest that intramolecular charge transfer (ICT) from donor to acceptor is involved in the π-conjugate system of HL because of the bathochromic shift (~56 nm) that happened with the addition of carbonate. Typically, K_2CO_3 is hydrolyzed to provide KOH, which abstracts the protons of HL. K^+ ion binding with HL had an impact on ICT efficiency, resulting in a drop in intensity at 287 nm.

Using UV-Vis spectroscopic technique, the anion sensing behaviours of the probe HL in a 1:1 v/v solution of methanol-tris HCl buffer (10 mM, pH 7.2) solutions were assessed at room temperature (Fig. 1b). The probe HL underwent absorption tests following the transfer of several anions SO_4^{2-}, SO_3^{2-}, NO_3^-, NO_2^-, Cl^-, Br^-, I^-, BF_4^-, AcO^-, HCO_3^-, CO_3^{2-}, $S_2O_3^{2-}$ and N_3^-. When CO_3^{2-} ions are present, the probe HL exhibits a significant change in absorbance, as seen in Fig. 1b. The π–π*

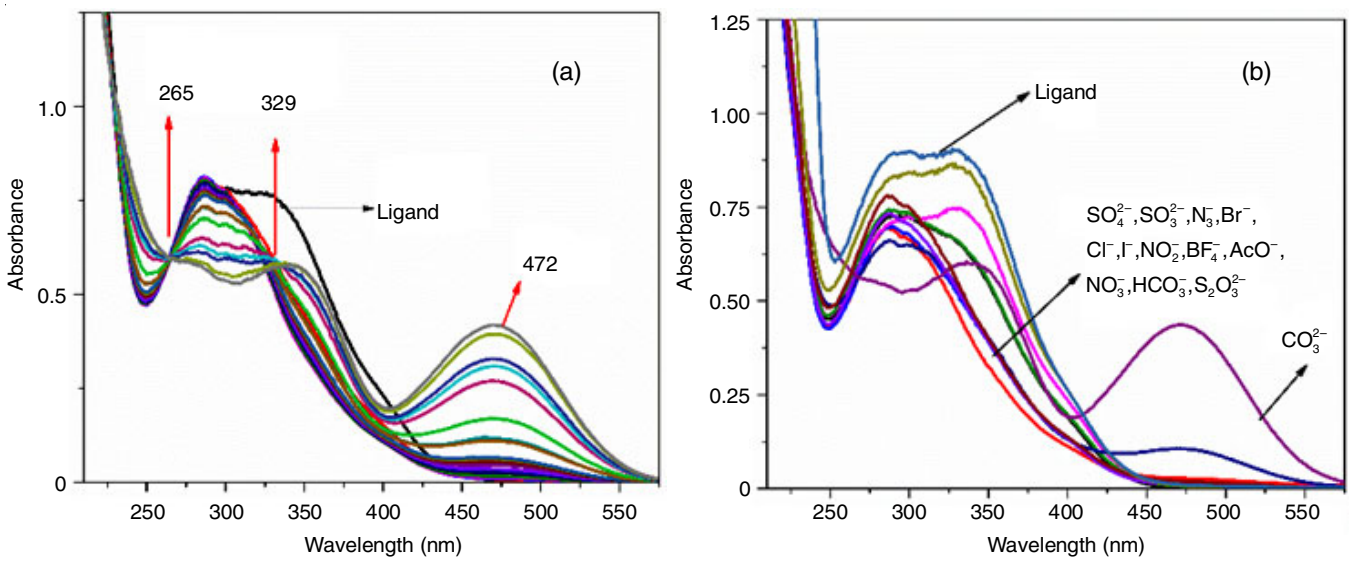


Fig. 1. (a) Absorption titration of HL•CO_3^{2-} in a 1:1 v/v solution of methanol-tris HCl buffer (10 mM, pH 7.2) (b) absorbance titration of HL with different anions in a 1:1 v/v solution of methanol-tris HCl buffer (10 mM, pH 7.2)

transition was responsible for the lowered band at (287 nm) and increased bands at (354 and 472 nm). At 287 nm, the probe HL without CO_3^{2-} displayed a strong absorption band. When CO_3^{2-} was added to the probe HL, there was a key enrichment in absorption at 472 nm and a corresponding decrease in intensity at 287 nm. When CO_3^{2-} was present, the colour of the probe HL solution changed from yellow to orange, but the π–π* transition prevented other solutions from causing any colour change (Fig. 1b).

Fluorescence studies: Experiments of fluorescence and the selective emissive characteristics of the chemosensor HL toward anion were carried out in a methanol-tris-HCl buffer (1:1 v/v, 10 mM, pH 7.2) solution using the same working media. Upon activation of the phenolate-thiadiazole fluorescent substance at 330 nm, the mild emission band at 382 nm was seen in free ligand HL. When two equivalents of each of the selected anions such as SO_4^{2-}, SO_3^{2-}, NO_3^-, NO_2^-, Cl^-, Br^-, I^-, BF_4^-, AcO^-, HCO_3^-, CO_3^{2-}, $S_2O_3^{2-}$ and N_3^- are sequentially added to the chemo-sensor HL, only the CO_3^{2-} ion can significantly increase the emission intensity as shown in Fig. 2a. The fluorometric reaction of the receptor HL is thought to be obtained only upon the presence of CO_3^{2-} ion because, similar to the fluorescence process, it is very difficult to distinguish the low-intensity signal from the false pulsing response caused by the background environment or by the precipitation of the receptor. In the competitive experiments, the CO_3^{2-} ion depending emission spectra of HL cannot be disturbed by the presence of other anion in equal concentration. Despite the interfering ions being five times more concentrated than the CO_3^{2-} ion, which slightly enhanced its intensity, the CO_3^{2-} ion remained detectable in the emission spectrum of the mixed solution (Fig. 3). The receptor HL forms a complex with the CO_3^{2-} ion, which reduces the photoinduced electron transfer (PET) and >C=N isomerization processes and increases emission intensity because

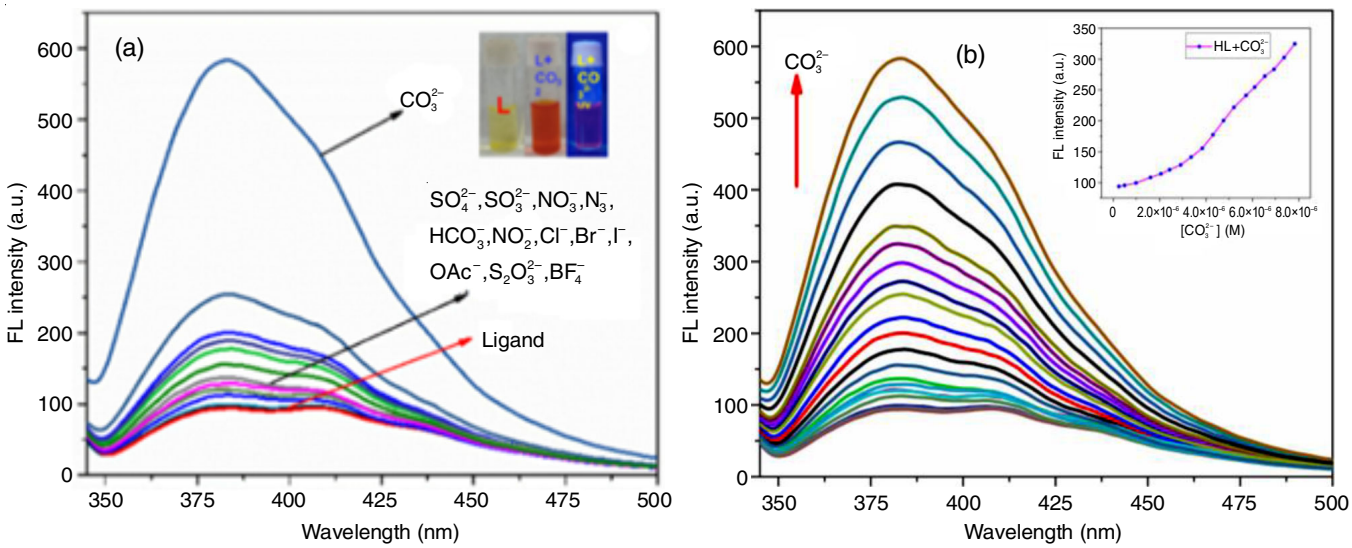


Fig. 2. (a) Fluorescence spectra of HL in a 1:1 v/v solution of methanol-tris HCl buffer (10 mM, pH 7.2) with two equivalent other anions present. (b) Fluorescence titration of HL with CO_3^{2-} in a 1:1 v/v solution of methanol-tris HCl buffer (10 mM, pH 7.2)

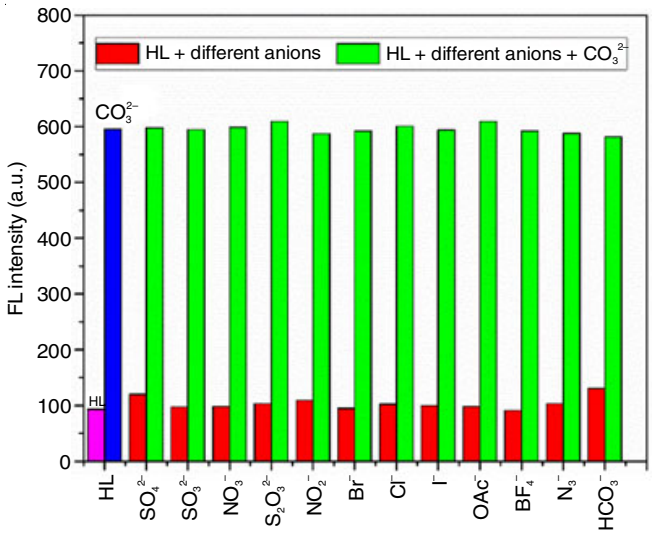


Fig. 3. Anion interference with and without CO_3^{2-} ions; red bars show HL + other anions, and green bars show HL + other anions + CO_3^{2-}

of the metal chelation-enhanced fluorescence (CHEF). Since of some radiative breakdown from the stimulated fluorophore phenolate-thiadiazole, the free receptor HL displayed moderate emission centred at 382 nm upon stimulation at 330 nm. In the titration tests, emission intensity at 382 nm grew progressively as the concentration of CO_3^{2-} ion was increased to the fixed solution of HL. It attained saturation when the concentration of CO_3^{2-} reached 1.1 equivalent. Fluorescence titration was used to determine the detection limit. Using the following formula, the limit of detection (LOD) of HL for CO_3^{2-} was calculated: LOD = K × σ; where σ = (Sb1)/(S), Sb1 is the standard deviation of the blank solution; S is the slope of calibration curve, and K = 3 in this equation [56]. The computed value of LOD is 0.435 µM (4.35×10^{-7} M) since the slope value is 2.6509×10^7 and its Sb1 value is 3.75198 (Fig. 4a). Fluorescent intensities at 382 nm (I_{382}) are shown against various carbonate ion concentrations (inset of Fig. 2b) to demonstrate that increases in I_{382} are proportional to CO_3^{2-} concentrations. The sigmoid shape of the curve indicates a substantial interaction between HL and CO_3^{2-} salt. The binding constant is determined using the Benesi-Hildebrand equation [57]. The formula is $(F_{max} - F_0/F_x - F_0)$ *vs.* $(1/[C]^n)$ (n = 1), where K is the binding constant and F_{max}, F_0, and F_x are the fluorescence intensities of HL in the presence of carbonate ions at saturation, free HL, and any intermediate carbonate ion concentration respectively. For HL–CO_3^{2-}, the binding constant values (K = 1/slope) are 1.86×10^5 M^{-1}. The resulting colour shift from yellow to orange of solution is clearly visible to the naked-eye (inset of Fig. 2a). The current probe can be used to detect CO_3^{2-} anions in naked-eye observation; it displays a pinkish-blue colour in UV lamps and orange colour in naked-eye in the presence of CO_3^{2-} ions.

TGA-DTG studies: The thermogravimetric analysis of probe HL shows a significant weight loss occur in the temperature range of 300 to 550 ºC due to the loss of structural unit, while it remains thermally stable up to 300 ºC. Moreover, the proposed molecular formulation of the complexes agrees with the TGA results. Complex (HL–CO_3^{2-}) shows a significant weight loss of 15% in the TGA study within a temperature range of 30.9-228.9 ºC, which is attributed to the loss of carbonate (Fig. 5).

Comparative studies: Table-1 lists some additional reported fluorescent, colorimetric Schiff base chemosensors that were compared to the Schiff base sensor HL's performance in terms of its fluorescent, colorimetric sensing action towards CO_3^{2-}. The proposed chemosensor HL can be synthesized in just two stages with fewer toxic chemicals and no hazardous byproducts. Table-1 shows that the current system has several appealing analytical characteristics in comparison to the other systems, including high sensitivity, wide linear range, high selectivity, lower detection limit, easy-to-use technology, good solubility, visualised sensitivity, and good practical applicability.

Conclusion

Thiadiazole based phenolate (HL) chemosensor is successfully synthesized and confirmed by mass, IR and NMR spectroscopy and selectivity was analyzed using various cations and

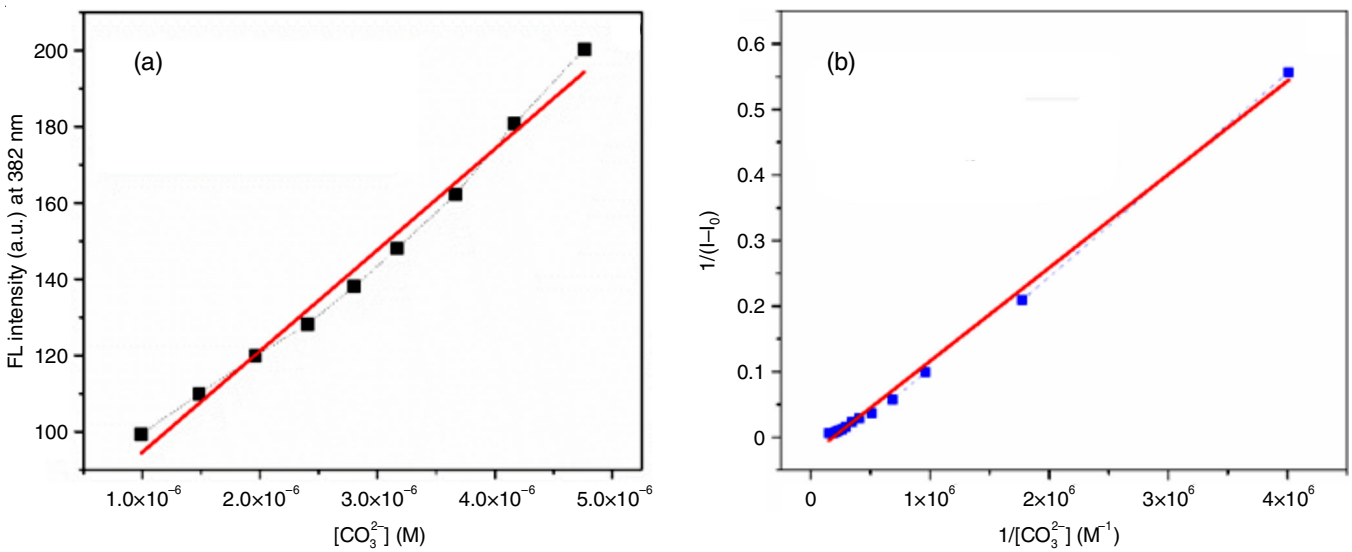


Fig. 4. (a) Fluorometric detection of detection limit of HL for CO_3^{2-} and (b) Determination of binding constant

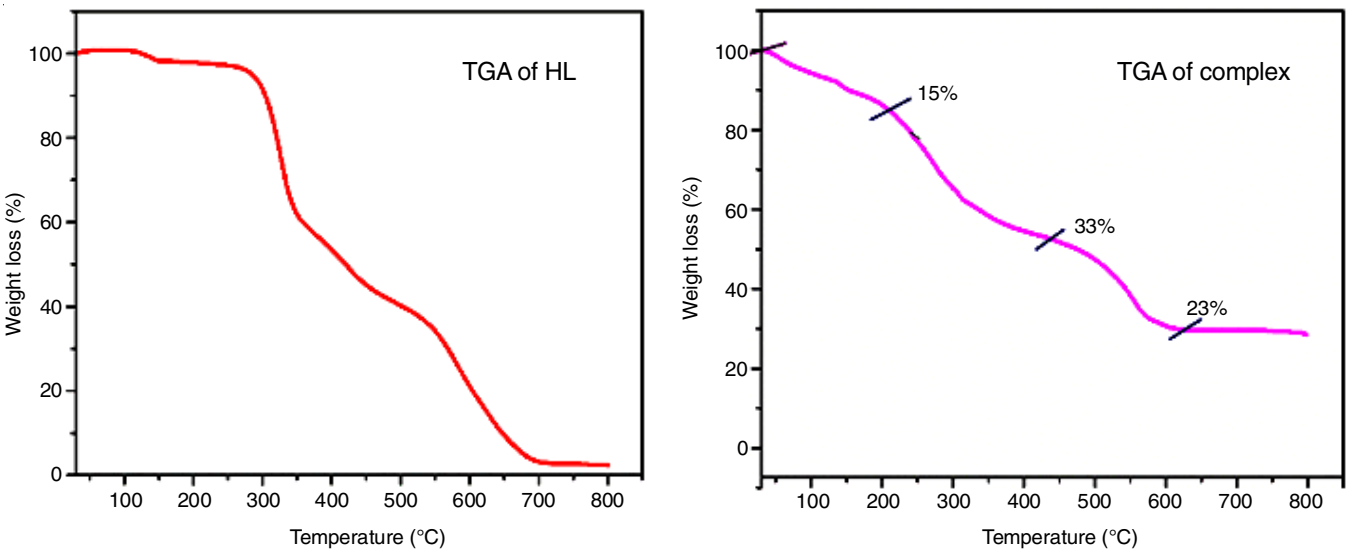
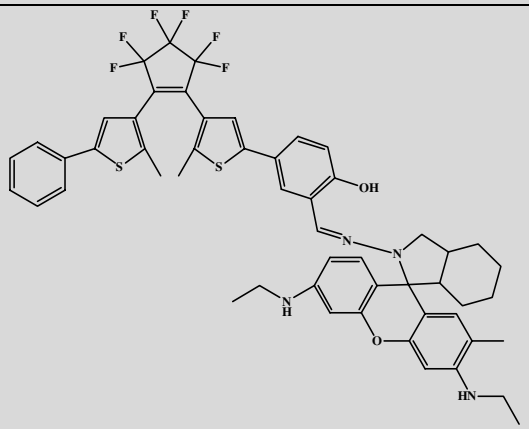
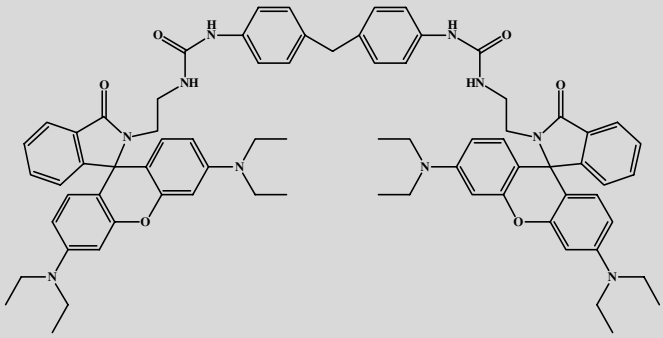
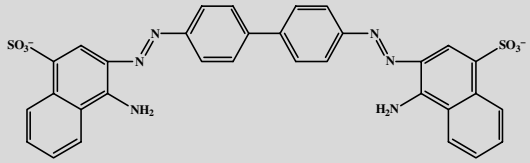
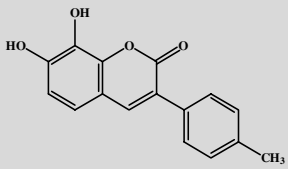
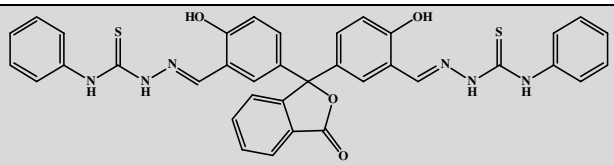
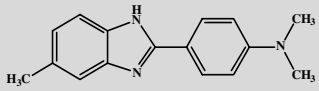
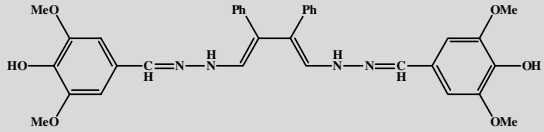
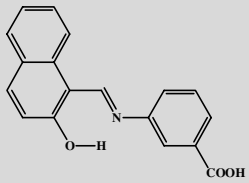
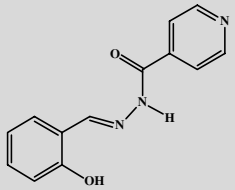
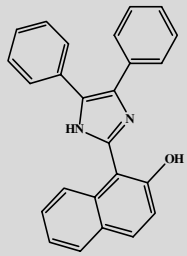
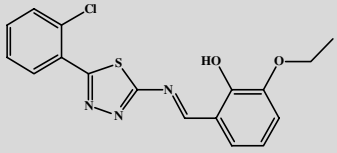


Fig. 5. Thermograms (TGA) of HL and its complex

TABLE-1
COMPARISON OF RECENTLY PUBLISHED PUBLICATIONS UTILIZING THE PROBE HL FOR CO_3^{2-} ION SENSING

Sensor	Sensing response	Solvent system	LOD (M)	Ref.
	turn-on	CH_3OH-H_2O (2/1, v/v)	96 nM	[21]
	turn-on	HEPES	2.76 ?M	[37]
	PET-OFF	DMSO–H_2O (1:1 v/v, 50 mM HEPES, pH-7.4)	3.57 ?M	[46]
	turn-on	MOPS BUFFER pH = 4.5, 7.1	96 nM	[58]

	turn-on	H_2O/CAN (99/1)v/v	1.03 μM	[59]
	turn-on	EtOH/H_2O (80/20) pH = 7.0	14.7 nM	[60]
	turn-off	(DMF/H_2O, 100/1-10/1), pH-5-14	10 μM	[61]
	turn-off	CH_3OH-H_2O (1:2)	1. (2-Fe^{3+})-5.10 μM 2. (BRU-Al^{3+})-5.60 μM	[62]
	turn-off	CH_3OH–H_2O (4/1)	0.88 μM fluorescence 0.26 μM uv/visible	[63]
	turn-off	HEPES Buffer	0.06 μM	[64]
	turn-on	1:1 v/v solution of methanol-tris HCl buffer	0.435 μM	Present work

anions. HL is also effectively employed as a selective "turn-on" chemosensor probe to identify the carbonate (CO_3^{2-}) anion in the aqueous medium. Due to the photoelectron transfer (PET) process, which is considerably red-shifted (~56 nm) with the addition of carbonate involving deprotonated aided intramolecular charge transfer (ICT), the structural distinctiveness of HL exhibits fluorescent features at 287 nm. The interaction of carbonate anion with probe HL result in fluorescence enhancement and bathochromic shift in UV-vis spectrum. One way to conceptualize the current probe's detecting ability is as a "naked-eye" carbonate indicator in aqueous solution. As for the chemosensor HL for CO_3^{2-}, its LOD value and binding constant were 0.435 μM and 1.86×10^5 M^{-1}, respectively.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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