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REVIEW ARTICLE

A Brief Overview on Luminescent Recognition and Chemosensing of Carbonate Ion

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Abstract:

Aim:

Despite the recent development of chromatographic and fluorogenic anions sensors, the hydrolysis of carbon dioxide into carbonic acid and subsequent transformation into carbonates and bicarbonate are harmful to the environment and the health of living creatures. This is why luminescence-based detection techniques are getting a lot of interest right now.

Background:

Despite the recent intention to create a naphthalene and triazole hybrid probe, ortho phenylenediamine (O-PDA) and two different aldehydes have been used in the present to successfully synthesize new fluorescent and colorimetric derivatives (AB). Aqueous solutions include colorimetrically detectable carbonate ions study. Additionally, we describe the creation and characterization of DHMC (7,8-dihydroxy-3-(4-methylphenyl)coumarin), a new coumarin-based molecule that responds to the carbonate ion in water and acetonitrile in terms of emission turn-on and naked-eye observability.

Object:

As part of current research, a 2:1 condensate of benzildihydrazone and syringaldehyde is being processed for the detection of carbonate ions in aqueous a solution.

Methods:

A luminescent lanthanide MOF-based thin film [{[Eu(HBPTC)(H_2O)]·2DMF}n] (BPTC = benzophenone-3,3',4,4'-tetracarboxylate) is successfully fabricated by electrodepositing in an anhydride system and new receptors as PDZ-1, PDZ-2, PDZ- 3 based on 2-(aryldenehydrazinyl) pyridine have been designed and for the detection of biologically and environmentally important ions. Moreover, fluorescent-colorimetric chemosensor which is based on a Schiff base for visual detection of CO_3^{2-} in an aqueous solution.

Results:

Many experiments were done to detect carbonate ions through various methods by using chemosensors like novel bis Schiff base, all these methods are eco-friendly, easy to synthesize, cost-effective, naked eye detectors, and have response towards absorbance and fluorescence intensity. It has a high binding association with carbonates. It has reversibility property. On the basis of the study and results, receptors may be useful as a valuable practical sensor for environmental analyses of carbonate.

Conclusion:

Detection of carbonate ions through various methods by using chemosensor like novel bis Schiff base is important for product quantity control and widely used in many daily basis products like cosmetics, glass, rayon, rubber, plastic, paper, printing ink, toothpaste and food. It has applications in therapeutic settings as well as in the fields of soil science, hydrology, and geology. Due to the hazardous effects of these, which might include death, collapse, vomiting, diarrhea, and stomach discomfort, it is also necessary to discover them. All of these techniques respond to absorbance and fluorescence intensity, are cost-effective, easy to synthesize, and visible to the naked eye.

Keywords: Colorimetric sensor, Fluorescent sensor, Carbonate sensor, Photo-induced electron transfer, Luminescent recognition, Chemosensing of carbonate ion.

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1. INTRODUCTION

Nature is home to a vast array of chemical species, all of which have a profound effect on biological and environmental processes. New sensitive and selective chemosensors that can identify and communicate the presence of anionic species through optical and naked-eye responses have garnered a lot of attention recently [1] due to their potential uses in the environmental, biological, and clinical areas. Because of its intrinsic simplicity and sensitivity to the unaided eye, the development of optical sensors based on the host-guest chemistry principle is becoming more and more popular in this field. One of the most important creatures in science is the anion, due to its fascinating physiological functions. Detection is then carried out. The examination of a metal ion has grown in popularity. This is due to the fact that the topic's ubiquity has raised interest in it [2 - 4]. The hydrolysis of carbon dioxide into carbonic acid and subsequent transformation into carbonates and bicarbonates are the main sources of carbonates, which are involved in mineral precipitation, ocean acidification, rock weathering, and climate change [5].

Anions include things like hydrogen carbonate and acetate, on the other hand. Due to their intense hydration energy and similar basicity, HCO_3^- (bicarbonate), a second (carbonate), are difficult to separate by force. The significant ion CO_3^{2-}, which acts as a soil-aggregating agent, is present in the earth's crust. Two ions are required to maintain the pH of saltwater. Carbonate is one of these anions and is widely used in toothpaste, food, rubber, glass, rayon, printing ink, and rechargeable Li ion batteries [6]. Food additives with various metal carbonates, ranging from E501 to E505, are necessary for the making of food.

Anions have historically played a significant role in the ecosystem. Genes are composed of biological reactions called phosphorases, for instance [7]. Fluoride in toothpaste therefore aids in the prevention of dental cavities [8 - 10]. Additionally, acetate facilitates the nerve impulses' transmission. In large quantities, carbonate ion is hazardous even though it is widely used in many different procedures. When anions exceed a safe threshold, they might be hazardous to one's health. An increasing number of diseases, such as osteoporosis, Bartter's syndrome, Pendred's syndrome, and cystic fibrosis, are being linked to anion flow interference across cell membranes [11]. In seawater, the chloride ion is a pollutant, and it also comes into contact with pollutant anions such as cyanide. Although CO_3^{2-} ions have many positive effects, their powerful caustic action on the gastrointestinal tract can lead to severe abdominal discomfort, vomiting, diarrhea, collapse, and even death if consumed in excess, according to the material safety data sheet [12]. Common adulterants in milk include CO_3^{2-} ions, which can interfere with hormone signals that control growth and reproduction.

One of the most significant subjects at the moment is the development of anionic chemosensors. Light is a flexible and valuable output signal that is used by several technologies, including optical illusion sensor systems. Anion sensors that are fluorogenic and chromatographic have recently been developed. In contrast, luminescence-based detection techniques are gaining a lot of attention due to their many advantages, including high sensitivity, selectivity, fast response times, and mobility [13 - 15].

Because of their potential uses in the biological, medical, and environmental domains, researchers have focused a great deal of attention on the design and synthesis of novel, sensitive, and selective chemosensors that can detect and signal the presence of anionic species through optical responses generate and the human eye [16, 17]. The identification and measurement of carbonate, one of the many anions that are frequently found in our surroundings, is crucial because of its prevalence and abundance in natural waterways and soil settings, where it mostly exists as metal carbonates [5]. The hydrolysis of carbon dioxide into carbonic acid and subsequent conversion into carbonates and bicarbonates are the main sources of carbonates. These processes are linked to ocean acidification, climate change, mineral precipitation, and rock weathering.The production of glass, rayon, rubber, plastic, paper, printing ink, toothpaste, cosmetics, and food all makes substantial use of carbonate compounds. Additionally, it is a leading contender for power sources in hybrid and electric vehicles, where vinylene carbonate is added as an electrolyte addition for Li-ion batteries that are rechargeable [18]. Carbonate is also essential for soil science, hydrology, geology, and agricultural planting [19]. Despite being widely used in many different processes, high dosages of the carbonate ion are hazardous. Due to carbonate's powerful caustic action on the gastrointestinal tract, severe stomach discomfort, vomiting, diarrhoea, collapse, and even death may result. Therefore, it is imperative to create a straightforward, reasonably priced chemosensor for carbonate that has the ability to analyse actual samples without intervention from endogenous substrates [20 - 23].

These aspects have piqued the interest of researchers, who have created a variety of methods to quantify CO_3^{2-} ions in real time, including the continuous-flow approach [19], the acoustic method [24], gas chromatography [25], pH ion-sensitive field effect transistor [26, 27], ion selective electrodes [28, 29], and the FT-IR method [30]. These techniques are costly or time-consuming. There are reportedly very few studies on carbonate sensors based on fluorescence. Patra *et al*. [31] reported, for example, the use of a Schiff base-based fluorescent-colorimetric chemosensor for CO_3^{2-} detection in an aqueous media. For Zn^{2+} and CO_3^{2-}detection, a different study [32] used a tetraphenyl ethylene-functioned salicylaldehyde-based AIE-activated Schiff-base (TEMPO). Similar to this, an organic compound that had been triazole functionalized was used to create a novel fluorogenic signaling probe for carbonate and bicarbonate ion detection. A different type of fluorescent probe that may be helpful is $[[Eu(HBPTC)(H_2O)_2]\bullet 2DDF_n]$ (where BPTC is benzophenone-3,3',4,4'-tetracarboxylate) and is based on a luminous lanthanide MOF. For instance, Ln^{3+} ions have distinct intra 4f - 4f transitions with extended excited state luminescence lifetimes that are fairly sharp, enabling effective excited state processes like luminescence resonance energy

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transfer (LRET) to take place [33, 34]. Similar to this, CO_3^{2-} detection uses a di cationic meso- Bis(benzimidazolium) Calix [4] pyrrole to recognize, sense, and trap bicarbonate anions.

2. LUMINESCENT RECOGNITION AND CHEMOSENSING OF CARBONATE IONS BY VARIOUS METHODS USING DIFFERENT RECEPTORS

- In 2014, Huiping Liu *et al* [35], proposed A luminescent lanthanide MOF-based thin film $[\{[Eu(HBPTC)(H_2O)_2]\cdot 2DMF\}_n]$ (BPTC = benzophenone-3,3',4,4'-tetracarboxylate) which is successfully created in an anhydride system by electrodepositing.

By applying a direct current in a nitrate solution, this method will cause OH^- anions to accumulate close to the cathode and hydrolyze benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA). This will then coordinate with the growth of Eu-HBPTC on the FTO surface, which will lead to the growth of MOFs directly on the electrode surface (Fig. **1**).

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2HO^- \qquad \textbf{(1)}$$

One could reasonably assume that the electrochemical production of the base in nitrate solution is the mechanism by which the thin films of Eu-HBPTC were deposited at the cathode [36]. As demonstrated in Fig. (**1**), the reaction (1) that raised the local concentration of HO^- and caused the BTDA to hydrolyze at the cathodic area resulted in the growth of MOFs directly on the FTO surface. The effects of conductive salt, electrolyte concentration, and current density on MOF film production are examined. They show that anhydride ligands can be used in place of carboxylic acid ligands in order to assemble the lanthanide MOF-based thin film using cathodic electrodeposition. Additionally, the MOF film's photoluminescent characteristics were examined, and the results of the photoluminescent measurement showed that the luminescent MOF thin film is an extremely effective carbonate in aqueous solution sensor (Fig. **2**).

The SEM, PXRD, and FT-IR were used to characterize the Ln-MOF film, which was found to have 80 luminous intensity and great stability in aqueous solution. Further evidence that this Ln-MOF thin film is a highly selective sensor for carbonate in aqueous solution comes from the observation of an evident luminescence quenching of the film for CO_3^{2-} aqueous solution whereas other anions exhibit no significant change in the same conditions (Fig. **3**). This carbonate sensor is currently being used in biological systems.

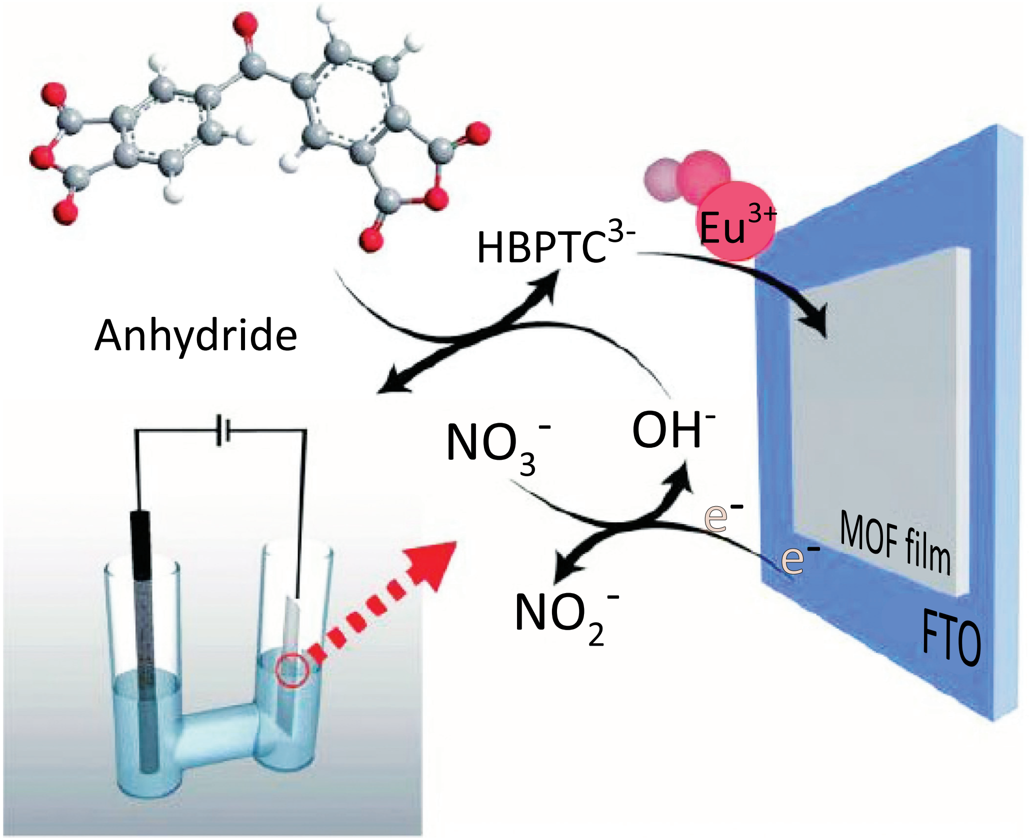


Fig. (1). General scheme for the cathodically induced electrodeposition of MOFs, involving the (**A**) reduction of nitrate and generation of HO95 (**B**) the hydrolysis of anhydride (BTDA), and (**C**) MOF crystallization from $HBPTC^{3-}$ and Eu^{3+}.

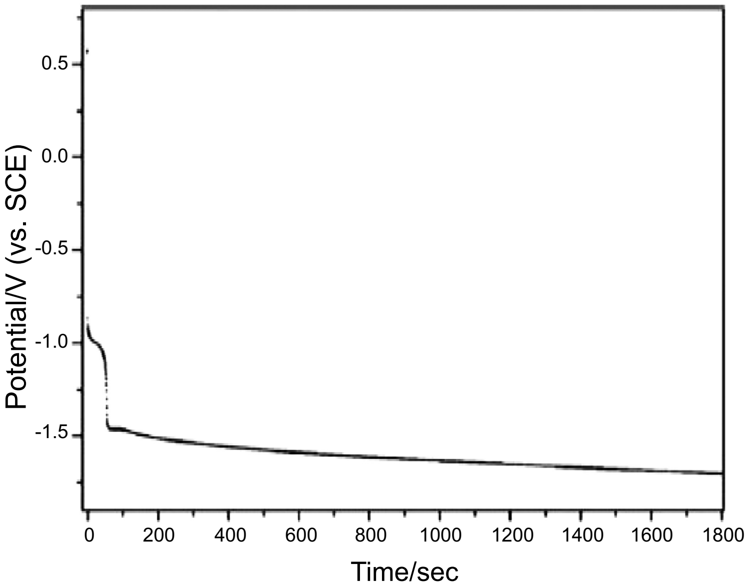


Fig. (2). Cyclic voltammograms of several solutions in DMF acquired at a 100mV scan rate using FTO working electrodes. The CVs of a 0.02 MBTDA solution and DMF employing a 75 FTO working electrode are displayed in the inset.

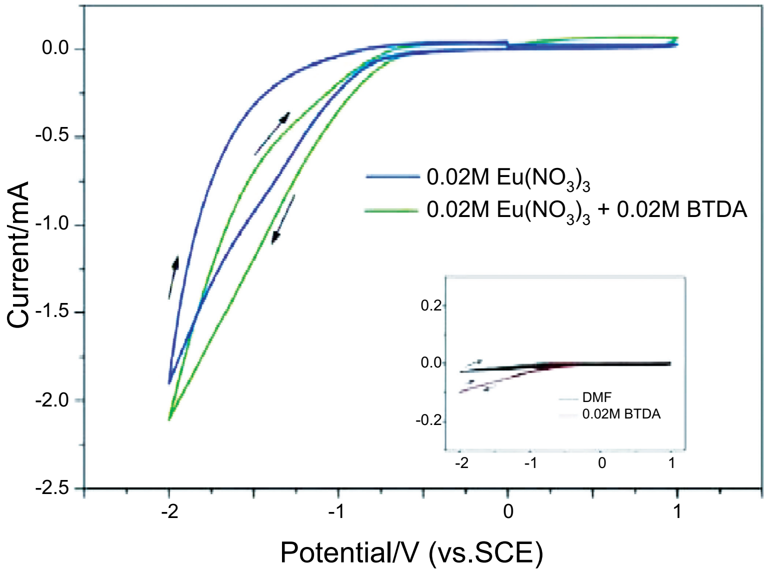


Fig. (3). Potential (*vs*. SCE) against time curve at constant current density during Eu-HBPTC film electrodeposition. At 298 K, the experiment was conducted at 0.4 mA·cm^{-2} in mixture 5 that contained 0.02 M Eu$(NO_3)_3$ and 0.02 M BTDA.

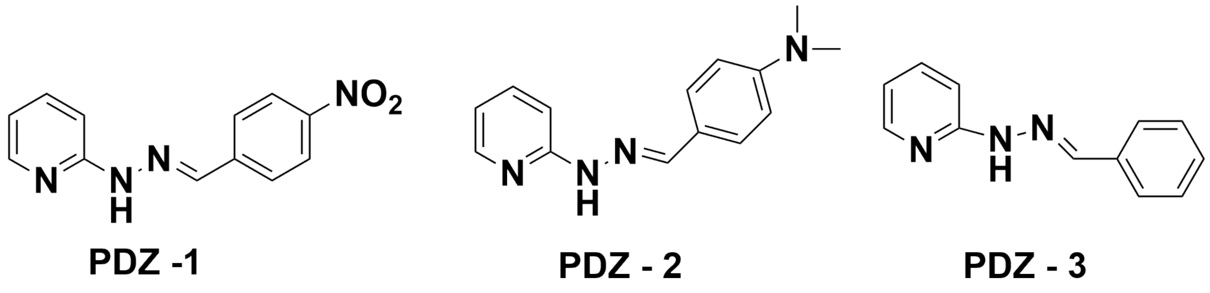


Fig. (4). Chemical structures of receptors PDZ-1, PDZ-2 and PDZ-3.

- Vikram Thimaradka and his groups [36], in 2017 prepared, a series of new receptors as PDZ-1, PDZ-2, PDZ- 3 based on 2-(aryldenehydrazinyl) pyridine have been designed for the detection of biologically and environmentally important ions (Fig. **4**).

As a binding site, PDZ-1 has a single-NH functionality. By adding -NO_2 functionality to the -NH proton, the strong acidity that results from the nearby pyridine moiety is further intensified. In general, a binding site-signaling subunit approach to the sensing of CO_3^{2-} ions is developed by the –NO_2 functionality, which also serves as a signaling subunit. When CO_3^{2-} ions are present, PDZ-1 exhibits a striking visual reaction that changes from yellow to green (Fig. **5**). Receptor PDZ-2 was created by adding PDZ-3, which does not have a substituent at the para position, and electron-releasing -NMe_2 (dimethylamine) to an NH proton carrying hydrazine-pyridine group.

Using the neutral organic receptor PDZ-1, colorimetric detection of CO_3^{-2} has been accomplished with a distinctive visual colour shift from yellow to green at 215 nm. UV–Vis spectroscopic and cyclic voltametric studies revealed the stoichiometry of binding and electrochemistry of host-guest complex formation. Moreover, the data of the UV–Vis spectral data corroborates well with the experimentally derived results confirming the associated colour change in the colorimetric experiment (Fig. **5**).

Fig. (5). The colour of PDZ-1, PDZ-2, and PDZ-3 (1×10^{-4} M in DMSO) changed as 18 equivalents of various anions (1×10^{-2} M in distilled water) were added in the following order: free receptor, From top to bottom, PDZ = PDZ-1, PDZ-2, and PDZ-3. PDZ + F^-, PDZ + Cl^-, PDZ + Br^-, PDZ + PO_4^{3-}, PDZ + HPO_4-, PDZ + ClO^-, PDZ + CO_3^{2-}, PDZ + HCO_3-, PDZ + SO_4^{2-}, PDZ + HSO_4^-, PDZ + NO_3^-, PDZ + AcO^- (Top to down: PDZ = PDZ-1, PDZ-2 and PDZ-3).

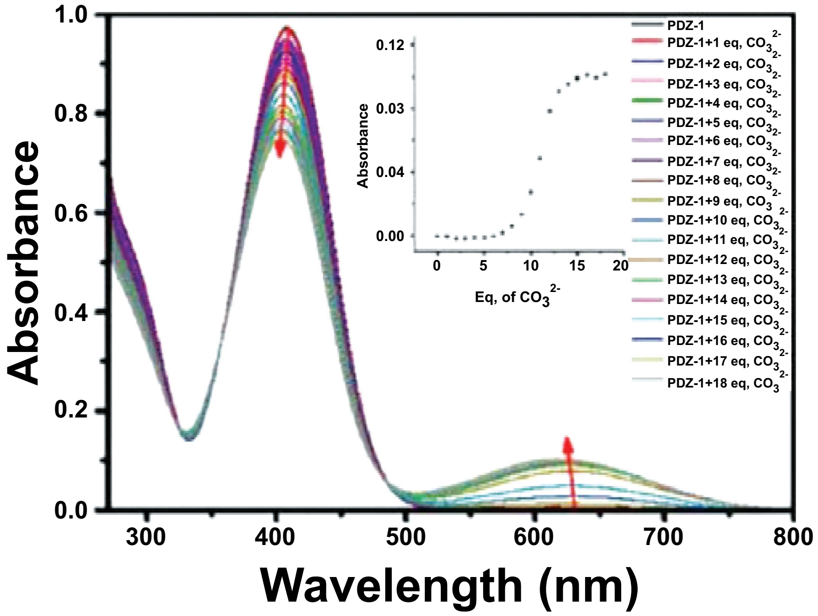


Fig. (6). UV-Vis titration spectra of the PDZ-1 receptor (1×10^{-4} M in DMSO) after one equivalent of CO_3^{2-} ions was added step-by-step (1×10^{-2} M in DMSO). The plot of the binding isotherm at 629 nm inset.

The pale-yellow hue of PDZ-1 is reflected in an absorption band at 408 nm in the UV-visible spectra of the compound. Using UV spectrophotometric titration data at 629 nm, the binding stoichiometry between receptor PDZ-1 and CO_3^{2-}ions was ascertained using the Benesi–Hildebrand Method (Fig. **6**).

The binding mechanism involved in the process of anion sensing was revealed by the PDZ-1 CO_3^{2-} complex, as demonstrated by electrochemical and DFT experiments. While PDZ-2 and PDZ-3 are inert in the ion detection process, PDZ-1 is highly selective for carbonate and exhibits no colorimetric reaction towards any other anions or cations (Fig. **7**).

The binding constant was measured and found to be 0.77×10^{-4} M^{-2}. PDZ-1 could successfully detect CO_3^{2-} ions at a concentration as low as 0.11 mM.

For carbonate, the PDZ-1 limit of quantification (LOQ) and limit of detection (LOD) were found to be 0.36 mM and 0.11 mM, respectively. PDZ-1 can be employed as a real-time carbonate sensor in biological and environmental samples due to its strong binding constant and detection limit. For the detection of CO_3^{2-}ion in aqueous conditions, PDZ-1 is a highly selective, aqueous-compatible small molecule colorimetric chemosensor based on 2-(arylidenehydrazinyl)pyridine. PDZ-1 can be effectively referred to as a selective sensor for an aqueous supply of carbonate ions, in contrast to the multi-ion sensing features of receptors that have been documented thus far [37 - 41].

The binding mechanism is shown by DFT analyses carried out on the PDZ-1 and PDZ-1 + CO_3^{2-} complex (Fig. **8**). It was discovered that the binding constant was 0.77×10^4 M^{2-}. An extremely selective optical sensor for an aqueous carbonate ion source is hydrazinyl pyridine. A highly selective fluorogenic sensor that may be applied to *in vivo* situations is currently in high demand. In the near future, fluorescent sensors for carbonate recognition could be developed using the approach made possible by the current work.

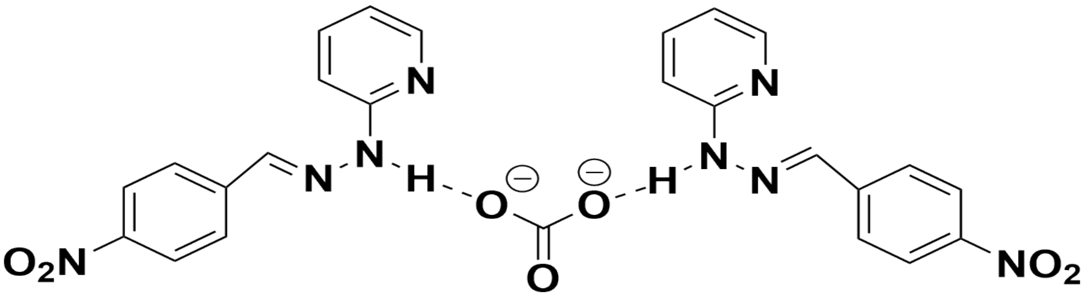


Fig. (7). Projected binding mechanism of PDZ-1 with CO_3^{-2}.

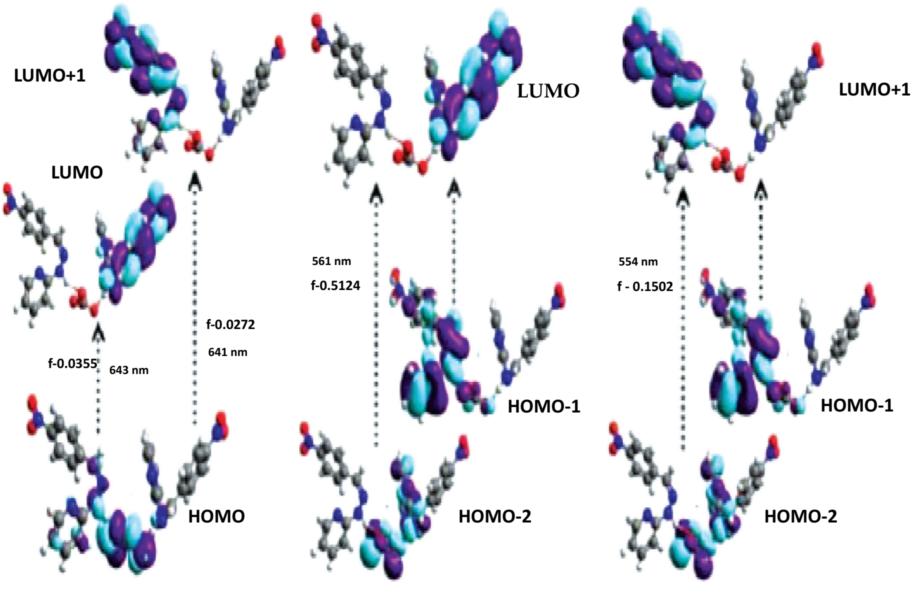


Fig. (8). Molecular orbitals of PDZ-1 and PDZ-1 + CO_3^{2-} complex with their energy levels at 6–31+GD.

Conclusively, PDZ-1 stands superior among all the colorimetric receptors reported. It is very selective, exhibiting a noticeable colour shift in visible light and a redshift in UV absorption spectra. It is also synthetically significant, as it can detect CO_3^{2-}ions with a single, strong binding site. This is the first time that a straightforward pyridine derivative has been investigated for CO_3^{2-} ion sensing.

A reversible fluorescent-colorimetric chemosensor based on a Schiff base was presented by Goutam K. Patra [31] and his groups for the visual detection of CO_3^{2-} in aqueous solution (Fig. **9**). Because of its exceptional sensitivity and selectivity towards carbonate ions, as evidenced by changes in both absorbance and fluorescence intensity and a colour shift from colourless to yellow, the chemosensor-L is utilized as a Schiff base. It costs less and is better for the environment. Chemosensor-L is a methanol-based solution of benzildihydrazone and syringaldehyde condensate in a 2:1 ratio.

According to the UV-Vis spectra, the presence of the carbonate ion in the L solution caused a rapid colour change from colourless to yellow, suggesting that receptor L can function as a "naked-eye" carbonate indicator in an aqueous solution. When the concentration of carbonate in the UV-visible titration experiment increased, Probe L showed two distinct isosbestic points in the absorption spectra at 285 and 375 nm. Additionally, the intensity of the newly red-shifted band at 423 nm, which was caused by the carbonate ion, increased steadily as more carbonate ions (0–30 equiv.) were added to the solution (Fig. **10**) [31].

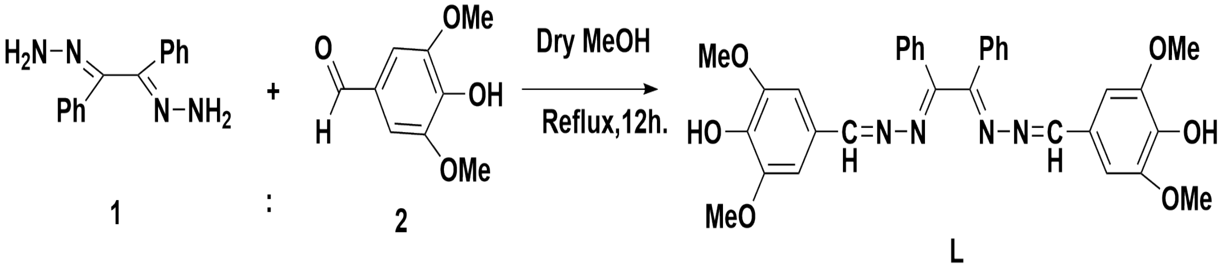


Fig. (9). Synthetic procedure for the preparation of receptor – L.

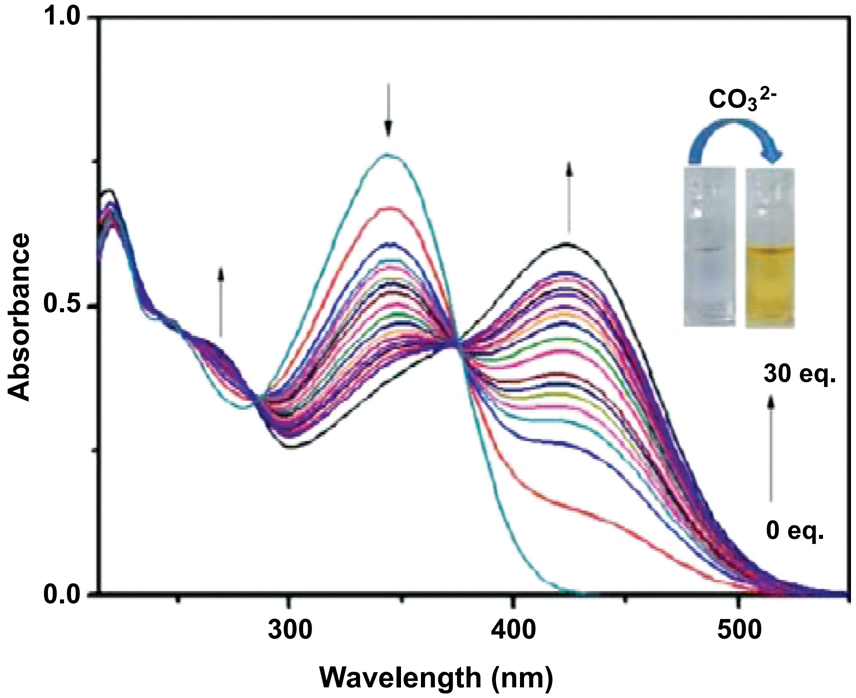


Fig. (10). Change in the absorption spectra of L after the addition of CO_3^{2-} up to 30 equiv.

Additionally, chemosensor L's behaviors are noteworthy in the fluorescence investigations for their ability to differentiate $CO_3^{2-}$from other anions (SO_3^{2-}, SO_4^{2-}, HSO_4^-, F^-, OAc^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HCO_3^-, N_3^-, NO_3^-). With the exception of CO_3^{2-}, **L** exhibits minimal emission and a poor fluorescence quantum yield at room temperature upon stimulation at 340 nm (Fig. **11**).

The NMR reports of the **L** have been also studied in this group. Hence, ^{1}H-NMR and HRMS spectral studies of the probe and the adduct define the chemical mechanism of carbonate ion binding with the receptor **L** (Fig. **12**). The two terminal hydroxyl groups of the Schiff base receptor were shown to be essential to the sensing process; the binding of the Na^+ ion to the receptor's terminal hydroxyl group caused the –OH proton in the free receptor to be slightly displaced by one equivalent of sodium carbonate. There is chemosensing property in L + Na_2CO_3. The L + Na_2CO_3 product exhibits van der Waals force of attraction, π–π stacking, and charge transfer.

Therefore, the noble Schiff base's reversible action is a necessity for creating innovative chemosensors with real-world applications. Ion reversibility in carbonate detection is a rare occurrence. By adding CH_3COOH, a Na^+ bonding agent, receptor L's recognition mechanism was made reversible. The regeneration of free receptor L was demonstrated by the formation of a peak at 345 nm and a decrease in absorbance strength at 423 nm when CH_3COOH was added to a combination of receptor L and Na_2CO_3 (Fig. **13**). Na_2CO_3 was added once again to regain the absorbance band at 423 nm. This reversibility is crucial for the creation of carbonate ion sensing devices.

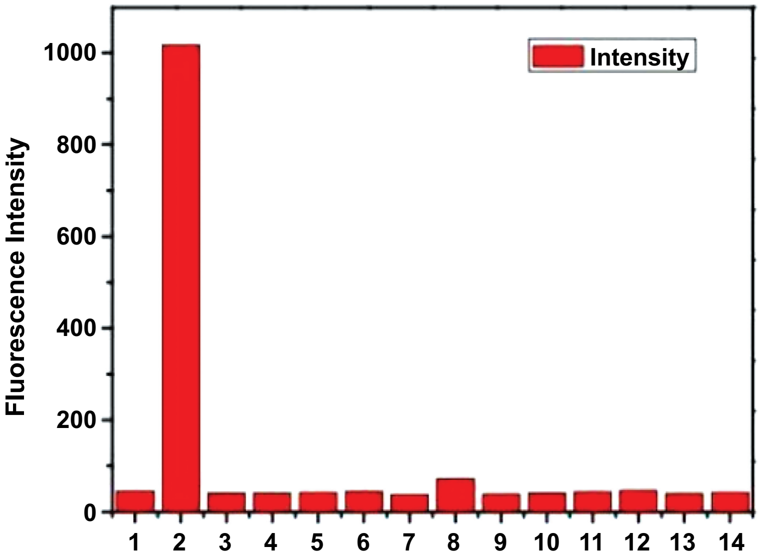


Fig. (11). Relative fluorescence of **L** in presence of different anions (1. Only L ;2. L+ CO_3^{2-} ; 3. L+ F^- ; 4. L + Cl^- ; 5. L+ Br^- ; 6.L+ I^- ; 7. L+ N_3^- ; 8.L+ HCO_3- ; 9. L+ NO_3- ; 10. L+ SO_4^{2-} ; 11. L + SO_3^{2-} ; 12. L+HSO_{3-} ; 13. L + OAc^- and 14. L+ H_2PO_4- using HEPES buffer.

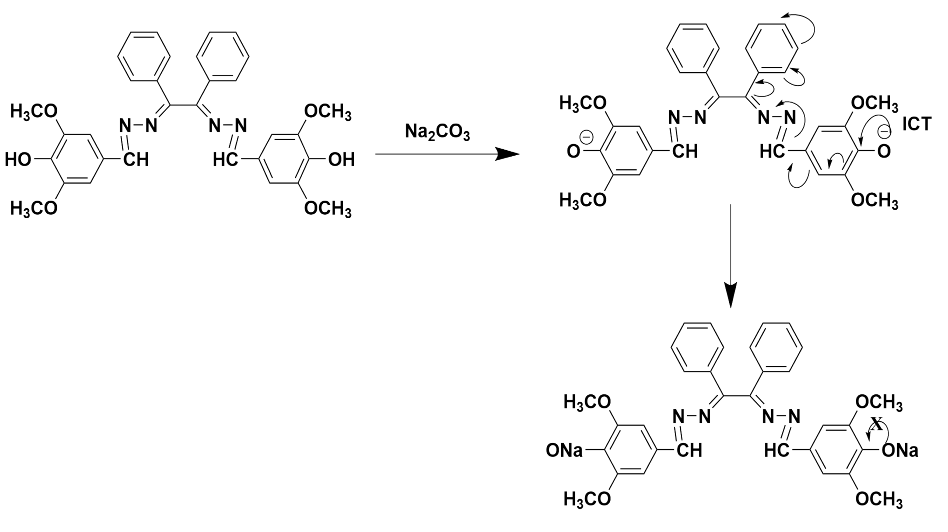


Fig. (12). Sensing mechanisms of **L** with Na_2CO_3.

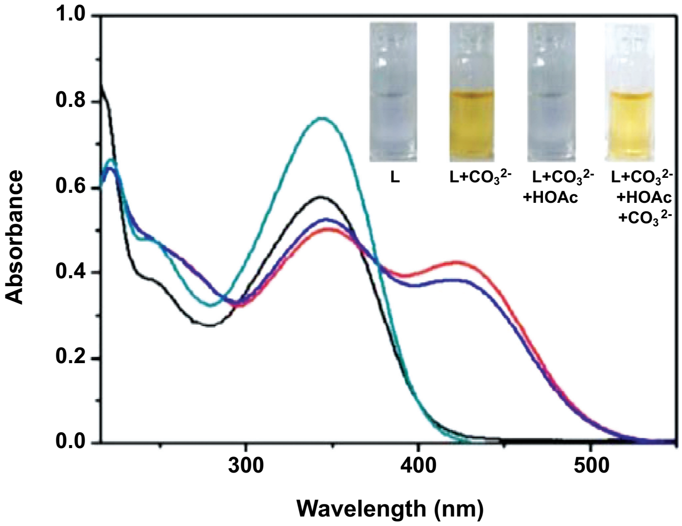


Fig. (13). Test of reversibility L with CH_3COOH (Green trace, L; red trace L+Na_2CO_3 ; black trace, L+Na_2CO_3 +$HOAc^-$ blue trace, L+Na_2CO_3+HOAc + Na_2CO_3).

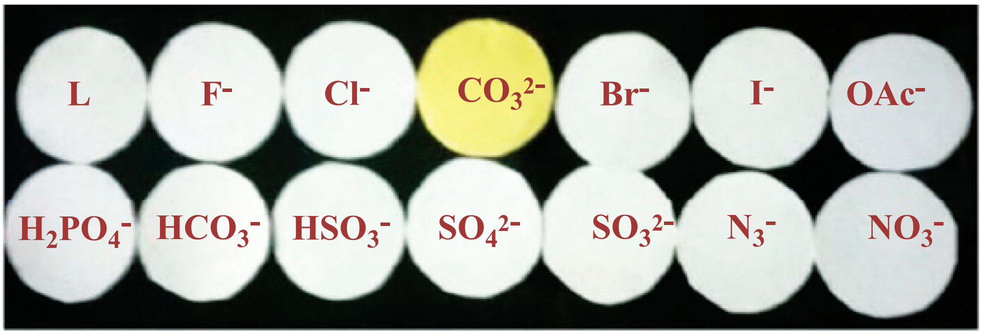


Fig. (14). Photograph of the test kits with **L** (0.5 mM) for detecting carbonate ions among other anions.

A unique bis Schiff base sensor is created in order to visually detect carbonate in an aqueous solution. One possible use for receptor L is as a "naked-eye" carbonate indicator. The chemosensor L is inexpensive, environmentally benign, and simple to assemble. Its exceptional selectivity and sensitivity to carbonate are demonstrated by variations in the intensity of its fluorescence and absorption. Studies also demonstrate that it is reversible. The suitability of the chemosensor L for actual sample analysis was examined using tap water, river water, and distilled water all in identical settings. Fluorescence enhancement was observed in the case of distilled water for all concentrations of carbonate ions with these chemosensor **L**. But in the case of tap water and river water, there is more enhancement in fluorescence intensity due to the presence of excessive carbonate ions in those water samples. **L** is greater receptor as competition with other anions in aqueous solution. The test kits coated with the chemosensor **L** solution would be convenient for detecting carbonate (Fig. **14**).

The development of a lansoprazole-based colorimetric was made possible in 2021 by Mehdieh Darroudi *et al.* [42] who presented chemosensor, a novel Schiff-based reversible chemosensor L in aqueous media that is utilised to detect CO_3^{2-} in aqueous media with the naked eye. The new benzimidazole-based receptor Lansoprazole has been used to detect carbonate anion by naked-eye and UV–Vis spectroscopy (Fig. **15**). The lansoprazole chemosensor selectively recognizes CO_3^{2-} ion over the other interference anions in the ethanol, followed by deprotonation and reflected 1:1 complex formation between the receptor and the carbonate ion. Lansoprazole exhibits splendid selectivity toward carbonate ions *via* a visible colour change from colourless to yellow with a detection limit of 57µM. The binding mode of CO_3^{2-} to the receptor **L** is supported by Density Functional Theory calculation (Fig. **16**).

Together with colleagues, Venkata N. K. B. Adusumalli [43] developed a luminescence resonance energy transfer-based technique for the detection of carbonate and bicarbonate ions in February 15, 2021. Gallic acid (GA) fulfills numerous functions in gallic acid-capped CaF_2:Tb^{3+} nanocrystals, which are used to achieve this. Due to the sensitivity of GA ligands, the gallic acid-capped CaF_2:Tb^{3+} luminous probe exhibits intense green emission at 544 nm (excitation at 296 nm). After the carbonate ions are added, the intensity of the green emission increases even further. The efficacy of the nanocrystal probe's detection is confirmed using both human blood and water samples (Fig. **16**).

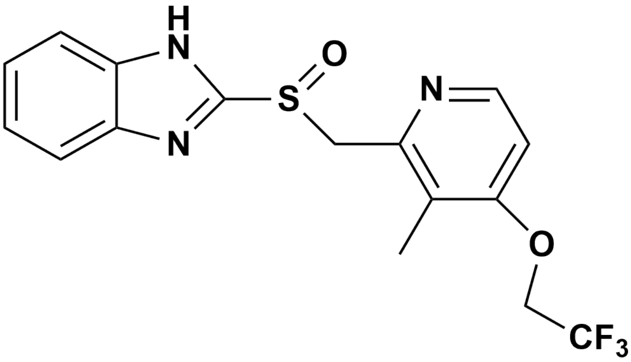


Fig. (15). 2-[3-methyl-4-(2,2,2,-trifluoroethoxy)-2-pyridil]sulfinyl-1Hbenzimidazole(Lansoprazole).

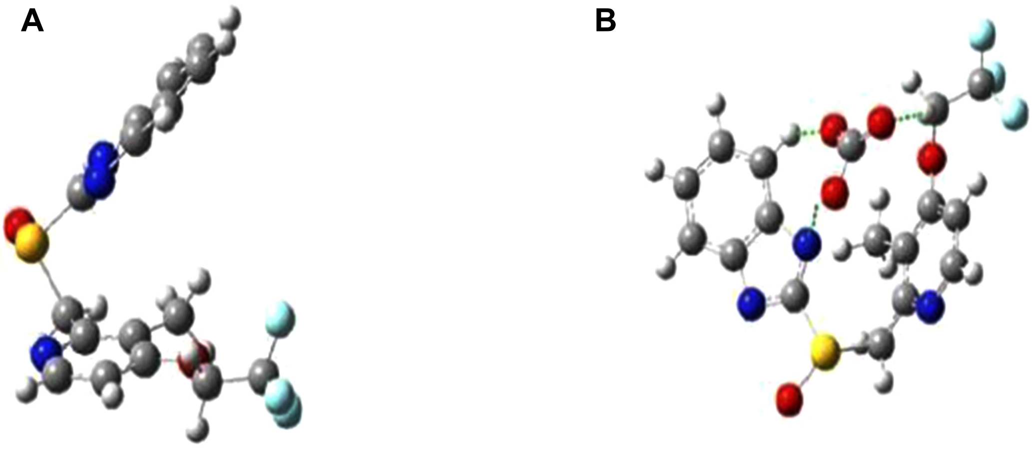


Fig. (16). Chemosensor (**A**) L, and (**B**) L-CO_3^{2-} optimized geometries.

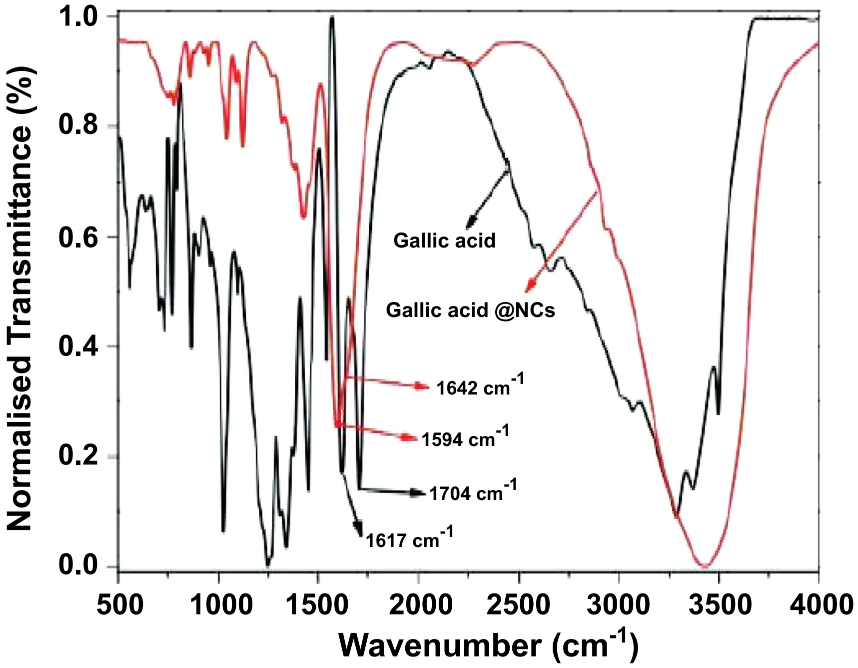


Fig. (17). FTIR spectra of pure gallic acid (GA) and GA-capped CaF_2:Tb^{3+} (2%) NCs.

GA-capped $CaF_2:Tb^{3+}$ (2 mol%) NCs were synthesized *via* a microwave irradiation method and the binding of the GA molecules to the $CaF_2:Tb^{3+}$ NCs was confirmed by using FT-IR analysis (Fig. **17**).

At room temperature, all luminescence studies were collected, and the NC solution had an initial pH of approximately 7.0. The following ions were present during the detection investigations in order to confirm that other ions did not interfere with the detection of CO_3^{2-} (Na_2CO_3): Mg^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Mn^{2+}, Fe^{2+}, Ca^{2+}, SO_4^{2-}, CH_3COO^-, NO_3^-, PO_4^{3-}, NaCl, NaF, and Hg^{2+} (Fig. **18**).

Water samples from a tap, pond, rain, and river were gathered for the actual water examination. Regarding the sample of tap water. Room temperature was used for the trials. The ability of the GA-capped $CaF_2:Tb^{3+}$ NCs to detect carbonate ions in actual water samples was examined using luminosity detection techniques (Fig. **19**).

After being placed in tubes with EDTA, human blood was centrifuged. The plasma with a pale yellow hue was divided. Different ratios of plasma components combined with distilled water were used to calculate the carbonates and bicarbonates in plasma, followed by GA-capped $CaF_2:Tb^{3+}$ (2%) Following the distribution of NCs throughout the aforementioned solution, luminescence measurements were taken (Fig. **20**) [32].

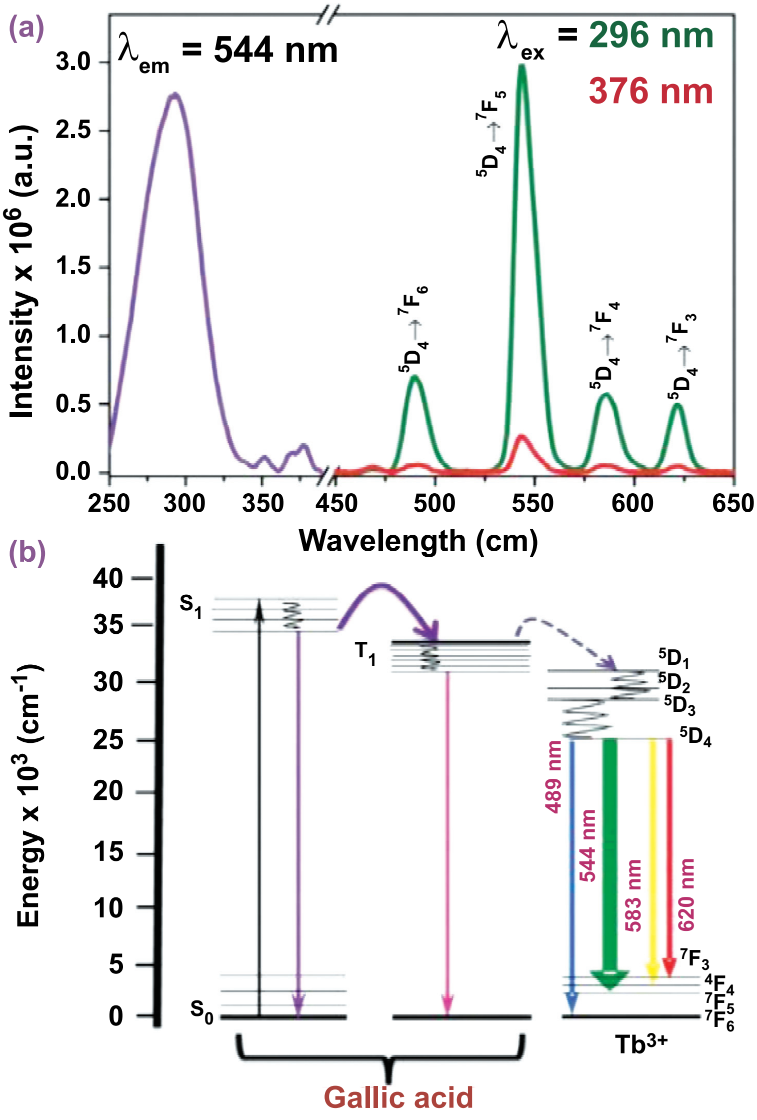


Fig. (18). (**A**) PL spectra and excitation of the GA-capped $CaF_2:Tb^{3+}$ (2%) NCs. (**B**) A schematic energy level diagram showing the suggested mechanisms for energy transfer between GA and Tb^{3+} ions.

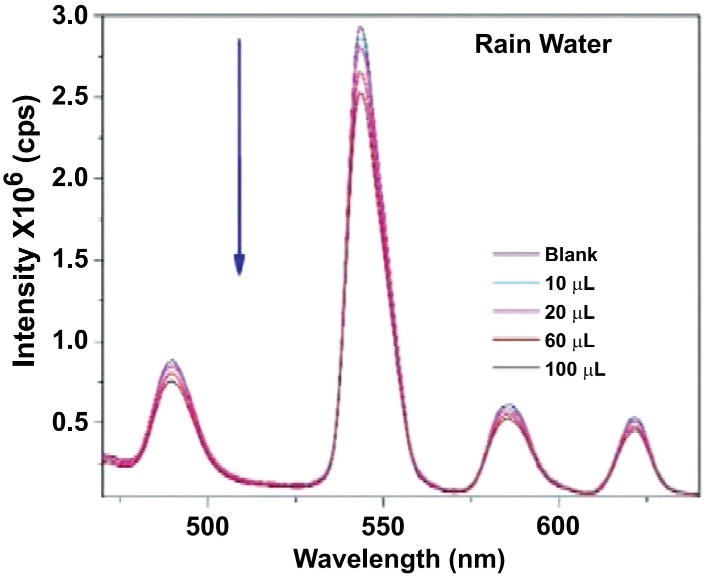


Fig. (19). Photoluminescence spectra of the GA-capped CaF_2:Tb^{3+} NCs collected with the addition of a different quantity of rainwater.

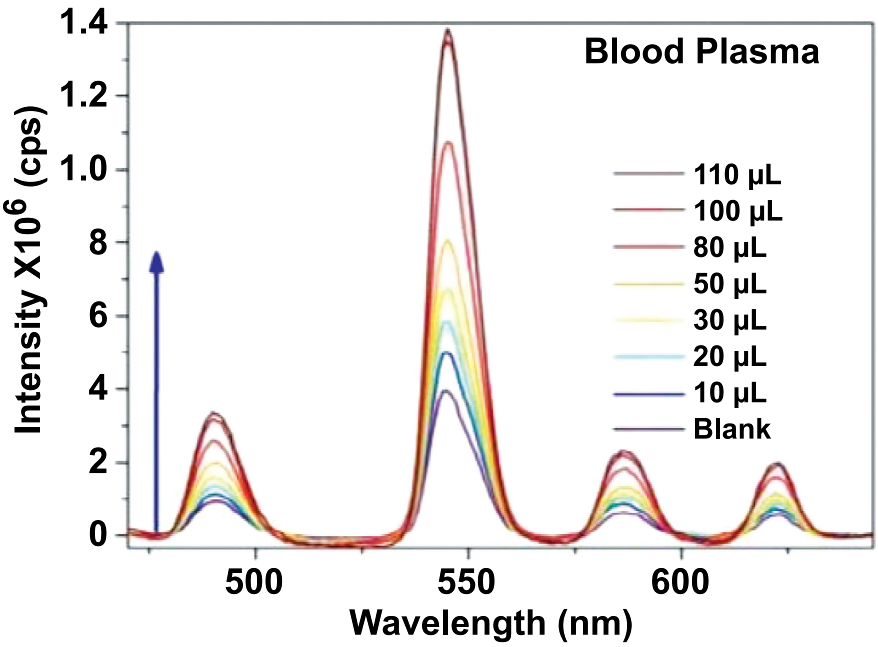


Fig. (20). The photoluminescence spectrum of the GA-capped CaF_2:Tb^{3+} NCs obtained after varying the amount of blood plasma added.

They do the experiment in D_2O solvent, and only when 300 mM concentration of CO_3^{2-}ions is added can the Tb^{3+} ion emission be noticed. As a result, in D_2O as opposed to H_2O, there is a substantially greater enhancement in the Tb^{3+} ion emission intensity with carbonate ions. This finding raises the possibility that the enhancement in emission intensity that has been observed is not the consequence of water molecules around the nanocrystals reducing non-radiative relaxation.

The brightness of green emission from a colloidal dispersion of NCs with carbonate ions (from 10 to 100 mM) increased, further confirming an increase in PL intensity of Tb^{3+} emission at 550 nm (Fig. **21**). The colloidal GA-capped CaF_2:Tb^{3+} NCs' digital pictures under UV light (Fig. **22**).

The rise in the luminescence intensity of the Tb^{3+} ions in the presence of CO_3^{2-} ions was analyzed using the Stern–Volmer equation (Fig. **23**) in order to assess the sensitivity of the GA-capped CaF_2:Tb^{3+} NCs towards the detection of CO_3^{2-} ions.

$$I/I_0=1+K_{SV}[C]$$

where I_0 and I represent the luminescence intensity of the NCs before and after the addition of CO_3^{2-}/HCO_3^- ions, respectively,

[C] is the concentration of CO_3^{2-}/HCO_3^- ions and K_{SV} is the quenching constant

The addition of carbonate ions is the only significant boost in the Tb^{3+} emission. An interference analysis was conducted to see if there was any interference from other analytes in the carbonate detection using GA-capped CaF_2:Tb^{3+} NCs. This method was expanded upon to identify CO_3^{2-} and HCO_3^- in blood samples. The measurement of CO_3^{2-}ions in clinical specimens is difficult but necessary. Heterogeneous organic (proteins), organic, and inorganic (metal ions, urea) components can be found in clinical samples. With the increasing blood plasma concentration from 10 mM to 110 mM for the NC dispersion, the luminescence intensity of Tb^{3+} ions in GA-capped CaF_2:Tb^{3+} NCs gradually enhanced (Fig. **24**).

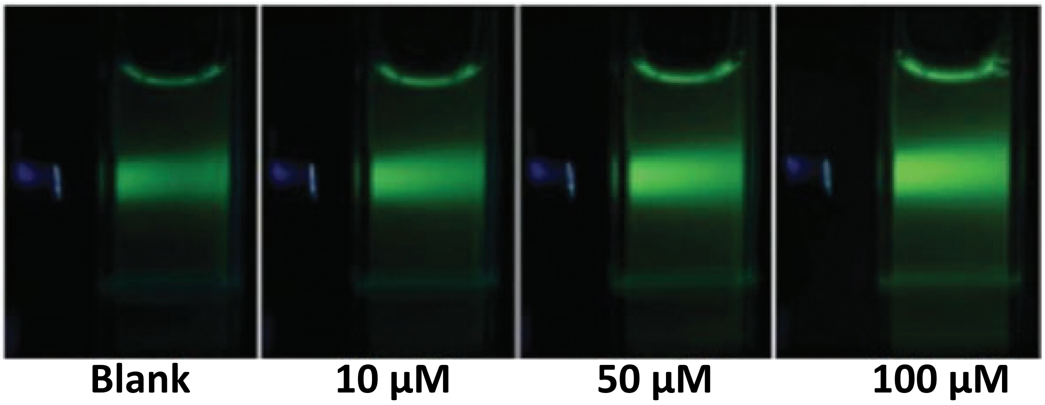


Fig. (21). Photoluminescence spectra of CaF_2:Tb^{3+} NCs with GA caps were obtained after adding Na_2CO_3 gradually. The bar diagram in the inset illustrates how the concentration of carbonate ions increases together with the intensity of Tb^{3+} luminescence.

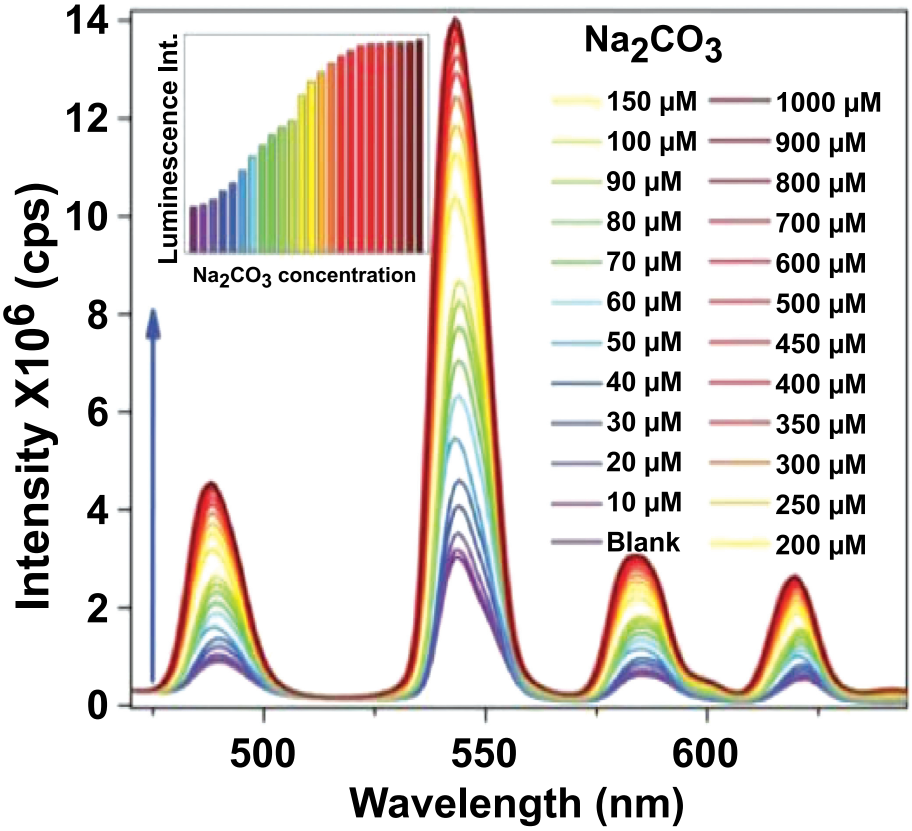


Fig. (22). Colloidal GA-capped CaF_2:Tb^{3+} (1 mg mL^{-1} ; blank) nanocrystals under UV light stimulation after adding 10, 50, and 100 mM CO_3^{2-} ions are shown in digital pictures.

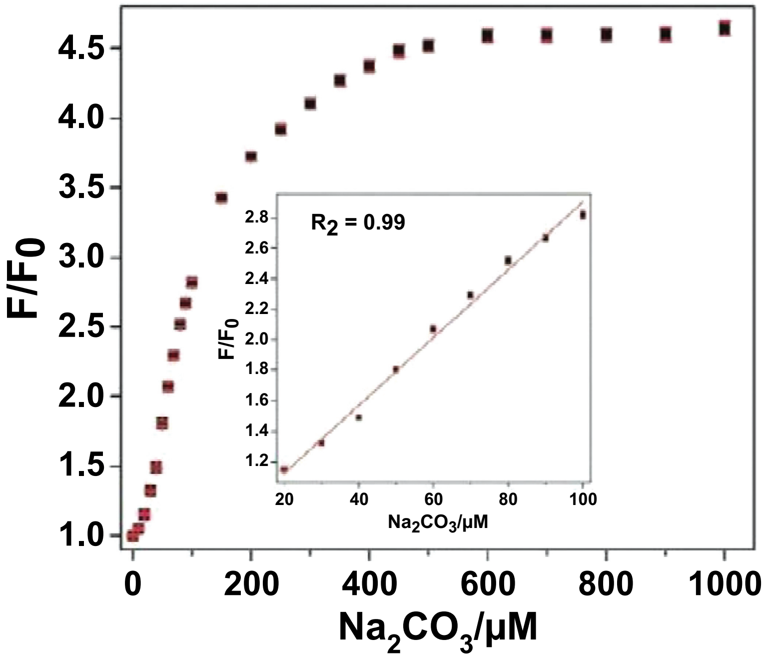


Fig. (23). The GA-capped $CaF_2:Tb^{3+}$ (2%) NCs' Stern-Volmer plot after increasing the amount of Na_2CO_3 added to the aqueous medium.

Conclusively Gallic acid plays a multifunctional role as a capping agent to control the nanoparticles' growth, as a sensitizer to enhance the luminescence of Tb^{3+} ions and as a linker to selectively bind to carbonate ions. The nanocrystals show bright green luminescence from the Tb^{3+} ions *via* energy transfer from GA's when excited in the UV region. The NCs increase the luminescence intensity of the Tb^{3+}ions, enabling them to detect carbonate ions in an aqueous solution with great selectivity. This is explained by the fact that in GA-capped $CaF_2:Tb^{3+}$ NCs with the aforementioned anions present, there is an increase in the energy transfer efficiency from gallic acid to Tb^{3+} ions. With this technique, carbonate and ions in an aqueous media can be detected with great selectivity and minimal interference from other analytes in the concentration range of 10 mM. To detect carbonate ions in actual water samples from a tap, pond, rain, or river, this research might be expanded. Last but not least, the GA-capped nanocrystals were able to identify carbonate in samples of human blood plasma, indicating that they are suitable for use in life science applications.

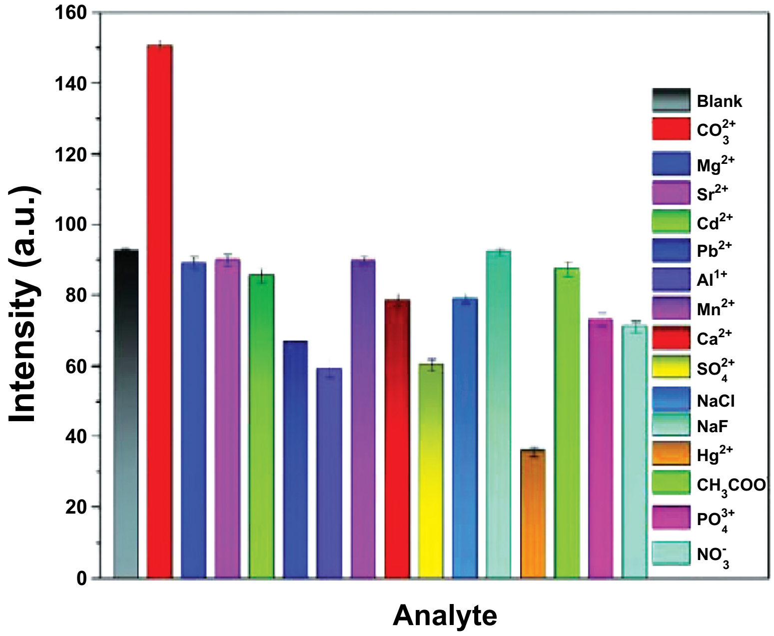


Fig. (24). The bar graph demonstrates the specific increase in Tb^{3+} emission intensity from GA-capped $CaF_2:Tb^{3+}$ (1 mg ML^{-1}) NCs containing 50 mM carbonate ions. On the other hand, very little improvement was observed when additional analytes (100 mM) were added.

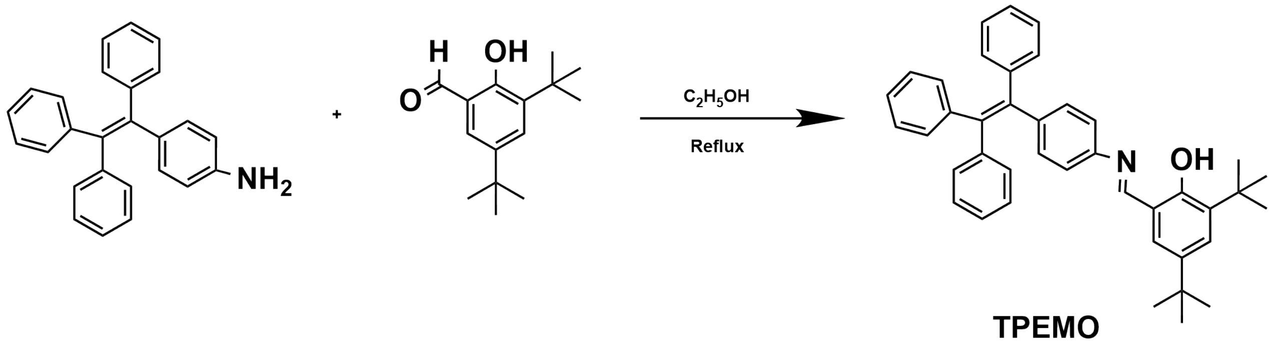


Fig. (25). Ligand system applied in the study.

- In October 2019, J. Jia and H. Zhao presented a different study that described a multi-responsive AIE-active tetraphenylethylene functioned salicylaldehyde-based base for reversible processes and CO_3^{2-} and Zn^{2+} detection [32].

Tetraphenylethylene-fuctioned salicylaldehyde -based AIE-active Schiff -base (TPEMO) had been designed and synthesized in solvent media (Fig. **25**).

Furthermore, upon grinding, this compound exhibits reversible mechanoflurochromism (MFC), resulting in a colour change from yellowish-green to orange-yellow. It exhibits selectivity and sensitivity towards Zn^{2+} and could sensitively detect CO_3^{2-} with a 1:1 ratio and emits an obvious fluorescence from blue to bright orange (Fig. **26**).

Graphical structure of Tetraphenylethylene-fuctioned salicylaldehyde -based AIE-active Schiff -base (TPEMO) (Fig. **27**).

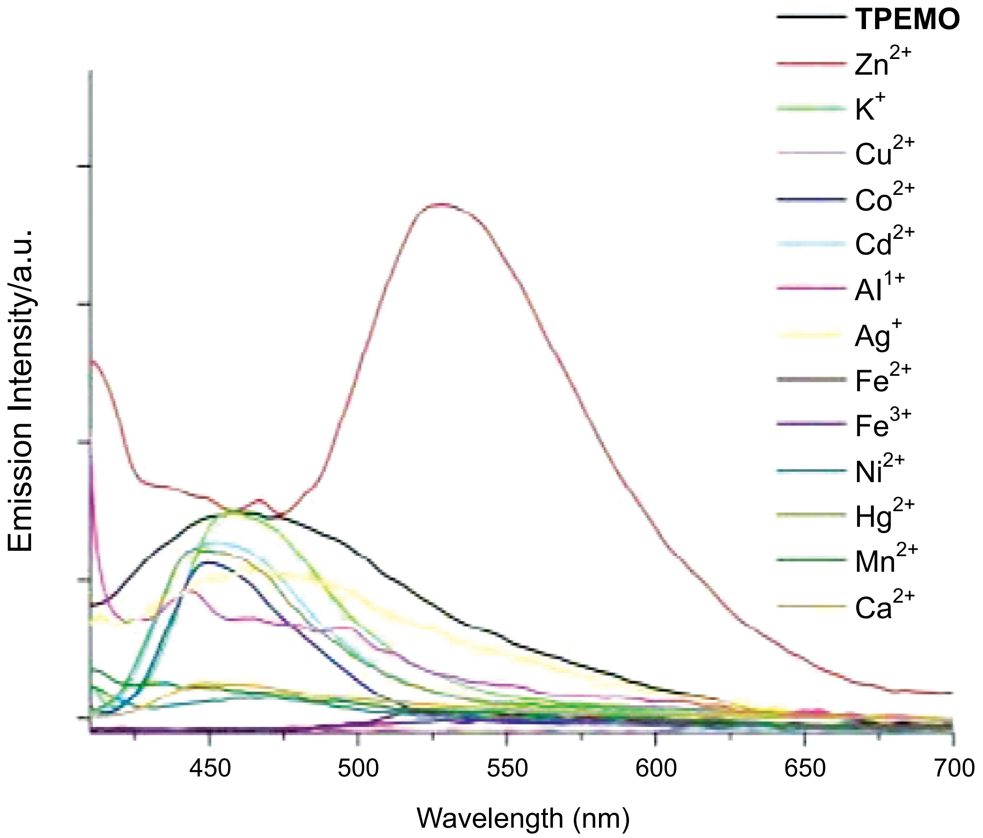


Fig. (26). Zn^{2+} has strong emission at 523 nm with many metals and CO_3^{2-} in the lowest range.

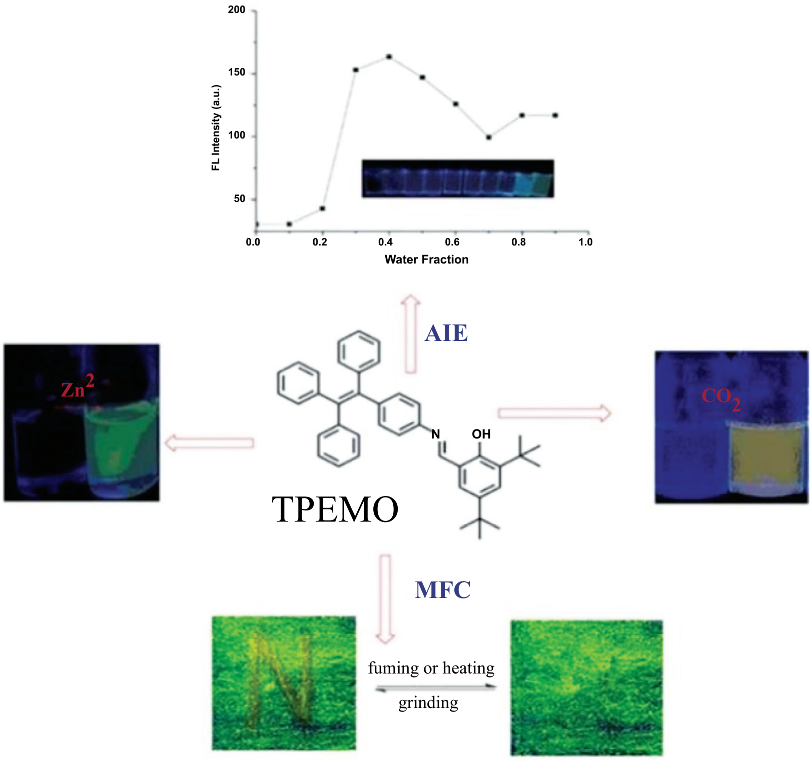


Fig. (27). AIE-active Schiff base based on tetraphenylethylene-functioned salicylaldehyde (TPEMO).

• The design and synthesis of a triazole-naphthalene hybrid for selective colorimetric and fluorometric sensing of carbonate ions was published by Harikrishnan Muniyasamy [44] and a collaborator on Aug, 2021. The probe has been extensively characterised using HRMS spectroscopy and ^{1}H and ^{13}C NMR spectroscopy. By exhibiting variations in both its UV–Vis absorption and emission spectra, CK demonstrates an exceptional selectivity and sensitivity towards carbonate ions over other anions. The carbonate ion's limit of detection in the emission and absorbance spectra is 1.8 µM and 7.2 nM, respectively. With the aid of the Job's plot, FTIR, NMR titration, and theoretical studies, the plausible sensing was verified. Additionally, the most obvious application of probe mechanism CK is the way of colourless to yellow carbonate detection with the naked eye. The receptor CK serves as a useful and practical sensor for carbonate ion environmental investigations. Furthermore, we use the carbonate ion's sensing performance with the probe to emulate a novel logic gate circuit (Fig. **28**).

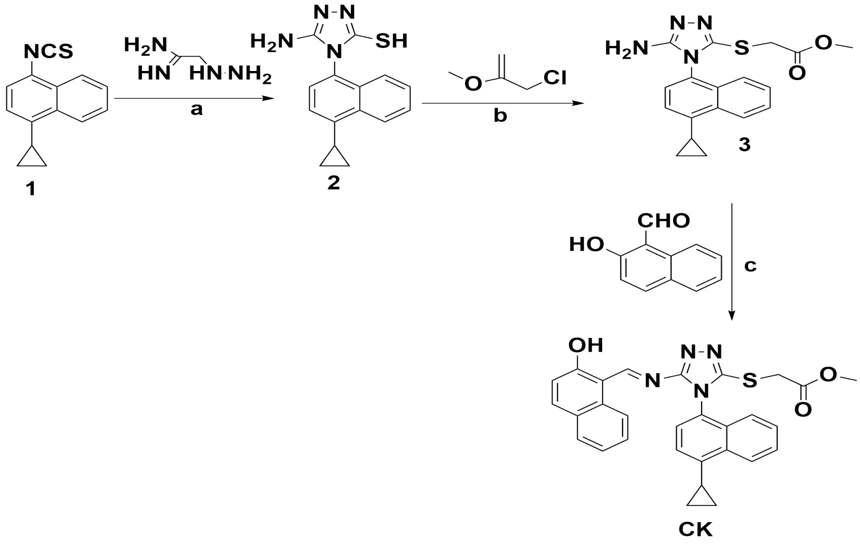


Fig. (28). The probe synthesis represented. The following are the conditions and reagents: (**a**) N, N-diisopropylethylamine, DMF, 50°C; (**b**) K_2CO_3, DMF, 50°C; (**c**) Methanol, Glacial acetic acid, 80°C.

Mahdieh Darroudi [45], *etal*. on May 3, 2021, using a simple, environmentally friendly catalytic reaction between ortho-phenylenediamine (O-PDA) and two distinct aldehydes in the presence of SBA-Pr-SO_3H, two new fluorescent and colorimetric chemosensors based on benzimidazole derivatives (A, B) have been successfully synthesised (Fig. **29**). Hg^{2+}, Ag^+, and CO_3^{2-} ions were successively detected by these chemosensors. In the instance of A, the stoichiometric ratio of the sensors towards Ag^+/CO_3^{2-} ions was 2:1, while for Hg^{2+} B, it was 1:1. The response times for both the A and B probes were quick (1 minute). Moreover, spectroscopic, DFT, and NCI simulations validated the optimised structures, binding processes, and electronic transitions with a high degree of concordance and correlation (Fig. **30**).

Competitive anions were added to the chemosensor A, and no discernible alterations were seen, indicating that the UV–Vis response was very selective for the CO_3^{2-} ion. Moreover, the addition of various ions was used to assess the UV–Vis spectral behaviour of chemosensor B (1×10^{-4} mol L^{-1}, in ethanol). Only the Hg^{2+} ion among all the anions under study significantly altered the UV-Vis absorption spectrum of chemosensor B; the other metal ions showed no discernible effects on the UV-visible spectra of chemosensor B (Figs. **31** and **32**).

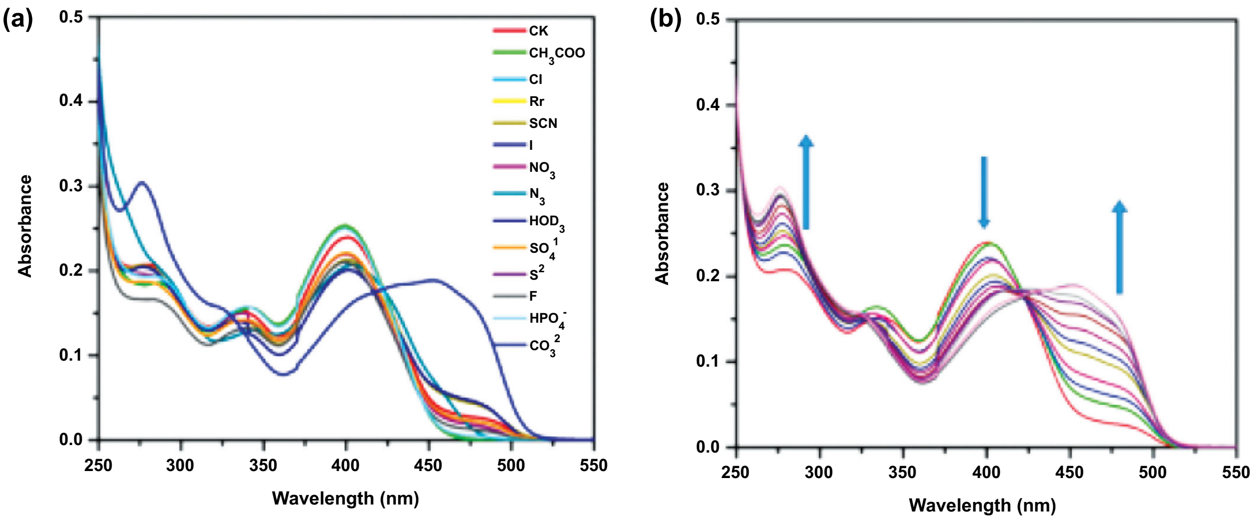


Fig. (29). (**A**, **B**) The selective spectra of CK (10 μM) with different anions (5 μM) and the sensitivity experiment of CK with varying carbonate ion concentrations (0.5 to 5.5 μM).

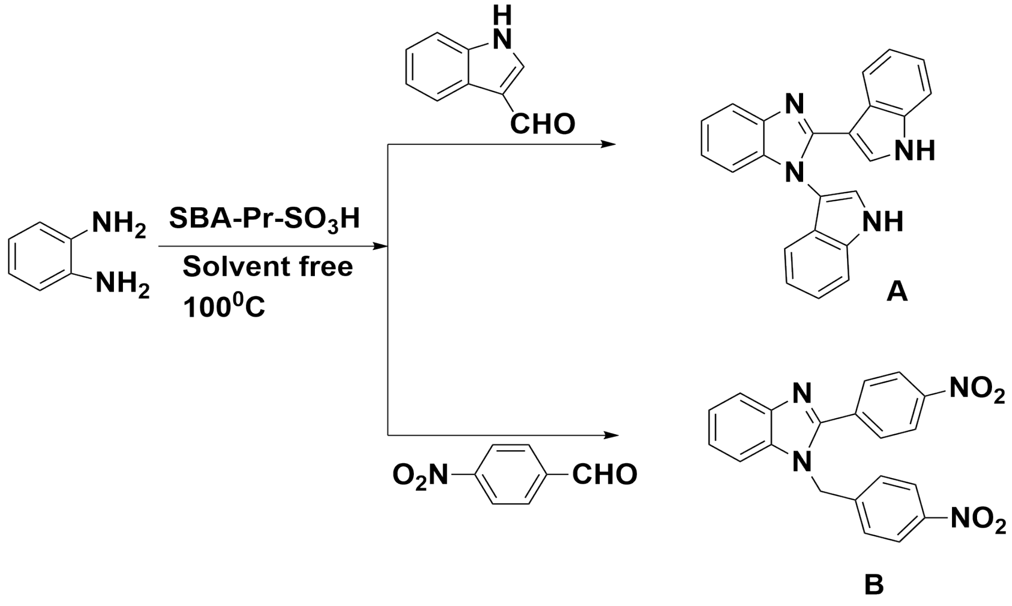
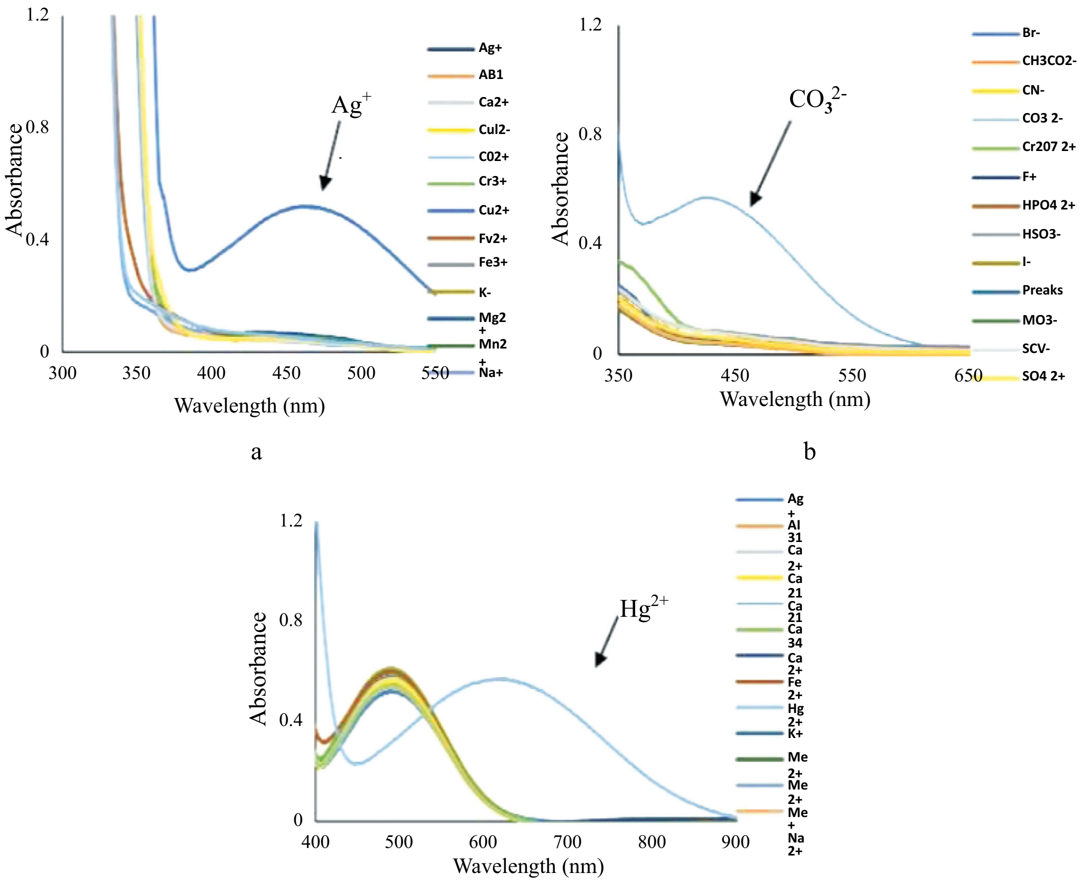


Fig. (30). Preparation of chemosensor **A>** and **B** in the presence of SBA-Pr-SO_3H.

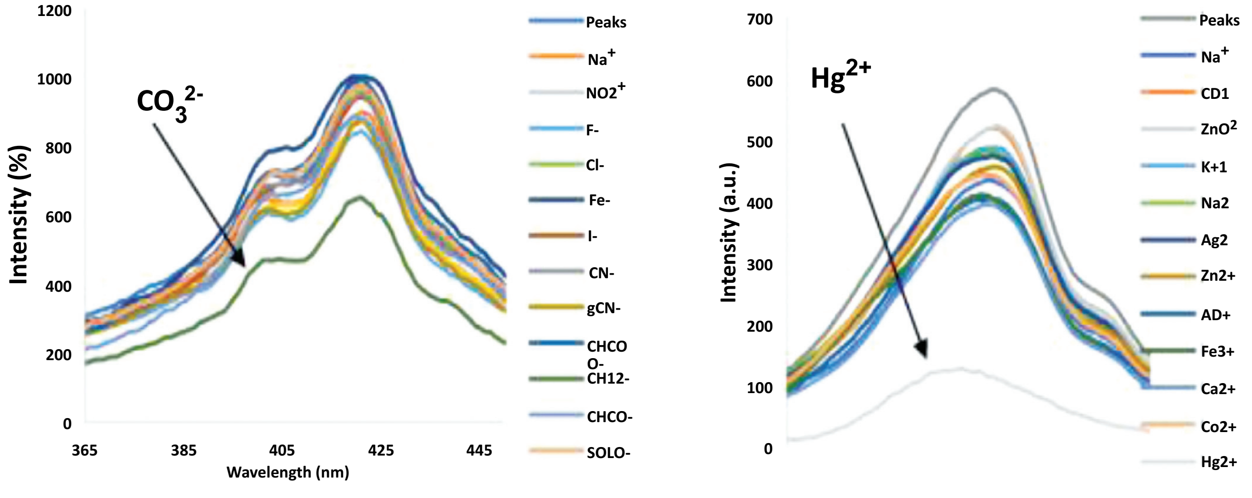


a

b

c

Fig. (31). The addition of different metal ions alters the absorption spectra of chemosensor A (5×10^{-5} mol L^{-1}, in ethanol) in response to Ag^+, chemosensor B (5×10^{-5} mol L^{-1}, in ethanol) in response to CO_3^{2-}, and chemosensor B (1×10^{-4} mol L^{-1}, in ethanol) in response to Hg^{2+}.



a

b

Fig. (32). The reaction of (**a**) chemosensor A (5×10^{-5} mol L^{-1}, in ethanol) to the addition of various anions (100 µL, L^{-1}, in ethanol) and metal ions (100 µL, 0.01 mol L^{-1}) with lamda$_{ex}$ at 425 nm is shown in the fluorescence spectrum.

Şükriye on June 15, 2018, Nihan Karuk Elmas [46] and associates created a novel colorimetric and fluorescent chemosensor for the visual assessment of carbonate ions using the solvent-free, microwave-assisted synthesis of 7,8-

dihydroxy-3-(4-methylphenyl) coumarin (DHMC) (Fig. **33**). By using spectroscopy techniques and microanalysis, the structural characterisation of DHMC was verified (MALDI-TOF, FT-IR, ^{1}H NMR, ^{13}C NMR, and 2D HETCOR). The binding behaviours of DHMC were examined using UV–vis and fluorescence spectroscopy towards different anions. When compared to other anions, DHMC exhibited a sensitive and selective fluorometric and colorimetric response to the carbonate ion. It was discovered that CO_3^{-2} has a detection limit of 1.03 μM. Furthermore, the utilisation of fluorescence imaging in living cells indicates that DHMC holds significant promise for biological imaging applications. Research has shown that DHMC can be used (Fig. **34**) as a rapid and reliable sensor for the determination of carbonate anion in a variety of practical applications.

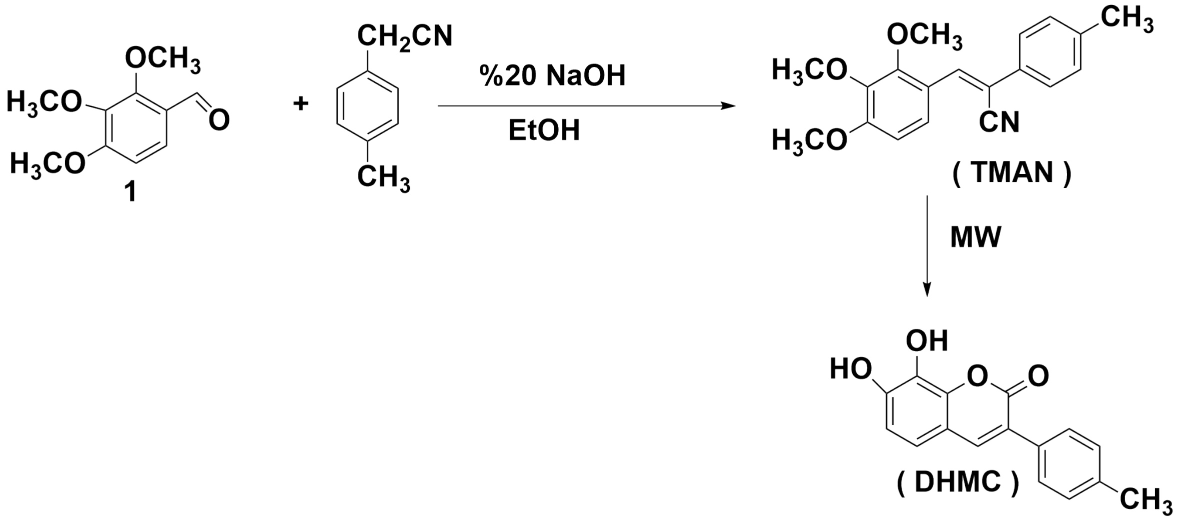


Fig. (33). Overview of the chemicals TMAN and DHMC.

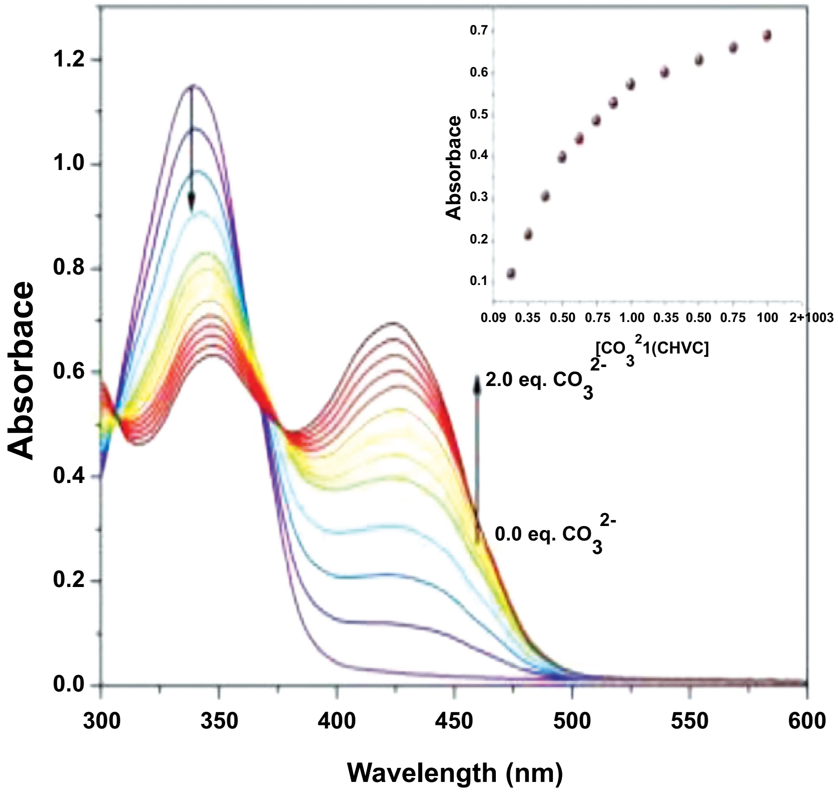


Fig. (34). UV-vis titration spectra of DHMC (50 μM) in H_2O/ACN (v/v, 99/1) with different concentrations of CO_3^{2-} (0.0 –5.0 equiv.).

CONCLUSION

Numerous studies were conducted to identify the carbonate ion using chemosensors, such as the novel bis Schiff base, the benzimidazole-based receptor Lensoprazole, optical sensors as a series of receptors (PDZ-1, PDZ-2, PDZ-3), gallic acid doping nanoparticles, and others. These methods were crucial for managing product quantity and were widely used in everyday products such as food, toothpaste, rubber, paper, glass, rayon, cosmetics, and many other products. It has applications in soil science, hydrology, geology, rock weathering, clinical areas, and agricultural planting. Due to their hazardous effects, which include vomiting, diarrhoea, collapse, and even death, it should also be necessary to detect these. These techniques respond to absorbance and fluorescence intensity and are all inexpensive, simple to synthesise, and eco-friendly. They can also be detected with the naked eye. It binds to carbonates with a strong affinity. It possesses reversibility. Based on the investigation and findings, receptors could serve as a helpful and practical sensor for carbonate environmental assessments. A simple, environmentally friendly, solvent-free procedure involving OPDA and benzaldehyde replaced in a good yield allowed for the effective synthesis of fluorescent and colorimetric chemosensors A and B, two benzimidazole-based turn-offs for the visual detection of metal ions and anions. In addition to fluorescence decrease, the dual-mode chemosensors A and B showed exceptional sensing capabilities towards CO_3^{2-} and Hg^{2+} ions, which can be attributed to the ICT process. Additionally, the chemosensors A and B may function as colorimetric sensors that detect Ag^+, CO_3^{2-}, and Hg^{2+} ions with the unaided eye, respectively. The fluorometric DLs for chemosensors A and B were determined to be 22 µM for CO_3^{2-} and 1.65 µM for Hg^{2+}, respectively. The colorimetric DLs for chemosensor A were projected to be as low as 1.82 for Ag+, 2.13 for CO_3^{2-}, and 9.73 for Hg^{2+} ion towards chemosensor B. We have developed a new hybrid sensor based on triazole and naphthalene that can detect carbonate ions with the unaided eye. The UV–Vis absorption and emission spectra of the chemosensor CK show improvements with respect to selectivity and sensitivity towards carbonate ions over other anions. The lowest detection limit of carbonate ions ever documented in the literature is 1.8 µM from emission spectroscopy and 7.2 nM from UV-visible spectroscope. Furthermore, a number of techniques, including Job's plot, FTIR, proton NMR titration, and theoretical research, supported the likely sensing mechanism. Our probe may also be used to detect carbonate ions in the solution phase with the unaided eye. Additionally, the probe CK is effectively used in environmental sample analysis for the quick detection of carbonate ions. Finally, we anticipate that the novel probe CK will prove to be an advantageous biological carbonate ion sensor. In H_2O/ACN (v/v, 99/1) solution, a turn-on fluorescence chemosensor based on 8-dihydroxy-3-(3-chlorophenyl) coumarin (DHMC) for CO_3^{2-} detection was created. The chemosensor demonstrated remarkable selectivity for CO_3^{2-} over other anions. There was a noticeable ten-fold increase in fluorescence intensity when CO_3^{2-} was present. Furthermore, it was discovered that the probe's detection limit was 1.03 µM. Additionally, it has been established that the fluorescent sensor can be used to monitor CO_3^{2-} anions in living cells. Consequently, the CO_3^{2-} anion can be determined using DHMC as a colorimetric and "turn-on" fluorescence sensor.

APPLICATION OF RESEARCH

To acquire knowledge for easy sensing of carbonate ions in real samples.

LIST OF ABBREVIATIONS

FRET = Fluorescence resonance energy transfer
CHEF = Chelation enhanced fluorescence
PET = Photon electron transfer

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

FUNDING

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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