Acetate ion augmented fluorescence sensing of Zn\(^{2+}\) by Salen-based probe, AIE character, and application for picric acid detection

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**Abstract**
Counter anion-triggered metal ion detection has been rarely reported by fluorimetric method. To address this challenging issue, a fluorescent probe (H_2L) has been synthesized from bromo-salicylaldehyde and hydrazine hydrate, and structurally characterized by single crystal X-ray diffraction. The probe shows very weak fluorescence itself. However, its emission intensity increases in the presence of Zn\(^{2+}\) over other metal ions. Surprisingly, the emission profile of this probe in presence of Zn\(^{2+}\) is augmented only when acetate anion (OAc\(^{-}\)) is present as counter anion, that allows for precise quantitative analysis by spectroscopic studies. The compositions and complexation among the probe, Zn\(^{2+}\) ion, and OAc\(^{-}\) are supported by ESI-MS, \(^1\)H-NMR, and Job’s plot. Based on these studies, it is confirmed that the binding ratio between probe: metal is 1:2 and the detection limit (LOD) for the Zn\(^{2+}\) is 2.18 \(\mu\)M. The probe is capable of recognizing Zn\(^{2+}\) ion in the wide range of pH \(\sim 6.5-9.5\), and it could be efficiently recycled by EDTA. Furthermore, the combinatorial molecular logic gate and memory device have been constructed from the fluorescent behavior of H_2L with Zn\(^{2+}\), OAc\(^{-}\), and EDTA input as based on NOT and AND gates. Interestingly, the aggregation-induced emission (AIEE) phenomenon is also perceived with greater than 50% water content in organic water mixtures, which are then useful for the detection of picric acid often used as explosive.

**KEYWORDS**
AIEE, counter anion, molecular logic gate, PET and CHEF, Picric acid, Schiff base, zinc sensor

1 | INTRODUCTION

Performing multiple tasks useful material is a significant and developing field of science in the cutting edge world. Such kind of materials makes an item modest, easy to use, and the time executives issue provides an endeavor and influence towards sustainable developments.\(^1,2\) Schiff base is a reasonable example of such type of materials because of its versatile application in different field of applied science including medicine and pharmacy (viz., antifungal, antibacterial, biocidal, antitumor, antiviral, and antimalarial properties), chemical synthesis...
and analysis, modern imaging technologies, molecular memory storage, photochromic materials and photodetectors in biological systems, and in colorimetric and fluorimetric ion/ molecule sensors.\textsuperscript{3–5} With that, the sensing of ions / small molecules by Schiff base has useful application in several interdisciplinary science like chemistry-biology, chemistry-physics, chemistry-mathematics, etc. due to its facile synthesis, superb selectivity and swift sensibility, exclusion of large instrument and huge cost unlike other several methods like atomic absorption spectroscopy (AAS), electrothermal atomization, inductively coupled plasma mass spectrometry, LC-GC/MS, solid-phase extraction (SPE), etc. Among the various metal ions present in the biosphere, Zn\textsuperscript{2+} is an important metal ion due to its direct and indirect involvement with the living species.\textsuperscript{5,6} Zinc, the second most abundant transition element in human body after iron, fills in as an extra flag for transition element in human body after iron, fills in as an extra flag-


down the process of the invention and lead to very high costs and against the principle of a green approach. Furthermore, acetate ion is a critical component of numerous metabolic processes.\textsuperscript{16,17} This anion is a possible tracer for malignancies and has been extensively investigated in prostate cancer and its metastases.\textsuperscript{18}

Further, aggregation-induced emission (AIE) is an important and emerging scientific phenomenon of Schiff base molecule started distinctly on earlier decade by the pioneer Prof. B.Z.Tang.\textsuperscript{19} In recent times, a number of organic luminogens display feeble emission in dilute solutions and become strong emissive in aggregated/solid-state.\textsuperscript{20} Molecule demonstrating fluorescence in aggregate or solid state has enormous application in opto-electronic gadget like OLED and in cutting edge innovation.\textsuperscript{21–24} Side by side, AIE phenomenon is a ready and enormous applied technique for nitroexplosive detection via fluorescence quenching.\textsuperscript{25,26}

In this connection, number of reports in literature on AIE property of salen based Schiff base.\textsuperscript{27–30} Zn\textsuperscript{2+} sensing with AIE property on salen derivative also reported.\textsuperscript{31,32} However, the anion viz., acetate triggered Zn\textsuperscript{2+} sensing by Salen type Schiff base are rarely reported.\textsuperscript{33,34}

Herein, we introduce a Schiff base fluorescent sensor \([2,2'-(\{1E,1'E\}-hydrazine-1,2-diyldienebis(methanyletheliden))bis(4-bromo phenol)], H\textsubscript{2}L for Zn\textsuperscript{2+}, derived from bromo-salicylaldehyde moiety which nearly covers all these requirements for Zn\textsuperscript{2+} over coexisting metal cations in a DMSO-water medium via a “turn on” signaling response assisted by only OAc\textsuperscript{-} with ~ 54 times emission intensity increment. Our as-synthesized chemosensor H\textsubscript{2}L is the example of chemosensor for simultaneous detection of Zn\textsuperscript{2+} and OAc\textsuperscript{-} ions in a co-operative fashion. The reversible sensing features enables us to construct an advanced level three input (Zn\textsuperscript{2+}, OAc\textsuperscript{-} and EDTA) single output molecular logic gate and molecular memory device. Simultaneously, by utilizing the benefit of AIE feature of H\textsubscript{2}L, it has been applied as a fast, simple, and economically practical fluorescent chemosensor for picric acid detection in mixed aqueous media as well as in paper strips through immediate naked eye on site recognition.

2 | EXPERIMENTAL SECTION

2.1 | Materials and Methods

All the chemicals used throughout the study were acquired from the commercial suppliers. 5-bromosalicylaldehyde (≥99.0%), hydrazine hydrate (≥99.0%), methanol (≥99.0%), HEPES (99.0%), Na\textsubscript{2}EDTA (98.0%), and glycerin were received from Merck India Ltd. Solvents used for spectroscopic studies were of analytical grade and distilled prior to their use. The progress of reaction monitored by TLC plate (F\textsubscript{254}) obtained from Merck India LTD. Instruments used for: Locally made melting point apparatus for melting point measurements, Bruker 400 MHz instruments for NMR spectra acquire, QTOF mass spectrometer for ESI-MS, Perkin Elmer-100 FT-IR spectrometers for IR spectral collection, HORIBA Jobin Yvon Fluorocube-01-NL fluorescence lifetime spectrometer for lifetime measuring. The stock solutions of different metal ions were made either from perchlorate, chloride, acetate or nitrate salts in methanol or water. The stock solutions of different anions were made from respective sodium, or potassium salts. Double beam UV-Visible spectrometer (model-evolution 201) and Jasco 8500 fluorimeter were used for absorbance and fluorescence data acquisition, respectively.

2.2 | Single crystal X-ray crystallography

The data based on single crystal X-ray diffraction of H\textsubscript{2}L was recorded (∼293K) on Bruker SMART APEX-III CCD diffractometer by graphite monochromated Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073\)Å). Bruker Apex-II suite was used to perform the data reduction, structure solution, refinement, and the integration of data by SAINT\textsuperscript{35} program and the absorption corrections using SADABS.\textsuperscript{35} SHELXL-2014\textsuperscript{36} on F\textsuperscript{2} is employed for full-matrix least-squares refinements using anisotropic refinement for all non-hydrogen atoms. All the hydrogen atoms become in their own geometrical places. The ORTEP vision is in Figure S1. The refinement data for H\textsubscript{2}L is given in Table 1.

2.3 | Synthesis of the chemosensor H\textsubscript{2}L

To the methanolic solution of 5-bromosalicylaldehyde (201 mg, 1.0 mmol), hydrazine hydrate (25 mg, 0.5 mmol) in methanol was added dropwise with continuous stirring. The reaction was monitored by TLC plate from time to time. Further stirring for another 24 hrs gave a yellow colored precipitate. The ensuing product was collected, filtered, and recrystallized from methanol to obtain a bright yellow crystalline
TABLE 1 Crystal data and structure refinement for H<sub>2</sub>L (CCDC No. 1961337)

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SCHEME 1 Synthetic route of the chemosensor H<sub>2</sub>L

solid H<sub>2</sub>L (Scheme 1). Yield: 93%, M. Pt.: 306-308° C (Lit. M. Pt.: 303-305 °C). Elemental analysis: C<sub>14</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub> Found (%): C, 42.61; H, 2.52; Br, 40.18; N, 7.02; O, 8.67. Calcd (%): C, 42.24; H, 2.53; Br, 40.15; N, 7.04; O, 8.04

2.4 Sample preparation for absorbance and photoluminescence studies

Stock solutions of various metal ions (1 × 10<sup>-2</sup> M) were prepared in de-ionized water. A stock solution of H<sub>2</sub>L (2 × 10<sup>-3</sup> M) was prepared in DMSO-H<sub>2</sub>O (9:1). The solution of H<sub>2</sub>L was then diluted to 10 × 10<sup>-6</sup> M with DMSO /aqueous HEPES buffer (5μM, pH 7.2; 9:1, v/v) for spectral studies by taking only 20 μL stock solution of H<sub>2</sub>L (1 × 10<sup>-3</sup> M) and making the final volume 2 mL adding DMSO. In selectivity experiments, 50 μL (1 × 10<sup>-2</sup> M) metal ion or anion solution were added into 2 mL of H<sub>2</sub>L solution (10 × 10<sup>-6</sup> M). For fluorescence measurements, excitation wavelength was provided at 410 nm.

2.5 Calculations of the detection limit

The detection limit is determined based on the fluorescence titration. The detection limit (LOD) of the probe H<sub>2</sub>L for Zn<sup>2+</sup> is determined using the following equation.

\[
\text{Detection limit (LOD)} = 3\sigma/k \tag{1}
\]

where σ and k are the standard deviation of blank measurement and slope between the fluorescence emission intensity versus metal ion concentration, respectively.

2.6 Binding constant evaluation

The binding constant (K<sub>a</sub>) for the H<sub>2</sub>L –Zn<sup>2+</sup> complex was calculated using the following Benesi–Hildebrand equations from fluorescence titration data.

\[
\frac{F_{\text{max}} - F}{F - F_0} = 1 + \frac{1}{K[Zn^{2+}]} \tag{2}
\]

where F<sub>0</sub>, F, and F<sub>max</sub> are the fluorescence intensity of H<sub>2</sub>L in the absence of externally added Zn<sup>2+</sup>, at different Zn<sup>2+</sup> and with Zn<sup>2+</sup> in large excess concentration, respectively. K (M<sup>-1</sup>) is the association constant.

2.7 Fluorescence lifetime measurements

Fluorescence lifetimes were determined by the method of Time-Correlated Single-Photon Counting (TCSPC). Laser diode at 375 nm was utilized as the excitation source and the signals were collected at the magic angle of 54.7° to eliminate fluorescence anisotropy decay. DAS-6 decay analysis programming was used for decay analysis. Mean (average) fluorescence lifetimes were measured using the following equation.

\[
\tau_{av} = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i} \tag{3}
\]

in which α<sub>i</sub> is the pre-exponential factor corresponding to the <i>i</i>th decay time constant, τ<sub>i</sub>.

2.8 Computational details

The geometry optimizations of ligand (H<sub>2</sub>L) and complex [Zn<sub>2</sub>(L)(OAc)<sub>2</sub>](1) were generated in ground-state calculations and in
FIGURE 1 In the picture the two molecules built from the two independent units are indicated in different colors: A, The H-bonded (4,4) net with molecular synthon R\textsuperscript{4}(32); B, The molecular assemblies e.g. CH⋯π and NH⋯O interactions; C, The H-bonded 2D network in crystallographic ac plane; D, The space filling of crystal packing viewed down crystallographic “c” axis

3 | RESULTS AND DISCUSSION

3.1 Synthesis of the chemosensor H\textsubscript{2}L

The H\textsubscript{2}L was prepared by a simple condensation reaction between hydrazine and 5-bromosalicylaldehyde. The structure of H\textsubscript{2}L was characterized by elemental analysis, SCXRD, \textsuperscript{1}H \& \textsuperscript{13}C NMR, ESI-MS, FTIR spectroscopy (Figure S1-S5). The SEM-morphology of H\textsubscript{2}L exhibits a rod-like shape (Figure 7).

3.2 Structural description of H\textsubscript{2}L

The \textsuperscript{1}H NMR spectrum of H\textsubscript{2}L shows characteristics singlet assignable to phenolic (-OH) and aldime (-CH = N) protons around δ 11.13 ppm and 8.94 ppm, respectively. The presence of base peak at m/z, 397.8 in the HRMS of probe corresponds to [H\textsubscript{2}L]+. The FT-IR spectrum of H\textsubscript{2}L shows a broad band at around 3562.5 cm\textsuperscript{−1} due to phenolic –OH group, whereas the band at 1566.9 cm\textsuperscript{−1} refers to the -C = N (for azomethine) stretching frequency.

The single-crystal X-ray diffraction study allows to establish the detailed structure of H\textsubscript{2}L and is comparable with the report\textsuperscript{50} in a different form which could be useful for comparison to the current structural characterization (Table 1). The diffraction study shows two half molecules arranged about a crystalloinversion centre. Two different bond lengths of C = N, 1.279(1) and 1.271 (2) Å are comparable with the reported data\textsuperscript{51} and the hydrazine N-N lengths of 1.395(7) and 1.401(9) Å, are also similar with published data.\textsuperscript{52} The two centro-symmetric H\textsubscript{2}L mononuclear unit is connected through H-bonding interactions (\textsuperscript{9}CH⋯O = 2.689Å, \textsuperscript{6}CH⋯Br = 3.044Å) with molecular synthon R\textsuperscript{4}(32) to form (4,4) net (Figure 1A). H\textsubscript{2}L unit exhibits the supramolecular assemblies e.g. CH⋯π (\textsuperscript{9}CH⋯π = 2.964-3.054Å) and \textsuperscript{4}NH⋯O = 1.922-1.965Å interactions (Figure 1B) to form

the gas phase by DFT\textsuperscript{41} method along with CPCM model (conductor-like polarizable continuum model).\textsuperscript{42-44} B3LYP\textsuperscript{55,46} function was employed for the study. The absorbance profile in DMSO medium for H\textsubscript{2}L and [Zn\textsubscript{2}(L)(OAc)\textsubscript{2}](1), were demonstrated by time-dependent density functional theory (TDDFT)\textsuperscript{47} and used the lowest 40 singlet – singlet transitions for these calculations.

The 6-31+g basis set for C, H, N, O, and Zn atoms were employed for all the calculations. The frontier molecular orbitals with electron-density plots were arranged using Gauss View 5.1 software and Gaussian 09W software package.\textsuperscript{48} Gauss Sum 2.1 program\textsuperscript{19} was introduced to analyze the molecular orbital contributions.
2D framework (Figure 1C) in crystallographic ac plane to enhance the structural stability of the probe. The two \( \text{H}_2\text{L} \) molecules are arranged in a herringbone fashion when seen down “c” axis (Figure 1D).

### 3.3 Photophysical (absorbance and fluorescence) investigations with metal ions

The absorption and fluorescence behavior of \( \text{H}_2\text{L} \) were studied in DMSO-\( \text{H}_2\text{O} \) (9:1, v/v, 5 μM HEPES buffer pH 7.2). In its absorption spectrum, \( \text{H}_2\text{L} \) (20 μM) exhibits two characteristic peaks centered at 295 nm and 365 nm originating from π-π* and n-π* transitions, respectively. To explore the potential use of \( \text{H}_2\text{L} \) as a chemosensor, the absorbance and fluorescence properties of \( \text{H}_2\text{L} \) were compared with before and after addition of 25 equiv. of the alkali metal ions, alkaline-earth metal ions, and transition-metal ions (viz., \( \text{Ba}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Mn}^{2+}, \text{Al}^{3+}, \text{Co}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{Na}^+, \text{K}^+, \text{Fe}^{3+}, \text{Zn}^{2+} \)) as perchlorate salt; \( \text{Fe}^{3+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Hg}^{2+}, \text{Na}^+, \text{K}^+ \), and \( \text{Zn}^{2+} \) as their perchlorate salt; \( \text{Fe}^{3+}, \text{Zn}^{2+} \) as chloride salt and also zinc acetate salts, separately. Out of the sixteen metal ions mentioned above, significant absorption spectral change of \( \text{H}_2\text{L} \) was observed with few metal ions like \( \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+} \) (Figure 2A). Such type of spectral shift indicates primarily moderate to strong interaction of the probe \( \text{H}_2\text{L} \) toward \( \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+} \) ions. In presence of \( \text{Cu}^{2+} \), the UV-spectrum character changes unlike as compared to other metal ions. Although the copper-mediated hydrolysis of the imine bond is a common phenomenon in presence of water as reported earlier,\(^5\) in our case, it is not due to hydrolysis. Further experiment has been performed to check whether the change in absorption is due to hydrolysis or complexation in presence of \( \text{Cu}^{2+} \) ion. As depicted in Figure S6, the characteristic peak at 365 nm of the probe \( \text{H}_2\text{L} \) has been restored upon the addition of chelating ligand EDTA to the \( \text{H}_2\text{L}-\text{Cu}^{2+} \) ensemble making the probe free and hence we observe the absorption spectrum of \( \text{H}_2\text{L} \). This confirms that the probe \( \text{H}_2\text{L} \) was not hydrolyzed in presence of \( \text{Cu}^{2+} \). While upon addition of \( \text{Fe}^{3+} \), it also displays a new absorption band appeared around 450 nm (its own absorption property), and the solution color became yellow. These intriguing absorption signatures of \( \text{H}_2\text{L} \) in the presence of \( \text{Co}^{2+}, \text{Ni}^{2+} \) and \( \text{Zn}^{2+} \) is attributed to the ligand to metal charge transfer (LMCT) after formation of individual metal–ligand complexes.

Interestingly, under UV light exposure (366 nm), only the \( \text{Zn}^{2+} \) added \( \text{H}_2\text{L} \) solution displayed a bright greenish-yellow fluorescence out of the 16 mentioned cations. With the sequential increase of \( \text{Zn(OAc)}_2 \) concentration from 0 μM up to 40 μM, there was a subsequent change of the actual absorption peak at 295 nm and 365 nm with synergic appearances of a new red-shifted (55 nm) band around 420 nm (Figure 2B). The well-defined formation of isosbestic point at 390 nm (Figure 2B) strongly supports the formation of a new complex of \( \text{H}_2\text{L} \) with \( \text{Zn}^{2+} \).

Likewise, in the UV-Visible spectral examination, the selectivity of the probe \( \text{H}_2\text{L} \) was verified within the sight of the previously mentioned metal ions through fluorescence study. Though first-row transition metal ions such as \( \text{Co}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+} \) could coordinate with \( \text{H}_2\text{L} \), as shown by UV–Vis spectra, they did not show any noticeable emission alternations (Figure 3A). In the emission spectrum, \( \text{H}_2\text{L} \) shows a weak broad two shoulder emission band near 513 nm upon excitation at 410 nm in a DMSO-\( \text{H}_2\text{O} \) (9:1, v/v, 5 μM HEPES buffer pH 7.2). The addition of \( \text{Cd}^{2+} \) or \( \text{Mg}^{2+} \) shows very little emission. (Figure 3B). In contrast, the addition of \( \text{Zn}^{2+} \) affords a very high-intensity emission in the middle region of the spectrum centering at 532 nm. Interestingly and also surprisingly it has been observed that in presence of particular anion (i.e. \( \text{OAc}^- \)) the emission intensity of \( \text{H}_2\text{L-Zn}^{2+} \)ensemble increases tremendously, and also with \( \text{SO}_4^{2-} \) but not much as that of \( \text{OAc}^- \) (Figure 3C). Furthermore, acetate salt of mentioned metal ion or different metal salt in presence of acetate ion fails to enhance emission intensity to a larger extent as \( \text{Zn(OAc)}_2 \) or \( \text{Zn}^{2+} \) (as perchlorate) in presence of \( \text{OAc}^- \) does (Figure 5). Moreover, we have examined the emission response of \( \text{H}_2\text{L} \) with zinc formate and zinc oxalate to demonstrate whether acetate or other carboxylate have any role to augment fluorescence. As depicted in Figure S8, it is observed that the formate and oxalate salts of zinc have a negligible effect to increase emission intensity in comparison to acetate salt of zinc. A gradual increment in the concentration of \( \text{Zn(OAc)}_2 \) to \( \text{H}_2\text{L} \), a systematic growth in the emission intensity with a 19 nm red-shifted emission maxima was observed (Figure 3D). The color of the solution changed from colorless to green
FIGURE 3  A, Image of H2L with different cations under UV-lamp. B, Emission signature of H2L with different cations. C, Effect of different counter anions on the emission intensity of the H2L-Zn2+ system. D, Emission profile of H2L (20 μM) upon incremental addition of Zn2+ in DMSO-H2O (9:1, v/v, 5 μM HEPES buffer pH 7.2), inset: color change upon the addition of Zn(OAc)2 to H2L under UV-lamp (λ = 366 nm). (λex = 410 nm)

during the titration process (Figure 3D, inset). It can likewise be noticed that the fluorescence quantum yield of H2L (ϕ = 0.03) expanded considerably upon cooperation with Zn2+ (ϕ = 0.20), Cd2+ (ϕ = 0.089) as their acetate salts. Again, solvent environment plays an important contribution to ion/molecule sensing. The H2L binds and sense Zn2+ fluorimetrically to the maximum extent in polar aprotic solvents, DMF, and DMSO (Figure S9, S10). Since water content makes an experiment ecofriendly towards real sample analysis, we choose DMSO-H2O as the medium (9:1, v/v, 5 μM HEPES buffer, pH 7.2) for our present investigation.

3.4 | TCSPC study

Fluorescence lifetime measurements of the H2L, and related compound have been done in DMSO-H2O (9:1) at λex = 375 nm. The decay behavior of H2L and its metal complex were well-fitted to biexponential functions. Bare H2L showed two components having lifetimes 0.04 (populations 0.99%) and 2.75 ns (populations 0.003%), respectively. The average lifetime of H2L was calculated to be 0.504 ns. After the addition of Zn(ClO4)2 solution, lifetime of H2L changes to 0.25 ns and 1.44 ns, having populations of 0.40 and 0.60%, respectively (Figure 4A). The average lifetime was calculated to be 1.31 ns (Table 2).

The OAc− salts of other metal ions increase the average lifetime of H2L from 0.504 ns to 1.00 ns. As appeared in Figure 4B, upon addition of NaOAc followed by Zn(ClO4)2, the average lifetime was calculated to be 1.53 ns. The direct inclusion of Zn(OAc)2 to H2L increases the life time to 2.36 ns (Figure 4C). Therefore, the average lifetime of the H2L increases extremely when both Zn2+ and OAc− ions are present. Hence, OAc− triggers up the sensing of Zn2+ of H2L. This is attributed to the formation of comparatively rigid structure imposed on the H2L by strong complexation with Zn2+ ion via acetate bridging (Scheme 2). Rigid structural architecture of H2L inside the complex limits the free movement of flexible bonds and thereby minimizes the radiationless transition and consequently, excited-state lifetime increases.

3.5 | Cross selectivity and sensitivity study

To assess the usefulness of H2L as a powerful ion-selective fluorescence chemosensor for Zn2+, the impact of competing metal ions is investigated by taking in excess concentration (10 equivalents) of different metal ions as that of Zn2+. The outcome demonstrates that the emission signature of H2L-Zn2+ (as its acetate salt) solution remains unchanged by the presence of common cations except by Cu2+, Fe3+,...
Co²⁺, and Cr³⁺. These four cations quench the emission intensity to a large extent (Figure 5A) due to their strong complexation tendency which replaces the Zn²⁺ from the formed complex, heavy atom effect and paramagnetic quenching efficiency.⁵⁴⁻⁵⁶

The possible disruption of anions was also investigated by the competitive experiments with excess (10 equivalent) of anions in a similar manner. The emission profile of H₂L-Zn²⁺ (in its acetate salt) solution remains almost unaffected by the presence of common anions such as F⁻, Cl⁻, Br⁻, I⁻, OAc⁻, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, SO₃²⁻, HSO₃⁻, H₂SO₄⁻. However, HSO₄⁻, HPO₄²⁻, and H₂PO₄⁻ quenches the intensity to a noticeable extent (Figure 5B) as seen in some literature.⁵⁷⁻⁵⁹ These all outcome suggesting that the probe H₂L is an AcO⁻ specific fluorescence chemosensor for Zn²⁺ even in the presence of most of the competing ions (cations and anions).

3.6 | Reversibility

To investigate the reversibility of the sensor toward Zn²⁺, strong chelating agent EDTA was added to the sensor H₂L-Zn²⁺ complex, and the absorbance, as well as fluorescence response, was noted (Figure S11a, 11b). With the addition of 1.0 equivalent EDTA as that of Zn²⁺ to the sensor H₂L-Zn²⁺ complex, the absorbance of the receptor recovered. Again, the greenish fluorescence is fully quenched on the addition of EDTA to the H₂L-Zn²⁺ ensembles and this indicates the metal ion is completely stripped away from the complex to make the ligand bare again. Further inclusion of Zn²⁺, the emission intensity was recovered. The fluorescence emission changes show a twisting response even after several cycles (Figure S12) and the sensor can be easily recovered for repeated use.

3.7 | pH effect on sensing behavior

The fluorescence intensity of the H₂L is very low or negligible and didn’t differ remarkably over a wide pH range from 2.0 to 8.0 (Figure 6). Beyond pH 8.0, the fluorescence intensity turned out to be high. At lower pH the imine protons get protonated or the compound may get hydrolyzed to discharges non-fluorescent beginning aldehyde. While in the moderate range of pH the ESIPT process (discussed later) prevails to show the two shoulders in its emission spectra. In the span
SCHEME 2  Plausible binding and sensing mode of the chemosensor H$_2$L towards Zn$^{2+}$

of higher pH (>10), deprotonation of hydroxyl group takes place and consequently able to dismiss the ESIPT procedure, thus results in high emission. Again, the emission profile of H$_2$L-Zn$^{2+}$ complex displayed remarkably higher intensity between the pH ranges from 6.5 to 9.5. Henceforth, the probe can be useful for Zn$^{2+}$-sensing under physiological pH ranges.

3.8  Detection limit and binding stoichiometry

From the emission titration, detection limit (LOD) for Zn$^{2+}$ is determined to be 2.18 μM using 3σ method (Figure S13), which is far better than the acceptable limit of 76 μM Zn$^{2+}$ recommended by the US-EPA and World Health Organization (WHO) for drinking water. Moreover, to determine the stoichiometry of the H$_2$L/Zn$^{2+}$ complex further, Job’s method using fluorescence intensity was applied to keep the total concentration of Zn$^{2+}$ and H$_2$L at 10 μM, but changing the molar ratio of Zn$^{2+}$ from 0 to 0.9. A plot of fluorescence intensity at 532 nm versus X$_M$ shows that the value goes through a maximum at a molar fraction of about 0.69 (Figure S14), indicating a 1:2 stoichiometric complex formation exactly. Again, the plot of [(F$_{max}$ - F$_0$)/(F - F$_0$)] vs. 1/[Zn$^{2+}$]$^2$ yields a straight line (Figure S15), indicating that H$_2$L binds with Zn$^{2+}$ in a 1: 2 stoichiometry with association constant (k$_a$) = 1.2 × 10$^{10}$ M$^{-2}$ determined from Benesi-Hildebrand equation. This illation was further ascertained from the ESI-MS spectrum (Figure S16), which exhibited peaks at m/z = 645.43 corresponding to 1: 2 [L$^2-$ + 2Zn$^{2+}$ + 2OAc$^-$/] complexation.

3.9  Plausible binding mode eluciation

In order to verify the binding site of ligand metal complex, $^1$H NMR titration were performed using 0 and 2.0 equivalent Zn$^{2+}$ ion in DMSO-$d_6$ (Figure S17). The bare ligand H$_2$L showed characteristic –O–H peak at 11.13 ppm, –CH = N- peak at 8.94 ppm and other remaining aromatic protons at desired position. When, Zn(ClO$_4$)$_2$ was added to probe the peaks corresponding to –O–H disappeared indicates the probe binds the metal ion through deprotonated hydroxyl group as shown in Scheme 2. FTIR of H$_2$L shows -OH stretching frequencies 3562.5 cm$^{-1}$ (hydrogen bonded, broad, Figure S5). Formation of the L–Zn$^{2+}$ complex shifts the –OH stretching frequency from 3562.5 cm$^{-1}$ to a broader value in the region 2955 cm$^{-1}$ indicates the co-ordination occurred hydroxyl oxygen atom since on binding to the metal center the electron density on the donating center decreases and hence made the related bonds weaker than before binding. The stretching band appeared at 1625 cm$^{-1}$ assign to be –C = N- bond in free H$_2$L shifted to 1600 cm$^{-1}$
3.10 Microscopic studies

Comparative analysis of the SEM images of H₂L in the absence and presence of Zn²⁺ ions shows major morphological variations, as shown in Figure 7. The probe H₂L exhibits a rod-like structure in its free state in complex lowered the bond strength by decreasing the electron density on imine N-atom in complex (Figure S18).

3.11 Plausible sensing mechanism

In the absence of a metal ion, H₂L did not show noticeable intense emission when excited at 410 nm because the cis-trans isomerization around -C≡N- bond may be the predominant decay process in the excited state.⁶¹ This was confirmed from the viscosity dependent emission of the probe as shown in Figure 8. With increase of viscous solvent glycerine in DMSO-glycerine mixture the emission intensity emerged. This supports free rotation around the -C≡N- inhibited resulting in the suppression of the non radiative decay process in the excited-state. When the probe binds Zn²⁺ associated with acetate ion (shown in Scheme 2) such type of isomerization process (Figure 7A). However, in complex molecule, obtained from the ligand with Zn salt, the structure is comparatively smaller (Figure 7B). This is due to the agglomeration of receptor H₂L with Zn²⁺ ions. EDAX analysis (Figure 7C) indicates the presence of carbon (C), oxygen (O), nitrogen (N) and bromine (Br) in receptor H₂L in atomic percentages are 70.42, 10.74, 9.13, and 9.70, respectively. EDAX analysis of H₂L–Zn²⁺ (Figure 7D) gives the result having atomic percentage carbon (C), oxygen (O), nitrogen (N), bromine (Br), and zinc (Zn) 57.71, 6.28, 22.81, 4.22, and 8.98, respectively. This outcome further confirms the complex formation with 1:2 stoichiometry.
From the viewpoint of ESIPT, nearness of acidic salicyl−OH and basic imine-N moieties favorable for six-membered ring structure via intramolecular H-bonding is of special interest. Upon excitation, the proton is transferred from the hydroxyl oxygen to the electronegative imine nitrogen of the internal hydrogen-bonded enol isomer framing an excited state K*, which happens extremely fast in the subpicosecond time scale. After the relaxation of the keto form (K*) to the ground state, the energetically favored enol form is recuperated spontaneously by reverse proton transfer, to finish the cyclic four-level scheme. Again, the intramolecular hydrogen bonding (−OH⋯N−) needed for the ESIPT process is interrupted in polar protic solvent via intermolecular H-bonding. Whereas, in polar aprotic
solvent intermolecular H-bonding also possible but it occurred only with phenolic H-atom, imine N-atom unable to form H-bond as in methanol.\textsuperscript{66} To confirm the phenomenon of photo-tautomerism, we have explored the solvents effects on photophysical behavior of the probe $H_2L$ and its $\text{Zn}^{2+}$ complex in terms of absorbance and emission study. We have chosen MeCN and DMSO as polar aprotic and MeOH as polar protic solvents in this context. The UV-Vis absorption peaks centered at 293 nm in MeOH, 294 nm in DMSO and 293 nm in MeCN can be attributed to $\pi-\pi^*$ transition. The longer absorbance peak at 365 nm in MeOH, 367 nm in DMSO and 368 nm in MeCN can be attributed to $n-\pi^*$ transition. The absorbance peaks of $H_2L$ appeared almost in the same position, demonstrating a comparable ground-state type in all solvents. The slightly blue-shifted in methanol is not consistent with simple polarity effects and may be due to specific H-bonding interaction with methanol donor and the imine nitrogen acceptor. The corresponding emission peaks were observed at 468 nm, 542 nm in MeOH; 470 nm, 529 nm in DMSO; 471 nm, 533 nm in MeCN, respectively. The Stokes shifts were 177 nm, 162 nm, and 165 nm in MeOH, DMSO, MeCN respectively [Table 3].

The emission wavelength and Stokes’ shift decrease with increasing solvent polarity (Figure S6, S7), suggesting in excited-state (K* state) has lower population than E* state. These findings are comparable to various other ESIPT systems.\textsuperscript{66,67} The bi-exponential decay fitting also supports the ESIPT process to take place, one from keto another from enol. The lifetime of the $\text{Zn}^{2+}$-receptor ensembles increases from 0.504 ns in free probe to 2.36 ns and this strongly supports the inhibition of the ESIPT process on complex formation. Again, highest lifetime for Zn-acetate associated receptor confirms that acetate ion makes an effective platform for $\text{Zn}^{2+}$ sensing. These collective experimental results like $^1$NMR, IR, UV-Vis absorbance, fluorescence (both steady-state and time-resolved), ESI-MS and SEM indicate Zn-acetate or $\text{Zn}^{2+}$ ion in the presence of acetate ion capable to lock the free rotation around $–C\equiv N$ bond completely, restrict ESIPT and PET process leading to sense fluorimetrically.

3.12 | Geometry optimization studies

To validate the interaction of the probe $H_2L$ and $\text{Zn}^{2+}$-L complex, we have performed density functional theory (DFT) utilizing Gaussian 09 software on their geometries. The theoretical geometries of $H_2L$ and its $\text{Zn}$(II) complex are revealed in Figure 9a. The conformation and coordination of the neutral complex as $[\text{Zn}_2(L)(\text{OAc})_2](1)$ is confirmed from ESI-MS spectra and then executed the theoretical optimization on it.
The main bond lengths and bond angles of the complex are tabulated in Table S1.

For complex 1, each metal atom Zn$^{2+}$ is being tetra-coordinated with mono-deprotonated (with NO donor sites) of one side of bi-compartmental tetra-dentate H$_2$L ligand and two acetate (OAc$^{-}$), co-ligands bridges to each metal centers to an arrangement of a tetrahedral geometry with inversion center and combined to form a binuclear complex with a frame of [Zn$_2$(L)(OAc)$_2$](1). The calculated Zn–N bond distances are in the range 2.028 Å and Zn–O bond distances are in the range 1.906–1.972 Å.

In the case of H$_2$L, the electron cloud remains mainly on HOMO–1, LUMO, and LUMO+2 orbital ensues at the phenoxo oxygen and phenyl ring, while the same for HOMO–3, HOMO, HOMO–2, and LUMO+1 orbitals reside at the phenyl ring and phenoxo oxygen, bromine atoms as well as at azine nitrogens atom with an energy difference between HOMO and LUMO of 3.31 eV (Figure 9B). Just in case of complex 1, HOMO, HOMO–1 and LUMO orbitals mostly originate from the involvement of azine nitrogen, phenyl ring, and phenoxo oxygen, and also LUMO+1, LUMO+2, LUMO+3, and HOMO–2 orbitals originate from azine nitrogen, phenoxo oxygen, and considerable contribution of metal centers with an energy difference between HOMO and LUMO of 3.00 eV (Figure 9B).

The absorbance spectra of the ligand used in the present work were studied at room temperature in DMSO. The ligand shows two well-resolved peaks at 295 nm and 365 nm that are in well agreement with theoretical values at 295.87 nm and 353.79 nm, respectively. These bands are assigned to S$_{0}$→ S$_{2}$ and S$_{0}$→ S$_{3}$ electronic transitions for H$_2$L.

The complex 1 shows well-consignable absorbance band at 418 nm (Figure 9C) in DMSO solvent at 298 K and the corresponding calculated absorption band is located at 413.20 nm which is in excellent agreement with experimental result (Table 4). This spectrum band can be assigned to the S$_{0}$→ S$_{2}$ transition.

### 3.13 Aggregation-induced emission characteristics of the probe H$_2$L

The nearness of ES1PT and C=N isomerization properties in H$_2$L influence to test its AIE character. The presence of bromine substituent boosts the emission intensity. SCXRD reveals that intermolecular Br⋯Br halogen bonds as well as multiple stronger intermolecular interactions in the crystal may lead to a more rigid environment, which can substantially suppress molecular motions and facilitates the emission process in its aggregate state. The sensor is well soluble in DMF and DMSO yet is insoluble in water. The probe H$_2$L in its absorption spectrum shows a longer wavelength level off pattern (due to Mie effect) with more than 60% water content in DMSO-H$_2$O binary mixture indicating formation of nano aggregate (Figure 10).

The probe H$_2$L in DMSO with increasing water fraction from 0% to 90% shows the solution color changing from a non-emissive to brightly greenish yellow under UV light (366 nm) exposure (Figure 11A). Upon excitation at 410 nm, the sensor H$_2$L is non-emissive and the emission profile of the sensor is nearly unaltered at 0%–40% water fraction at 530 nm (Figure 11B). The fluorescent intensity increases surprisingly at 560 nm when the water fraction becomes ≥50%. Beyond the 70% water content in the binary mixture the intensity gets to fall. The different organic solvent and water mixture (3:7) like DMF-H$_2$O, DMSO-H$_2$O, MeCN-H$_2$O, MeOH-H$_2$O, EtOH-H$_2$O, THF-H$_2$O also show the same type of emissive character of H$_2$L (Figure S19). The actual emission color perception for H$_2$L+Zn$^{2+}$ is best viewed by popular CIE 1931 diagram (Commission International de L’Eclairage) by using the co-ordinates CIE-X 0.28 and CIE-Y 0.60 for its emission that dictates its color in green region. The AIE state have the co-ordinates CIE-X 0.42 and CIE-Y 0.51 that indicates the color toward more yellow color (Figure 11C).

The DLS based particle size analysis of H$_2$L (20 μM) in different DMSO-H$_2$O ratio

<table>
<thead>
<tr>
<th>Ligand and Complexes</th>
<th>Theoretical (nm)</th>
<th>Experimental (nm)</th>
<th>Composition</th>
<th>Electronic Transition</th>
<th>Energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>H$_2$L</td>
<td>295 354</td>
<td>295 365</td>
<td>HOMO→LUMO+1 HOMO–2→LUMO</td>
<td>S$<em>{0}$→S$</em>{2}$→S$_{3}$</td>
<td>4.1905 3.6382</td>
<td>0.0975 0.0726</td>
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<tr>
<td>L-Zn$^{2+}$</td>
<td>413</td>
<td>418</td>
<td>HOMO–1→LUMO</td>
<td>S$<em>{0}$→S$</em>{2}$</td>
<td>3.0006 0.0131</td>
<td></td>
</tr>
</tbody>
</table>
agglomeration begins. This phenomenon demonstrated that the sensor is an AIE-active compound.

3.14 Molecular logic gate

The variation of the optical outputs with a reasonable mix of different ionic inputs can be utilized to impersonate different Boolean logic operations. The function of the memory device in the current case is based on Boolean logic which switches between two crisp states, either "0" or "1." By utilizing Zn²⁺, OAc⁻, and EDTA as the three input and ensuing changes of emission intensity on the interaction of H₂L with the mentioned three analytes as output signal, a combinational logic gate can be constructed based on NOT and AND gates.

The three chemical inputs of Zn²⁺, OAc⁻, and EDTA ions are assigned as input 1, input 2, and input 3, respectively, and considered as logic 1 when they are available and logic 0 stands for no addition of Zn²⁺, OAc⁻, EDTA. The output corresponds to the turn-off and turn-on fluorescence emission at 532 nm denoted by Logic 0 and Logic 1, respectively. The three possible input and fluorescence signal as output meet the character of a combined NOT and AND type molecular logic gate as shown in Figure 12A. Under the conceivable eight combinations of these inputs, the condition (110) displays the output as 'ON' with the readout signal '1'. However, the rest of the seven combinations exhibits no change in the fluorescence intensity of H₂L through displaying the output as 'OFF' with the readout signal as 0 (Figure 12B, table).

3.15 Molecular memory device

Memory devices are gadgets that are fit for taking care of information and can be created by sequential logic circuits. These circuits function through the feedback loop in which one of the outputs of the device fills in as the input information and it is remembered as a "memory element". So by utilizing binary logic function, a sequential logic circuit has been designed displaying "Write-Read-Erase-Read" kind of behavior.

In our system, high emission output at 532 nm and weak emission output at the same wave-length have been considered as ON

**FIGURE 11**  A, Image of the probe H₂L (20 μM) in different DMSO-H₂O ratio under UV-cabinet (λ = 366 nm) B, Emission profile of the probe H₂L (20 μM) in different DMSO-H₂O ratio. (λex = 410 nm, slit width = 2.5 nm/2.5 nm). C, Chromaticity diagram from PL spectra of H₂L+Zn²⁺ and H₂L in aggregate state

**FIGURE 12**  A, Representative combinational logic gate circuit. B, Corresponding truth table
state (1) as OFF state (0), respectively. Now for the construction of useful mimic of memory element of our receptor $H_2L$, we took $\text{Zn(OAc)}_2$ and EDTA as the inputs for the Set (S) and Reset (R) process, respectively and emission intensity at 532 nm is considered as the output signal (Figure 13A,B). In this memory function, the system writes when it gets input A (Zn-acetate) i.e. high emission value and it memorizes binary number “1” that results in writing 1. But the input B (EDTA), which is a reset input, erases the data resulting in writing and then memorize the binary number 0 (Figure 13C). The most noteworthy thing is that these cycles could be repeated many times (Figure S12) with the same concentration of the input without a remarkable decrease in emission intensity. Thus, this molecular sequential logic function based circuits shows near sort of behavior like the traditional semiconductor based logic devices, and it may be a well tool for improvement of molecular microprocessor in near future.

The novelty of our as-synthesized probe on the basis of synergistic sensing shown in the Table 5 presents that $H_2L$ is an outstanding performer as a chemosensor of $\text{Zn}^{2+}$ and $\text{OAc}^–$.

### 3.16 Application of probe $H_2L$-aggregate as a picric acid (PA) sensor

The photoluminescence property of the probe in solid-state as well as with a higher percentage of water inspired us to check or develop it as a picric acid sensor, for this goal we used 70% water content of $H_2L$ (20 μM) solution in acetonitrile and various nitro-aromatics was added. The selectivity and sensitivity of the probe were investigated using various analytes (150 μM) such as nitrobenzene (NB), 2-aminophenol (2-AP), 2-nitrotoluene (2-NT), $p$-nitrobenzoic acid (4-NBA), 1,3-dinitrobenzene (DNB), $o$-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (DNP), and picric acid/trinitrophenol (PA/TNP) by means of emission changes. The emission spectra show that only PA and 2,4-DNP quench the luminescence properties of which former quenches a large extent (Figure 14A). Successive addition of PA decreases the emission intensity at 560 nm gradually (Figure 14B).

It is fascinating to note that among various investigated nitroaromatics, only PA cause to be significant fluorescence turn-off responses,

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**TABLE 5** Brief comparison between recently published works based on synergistic sensing with our probe $H_2L$

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Probe</th>
<th>Analytes</th>
<th>Detection limit</th>
<th>Mechanism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Probe 1</td>
<td>$\text{Zn}^{2+}$, $\text{F}^–$</td>
<td>LOD not given</td>
<td>ESIPT</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>Probe 2</td>
<td>$\text{Mg}^{2+}$, $\text{Na}^+$</td>
<td>LOD not given</td>
<td>ICT</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>Probe 3</td>
<td>$\text{Zn}^{2+}$ and $\text{Pb}^{2+}$ via $\text{Au}^+$</td>
<td>LOD not given</td>
<td>AIE</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>Probe 4</td>
<td>Cu$^{2+}$ ions via Zn$^{2+}$ or Cd$^{2+}$</td>
<td>$5.07 \times 10^{-8}$ M for Zn$^{2+}$ and $4.68 \times 10^{-8}$ M for Cd$^{2+}$,</td>
<td>PET</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>Probe 5</td>
<td>Zn$^{2+}$, OAc$^-_2$</td>
<td>$2.4 \times 10^{-7}$ M for Zn$^{2+}$</td>
<td>ESIPT</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>Probe $H_2L$</td>
<td>Zn$^{2+}$, OAc$^-_2$</td>
<td>$2.18 \times 10^{-6}$ M for Zn$^{2+}$</td>
<td>PET, CHEF, C = N isomerization, ESIPT, AIE</td>
<td>This work</td>
</tr>
</tbody>
</table>

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**FIGURE 13** A, Truth table of the logic circuit. B, Schematic circuit diagram of logic gate for molecular memory device; C, Schematic representation for the memory element with “writing-reading-erasing-reading” property.
which undoubtedly indicates that strong ground state complexation between highly electron deficient PA and more electron-rich fluorescent hydrosol causes fluorescence quenching more easily via charge transfer pathway. Again, as the absorption band of PA falls (365 nm) within the area of absorption maxima of aggregated H$_2$L, the quenching in emission intensities on excitation at higher wavelength (410 nm) eliminated the scope of inner filter effect (Figure S21). Again, the optimized DFT calculation shows energy of HOMO and LUMO of picric acid is far below the HOMO and LUMO of the probe H$_2$L (Figure S22). Therefore the charge transfer mechanism is responsible for PL quenching phenomenon. Due to the presence of three strong electron-accepting group in PA, it is an effective molecule over other nitroaromatics for reducing the emission intensity. In solution, the quenching was observed under UV- light (366 nm) (Figure S23a). Furthermore, to develop an inexpensive and convenient tool for PA detection, test strips were prepared from Whatman 41 filter paper using probe H$_2$L solution (20 μM). The test strips were spotted by solution of H$_2$L and then dried in air. The probe H$_2$L-immersed filter paper strip showed an intense yellowish fluorescence on exposure to UV-light. Insignificant quenching of yellowish emission intensity upon the addition of different analytes (50 μM) was observed except PA and 2,4-DNP quench to marked extent (Figure S23b). Furthermore, PA solutions of different concentrations (10$^{-2}$ – 10$^{-7}$ M) were prepared and 0.02 mL of each was dropped on each fresh test strips (Figure S23c). Visual color changes were noticed from colorless to yellow in the case of 10$^{-5}$ M concentration while on the addition of further diluted concentration, no color change was observed. Under the UV light (366 nm), detectable dark spot was observed in the case of 10$^{-3}$ M concentration which faded upon further dilution. Thus, paper strips application pave a cheap onsite kit for picric acid detection.

4 | CONCLUSIONS

We have successfully synthesized and characterized a salen-based inexpensive turn-on fluorescent probe for the selective determination of Zn$^{2+}$ in presence of OAc$^{-}$ ion. Zn$^{2+}$ produces a pronounced fluorescence enhancement response under an OAc$^{-}$ triggered synergistic effect which is reported for the first time in the current study. Our as-synthesized probe offers selective Zn$^{2+}$ detection in the presence of several other metal ions up to micromolar limits. Fluorescence enhancement is attributed to the Zn$^{2+}$ assisted CHEF process, and inhibition of PET and ESIPT process. The binding mode was well corroborated with the theoretical study. Based on the three chemical inputs of Zn$^{2+}$, OAc$^{-}$, and EDTA ions, and emission intensity as output advanced level molecular logic gates including memory device is possible with suitable selection of inputs. Our fundamental findings will pave the way for design and synthesis of counter anion triggered chemosensors which will also be highly beneficial as solid-state emitter. Moreover, the application for picric acid detection using the AIE probe is also promising.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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