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Highly Selective Dual Channel Chemosensor Based on benzo[*d*]thiazole for Detection of Zn^{2+} ions

Lokesh Kumar Kumawat, Vinod Kumar Gupta[*],

Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
[*]E-mail: vinodg@uj.ac.za

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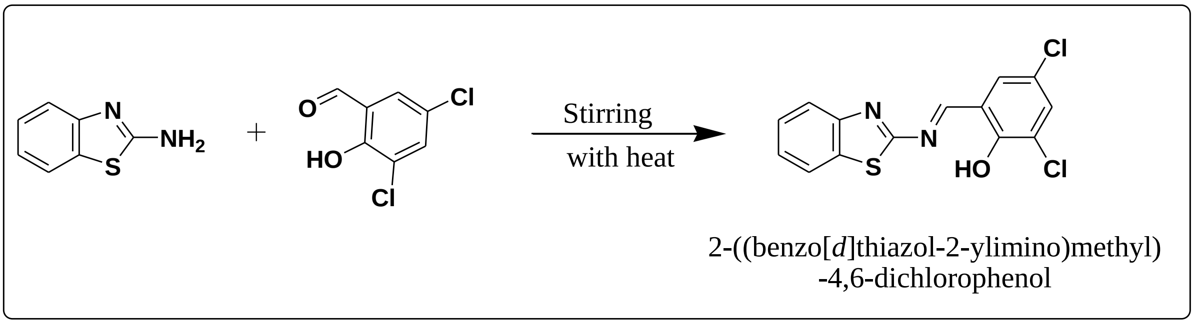
A cost effective reversible dual channel chemosensor (BT-1) has been synthesized for detection of Zn^{2+} ion based on a benzo[*d*]thiazole Schiff base. It exhibits high selective and sensitive optical changes in fluorescence intensity for zinc metal ions. Optical chemosensor (BT-1) exhibited fluorescence off-on effect with Zn^{2+} without any significant interference of other metal ions. The LOD of the optical chemosensors was calculated 0.11 μM for Zn^{2+} ion. Probe BT-1 is applicable to electroanalytical recognition of Zn^{2+} metal ion with polyvinyl chloride membrane sensing response. Reported chemosensor was provided high sensing response in real environmental sample with quick response time.

Keywords: Chemosensor, reversibility, membrane sensor, real sample, EDTA, Zn^{2+}.

1. INTRODUCTION

In last two decade, the design and synthesis of new high sensitive and selective optical chemosensors has been received expressive attention due to their high potential role in the biological and environmental applications [1–5]. Among various metal ions zinc is the second most abundant transition metal ion in our environment. It plays a crucial role in different biological process in human body like as gene transcription, neural signal transmission catalytic cofactors, and regulation of metalloenzymes. In industry, zinc is mostly used in galvanize process with iron metals to prevent rusting and die-castings in electrical, automobile, and hardware industries. Zinc oxide and sulfide are highly known in pharmaceuticals, paints and rubber industries, cosmetics and soaps industries, and fluorescent lights industries. But the exposure to high levels of Zn^{2+} ion can generate some hazardous symptoms like “oxide shakes” and neurodegenerative disorders [6–15].

Owing to high importance role in human life it is essential to monitoring of Zn^{2+} concentration level in environmental and biological sample. Different analytical instrumental techniques are available to detect low level metal ion concentration like as voltammetry, inductively coupled plasma mass-spectroscopy (ICP-MS), Liquid Cromatography, atomic absorption spectrometry [16–23]. But these techniques have some limitation like high cost instrument, expert handling and less effective in *vivo* cell study. Optical chemical sensors (colorimetric and fluorometric) and PVC membrane electrode have attractive distinct advantages of quick response, high sensitivity and selectivity, low cost, and online monitoring [24–32]. A great number chemosensors for zinc metal ion based on rhodamine, coumarin, quinoline and anthracene moiety have been developed [33–43], Most of these optical sensors exhibited shortcomings limit like as high cost reacting material, complicated synthesis process, selectivity interference. Thus it is highly demanded to develop a simply synthesized low cost dual channel chemosensor for zinc metal ions without interference.



Scheme 1. Synthesis of chemosensor **BT-1.**

Our research group is working with this task to design and synthesis of new low cost small molecular chemosensor series [44–50]. As a part of our ongoing research work, we decided to explore new chemosensor BT-1 with benzo[*d*]thiazole moiety for detection of zinc ion with dual channel sensing application. We have synthesized new 2-((benzo[d]thiazol-2-ylimino)methyl)-4,6-dichlorophenol (BT-1) for the detection of zinc ion in aqueous methanolic solution. The chemosensor (BT-1) demonstrated naked eye switch “off-on” sensing phenomena in the presence of zinc ion with the formation of 1 : 1 stoichiometric complex.

2. EXPERIMENTAL SECTION

2.1. General information

All the reactant and other chemicals were purchased from Sigma Aldrich. All the metal chloride and nitrate salts were purchased through Sigma and Merck, and used without recrystallized. For characterization ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 400 using $CDCl_3$ solvent and chemical shifts were reported in *d* values (ppm) relative to TMS and spectra were processed using MestReNova software. Molecular weight of compound with and without metal ions were recognized through high resolution mass (HRMS) spectra by using HPLC grade methanol solvent and triple distilled water. Absorbance and fluorescence spectra were recorded on a Shimadzu UV 1800 spectrophotometer and Perkin Elmer LS-45 luminescence spectrometer using a 10 mm path length quartz cuvette. ChemDraw Ultra 8.0 was used for drawing structures and Origin 6.0 was used for mathematical and graphical work.

2.2. Synthesis of chemosensor

2-((benzo[d]thiazol-2-ylimino)methyl)-4,6-dichlorophenol (BT-1) was synthesized accordingly modified reported method [51,52]. 3,5-Dichlorosalicylaldehyde (5.0 mmol), benzo[d]thiazol-2-amine (5.0 mol) were taken in 25 ml stoppered round bottom flask and mixed in 10 ml anhydrous methanol. This mixture was stirred and heated at 80 °C in water bath for about 4 hours. Reaction was monitored by TLC plates. A yellowish solid product was occurred and recrystallized from cold EtOH. Compound BT-1 was characterized by ^{1}H NMR, ^{13}C NMR and HRMS analysis. (Yield 40%), ^{1}H NMR spectrum (in $CDCl_3$), δ, ppm: 13.16 (s, –OH), 9.94 (s, 1H), 7.99–7.97 (t, 2H), 7.64–7.60 (td, 1H), 7.49–7.41 (3, 2H), 7.39–7.36 (dd, 1H). ^{13}C NMR spectrum (in $CDCl_3$), δ, ppm: 163.83, 163.57, 153.77, 153.25, 151.43, 137.67, 132.62, 130.64, 127.98, 126.94, 123.49, 121.78, 119.38, 116.94. ESI MS m/z (M+H): 322.9804, Calculated for $C_{14}H_9Cl_2N_2OS$ = 322.9813 (Fig. 1–3).

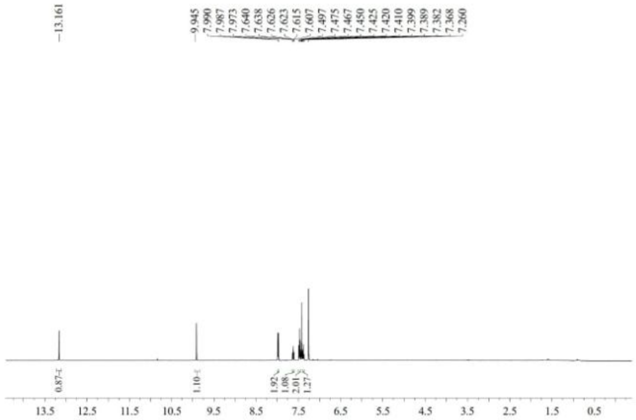


Figure 1. ^{1}H NMR spectra of **BT-1** recorded in $CDCl_3$ solvent.

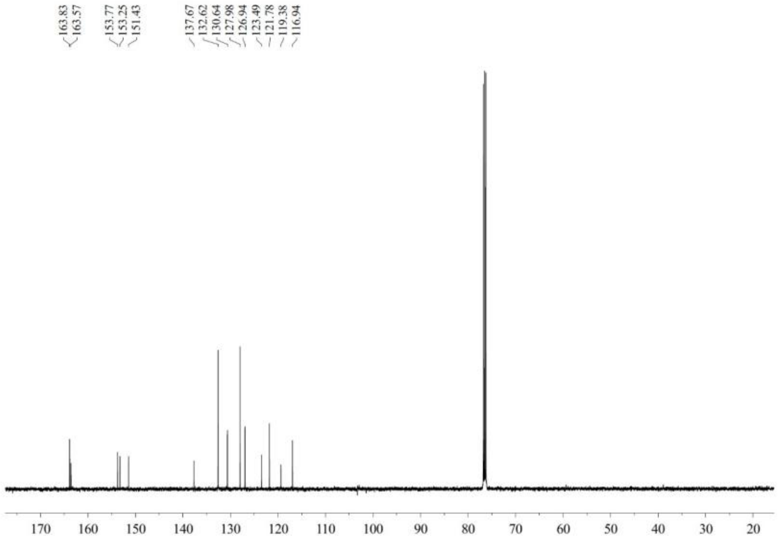


Figure 2. ^{13}C NMR spectra of **BT-1** recorded in $CDCl_3$ solvent.

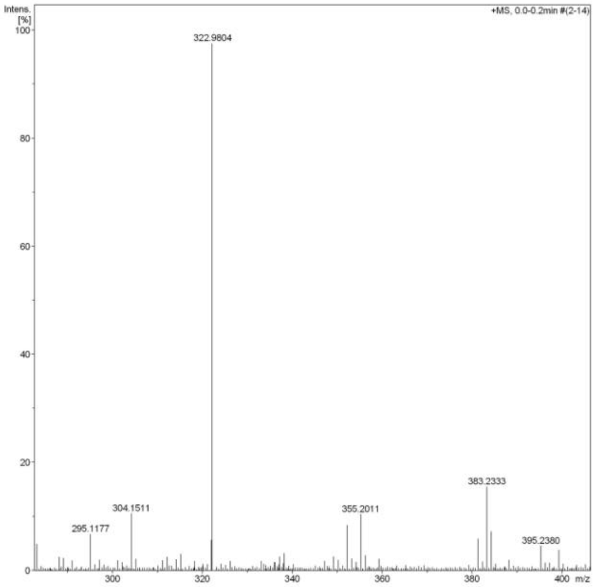


Figure 3. HRMS spectra of **BT-1**.

2.3. Absorbance and Emission analysis

For UV and fluorescence studies, solutions of the chemosensor BT-1 (1 x 10^{-4} M) and different metal ions Ca^{2+}, Cd^{2+}, Na^{+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, K^{+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+} and Fe^{3+} (1 x 10^{-3} M) were prepared in $CH_3OH–H_2O$ (2/1, v/v) and further diluted. All fluorescence spectra for chemosensor BT-1 was recorded at room temperature from 370 to 700 nm in a quartz cell (1 cm path length) with 5.0 nm excitation and emission slit.

2.4. Electrode preparation

The PVC based membrane electrodes were formed through mixing of suitable amounts of anionic additive (NaTPB), ionophore (BT-1), plasticizer and polyvinyl chloride in THF (5 ml) solvent. Obtained homogenous mixture was poured into polyacrylate rings placed on a smooth glass plate. After full night evaporation, transparent membranes were glued to 2 cm diameter pyrex glass tube and kept it for soaking in solution of (1.0 x 10^{-2} M) for 48 hour.

3. RESULTS AND DISCUSSION

3.1. Optical sensing studies

3.1.1. Absorbance and Fluorescence sensing

In an initial analysis, UV-Vis studies of optical chemosensor (BT-1) were examined in MeOH/ H_2O (2/1, v/v) solution. Chemosensor BT-1 (2.0 × 10^{-5} M) exhibited strong absorbance band located at

415 nm. After the addition of different metal ion (like as Co^{2+}, K^{+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ca^{2+}, Cr^{3+}, Ni^{2+}, Na^{+}, Cd^{2+}, Al^{3+} and Pb^{2+} ions), chemosensor didn't produce any remarkable variations in UV-Vis band (figure 4) however, absorbance band sifted to higher wavelength with Cu^{2+}, Mg^{2+} and Zn^{2+}.

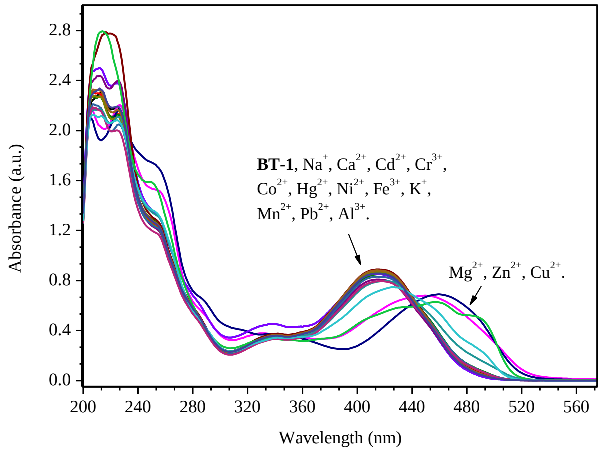


Figure 4. Absorbance spectra of **BT-1** (20 µM) with various metal ions (20 µM) such as Na^{+}, K^{+}, Cu^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Mg^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+} and Al^{3+} in methanol:H_2O (2/1, v/v) solution.

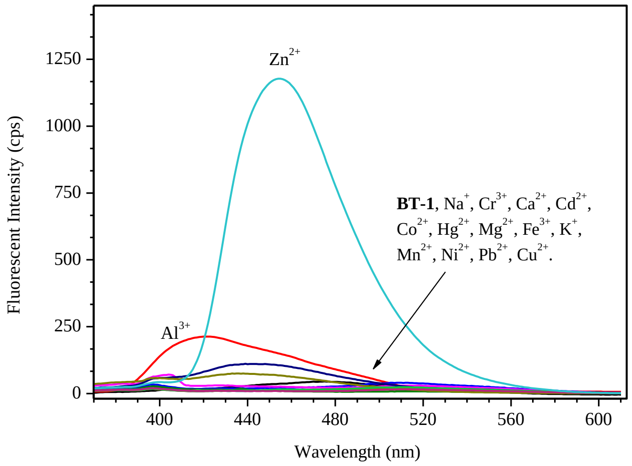


Figure 5. Fluorescence emission spectra of chemosensor **BT-1** (20 µM) in MeOH:H_2O (2/1, v/v) with equimolar amount of different metal ions.

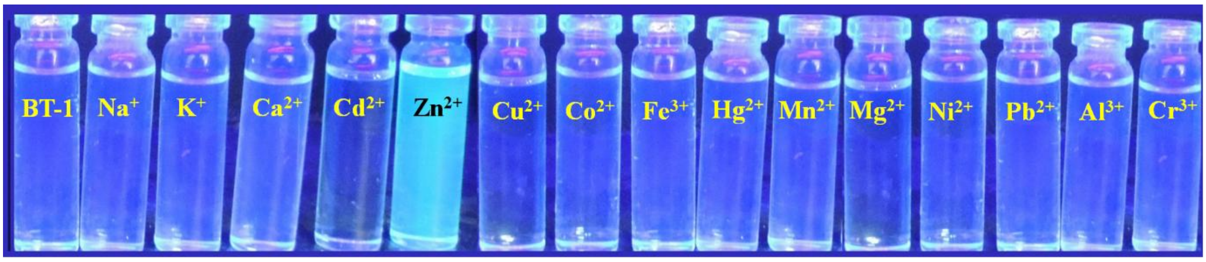


Figure 6. Naked eye fluorescence responses of **BT-1** with different metal ion in MeOH/H_2O (2/1, v/v) solution.

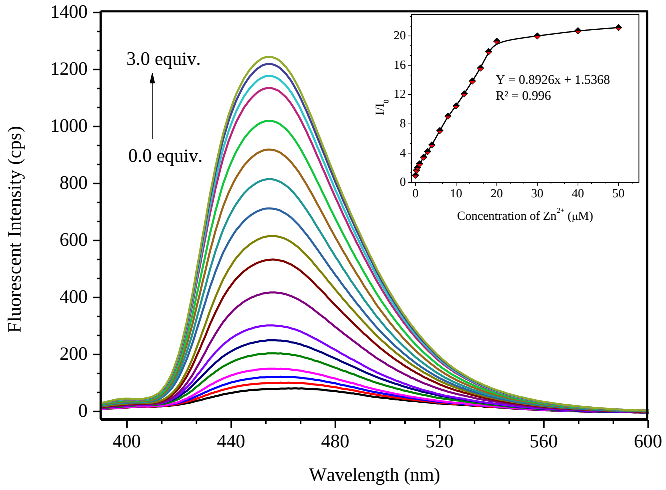


Figure 7. The fluorescence emission enhancement of **BT-1** with progressive addition (0 to 3.0 equiv.) of Zn^{2+} ion.

Fluorescence sensing study of optical selective probe was performed on perkin elmer LS-45 luminescence spectrometer. The chemosensor BT-1 (20 μM) exhibited very low emission intensity at 454 nm in aqueous methanolic solution (2/1, v/v). This emission band remain unaffected upon the addition of equal concentration (20 μM) of different metal ions viz., K^+, Cu^{2+}, Mg^{2+}, Na^+, Hg^{2+}, Ca^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+}, Fe^{3+} and Cr^{3+} ion. Interestingly, in the presence of Zn^{2+} fluorescence emission intensity enhanced more than 20 fold at maxima 454 nm (Fig. 5). Resultant, probe BT-1 exhibited switch off-on blue-green fluorescence which is feasible for naked-eye detection (figure 6). Furthermore, the fluorescence titration studies was performed for quantitative evaluation of Zn^{2+} ions. In titration, the concentration of optical probe remain constant and zinc metal ion concentration regularly varied from 0.0 equivalents to 3.0 equivalents. The fluorescence intensity of probe BT-1 was gradually increased with a linear range ($R^2 = 0.996$) at maximum wavelength (454 nm) as evaluated in Fig. 7. Moreover, the limit of detection (LOD) of optical probe (BT-1) towards Zn^{2+} was examined through the standard method (3σ/slope), slope were determined by fluorescence titration. LODs for sensor BT-1 were calculated 1.12×10^{-7} M.

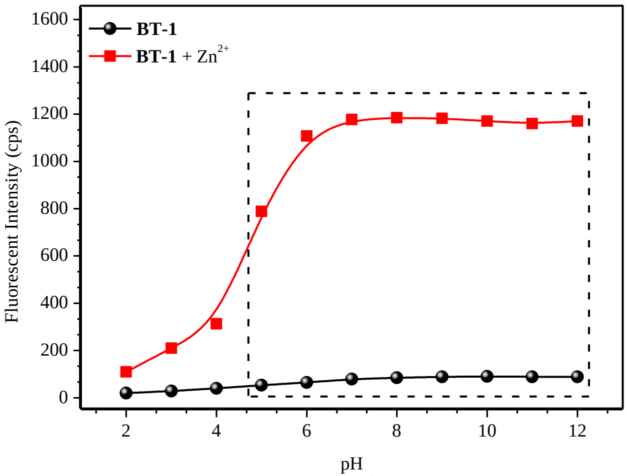


Figure 8. Fluorescence response of **BT-1** and **BT-1**+Zn^{2+} over variable pH medium (λmax. = 454 nm).

Additionally, pH response on the fluorescence emission changes of BT-1 and BT-1 +Zn^{2+} (20 µM) was studied in 2.0–12.0 pH range. We observed in figure 8, probe BT-1 showed optimum fluorescent sensing for Zn^{2+} in the pH range 5–12 but in case of high acidic medium significant fluorescence quenching occurred at maximum wavelength 454 nm due to interference with H^+ ions. Thus, Optical sensor BT-1 is highly effective for Zn^{2+} detection in environmental sample.

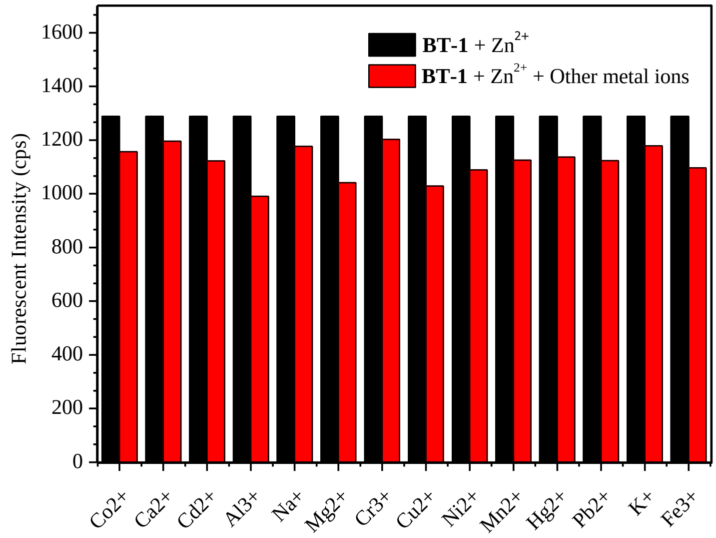


Figure 9. Examination of selectivity of optical probe **BT-1** (20 µM) in MeOH/H_2O (2/1, v/v) toward Zn^{2+} at 454 nm in the presence of various metal ions.

Furthermore, the selectivity of optical probe BT-1 towards Zn^{2+} was examined with competitive experimental method, the equal concentration of various metal Na^+, K^+, Ca^{2+}, Cr^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Hg^{2+}, Fe^{3+}, Al^{3+} and Cd^{2+} ion added in aqueous methanolic solution (2/1, v/v) of BT-1+Zn^{2+}. The 'turn-on' fluorescence intensity of probe at 454 nm remain unchanged (Fig. 9). Additionally, the binding constant value for BT-1+Zn^{2+} complex calculated through the linear plot of concentration titration [53]. The binding constant (Ka) was observed 1.07 x 10^5 M^{-1} (BT-1+Zn^{2+}) *via* Benesi−Hildebrand method (Fig. 10).

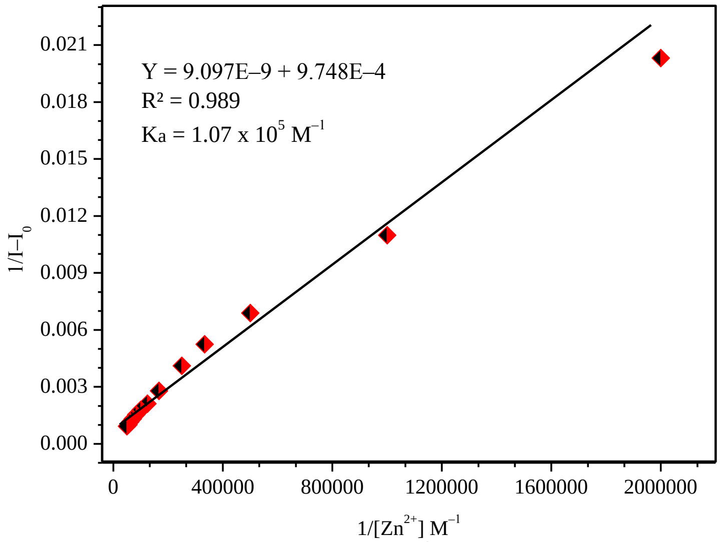


Figure 10. Benesi−Hildebrand plot for probe **BT-1**+Zn^{2+} at maximum emission wavelength 454 nm,

3.1.2. Job's plot analysis

Stoichiometry of BT-1+Zn^{2+} complex was evaluated through Job's titration method. In titration method, molar ratio of zinc ions regularly changed from 0.1 to 0.9 equivalent with the total concentration (20.0 μM) of chemosensor (BT-1) and Zn^{2+}. In result, maximum fluorescence intensity observed at 0.5 molar fraction (figure 11) that suggesting 1:1 stoichiometric complex between probe and Zn^{2+} ions. Experiment was further verified by HRMS data, [BT-1+Zn^{2+}+H_2O + Na^++ H]$^+$ calculated 426.9029 and obtained 426.9007 (figure 12).

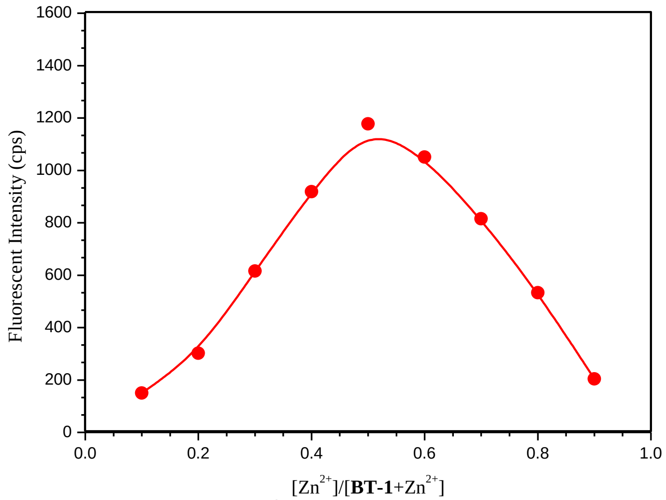


Figure 11. Job's plot spectra of **BT-1** with Zn^{2+} (20.0 μM) at maximum emission wavelength 454 nm in methanol/H_2O (2/1, v/v) solution.

3.1.3. Reversible sensing natures

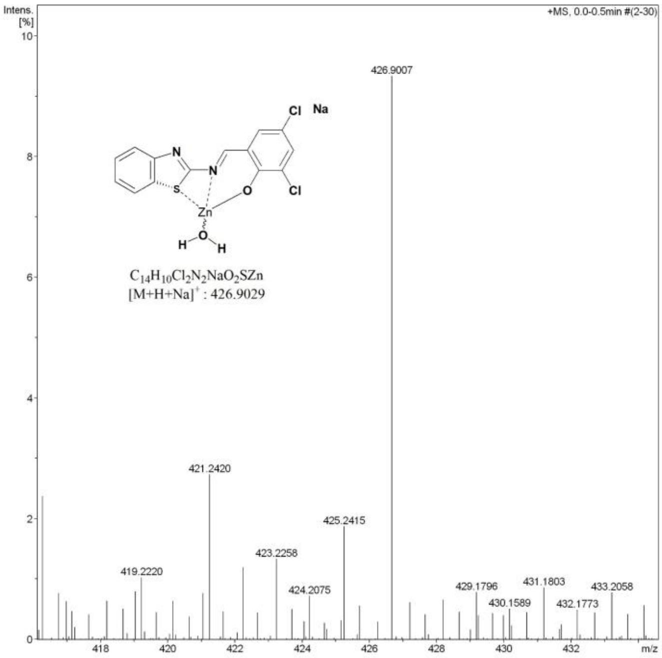


Figure 12. HRMS spectra of chemosensor **BT-1** with 1:1 stoichiometry complex with Zn^{2+}.

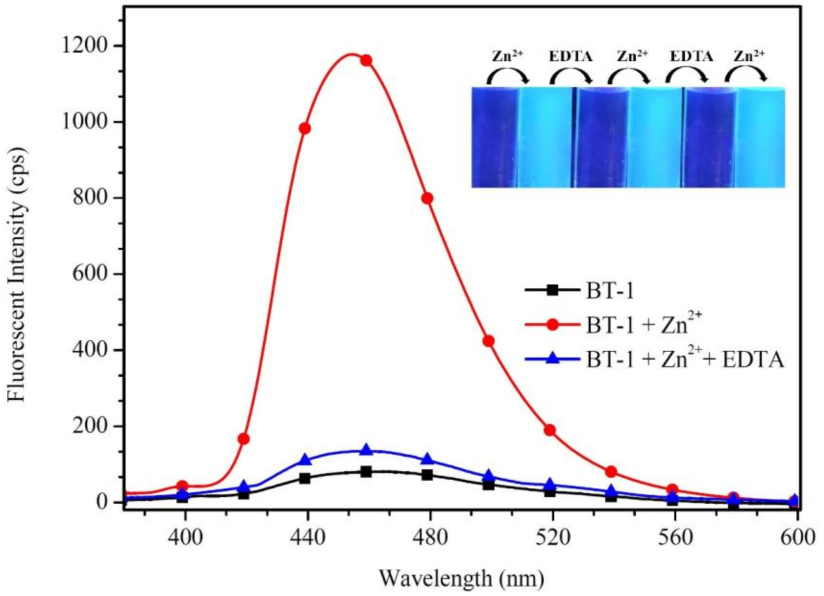


Figure 13. Reversible sensing nature of optical probe **BT-1** with EDTA.

Recyclability and reusability are important parameter of the optical sensing phenomena. Optical probe BT-1 also showed reversible sensing phenomena in the existence of EDTA. After addition of 1.5 equimolar amount of EDTA (at neutral pH) in the solution of BT-1+Zn^{2+}, the fluorescence intensity of BT-1+Zn^{2+} was quenched at lower level due to formation of EDTA+Zn^{2+} complex and probe BT-1 can be a recovered from this solution [54]. This experimental cycle repeated 4-5 times and we observe related level of sensing efficiency (figure 13).

3.2. Electroanalytical sensing of Zn^{2+}

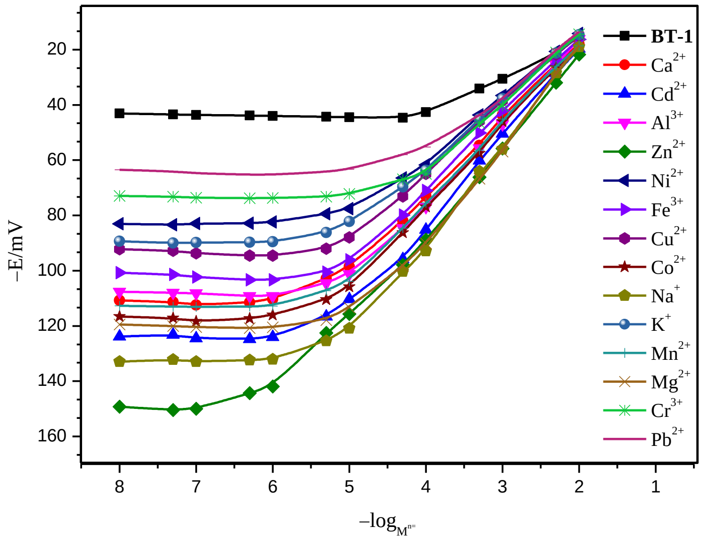


Figure 14. Response study of **BT-1** based membrane sensors with different metal ions.

We also explored the possibility of benzo[d]thiazol (BT-1) as a neutral ionophore for Zn^{2+} as a membrane electrode sensor. PVC membrane electrodes were designed by mixing of appropriate ratio of ionophores, polyvinyl chloride, plasticizer and anionic additive (see experimental section for more detail). For all potentiometric measurements following cell setup was applied:

SCE || test solution | PVC membrane | 1.0 x 10^{-2} M M^{n+} || SCE

As shown in Figure 14, all metal ions (exception of Zn^{2+} ions) displayed poor response in concentration range 1.0 x 10^{-8} to 1.0 x 10^{-2} M with lower Nernstian slop (expected slopes of 59, 29.5 & 20 mV per decade respectively for mono, di & trivalent cations) signifying higher selective response of ionophore BT-1 toward Zn^{2+} [55].

Table 1. Effect of plasticizer on the potentiometric response of ionophores **BT-1** based membrane sensors.

Mem. no.	Composition of membrane (mg)				Linear range (M)	Slope (±0.5mV/ decade)	Response time (s)
	Ionophore	Plasticizer	NaTPB	PVC			
1	2	65 (TBP)	3	30	3.28×10^{-6} – 1.0×10^{-2}	28.7	19
2	2	65 (CN)	3	30	1.75×10^{-6} – 1.0×10^{-2}	30.2	18
3	2	65 (DBP)	3	30	9.73×10^{-7} – 1.0×10^{-2}	25.9	21
4	2	65(o-NPOE)	3	30	3.68×10^{-7} – 1.0×10^{-2}	29.4	12
5	2	65 (DOP)	3	30	6.50×10^{-6} – 1.0×10^{-2}	27.1	19
6	2	–	3	30	3.45×10^{-5} – 1.0×10^{-2}	18.4	29

The different aspect of membrane sensing like as selectivity, sensitivity and linear working range are highly depended on the composition of the membrane, so electrodes were adjusted to achieve optimum composition. The effect of different plasticizers (TBP, CN, DOP, DBP and o-NPOE) were studied on the performance of the membrane electrode. As showed in figure 15 and table 1, PVC membrane electrode with o-NPOE (plasticizer) has better operational range and low response time. The membrane with a composition of ionophores (BT-1) : Plasticizer (o-NPOE) : Additive (sodium tetraphenylborate) : PVC in the ratio of 2 : 65 : 3 : 30 exhibited optimum response with a Nernst slope of 29.4±0.4 mV per decade of zinc activity.

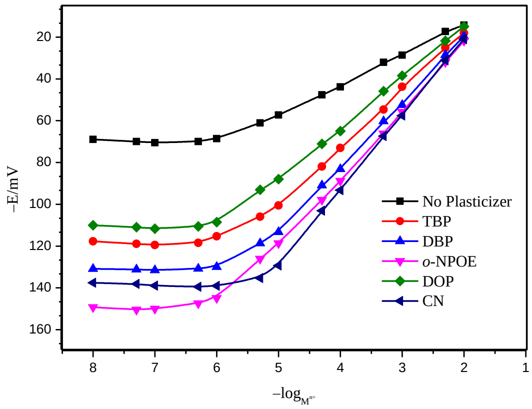


Figure 15. Potential deviation of **BT-1** based membrane sensors with different plasticizers.

3.3. Application of chemosensor

3.3.1. Real sample analysis

Table 2. Real time analysis of Zn^{2+} concentration in $MeOH/H_2O$ (2/1, v/v,) solution, proposed optical sensor **BT-1** and AAS.

Sample Methanol/Water (2/1, v/v)	Concentration of metal sample (μg/L) (AAS)	Concentration of metal sample (μg/L) (Sensor BT-1)
Drinking water	15.22	15.02
Rain water	26.75	26.25
Industrial water	96.83	94.15

Present work based fluorescence optical sensor BT-1 showed a strong binding for Zn^{2+} without any interference. Hence this optical probe is highly suitable in ecological sample analysis for trace level quantification of Zn^{2+} ion. For accuracy, concentration of sample were also resolute by AAS and comparative data provided in (Table 2). The obtained results were showed good selective response.

4. CONCLUSION

A new probe 2-((benzo[d]thiazol-2-ylimino)methyl)-4,6-dichlorophenol (BT-1) was synthesized through simple chemical process and executed as dual channel chemosensor. BT-1 displayed a high sensitive and selective reversible optical fluorescence sensing response towards Zn^{2+} ions in the presence of various metal ions. Chemosensor BT-1 designed 1:1 stoichiometry complex with Zn^{2+} that was obtained by Job's method and HRMS spectra. The high binding response toward Zn^{2+} was verified by high binding constant 1.07×10^5 M^{-1} and low limit of detection (LOD) 1.12×10^{-7} M calculated by slandered methods. Probe BT-1 is also exhibited electroanalytical selectivity towards Zn^{2+} metal ion as a PVC membrane electrode with Nernstian behavior. Reported chemosensor could be functionalized as sensing kit to naked eye analysis of Zn^{2+}.

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