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Synthesis of New Schiff Bases Including of Terephthalohydrazide and Sensor Application

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Abstract: Schiff bases are compounds that are formed by the reaction of aldehydes or ketones with primary amines, usually in alcoholic solution and in a neutral environment, and contain carbon-nitrogen (C=N) double bonds, called the azomethine or imine group, in their structure because of the condensation reaction. In recent years, Schiff Base-based molecular sensors have been one of the most emphasized topics by scientists. In this study, the 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile was obtained as literature information (Alici & Erdemir, 2015). Then, for the target compound, which is Schiff base derivative, was obtained from the condensation reaction of the 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile with terephthalohydrazide. Chemical structure of synthesized Schiff base compound was confirmed as using various spectroscopic techniques (^{1}H-NMR and ^{13}C-NMR). Then, the interactions of the synthesized Schiff base compound with metals (Fe^{3+}, Ag^+, Ca^{2+}, Cr^{3+}, Li^+, Sr^{2+}, Ni^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Cs^+, Na^+, Mg^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+}) under convenient conditions were investigated using fluorescence spectrophotometry. In the fluorimetric investigations, primarily, the selectivity study was carried out. The free sensor target compound at 489 nm did not produce any significant emission intensity with excitation at 360 nm. The each of the cations (10.0 equiv) were separately added to target compound, only Al^{3+} caused to a single band at 489 nm with a notable emission enhancement. As a result of the measurements, it was determined that the target compound had fluorimetric selectivity against only Al^{3+} metal within all metals (Fe^{3+}, Ag^+, Ca^{2+}, Cr^{3+}, Li^+, Sr^{2+}, Ni^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Cs^+, Na^+, Mg^{2+}, Fe^{2+}, Zn^{2+}).

Keywords: Hydrazide, Fluorescence, Al^{3+}, Schiff base.

Introduction

Aluminum is a widespread and essential element in both the environment and daily life. Aluminum is widely used in industrial sectors such as water treatment, food additives, pharmaceuticals, and household appliances (Alici & D., 2021; Alici & Erdemir, 2015). Since all these uses are directly related to human life, it is possible that we consume too much aluminum without realizing it. According to the data of the United Nations World Health Organization (WHO), the human body can absorb only 7 mg/kg Al^{3+}. Numerous diseases, including neurological conditions such as Alzheimer's disease, osteoporosis, and kidney disease, are caused by excessive exposure to Al^{3+} (Deibel, Ehmann, & Markesbery, 1996). Considering such situations, Al^{3+} pollution is of serious importance to the environment and humanity.

In order to look into Al^{3+} pollution, UV-vis and fluorescence spectroscopies have been the most popular methods in recent years. Due to its advanced properties, which include low cost, ease of use, quick reaction time, and superior selectivity, fluorescent probes that are capable of selectively detecting biological and environmental metal cations have garnered significant attention from researchers (Yue, Dong, Zhang, Sun, & Gong, 2015; Fu, et al., 2019; Xu, Chen, Zhang, Ju, & Lu, 2020; Chen, Xu, Ju, & Lu, 2021). Fluorescent

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chemosensors for Al^{3+} detection have been the subject of numerous studies published in recent years (Sen, et al., 2012; Mahalakshmi, et al., 2020; Ali, Alminderej, Messaoudi, & Saleh, 2021; Erdemir, Malkondu, & Karakurt, 2020).

The significance of Schiff base ligands with various donor atoms and their possible applications as fundamental components in macrocyclic chemistry is well-known in the fields of biomedical engineering and environmental chemistry (Keypour, et al., 2019; Nemati, Keypour, Shahabadi, Hadidi, & Gable, 2021; Zeynali, Keypour, Hosseinzadeh, & Gable, 2021; Hajari, Keypour, Rezaei, Farida, & Gable, 2022). Schiff bases exhibit exceptional detection capabilities and stability for specific metal ions, attributed to their effective electronic and structural characteristics in the host-guest complex (Golbedaghi, Ildiz, Azadbakht, & Fausto, 2022).

In this study, the 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile was obtained as literature information (Alici & Erdemir, 2015). Then, for the target compound, which is Schiff base derivative, was obtained from the condensation reaction of the 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile with terephthalohydrazide. Chemical structure of synthesized Schiff base compound was confirmed as using various spectroscopic techniques (^{1}H-NMR and ^{13}C-NMR). Then, the interactions of the synthesized Schiff base compound with metals (Fe^{3+}, Ag^{+}, Ca^{2+}, Cr^{3+}, Li^{+}, Sr^{2+}, Ni^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Cs^{+}, Na^{+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+}) under convenient conditions were investigated using fluorescence spectrophotometry. In the fluorimetric investigations, primarily, the selectivity study was carried out. The free sensor target compound at 489 nm did not produce any significant emission intensity with excitation at 360 nm. The each of the cations (10.0 equiv) were separately added to target compound, only Al^{3+} caused to a single band at 489 nm with a notable emission enhancement. As a result of the measurements, it was determined that the target compound had fluorimetric selectivity against only Al^{3+} metal within all metals (Fe^{3+}, Ag^{+}, Ca^{2+}, Cr^{3+}, Li^{+}, Sr^{2+}, Ni^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Cs^{+}, Na^{+}, Mg^{2+}, Fe^{2+}, Zn^{2+}).

Method

Chemicals and Instruments

All necessitated chemicals are analytical grade and were obtained from Sigma-Aldrich Chemicals (Zwijndrecht, The Netherlands) and utilized with no further processing. The perchlorate salts of the cations were utilized in this study. ^{1}H and ^{13}C-NMR spectral studies were measured by a Spinsol and Magritek NMR spectrometer and emission spectra of the chemosensor **TDH-CB** were recorded in a Varian Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies Inc, Santa Clara, CA, USA).

Synthesis of 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (CBA)

Compound (**CBA**) was prepared according in the literature (Alici & Erdemir, 2015).

Synthesis of the receptor bis((4'-cyano-4-hydroxy-[1,1'-biphenyl]-3-yl)methylene)terephthalohydrazide (TDH-CB)

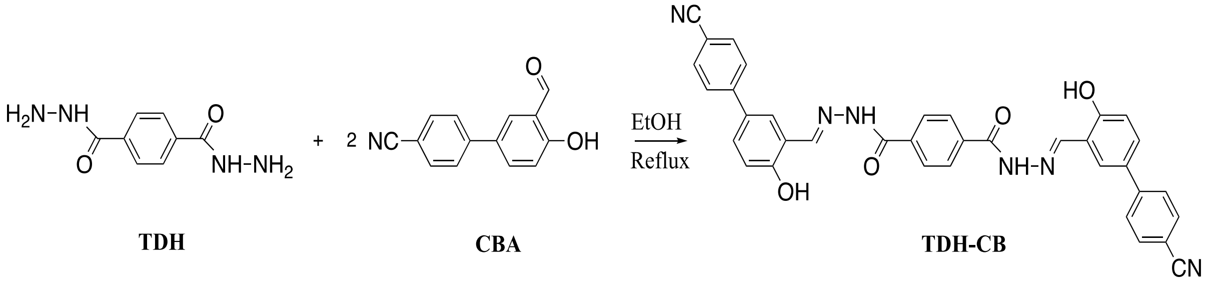
Absolute ethanolic solutions (25 mL) of 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (120.70 mg, 0.451mmol) was added to terephthalohydrazide (50.00 mg, 0.257 mmol) in absolute EtOH and stirred under reflux for 48 hours. After completion of the reaction, the precipitate formed was filtered off. The precipitate was washed three times with water and ethanol, dried in a vacuum oven. Finally, the Schiff base compound (**TDH-CB**) was recrystallized with hot ethanol to obtain yellow crystals.

Yield: 65 %, Melting Point: 344-346 ^{0}C, ^{1}H NMR (400 MHz, DMSO) δ 12.38 (s, 2H), 11.60 (s, 2H), 8.74 (s, 2H), 8.16 – 8.04 (m, 4H), 8.03 – 7.93 (m, 3H), 7.93 – 7.80 (m, 6H), 7.72 (d, J = 8.2 Hz, 3H), 7.07 (d, J = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 162.77, 158.60, 148.43, 144.41, 133.32, 129.92, 128.65, 128.41, 128.23, 127.37, 119.84, 117.80, 109.75.

Results and Discussion

Preparation of the Chemosensor TDH-CB

The synthesis of TDH-CB involves two distinct steps: the preparation of compound 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (CBA) was prepared by the reaction of 4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile by the Duff reaction with HMTA in trifluoroacetic acid. Then, TDH-CB was easily synthesized by the condensation reaction of CBA with terephthalodihydrazide with 65 % yield as illustrated in Schema 1.



Schema 1. The Synthesis procedure for the **TDH-CB**

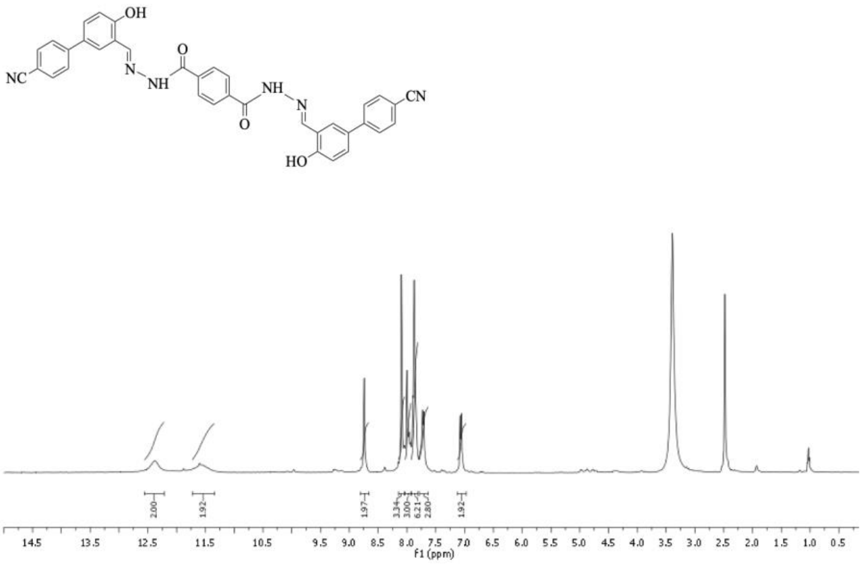


Figure 1. ^{1}H-NMR spectrum of Compound **TDH-CB**

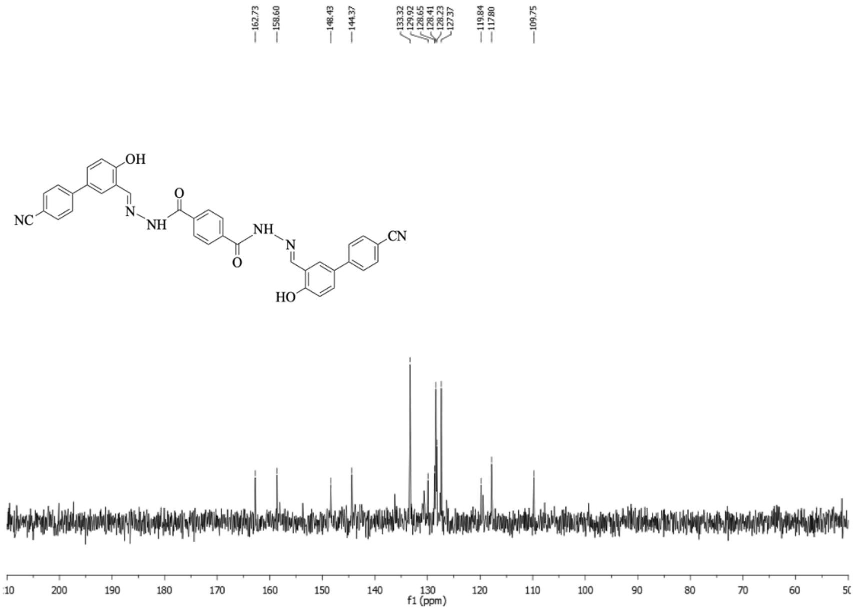


Figure 2. ^{13}C-NMR spectrum of compound **TDH-CB**

Emission Study

The stock solution of **TDH-CB** (10 mM) was prepared in DMSO and then diluted 5 µM in EtOH/HEPES (9/1, v/v). The tested metal perchlorate salts were utilized as (10^{-2} M).

Fluorescence Studies of TDH-CB versus Al^{3+}

Firstly, selectivity determination was made within metals (Fe^{3+}, Ag^{+}, Ca^{2+}, Cr^{3+}, Li^{+}, Sr^{2+}, Ni^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Cs^{+}, Na^{+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+}). For this study, the interaction between the solution of TDH-CB compound prepared in EtOH/HEPES (9:1) solvent medium and metal ions was investigated by fluorescence spectroscopy and for this investigation, various metal (Fe^{3+}, Ag^{+}, Ca^{2+}, Cr^{3+}, Li^{+}, Sr^{2+}, Ni^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Cs^{+}, Na^{+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+})) ions (10 equiv.) were added to 5 µM TDH-CB solution. As a result of this study, it was determined that it was selective against Al^{3+} metal (Fig.3).

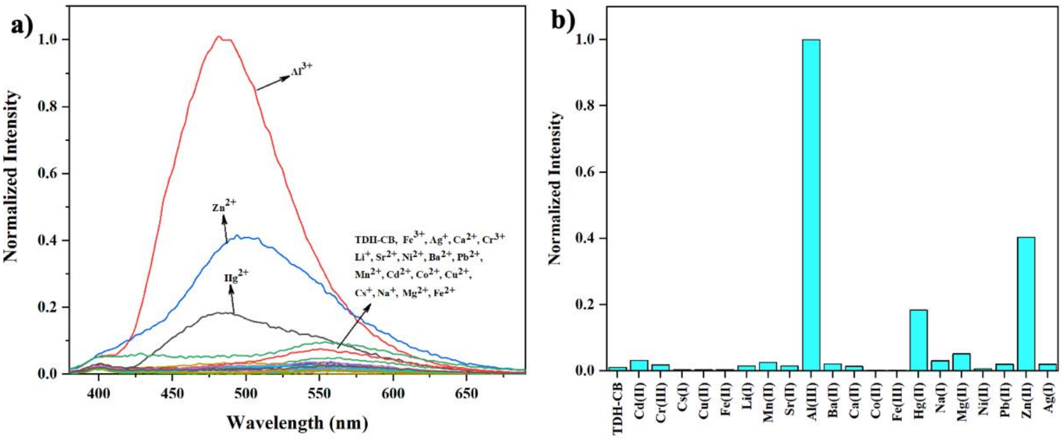


Figure 3. a) Fluorescence spectrum of **TDH-CB** compound in the presence of different metals (λ_{ex}: 360 nm; Ex-Slit: 10, Em-Slit: 8; λ_{em}: 489 nm), b) Fluorescence selectivity column graph of **TDH-CB** compound in the presence of different metals.

Fluorescence titration experiments were performed to better understand the interactions of **TDH-CB** and Al^{3+} metal (Figure 4.a). As seen in Figure 4.a, a significant increase in fluorescence is observed at 489 nm because of the addition of different concentrations of Al^{3+} metal solutions to the **TDH-CB** compound solution (5 µM). In addition, the JOB method was used to examine the **TDH-CB-Al^{3+}** complexation. Upon examining the JOB Plot graph, it is evident that the peak occurs at 0.5 (Figure 4.b). This indicates that the complexation of **TDH-CB** with Al^{3+} occurs in a 1:1 ratio.

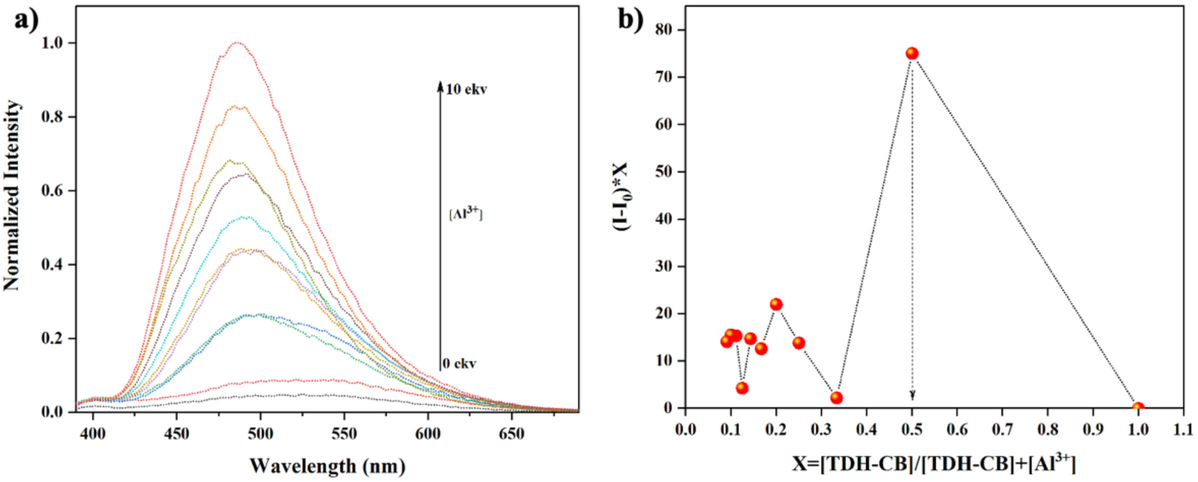


Figure 4. a) FL response of **TDH-CB** with increasing amount of Al^{3+} (0–10 eqv). **b)** Job's plot showing the 1:1 stoichiometry

Apart from the above-mentioned studies, research was carried out to determine the optimum pH range for **TDH-CB-Al^{3+}** complexation (Figure 5.a). From Figure 5.a, it is understood that the pH range of 6-7 is the most suitable range for the studies. In addition, a plot of the fluorescence intensity of the complexation of **TDH-CB** receptor with Al^{3+} was made against time (Figure 5.b). The graph shows how quickly (less than a minute) the receptor **TDH-CB** chemosensor forms a stable complex with the Al^{3+} metal.

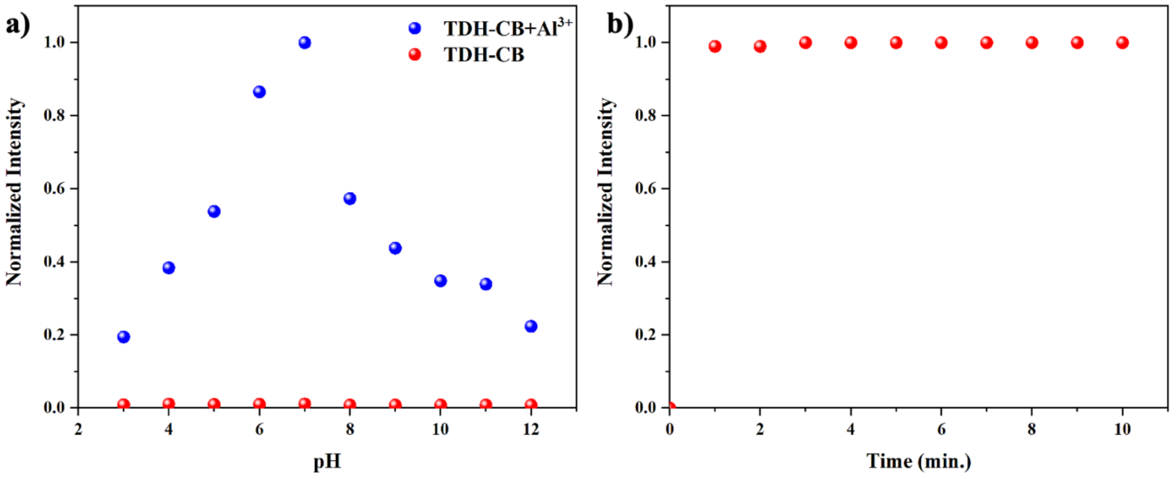


Figure 5. a) Effect of pH on the fluorescence intensity of TDH-CB and TDH-CB-Al^{3+} complex. b) Time-dependent fluorescence intensity changes of **TDH-CB** in the presence of Al^{3+}

It is crucial to ascertain whether the selective metal ion competition is with other metal ions for the compounds to be a useful sensor in terms of fluorimetric. The competition of the **TDH-CB** combination against Al^{3+} ions was conducted in the presence of additional metal ions to elucidate this situation (Figure 6). Examining the competition graph reveals that the Al^{3+} metal interacts with Cu2+, Fe3+, and Fe2+ metals, causing some quenching of the **TDH-CB-Al^{3+}** complex's fluorescence intensity.

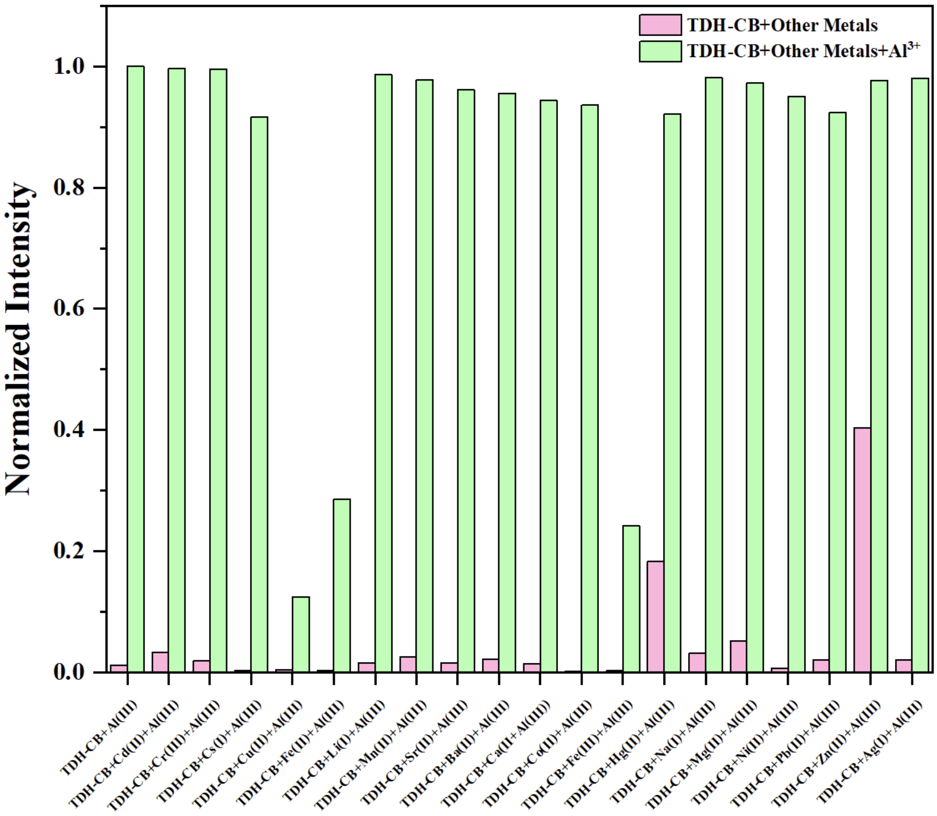


Figure 6. Fluorescence intensity at 489 nm of TDH-CB in response to Al^{3+} in the presence of interfering cations (10.0 eqv).

Conclusion

In summary, a new Schiff bases including of terephthalohydrazide fluorogenic chemosensor for Al^{3+} detection has been successfully synthesized. Fluorescence studies of **TDH-CB** chemosensor clearly showed that it is a selective Schiff base for Al^{3+} metal. For the detection of Al^{3+} on a range of pertinent competitor metal ions, the chemosensor **TDH-CB** demonstrated good performance. Chemosensor **TDH-CB** can fluorimetrically detect Al^{3+} metal ions in the neutral pH range and in a short time (less than 1 min). When all these conditions are evaluated, it can be said that the **TDH-CB** chemosensor is a usable sensor for the fluorimetric detection of Al^{3+} metal ions.

Scientific Ethics Declaration

The author declares that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the author.

Acknowledgements or Notes

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