TheEurasiaProceedings of Science, Technology, Engineering&Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2022

Volume 17, Pages 53-59

ICRETS2022: International Conference on Research in Engineering, Technology and Science

Synthesis and Fluorimetric Application of Novel Schiff Base Compound Containing Imidazole

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Abstract: This study describes the synthesis and application of 2-(2-hydroxy-5-(1H-phenanthro [9,10-d]imidazol-2-yl)benzylidene)-N-phenylhydrazine-1-carboxamide (**TC**) as a fluorogenic chemosensor toward for Zn^{2+} sensing in EtOH-H_2O (9:1, v/v) media. The chemosensor **TC** could sensitively determine Zn^{2+} ions with a low detection limit (LOD) and LOD value was found to be 5.73 nM. The fluorogenic titration spectrum indicated that the Zn^{2+} concentration was proportional to emission and gave a good linear alteration in emission in response to the equivalent of Zn^{2+}, the complexation ratio between chemosensor TC and Zn^{2+} was calculated as 1:1 by the method of continuous variation (Job's plot) from the obtained titration study. Moreover, the Ka value for the TC-Zn^{2+} complexation was found as 6.7×10^{-3} M^{-1} according to the Benesi–Hildebrand value of the changess in the titration of the chemosensor TC against Zn^{2+} ions. As a result of obtained data, chemosensor TC could be utilized to be an effective fluorogenic chemosensor for recognizing Zn^{2+} ions.

Keywords: Fluorogenic chemosensor, Schiff base, Zn^{2+}

Introduction

The design and construction of high performance fluorogenic chemosensors for sensitive and selective recognition of cations (such as Zn2+ recognition) have a significant value. Zinc metal in the human body after Fe is the second essential and most abundant transition element and zinc ions have a key role in neural signal transmission, regulating the immune system, cell nucleic acid and protein and a lot of molecular mechanisms. Zinc in the cell membrane plays an important role in preventing damage to the cell via the oxidative reactions. However, a lot of investigations displayed that an excess value of Zn2+ in the human body can gradually cause a lot of diseases, for example epilepsy, osteoporosis, prostate and breast cancers, and neurodegenerative diseases like Alzheimer's disease (Sethupathi et al., 2020; Erdemir & Malkondu, 2020; Ghaedi et al., 2009). Hence, it is very important to control and monitor the amount of Zn2+ to prevent the side effects of Zn2+ ions for the human body.

In the past few years, a lot of conventional analytical methodologies such as differential pulse stripping anodic voltammetry, electrochemical analysis, atomic absorption spectroscopy, flame atomic absorption spectrometry, isotope chromatography, and chromatography have been generally applied for the recognition of Zn2+ ions. Conversely, these conventional detection methods have some issues such as the necessity of time-consuming recognition, complex pretreatment, the necessity of sophisticated and high expensive equipment, and cumbersome operation, which make them not convenient for real-time and large-scale monitoring of samples. Compared with conventional analytical methodologies for the recognition of Zn2+ ions, fluorescence-based recognition technique is highly sensitive and selective. Additionally, this recognition technology has a lot of advantages for example, fast response time, easy sample preparation and so on (Sethupathi et al., 2020; Erdemir, & Malkondu, 2020; Ghaedi et al., 2009). In addition, fluorescence-based technique is superior sensitive and

selective, and it has a simple operation. Therefore, fluorescence-based recognition technique for cations detection has been extensively employed in medicine, chemistry, life science, environmental science, and many other research areas. There are a lot of synthesized fluorescence-based molecules for the fluorescence recognition of Zn2+ ions in the literature. These molecules are generally coumarin, fluorescein, calixarene, and thiazole based molecules (Erdemir & Malkondu, 2020; Aydin et al., 2021). Many of them have high detection limits or low selectivity behavior for the recognition of Zn2+ ions. Hence, it is exceedingly meaningful to construct novel fluorogenic chemosensors for effect and fast fluorescence analysis of Zn2+ recognition in environmental waste.

In this study, phenanthro imidazol based fluorogenic sensor TC (2- (2-hydroxy 5-(1H-phenanthro [9,10-d] imidazol-2-yl) benzylidene) N-phenyl hydrazine 1-carboxamide) was designed and constructed for the sensitively and selectively determination of environmentally significant Zn2+ ions. Preparation fluorogenic probe TC was characterized by 1H and 13C NMR spectroscopy. The fluorogenic sensing of Zn2+ ions with fluorogenic chemosensor TC in EtOH: H2O (9/1, v/v) medium has been accomplished with a great alteration in fluorescence emission spectra. The binding stoichiometry for TC and Zn2+ was computed to be 1:1 by Job's plot method. Furthermore, the binding constant between the TC and Zn2+ ions was found to be 6.7×10^{-3} M^{-1} from the Benesi–Hildebrand graph. In addition, the calculated limit of the detection (from the formula of $3\sigma/s$) value of fluorogenic sensor TC for the recognition of Zn2+ ions in EtOH: H2O (9/1, v/v) medium was as low as 5.73 nM and this obtained value was lower than the determined value in drinking water by WHO (World Health Organization). As a result of obtained results, newly designed and synthesized fluorogenic chemosensor TC could be successfully utilized to be a fluorogenic chemosensor for the recognition of Zn2+ ions in environmental samples and solution.

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. 1H and 13C-NMR spectral studies were measured by a Spinsol and Magritek NMR spectrometer and emission spectra of the chemosensor TC were recorded in a Varian Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies Inc, Santa Clara, CA, USA).

Synthesis of 2-hydroxy-5-(1H-phenanthro[9,10-d]imidazol-2-yl)benzaldehyde (1)

Compound **(1)** was prepared according in the literature (Kutluca Alici, 2020).

Synthesis of the chemosensor TC

Absolute ethanolic solutions (10 mL) of compound(1) (0.1 g, 0.295 mmol) was added to 4-phenylsemicarbazide(0.05 g, 0.33 mmol) in absolute EtOH and stirred under reflux for 20 hours. After completion of the reaction, the precipitate formed was filtered off. The precipitate was washed three times with water and ethanol, and dried in a vacuum oven. Finally, the Schiff base compound (TC) was recrystallized with hot ethanol to obtain white crystals.

Yield: 75 %, Melting Point: 225 0C, FTIR (ATR-cm-1): 3054 (N-H), 1658 (HC=N) 1H-NMR (400 MHz, DMSO-d6) δ 11.27 (s, 1H), 11.06 (s, 1H), 9.04 (s, 1H), 8.89 (d, J = 8.4 Hz, 2H), 8.78 (s, 1H), 8.58 (d, J = 7.9 Hz, 2H), 8.36 (s, 1H), 8.13 (d, J = 8.6 Hz, 1H), 7.81 (t, J = 7.5 Hz, 2H), 7.72 (t, J = 8.3 Hz, 4H), 7.33 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.5 Hz, 1H), 7.03 (t, J = 7.3 Hz, 1H). 13C NMR (100 MHz, DMSO-d6) δ 176.2, 158.13, 149.78, 139.57, 130.28, 128.67, 127.94, 127.53, 125.86, 125.76, 125.58, 124.37, 122.54, 122.33, 121.01, 117.23, 66.82.

Results and Discussion

Preparation of the chemosensor TC

The synthesis routes of TC include three steps: the preparation of compound 4-(1H-Phenanthro[9,10-d]imidazol-2-yl)phenol was prepared by the reaction of 9,10-Phenanthrenedioneand 4-Hydroxybenzaldehyde,

and 2-hydroxy-5-(1H-phenanthro[9,10-d]imidazol-2-yl)benzaldehydesynthesized by the Duff reactionwith HMTA in trifluoroacetic acid. The chemosensor TC was easily prepared by the condensation reaction of2-hydroxy-5-(1H-phenanthro[9,10-d]imidazol-2-yl)benzaldehyde (1) and 4-phenylsemicarbazide (2) in ethanol with 75 % yield as illustrated in Scheme 1. 1H-NMR, 13C-NMRand FT-IR were utilized to verify the structure of newly proposed chemosensor TC.

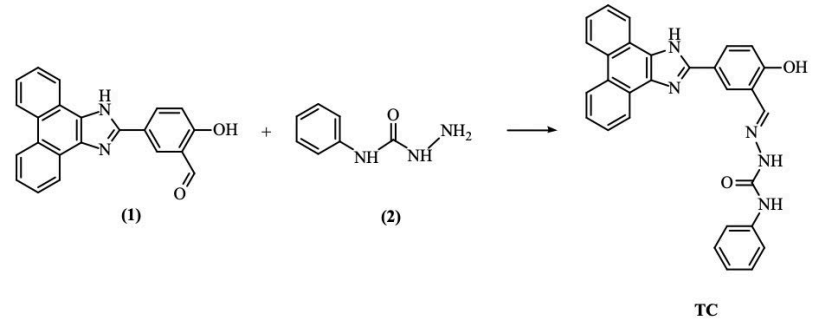

Figure 1. Synthesis of Compound TC

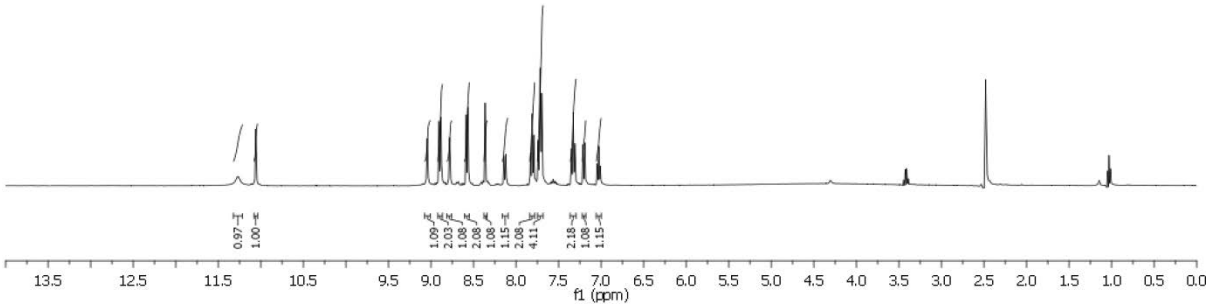

Figure 2. ^{1}H-NMR spectrum of Compound TC

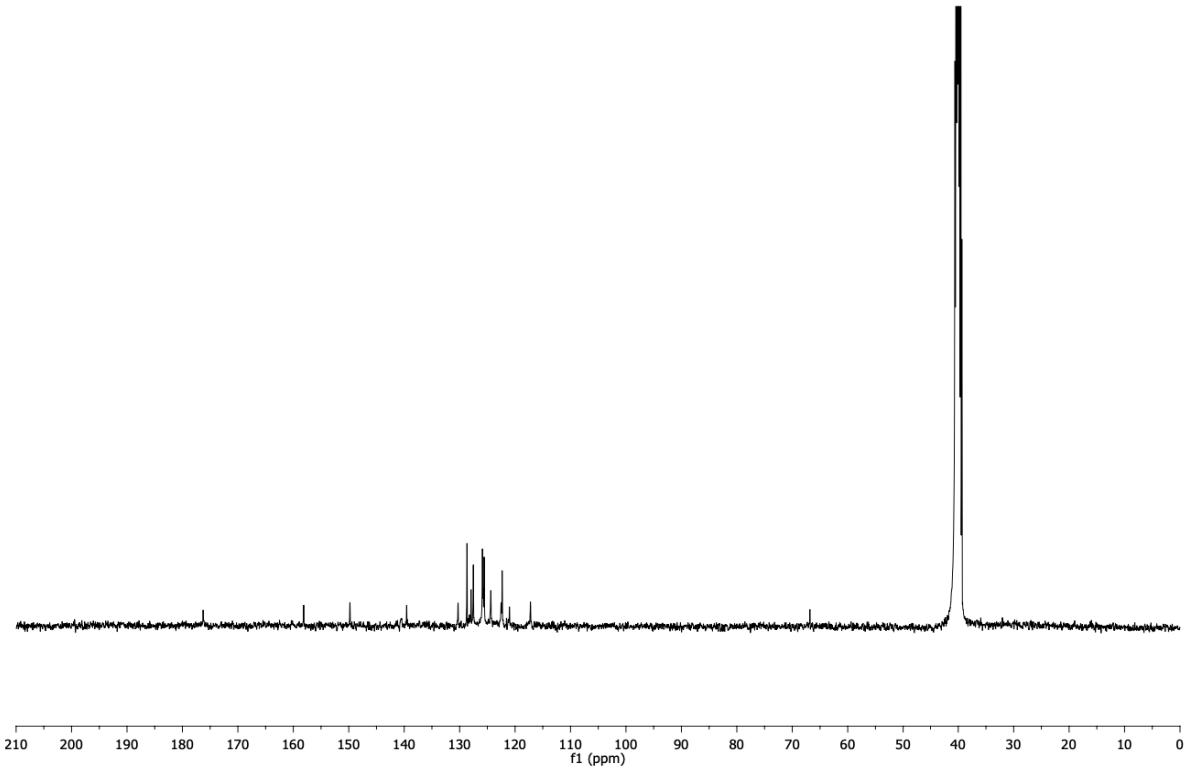

Figure 3. ^{13}C-NMR spectrum of Compound TC

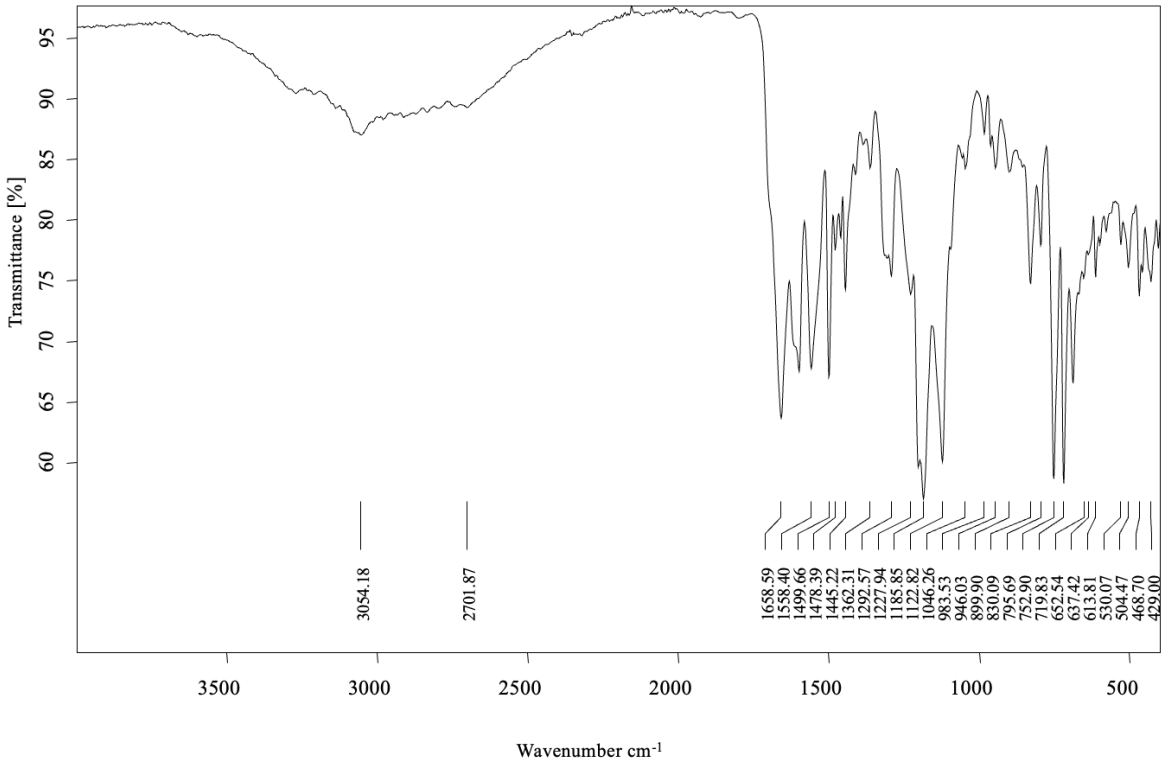

Figure 4. FT-IR spectrum of Compound TC

Emission study

The stock solution of TC (10 mM) was prepared in DMSO and then diluted 50 µM in EtOH/H2O (9/1, v/v). The tested metal perchlorate salts were utilized as (10-2 M).

Photophysical Studies of TC toward Zn^{2+}

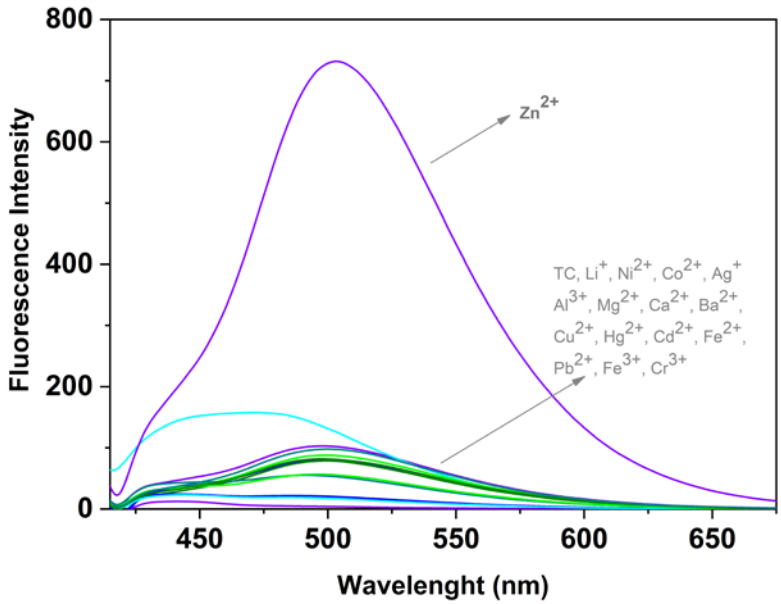

Figure 5. Emission intensity alterations of TC (50 µM) in the presence of various tested cations.

The fluorescent study of TC was carried out in EtOH−H_2O (9:1, v/v) with Li^+, Ni^{2+}, Co^{2+}, Ag^+, Al^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Fe^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+} ve Zn^{2+}. Initially, TC had no emission at 512 nm and then the adding of Zn^{2+} in TC led to significant intensity enhancement at 512 nm. Other mentioned cations introduced into the TC solution did not produce any spectral alteration at 512 nm (Fig 4). The corresponding change in This remarkable enhancement of the intensity exhibits the strong interaction between TC and Zn^{2+}.

To evaluate the sensitivity and quantitative appraisal of TC toward Zn^{2+}, the standard titration analysis was utilized as depicted in Fig. 2. The TC intensity at 512 nm enhanced with the increasing of the concentration of Zn^{2+}. The fluorescent spectral trend of the solution of TC with the addition of increasing concentration of Zn^{2+} was performed as illustrated in Fig 5. The TC intensity enhanced with the increasing Zn^{2+} concentration.

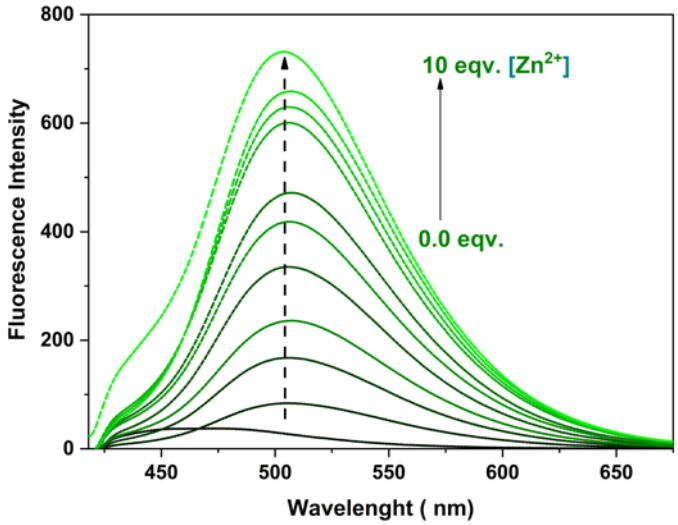

Figure 6. Emission spectra of TC with various concentrations of Zn^{2+}

The emission values were plotted as a function of the concentrations of Zn^{2+} Fig 6a to investigate the limit of detection (LOD) value of TC for Zn^{2+} determination The LOD value of compound **TC** was determined as 5.73 nM according to the equation: LOD = 3σ/k (σ: symbolizes the root-mean-square of blank measurements, k: the slope of the linear calibration curve). Furthermore, the Ka value for the TC-Zn^{2+} system was 6.7×10^{-3} M^{-1} in accordance with the Benesi–Hildebrand plot of the alterations in the titration of the TC toward Zn^{2+}.

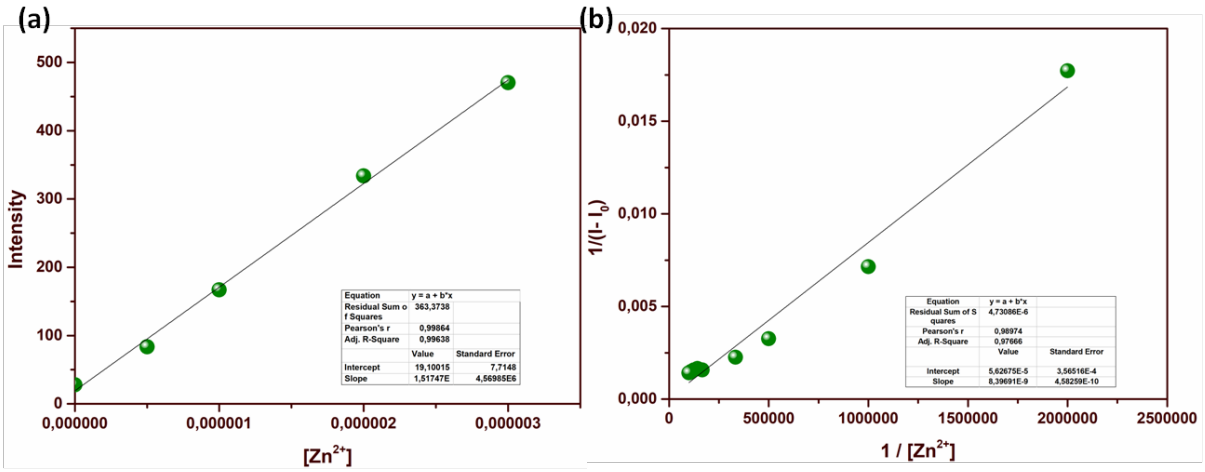

Figure 7. (a) The plot of emissions of TC versus with various Zn^{2+} concentration, (b) Benesi–Hildebrand plot of TC- Zn^{2+}

The complexation ratio between TC-Zn^{2+} was investigated by the method of continuous variation (Job's plot). As depicted in Fig. 7, the turning point happened at 0.5 of Zn^{2+} concentration ratio, indicating that the stoichiometric ratio of TC-Zn^{2+} was 1:1.

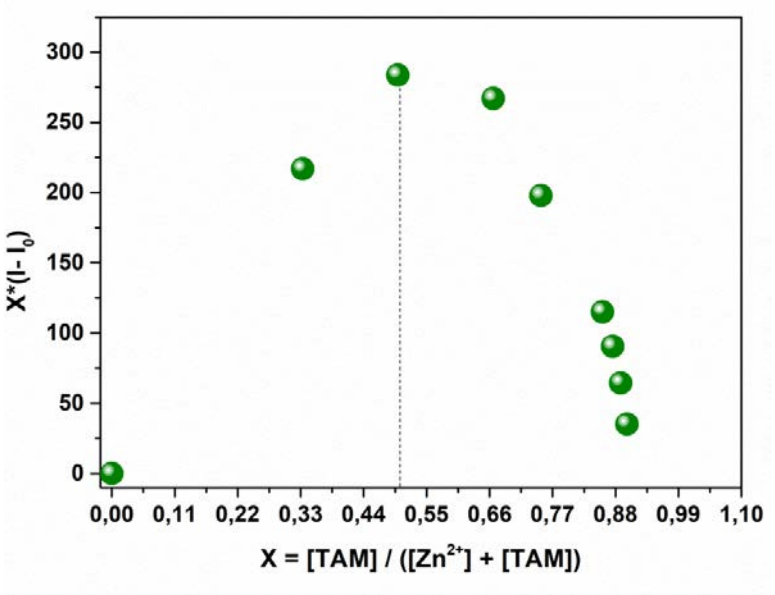

Figure 8. Job's plots of TC with Zn^{2+}

Conclusion

In conclusion, a novel imidazole-derived fluorogenic chemosensor for Zn^{2+} sensing has been developed. As a result of the coordination of the TC with Zn^{2+}, the intensity alteration of TC solution has occurred because of the strong affinity between TC and Zn^{2+}. This proposed fluorogenic chemosensor TC can become an easy recognition tool for Zn^{2+} in solutions and can reveal the design of various fluorogenic probes for Zn^{2+} recognition.

Scientific Ethics Declaration

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

Acknowledgements or Notes

This article was presented as an oral presentation at the International Conference on Research in Engineering, Technology and Science (www.icrets.net) conference held in Baku/Azerbaijan on July 01-04, 2022.

*This work was supported by the SU with the financial support (SU, BAP-Grant Number: 20401031).

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To cite this article:

Alici, O. & Aydin, D. (2022). Synthesis and fluorimetric application of novel schiff base compound containing imidazole. *The Eurasia Proceedings of Science, Technology,Engineering & Mathematics (EPSTEM), 17*, 53-59.