

## PHENYLETHYLAMINE DERIVATIVE OF CALIX[4]ARENE SCHIFF BASE FOR FLUOROMETRIC DETECTION OF ZINC ION

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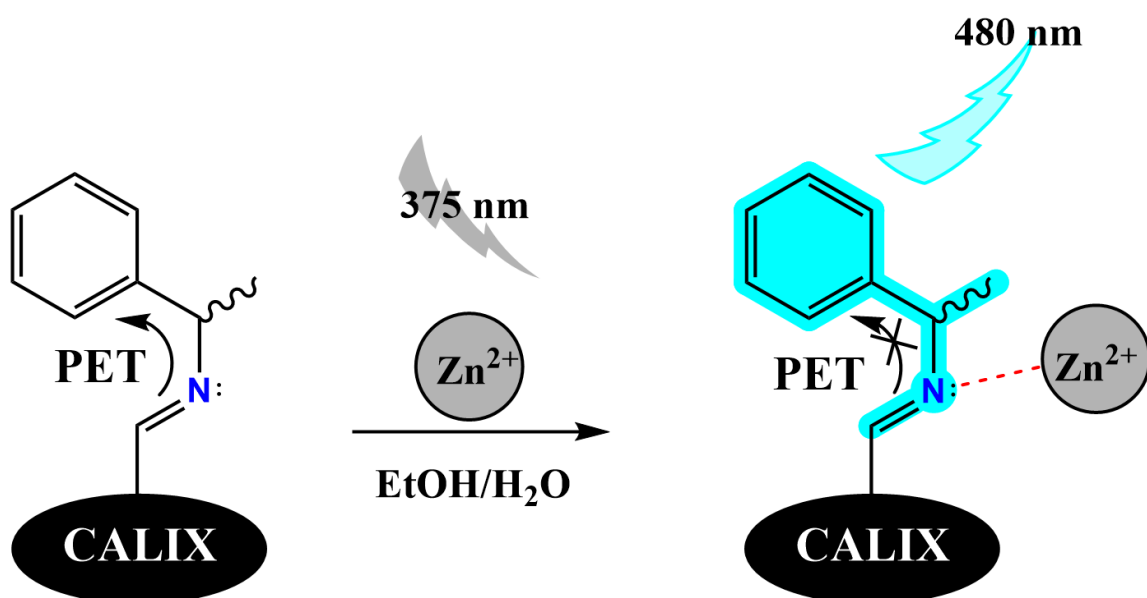
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### Highlights

- It was synthesized a new type of calixarene Schiff-base ligand (L) as the fluorophore and the receptor.
- Fluorescent L demonstrated high selectivity and sensitivity towards Zn<sup>2+</sup> compared to other metal ions.
- Limit of detection (LOD) reached 4.8 x 10<sup>-7</sup> M.
- It was determined that probe L can be utilized for the detection and monitoring of Zn<sup>2+</sup> in the environment.

### Graphical Abstract



Possible interaction presentation of calixarene-based probe (L) and Zn<sup>2+</sup> ion.



## PHENYLETHYLAMINE DERIVATIVE OF CALIX[4]ARENE SCHIFF BASE FOR FLUOROMETRIC DETECTION OF ZINC ION

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**ABSTRACT:** As a Zn<sup>2+</sup> fluorescent probe, we have designed and synthesized a new type of calixarene Schiff-base ligand (L) possessing a 1-phenylethylamine group as the fluorophore and the receptor. As only Zn<sup>2+</sup> caused a significant increase in fluorescence emission intensity at 480 nm and the limit of detection (LOD) reached 4.8 × 10<sup>-7</sup> M, the synthesized fluorescent probe L demonstrated high selectivity and sensitivity towards Zn<sup>2+</sup> compared to other metal ions. In addition, the formation of a 1:1 complex between probe L and Zn<sup>2+</sup> was determined. As a consequence, it was determined that probe L can be utilized for the detection and monitoring of Zn<sup>2+</sup> in the environment.

**Keywords:** Calixarene, Schiff Base, Fluorometric Detection, Zinc, Sensor

### 1. INTRODUCTION

The exponential advancement in the application of heavy metals in pharmaceuticals, waste-water treatment and manufacturing industry has consequently elevated their levels in the environment and atmosphere [1, 2]. Heavy metal pollution has the potential to cause adverse impact on the ecosystem and therefore, the detection of these elements at trace concentrations is of paramount importance [3]. Zinc is one of the most abundant transitional metal elements in the earth's crust and it is the second most prevalent trace element in the human body after aluminium. It is extensively involved in diverse and significant biological processes such as gene expression, neurotransmission, apoptosis, as well as catalysis by functioning as a cofactor in more than 300 metalloenzymes [4-9]. Nonetheless, excessive accumulation of zinc in the body may disrupt the nervous and immune system thereby causing detrimental neurological effects such as Alzheimer's disease, cerebral ischemia, epilepsy and prostate cancer. In addition, toxic levels of zinc in the soil may inhibit the growth and development of plants due to nutrient imbalance and reduced photosynthetic rate [10, 11]. Therefore, many heavy metals such as Zn<sup>2+</sup> ion need to be detected in a sensitive and selective way. In recent years, many different molecules have been studied in the literature for the optical detection of Zn<sup>2+</sup> ion by using benzothiazole [12, 13], anthracene [14], benzidine [15], triphenylamine [16, 17], cyanobiphenyl [18], benzotriazole [19], tetrahydroquinazole [20], dinitrophenyl [21], thiophene [22], rhodanine [23], benzoimidazole [24], phenanthroline [25], naphthalene [26], 1,10-phenanthroline [27], BINOL [28] and sulphonamide [29]. Among these molecules, calixarenes play an important role. Heterocyclic structures formed as a result of the condensation reaction of p-terbutylphenol with formaldehyde in basic medium may have different functional groups in their structure and may have different uses. In the literature about calixarene derivatives, pyrene [30, 31], 4-biphenylcarbonitrile [32], bis(iminomethyl)phenyl [33], bis-terpyridinyl [34], 2,2'-bipyridine [35], imidazobenzimidazole [36], salicylidene imine [37] and triazole [38] structures are used for the optical detection of Zn<sup>2+</sup> ion. In these studies, especially the efficiency of Schiff base (-C=N-) functional groups for the detection of Zn<sup>2+</sup> ion is remarkable. During complexation, fluorescence properties emerge with the electron transfer disrupted as a result of the interaction of the nitrogen group in the Schiff base with ions [39]. In this study, a calix[4]arene-based ligand functionalized with a simple 1-phenylethylamine structure

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was synthesized and its optical properties against different cations in solution were investigated by fluorescence spectroscopy.

## 2. MATERIAL AND METHODS

### 2.1. Chemicals and Equipment

In this study, the characterization of the synthesized calix[4]arene derivatives were performed with Varian brand 400 MHz NMR spectroscopy. The PerkinElmer brand Spectrum 100 FT-IR spectrometer model was used for the FTIR spectrum analysis. During synthesis, the progress of the reactions were monitored using thin layer chromatography Merck brand Kieselgel 60 F254. Fluorescence studies were performed using PerkinElmer brand LS55 spectrometer. While UV-Vis studies were carried out with PG Instrument brand T80+ UV/Vis spectrophotometer model. All chemicals and reagents used during the study were of analytical quality acquired from Merck, Sigma Aldrich, Alfa Aesar, Acros Organics, ISOLAB.

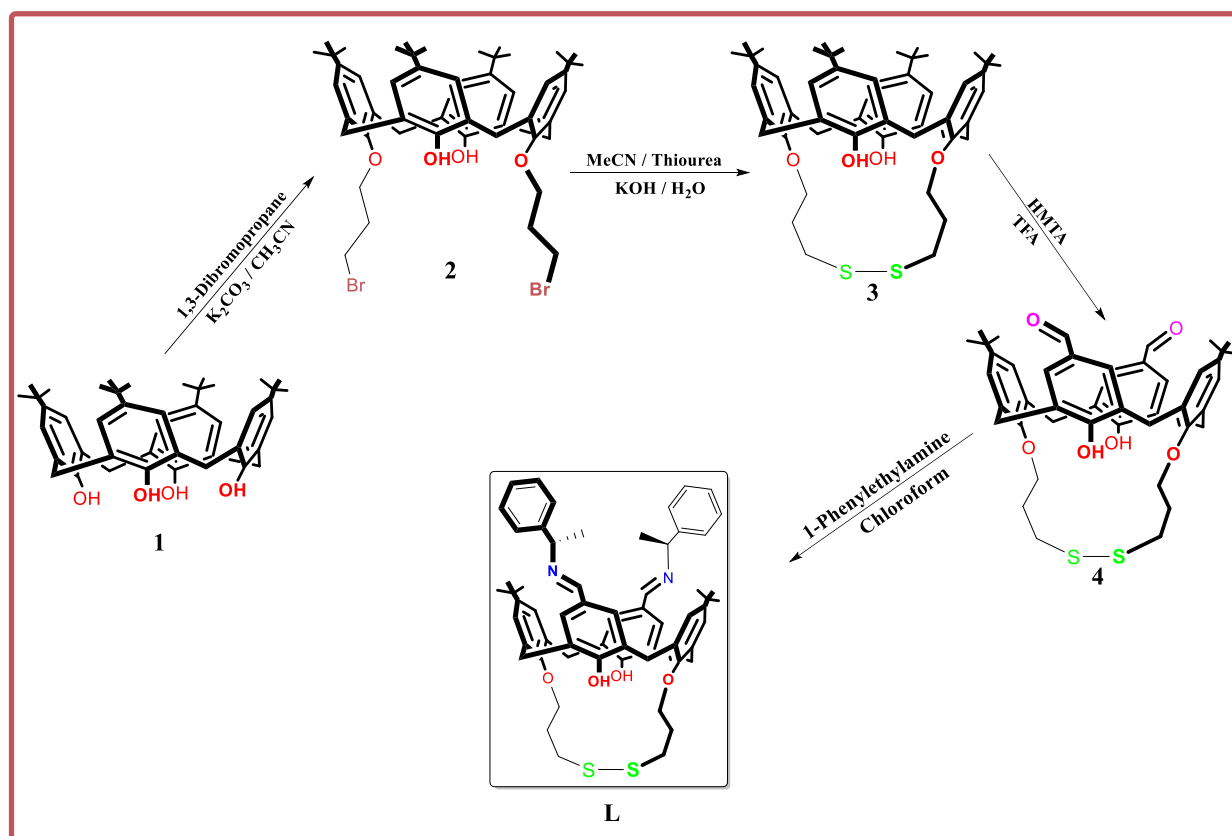


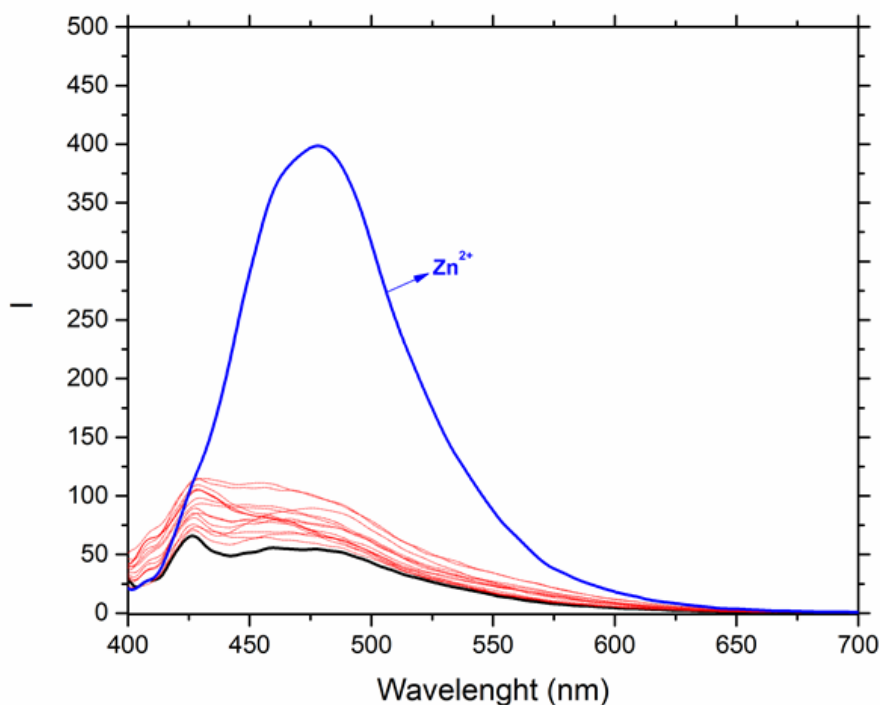
Figure 1. Presentation of synthesis scheme of calixarene based ligand (L).

### 2.2. Synthesis of Calixarene Based Ligand and Investigation of Sensing Properties

The final calix[4]arene derivative (L) using as a ligand in the study given in Figure 1 was synthesized according to the method in literature [40] and its structural characterization was performed.

For the spectroscopic measurements, the stock solutions ( $10^{-2}$  M) of various metal ions ( $Li^+$ ,  $Na^+$ ,  $Cs^+$ ,  $Ag^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Hg^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ , and  $Al^{3+}$ ) were separately prepared in deionized water using their perchlorate salt. On the other hand, the solution of L ( $3 \times 10^{-6}$  M) was prepared in 3 mL of ethanol and water (99:1, v/v) at room temperature.

The fluorescence titration study was conducted for **L** in 3 mL ethanol-water (99/1, V/V) system at a concentration of  $3 \times 10^{-6}$  M. Fluorescence spectrums of the solutions were taken by adding different cation solutions in certain volumes to realize the fluorescence titration on the solution. Excitation wavelength of the probe was 375 nm, the maximum emission wavelength was 480 nm and the slit width is 8/8 nm. In the UV-vis titration experiments, the solution of **L** was firstly added, followed by metal ions with different concentrations in a 3 mL of sample cuvette, the UV-vis spectral intensity of the mixture was tested after the reaction was complete, with scanning wavelength 200–800 nm.



**Figure 2.** Fluorescence spectra of **L** towards various ion in ethanol-water media ( $[L] = 3 \times 10^{-6}$  M,  $[M] = 3 \times 10^{-6}$  M, ( $\lambda_{ex} = 375$  nm).

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Synthesis of Calixarene Based Ligand (**L**)

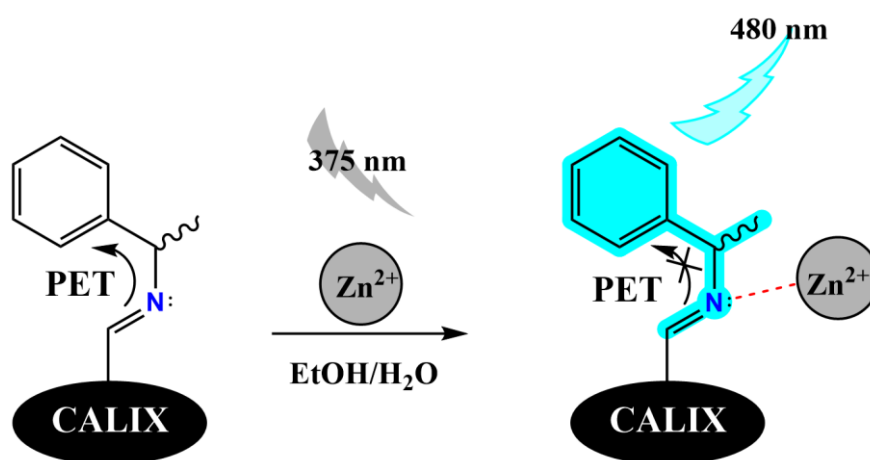
The amount of pollution caused by different cationic compounds in an aqueous environment should be measured accurately and efficiently. Thanks to the optical sensors developed for this purpose, compounds can be detected by selective, sensitive and reliable fluorimetric or colorimetric means. Among the fluorescence sensors, perception of different cations can be carried out by structures that contain different fluorophore groups. In this study, a 1-phenylethylamine functionalized Schiff base calix[4]arene (**L**) was prepared and its optical properties against various cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Al}^{3+}$ ) were examined. Following the synthesis scheme given in Figure 1, calix[4]arene derivatives were synthesized according to literature [40]. Firstly, the basic calix[4]arene **1** was synthesized according to literature, then the calix[4]arene derivative **2** consisting of the 3-bromopropoxyl group was synthesized in acetonitrile and 1,3-dibromopropane by the Williamson ether synthesis. As a result of the oxidation reaction of the obtained halide-containing calix[4]arene derivative with thiourea, the disulfide-linked calix[4]arene derivative **3** was synthesized and characterized. Then, calix[4]arene derivative **4** containing aldehyde groups was synthesized by the Duff

reaction with hexamethylenetetramine in trifluoroacetic acid medium. And finally, as a result of the condensation reaction of the calix[4]arene derivative containing aldehyde groups 4 and 1-phenylethylamine, L was synthesized and its characterization was carried out according to literature [40].

### 3.2. Investigation of Sensing Properties of Calixarene Based Ligand (L) Towards Various Ions

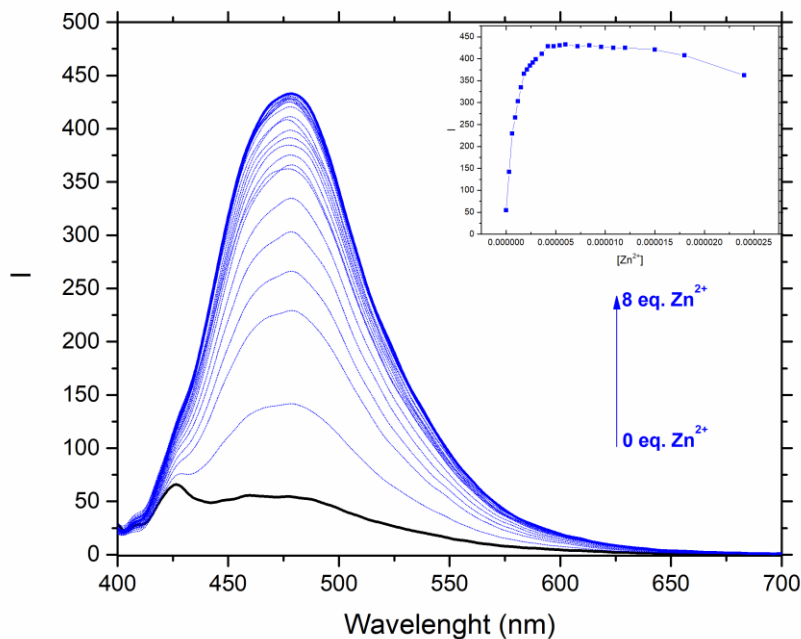
Examination of the optical properties of the prepared calix[4]arene-based ligand (L) against different cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Al}^{3+}$ ) was conducted at a concentration value of  $3 \times 10^{-6}$  M in an ethanol-water medium (99/1, v/v). The plot of the change in the fluorescence spectrum obtained is given in Figure 2. When the fluorescence spectrum of L is examined, it is observed that it emits weakly at 430 nm and 470 nm as a result of inhibition of photoinduced electron-transfer (PET) and C=N isomerization by excitation at 375 nm.

PET occurs towards the aromatic ring *via* the unshared electron pair on the nitrogen donor in the C=N group in the structure of L. Emission occurs when this PET mechanism breaks down after the addition of  $\text{Zn}^{2+}$  ion. According to literature, Zhu et al. (2017), Li et al. (2023) and Mu et al. (2021), in their study, determined that there is a PET mechanism towards the aromatic ring through the imine group in the ligands they have prepared, and this is deteriorated with the addition of  $\text{Zn}^{2+}$  to the medium [26, 41, 42]. In addition, due to the selective feature of the C=N structure, which is the chelating group, against transition metals [32], this PET mechanism is interrupted as a result of the interaction of the unshared electron pair on the nitrogen donor and the  $\text{Zn}^{2+}$  ion, which occurs as a result of the interaction of the  $\text{Zn}^{2+}$  ion after stimulation and the interaction of the  $\text{Zn}^{2+}$  ion. As a result of its interaction with the nitrogen donor, an emission peak occurred at 480 nm. The resulting interaction mechanism is given in Figure 3.

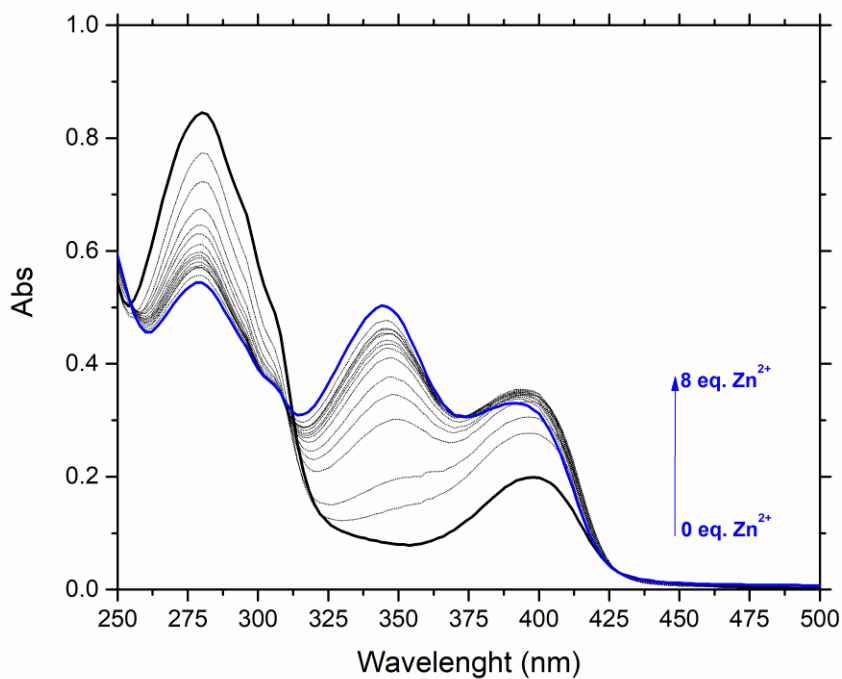


**Figure 3.** Possible interaction presentation of calixarene-based fluorescent probe (L) and  $\text{Zn}^{2+}$  ion.

In order to better examine the interactions between L and  $\text{Zn}^{2+}$  ion, both fluorescence and UV titration studies were performed by the addition of different amounts of  $\text{Zn}^{2+}$  ion. The changes in the fluorescence spectrum were recorded by adding 0-8 equivalents  $\text{Zn}^{2+}$  ion upon the solution of L at  $3 \times 10^{-6}$  M concentration in ethanol-water (99/1, v/v). It is observed that the fluorescence intensity increases at 480 nm in the spectrum however, this increase rate decreases, after the addition of 0.6 eq.  $\text{Zn}^{2+}$ . In case of UV titration, it is seen that the absorbance value increases at 340 nm in the spectrum, but this increase rate decreases, after the addition of 0.6 eq.  $\text{Zn}^{2+}$ .



**Figure 4.** Fluorescence spectra of L solution (EtOH/H<sub>2</sub>O, 99:1, v/v) upon addition of different amounts of Zn<sup>2+</sup> ion (0-8 equivalents) ( $\lambda_{ex} = 375$  nm).



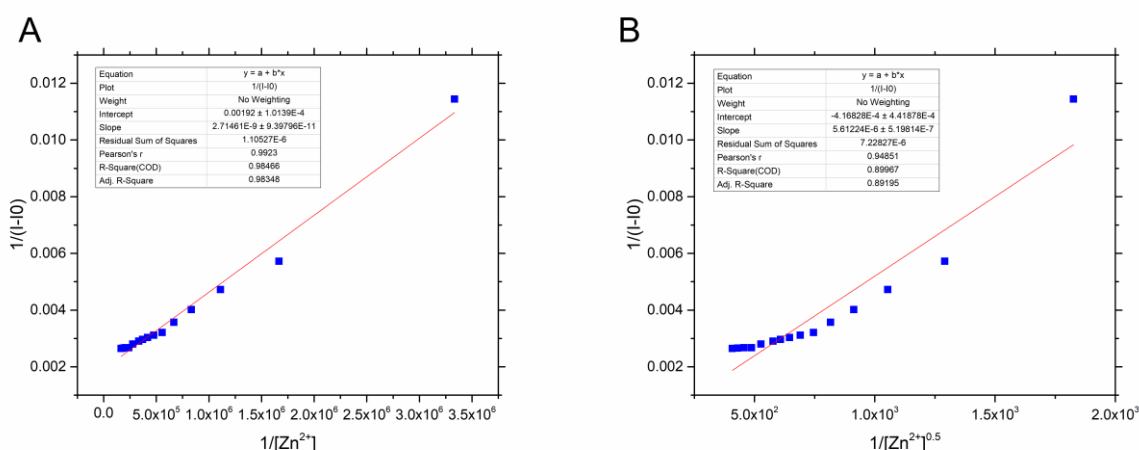
**Figure 5.** UV spectra of L solution (EtOH/H<sub>2</sub>O, 99:1, v/v) upon addition of different amounts of Zn<sup>2+</sup> ion (0-8 equivalents).

In order to determine the stoichiometry of the complex formed between the L and the Zn<sup>2+</sup> ion, the Job plot was drawn using the titration data and is given in Figure 6. When the obtained data was examined,

the fact that the peak of the mole fraction was close to the value of 0.66 suggested that the complexation occurred at a ratio of 2:1, that is, the two ligand L molecules complexed with a  $Zn^{2+}$  ion. On the other hand, in the fluorescence studies, as a result of the interaction with the unshared electron pairs on the nitrogen donor L possesses, it is seen that emission occurs with the inhibition of the PET mechanism. More, since L has two functional groups in its structure, the binding phenomena at the same conditions were examined using the Benesi-Hildebrand equation to better determine the complexation stoichiometry. Thus, the binding coefficient ( $K$ ) was calculated by the Benesi-Hildebrand equation using titration data to calculate the binding coefficient.

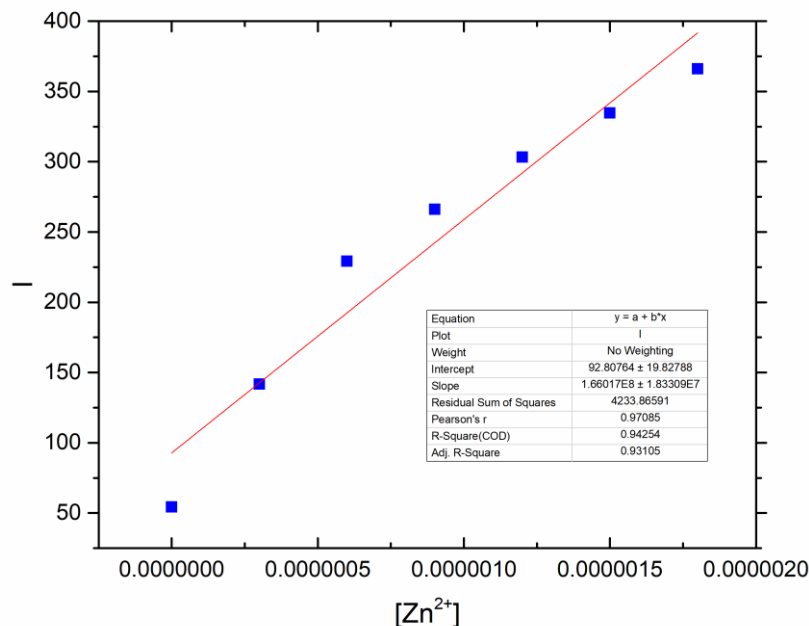
$$\frac{1}{I - I_0} = \frac{1}{\left\{ K (I_{\max} - I) [Zn^{2+}]^n \right\}} + \frac{1}{(I_{\max} - I)}$$

Here,  $I_0$  is the initial fluorescence intensity,  $I$  is the fluorescence intensity after cation addition,  $I_{\max}$  is the maximum absorbance value obtained and  $K$  is the binding constant ( $1/M$ ). In order to confirm the complexation between  $Zn^{2+}$  ion and L, Benesi-Hildebrand plots were plotted for assuming both 1:1 complexation and 2:1 complexation and given in Figure 6A and Figure 6B, respectively. According to the results obtained, it is seen that the slope of the graph obtained for 1:1 complexation has a higher linearity ( $R^2 = 0.9847$ ). When the results obtained with Job's graph are analyzed together, it is thought that a weak complex is formed between L and  $Zn^{2+}$  ion. The value of the binding constant ( $K = 1.8 \text{ M}^{-1}$ ) calculated from the slope of the  $1/[Zn^{2+}]$  versus  $1/(I - I_0)$  graph seems to confirm this.

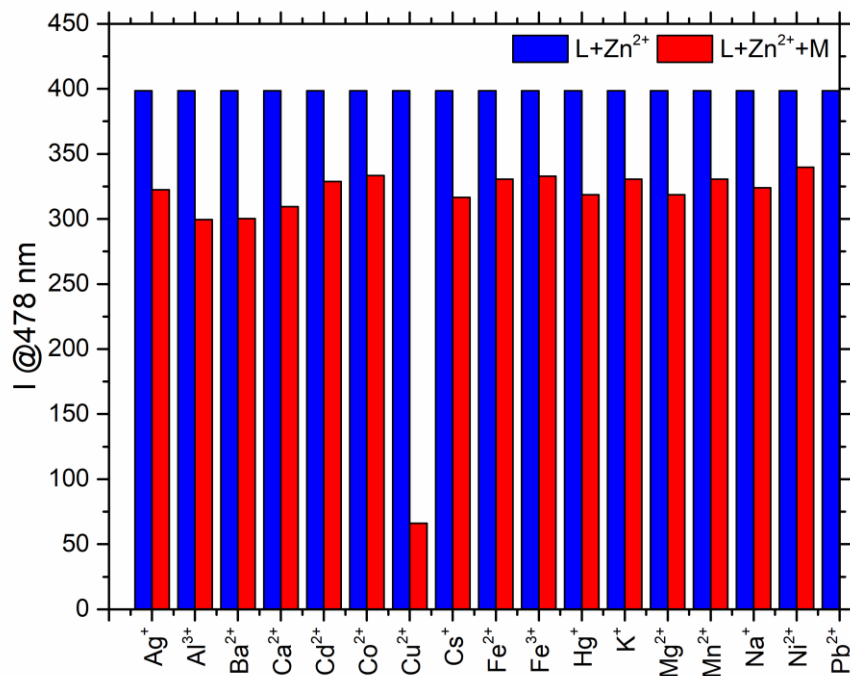


**Figure 6.** Benesi-Hildebrand plots for assuming (A) 1:1 complexation and (B) 2:1 complexation.

Using the data obtained as a result of the titration study, a graph of fluorescence intensity versus  $Zn^{2+}$  concentration was drawn as given in Figure 7. Using the data in the linear part of this graph, the limit detection (LOD) value was calculated as  $4.8 \times 10^{-7} \text{ M}$  using the formula  $LOD = 3\sigma/m$ , where  $\sigma$  denotes the standard deviation of the 10 blank samples, and  $m$  denotes the slope of the linear regression (Figure 7). This limit is discovered to be substantially lower than the WHO recommended limit for  $Zn^{2+}$  in drinking water ( $7.65 \times 10^{-5} \text{ M}$ ). As a result, with an increase in fluorescence, the probe would have extremely low detection limits and be suitable for usage in real-world scenarios.



**Figure 7.** The graph of change in fluorescence intensity towards  $Zn^{2+}$  ion in different concentrations.



**Figure 8.** Fluorescence intensities of L ( $3 \times 10^{-6}$  M) upon addition of various metal ions ( $6 \times 10^{-6}$  M) ( $Zn^{2+}$ ,  $Al^{3+}$ ,  $Ag^+$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Na^+$ ,  $Pb^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Ba^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Hg^{2+}$ , and  $Ni^{2+}$ ) and that of the respective solution added  $Zn^{2+}$  ( $3 \times 10^{-6}$  M). EtOH/ $H_2O$  solution (99:1, v/v),  $\lambda_{ex} = 375$  nm.

Upon the determination that L is selective against  $Zn^{2+}$  ion among different cations, the effect of other



cations on the L - Zn<sup>2+</sup> complex was investigated and the changes obtained are given in Figure 8. When the changes in fluorescence intensity obtained as a result of the addition of different cations as 2 equivalents on the L - Zn<sup>2+</sup> complex are examined, it is seen that the fluorescence intensity is seriously quenched with the addition of Cu<sup>2+</sup> ion. The results demonstrate that, with the exception of Cu<sup>2+</sup> ion, other interferences on Zn<sup>2+</sup> detection can be disregarded. In order to as far as feasible, the probe can be used in the environment to detect zinc ions without Cu<sup>2+</sup> ions.

#### 4. CONCLUSIONS

In this study, a 1-phenylethylamine-functionalized calix[4]arene-based ligand (L) was prepared and its optical properties against different cations were investigated. In the case of Zn<sup>2+</sup>, L exhibited an intense fluorescence at 480 nm when excited at 375 nm in an ethanol-water medium, which indicated that it is a selective sensor for the Zn<sup>2+</sup> ion among cations. This is due to the inhibition of the PET mechanism on the L probe as a result of its interaction with the Zn<sup>2+</sup> ion and the interaction mechanism with the C=N isomerization *via* its imine group. It was found that the composition of the complex formed by the coordination of L with Zn<sup>2+</sup> is 1:1. On the basis of fluorescence titration studies, the complex binding constant and the detection limit of the L probe were calculated to be 4.8x10<sup>-7</sup> M and 1.8 M<sup>-1</sup>, respectively. Consequently, this study presents that the 1-phenylethylamine-functionalized calix[4]arene-based ligand (L) prepared in this study can be an efficient and effective fluorescence sensor for Zn<sup>2+</sup> ions.

#### Declaration of Ethical Standards

The authors declare that all ethical guidelines including authorship, citation, data reporting, and publishing original research are followed.

#### Declaration of Competing Interest

The authors declare that there is no conflict of interest.

#### Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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