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Araştırma Makalesi

Employing of 2-Acetylpyridine Based Chalcone as Hg^{2+} Sensing Material: Experimental and Theoretical Examination

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ABSTRACT

This study reports the evaluation of 2-acetylpyridine based chalcone structure as a useful sensing material for Hg^{2+} ion detection by the means of UV-visible spectroscopy. In this context, firstly, the most common twenty metal ions were treated by the chalcone structure which was synthesized from 2-acetylpyridine and 4-diphenylaminobenzaldehyde according to the known procedures. As result, the studied chalcone compound exhibited good sensing activity towards Hg^{2+} ion in acetonitrile/water medium with significant red-shift phenomenon. In addition, some photophysical/electronic parameters of the chalcone and its Hg^{2+} complex were determined experimentally and theoretically. B3LYP, PBE0 methods and SVP, TVZP, and TVZPP basis sets were used for theoretical calculations in acetonitrile media. Finally, experimental results were explained and the proposed sensing mechanism was supported via density functional theory (DFT) outputs.

Keywords: *Chalcone, Sensors, UV/Vis Spectroscopy, Density functional theory*

2-Asetilpiridin Bazlı Kalkonun Hg^{2+} Sensör Malzemesi Olarak Kullanılması: Deneysel ve Teorik İnceleme

ÖZ

Bu çalışma, Hg^{2+} iyonunun belirlenmesinde 2-asetilpiridin bazlı kalkon yapısının UV-görünür bölge spektroskopisi yardımıyla kullanışlı bir sensör malzemesi olarak değerlendirilmesini rapor etmektedir. Bu bağlamda, ilk olarak, en yaygın yirmi metal iyonu, bilinen reaksiyonlara göre 2-asetilpiridin ve 4-difenilaminobenzaldehitten sentezlenen kalkon yapısı ile etkileştirildi. Sonuç olarak, çalışılan kalkon bileşiği asetonitril/su ortamında önemli oranda kırmızıya kayarak Hg^{2+} iyonuna karşı oldukça iyi sensör aktivitesi gösterdi. Ayrıca, kalkonun ve onun Hg^{2+} kompleksinin bazı fotofiziksel/elektronik parametreleri deneysel ve teorik olarak belirlendi. Asetonitril ortamındaki teorik hesaplamalar için B3LYP, PBE0 metotları ile SVP, TVZP ve TVZPP temel setleri kullanıldı. En son olarak ise, deneysel sonuçlar açıklandı ve önerilen sensör mekanizması yoğunluk fonksiyon teorisi (DFT) çıktıları ile desteklendi.

Anahtar Kelimeler: *Kalkon, Sensörler, UV/Vis Spektroskopisi, Yoğunluk fonksiyon teorisi*

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I. INTRODUCTION

Toxicology of mercury is well known by human being and exposure to all forms of it results in severe diseases [1]. For example, direct inhalation of mercury causes pulmonary diseases and chronic exposure to mercury results neurological and renal disorders [2]. Emitted mercury to the atmosphere later accumulated to aquatic media, then bioaccumulated to food chain [3]. There are many works on toxicology and measurement techniques of mercury in the literature [4-6].

Being one of the most toxic heavy metal, mercury, is a glossy white silver, odourless liquid and becomes colorless and odourless gas when it was heated. Mercury can exist mainly in three forms: metallic form, inorganic salt form and as organic complex. Every form has its own toxicity and biological activity effects. It has a severe, massive threat on the health in general beside its toxicity effects on the human beings even for other creatures as well. In general, numerous health measures have been undergoing to control and prevent metal toxicity at different levels [7]. Due to this reason, sensing and determination of mercury have been important for many years [8].

In addition to expensive instrumental techniques such as AAS and ICP, some inexpensive techniques using simple sensing materials are also available. In this context, some specially designed organic structures can serve as sensing materials against metal ions in these techniques. They can hold a metal ion by heteroatoms forming new complexes [9-12].

Chalcones, are a member of naturally occurring flavonoid family and have huge attracting potential as naturally occurred products due to their remarkable biological properties such as anticancer, enzyme inhibitor, antibacterial, and antifungal [13-16], can also be used as sensing materials in mentioned techniques. Thus, numerous studies investigating of the synthesis methods and evaluation in novel applications of these compounds have been reported [17-20].

In this study, we have reported an easy, cheap and rapid method for the detection of Hg^{2+} ions by a known chalcone ligand (ChL) structure, (E)-3-[4-(diphenylamino)phenyl]-1-(pyridin-2-yl)prop-2-en-1-one, using spectrophotometric techniques. In addition, geometric optimizations, electronic structures, and other energy parameters of the mentioned ligand and complex structures were studied by the help of computational calculations to illustrate the sensing mechanism. The B3LYP and PBE0 functionals were tested for the geometry and other electronic calculations by using different basis sets (SVP, TVZP, and TVZPP).

II. RESULTS AND DISCUSSION

A. SYNTHESIS

The studied chalcone based chemosensor ligand (ChL: (E)-3-[4-(diphenylamino)phenyl]-1-(pyridin-2-yl)prop-2-en-1-one) was obtained as in Fig. 1 according to the previous literature procedures. [21-23] ^{1}H-NMR and ^{13}C-NMR spectra were compared with related literature and the structure of chalcone based ligand (ChL) was verified as in Fig 1.

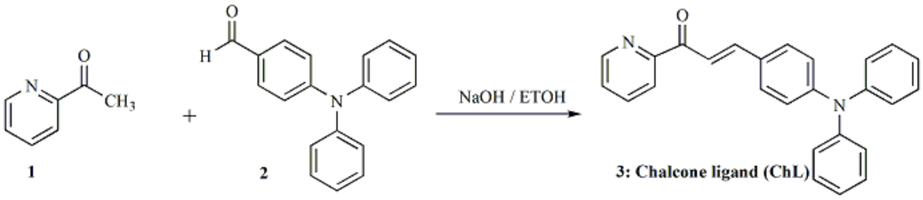

***Fig. 1** Synthesis of chalcone ligand (ChL).*

B. SENSING STUDIES

In this study, the synthesized chalcone ligand (ChL) has been investigated for its sensing behavior against common metal ions. In the chalcone structure, 2-acetylpyridine residue provides binding site for potential ion selectivity. Besides, triphenylamine derived aldehyde residue provides electron donation throughout the chalcone skeleton to advance the photophysical properties. In order to authenticate the photophysical nature of the ChL, firstly, absorption spectrum has been recorded in acetonitrile (10^{-5} M). In this medium, the main absorption band related with π-π^* transition was observed at around 432 nm. At this point, any changing on this spectrum by the coordination of any metal ion may signify that the chalcone compound can be used as a turn-on chemosensor. For this reason, to find out the considerable changes in the spectrum of the ChL by the interaction with any metal ions, subsequent experiments were carried out. The interaction between the ChL and a series of common metal ions such as Na^+, Cd^{2+}, Ag^+, K^+, Li^+, Mg^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Cu^{2+}, Hg^{2+}, Cr^{3+}, Pb^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+} were monitored by UV−Vis spectroscopy. For this target, 10^{-4} M water solutions (0.5 ml) of metal nitrate salts were added to 10^{-5} M ChL solution (5.0 ml). During this detection process, a strong red-shift was shown only by addition of Hg^{2+} ion and the color of the solution has clearly turned to blue from yellow (Fig. 2). This red-shift phenomenon may signify the interaction between the ChL and Hg^{2+} ion in the mixture of acetonitrile/water (10:1, v/v). The resulting new signal appeared at 592 nm in the absorption spectrum (Fig. 3) of the mixture. Based on the absorption responses of chalcone derivative against studied metal ions, it can be suggested that the ChL can serve as a highly selective Hg^{2+} ion sensing material.

Fig. 2 *Colorimetric change of ChL solution after addition of metal ions (1:1 metal-ligand stoichiometry in acetonitrile/water 10:1).*

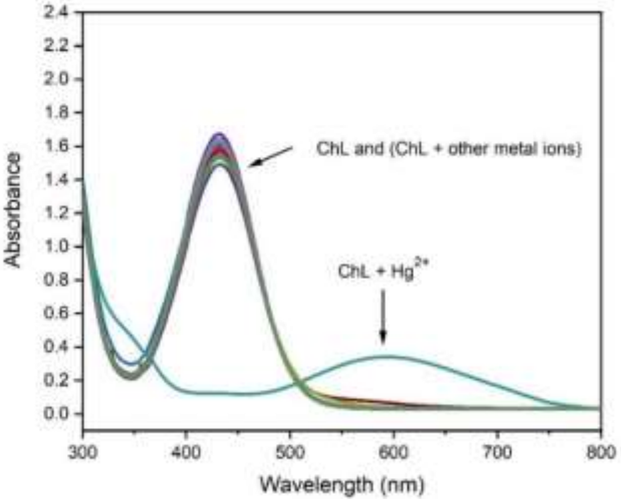

Fig. 3 *Absorption spectra of the ChL with different metal ions (1:1 metal-ligand stoichiometry in acetonitrile/water 10:1).*

To illuminate the binding stoichiometry between the ChL and Hg^{2+}, Job's plot experiments were performed. The intensity of the absorbance (592 nm) was monitored by increasing the molar ratio of Hg^{2+}. It can be clearly seen from Fig. 4A, measured absorbances exhibit a maximum at 0.5 molar fraction indicating the formation of 1:1 ratio of the ChL and Hg^{2+} ion. In order to obtain more evidence about binding mechanism of ChL toward Hg^{2+} ions, titration experiment was carried out using the solution of the ChL (10^{-5} M) in presence of increasing equimolar amounts of Hg^{2+} (0.25, 0.5, 1.0, 2.0, 4.0). In the titration study, the addition of Hg^{2+} gradually increased absorbance for the band at 592 nm up to 1.0 equivalent which support a 1:1 stoichiometry (Fig. 4B). Besides, addition of more Hg^{2+} exhibited no significant change in the absorption intensity. Further, binding stoichiometry was supported via mass analysis. The peak at 721.28 m/z indicates the structure of $[(ChL)+Hg^{2+}+2xNO_3^-+H_2O+H^+]$ (calcd: 721.12). Because of the formation of more rigid and planar orientation and restriction of the rotation of pyridine ring, a new transition band was appeared in absorption spectrum of the final structure. Thus, the ChL serves as a Hg^{2+} ion sensor by the absorbance based process with 1:1 stoichiometric factor.

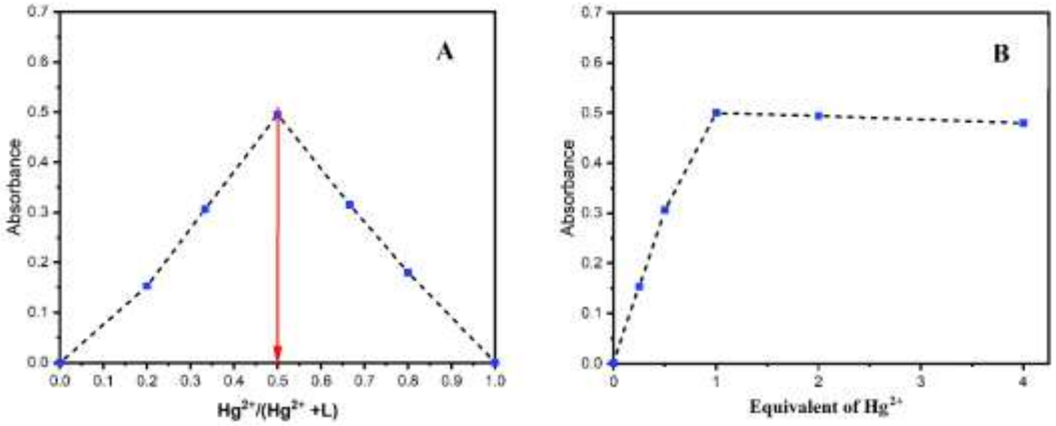

Fig. 4 *Job's plot (**A:** 2x10^{-5} M total concentration) and titration (**B**) experiments in acetonitrile/water mixture.*

One of the most important factors is the response time which should be considered in the detection process of an analyte for practical applications. It is expected that the response to an analyte should be as rapid as possible. From Fig. 5A, it can be clearly seen that the maximum value of absorption intensity was almost shown within 15-30 minutes due to the rapid response performance of the ChL towards Hg^{2+} ions at ambient temperature. Therefore, all spectra were recorded after standing an hour upon addition of Hg^{2+} unless otherwise mentioned. Moreover, the absorbance profile of the ChL and Hg^{2+} mixture remained unchanged during a long time (24 hours) indicating that the ChL-Hg^{2+} complex is quite stable. On the other hand, slightly heating up of the mixture up to 40-50 °C resulted in a faster response in a few minutes. Based on its good response time and stability of the resulting complex, the ChL presents a rapid and reasonable detection strategy for Hg^{2+}. On the other hand, a different important factor is actually pH effect on the sensing behavior and this parameter may affect the reliable working range of the sensor. Herein, the pH effect investigations showed that the determination of Hg^{2+} ions is operative only under acidic conditions ($pH \leq 6$) (Fig. 5B). Neutral and basic conditions did not response for the determination of Hg^{2+} ions.

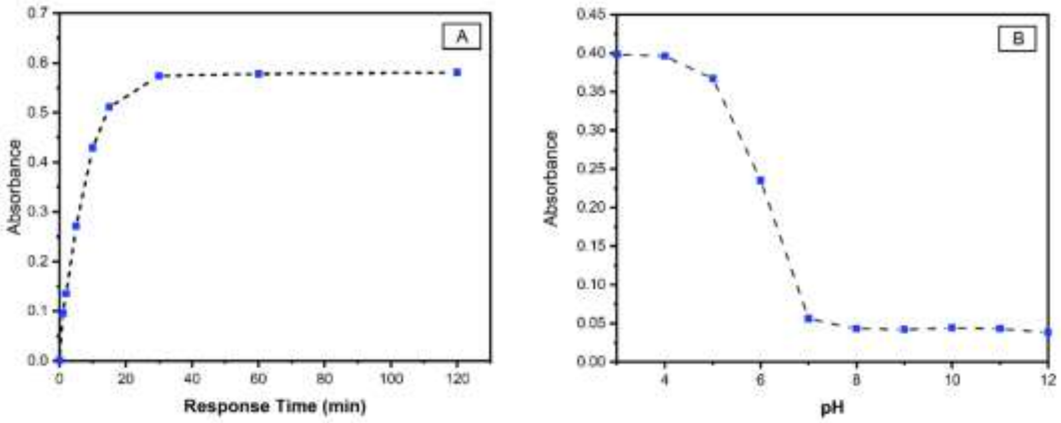

Fig. 5 *Response time of the ChL towards Hg^{2+} ion (**A**) and pH effect on Hg^{2+} detection (**B**) (1:1 metal-ligand stoichiometry).*

To investigate the effect of other metal ions during Hg^{2+} ion sensing of the ChL, interference tests were performed by mixing of the ChL, Hg^{2+} and other competitive metal ion. Absorption intensities of each solution at 592 nm were measured one hour later and the obtained results were illustrated in Fig. 6. As seen in Fig. 6, the test mixtures including other competitive metal ions displayed almost same absorption profile compared to the ChL+Hg^{2+} mixture. This indicates that Hg^{2+} ion sensing ability of the ChL was not considerably affected by the presence of other ions and this means that the ChL exhibited promising selectivity for Hg^{2+} ion compared to other metal ions.

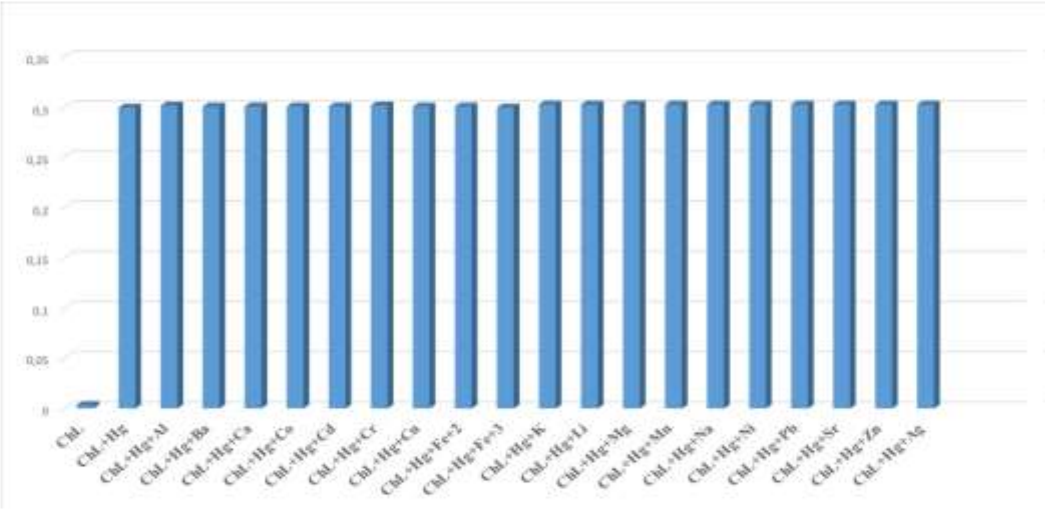

Fig. 6 *The effects of other metal ions on Hg^{2+} detection (~10^{-5} M, 1:1:1 stoichiometry in acetonitrile/water 10:2).*

Finally, considering the sensing studies, the Job's plot, titration experiment, and mass analysis result, Hg^{2+} ion has been clearly bonded to the studied ligand compound (ChL) at 1:1 equivalent and it can be said that the final structure of the resulting complex is as in Fig 7.

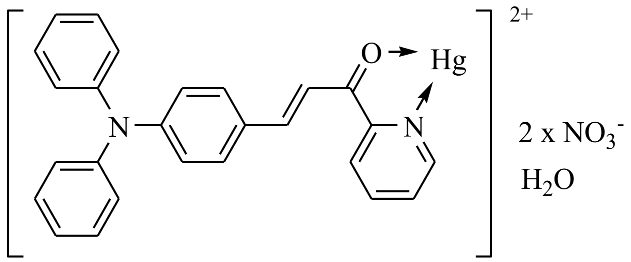

__Fig. 7__ Proposed structure of the ChL-Hg^{2+} complex.

C. THEORETICAL STUDIES

In order to verify the proposed sensing mechanism, geometric optimizations and theoretical calculations of the ChL and ChL-Hg^{2+} complex were performed. Thanks to TD-DFT calculations, frontier orbital energy differences, and absorption profiles of the studied compounds (ChL and ChL-Hg^{2+}) were determined. Then, the obtained energy differences and absorbance results were organised in Table 1. Moreover, experimental energy differences between HOMO and LUMO were also calculated by the Tauc-Plot method [24]. When looked at the calculation results in Table 1, it can be seen the differences in frontier MO energies and λ_{max} values before and after Hg^{2+} binding to the ChL. Considering the experimental and theoretical frontier orbital energy differences, B3LYP was more suitable method for the chalcone ligand (ChL) while PBE0 is better for ligand-metal structure (Fig. 8). On the other hand, theoretical absorption λ_{max} values were close to experimental result for both the ChL and ChL-Hg^{2+} for studied methods (Fig. 9). As result, calculated HOMO-LUMO energy differences and significant red-shift in theoretical UV spectra were in accordance with observed experimental results.

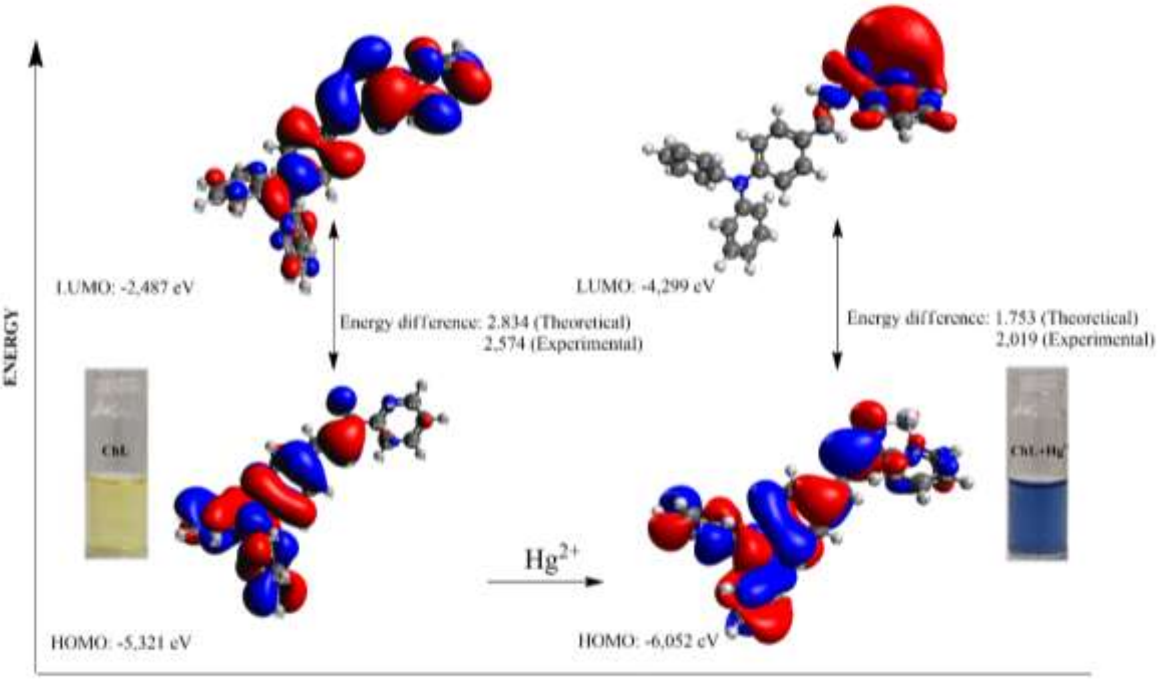

__Fig. 8__ HOMO and LUMO diagrams of the ChL and ChL-Hg^{2+} complex.

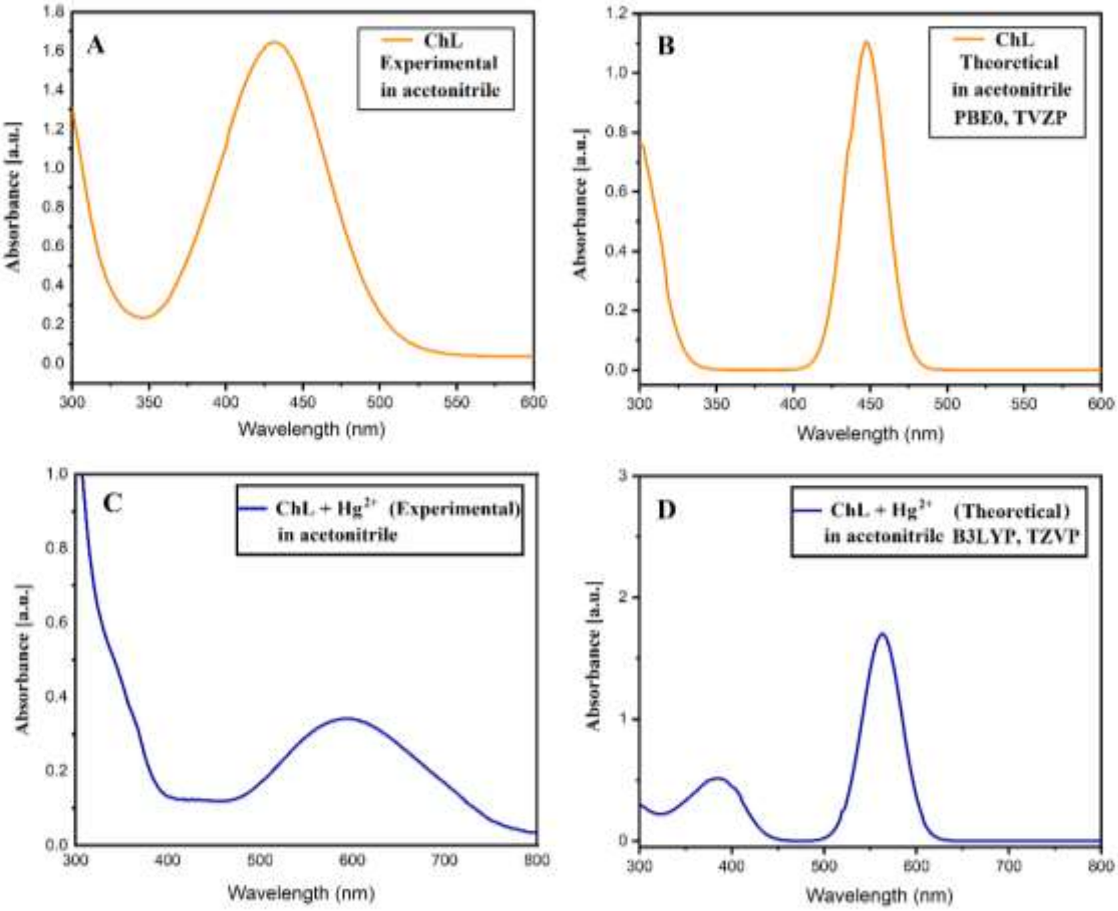

Fig. 9 *Comparison of the experimental and theoretical UV/vis spectra of the ChL and ChL-Hg^{2+} complex.*

Table 1. *Theoretical and experimental UV spectra of the ChL and ChL-Hg^{2+} complex.*

		Energy difference (*eV*)			**λmax** (*Abs., nm*)		
	Method/ Basis sets	**B3LYP**	**PBE0**	**Exp.**	**B3LYP**	**PBE0**	**Exp.**
ChL	SVP	2.904	3.232	2.574	462	438	432
	TZVP	2.834	3.151		473	451	
	TZVPP	2.833	3.151		473	451	
ChL+Hg^{2+}	SVP	1.132	1.765	2.019	560	538	592
	TZVP	1.155	1.753		555	538	
	TZVPP	1.155	1.754		555	538	

III. EXPERIMENTAL

A. GENERAL

All chemicals were purchased from the Sigma-Aldrich, Merck, and Fluka with high-grade purity and used without further purification. The used solvents were distilled according to the standard procedures. Ultrapure distilled water was used to prepare metal solutions. Acetonitrile with gradient grade for liquid chromatography was used as a solvent in metal sensing studies. The NMR spectra were obtained by a Bruker 400 MHz instrument in $CDCl_3$ using TMS as internal standard. The UV measurements were realized in a quartz cell of 1 cm optical path length by PG instruments T80+ double beam UV-vis spectrophotometer at room temperature. The melting point was measured by Electrothermal IA 9100. The geometric optimizations and theoretical calculations were performed via ORCA 5.0.2 [25,26] open source code. These theoretical calculations were performed for acetonitrile media and the outputs visualized Avogadro 1.2.0 [27,28] as graphical user interface.

B. SYNTHESIS

The studied chalcone based chemosensor ligand (**ChL**: (E)-3-[4-(diphenylamino)phenyl]-1-(pyridin-2-yl)prop-2-en-1-one) was obtained as in Fig. 1 according to the previous literature procedures [21-23]. First of all, 0.242g of 1-(pyridin-2-yl)ethanone and 0.546g of 4-(diphenylamino)benzaldehyde were dissolved in 20 ml of ethanol in the presence of 0.08 g of NaOH at room temperature. After completing reaction, 20 mL water was added to the mixture and neutralised with addition of diluted HCl solution. Then, the mixture was extracted by using 3x20 ml of dichloromethane and organic phase dried on Na_2SO_4. After filtration and evaporation of volatiles, the crude product recrystallized in MeOH/DCM solvent system. The structure of chalcone based chemosensor compound (ChL) was verified by NMR techniques. Melting point was found as 193 °C (Ref: 467 K). ^{1}H-NMR, ^{13}C-NMR spectra and melting point were found to be identical with the ones described in Ref. [21-23].

C. SENSING STUDIES

The stock solutions of ChL in acetonitrile (10^{-5} M) and metal solutions (10^{-4} M) in pure water were freshly prepared and metal sensing studies were performed with 1:1 stoichiometry by addition of metal solution (0.5 ml) to the ChL solution (5 ml). Using the UV spectrophotometric technique after one-hour timing, we investigated the changes in absorbance of chalcone ligand after addition of metal solutions. The results showed that the chalcone compound can be specific and selectively detecting substance for Hg^{2+} ions, and then cause a remarkable color change from yellow to blue. The Britton-Robinson buffer solutions were used to determine pH effect on sensing behavior. Time-dependent absorbance changings were monitored after mixing the chalcone ligand with Hg^{2+} solution at 1:1 equivalents in 24 hours period. The interaction between metal and ligand was investigated with the Job's plot method. Spectrophotometric titrations were made at constant ligand concentration [10^{-5} M] and varying Hg^{2+} equivalents [0-4 equivalents]. Competition tests were performed by using a mixture of ChL (1.0 eq.), Hg^{2+} ion (1.0 eq.) and other competitive metal ions (1.0 eq.).

D. THEORETICAL STUDIES

In order to calculate the electronic properties of ground state ChL and ChL-Hg^{2+} complex, we performed DFT and TD-DFT studies via ORCA 5.0.2 [25,26] open source DFT code by using an overclocked CPU Ryzen 5 3600 (4.1 GHz) with 24 GB of RAM. These calculations were carried out using two methods (B3LYP, PBE0) and three basis sets (def2-SVP, def2-TVZP, def2-TVZPP) in acetonitrile as solvent. Implicit solvation was included through the C-PCM model [29]. Also, the outputs visualized by Avogadro 1.2.0 [27, 28] as graphical user interface and the obtained HOMO-LUMO energy difference results and absorption data were tabulated in Table 1.

IV. CONCLUSION

In summary, a known compound, (E)-3-[4-(diphenylamino)phenyl]-1- (pyridin-2-yl)prop-2-en-1-one, has been re-synthesized and evaluated as a Hg^{2+} ion sensing material. The ChL showed an absorption band at 432 nm and a significant naked eye red-shift response towards Hg^{2+} ions in 10:1 acetonitrile-water medium. New absorption band has been shown at 592 nm and it can be said that this absorption band was observed due to the formation of Hg^{2+} complex resulting new electronic transitions and blocking conformational rotations. By considering this and other experimental results, it can be deduced 1:1 binding stoichiometry for the resulting ChL-Hg^{2+} structure. Also, the ChL exhibited acceptable response time and quite good sensitivity towards Hg^{2+} ions. In contrast to promising selectivity, sensitivity and response time of ChL, the reliable working range is limited only under acidic conditions. In addition, theoretical studies were performed to explain the sensing mechanism and the outputs supported this complex formation in 1:1 stoichiometry by the means of frontier molecular orbital energy differences and calculated absorption results. Consequently, this report presents a quite convenient method to detect Hg^{2+} ions by a 2-acetyl pyridine based chalcone structure.

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