**Zn$^{2+}$-Schiff’s Base Complex as an “On–Off-On” Molecular Switch and a Fluorescence Probe for Cu$^{2+}$ and Ag$^{+}$ Ions**

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**Abstract**

The present study presents a thorough theoretical analysis of the electronic structure and conformational preference of Schiff’s base ligand N,N-bis(2-hydroxybenzilidene)-2,4,6-trimethyl benzene-1,3-diamine (H$_2$L) and its metal complexes with Zn$^{2+}$, Cu$^{2+}$ and Ag$^{+}$ ions. This study aims to investigate the behavior of H$_2$L and the binuclear Zn$^{2+}$ complex (1) as fluorescent probes for the detection of metal ions (Zn$^{2+}$, Cu$^{2+}$ and Ag$^{+}$) using density functional theory (DFT) and time-dependent density functional theory (TDDFT). The six conformers of the H$_2$L ligand were optimized using the B3LYP/6–311+G* level of theory, while the L−2-metal complexes were optimized by applying the B3LYP functional with the LANL2DZ/6–311+G** mixed basis set. The gas-phase and solvated Enol-cis isomer (E-cis) was found to be the most stable species. The absorption spectra of the E-cis isomer and its metal complexes were simulated using B3LYP, CAM-B3LYP, M06-2X and ωB97X functionals with a 6–311 + +G** basis set for C, O, N and H atoms and a LANL2DZ basis set for the metal ions (Zn$^{2+}$, Cu$^{2+}$ and Ag$^{+}$). The computational results of the B3LYP functional were in excellent agreement with the experimental results. Hence, it was adopted for performing the emission calculations. The results indicated that metal complex (1) can act as a fluorescent chemosensor for the detection of Ag$^{+}$ and Cu$^{2+}$ ions through the mechanism of intermolecular charge transfer (ICT) and as a molecular switch “On–Off-On” via the replacement of Cu$^{2+}$ by Ag$^{+}$ ions, as proved experimentally.

**Keywords** Photoinduced electron transfer (PET) · Fluorescence probe molecular switch · Schiff base · Density functional theory (DFT) and time-dependent density functional theory (TDDFT)

**Introduction**

Due to their operational simplicity, high sensitivity, and high response speed, fluorescent probes have been widely applied in diverse fields, such as chemical biology, medicinal chemistry, analytical chemistry, and molecular biology [1]. The employment of fluorescent probes has revolutionized our understanding of several physiological or pathological processes and has provided effective sensing protocols for the detection of harmful species that may have been released into the environment (aqueous and gaseous). Fluorescent probes use either specific host–guest interactions or selective chemical reactions to affect changes in fluorescence properties. If the binding between the host and guest is noncovalent and reversible, then the fluorescent probe is known as a chemosensor. Alternatively, if the interaction between the host and guest leads to an irreversible chemical reaction, then the fluorescent probe is known as a chemodosimeter [2].

The chemical compounds with azomethine (-CH=N-) groups are called Schiff’s bases. They are excellent classes of ligands and enjoyed popular use in coordination chemistry because they form coordinate bonds with metal ions to produce coordination metal complexes. Metal complexes
incorporating Schiff bases have played important roles in the advancement of inorganic chemistry. They were discovered by Hugo Schiff’s (Germanist) [3]. Schiff bases have considerable chemical and biological importance because of their easy method of preparation, excellent chelating ability and synthetic flexibility [4, 5].

Schiff bases show photochromism and thermochromism in the solid state through proton transfer from the hydroxyl (O) atom to the imine (N) atom [6–9]. Salicyldeneanilines Schiff’s bases (SAS) are dynamical systems, usually referred to as molecular switches [10] that exhibit thermochromism [11–15], photochromism [12, 13, 16–19], solvatochromism [13, 20, 21], and nonlinear optical (NLO) switching properties [20–24], both in solution and solid state. SAS molecules can undergo keto-enol tautomerism when triggered by light or temperature changes [25, 26]. This behavior is shown by their Cis and Trans isomers, which are characterized by one or two intramolecular H-bonds. Schiff base probes possess –OH (phenolic) and –N= (imine) functional groups close to each other and hence become excellent hydrogen donor and acceptor sites, respectively, for constructing excited-state intramolecular proton transfer (ESIPT) entities that can be used as metal ion-specific probes [27–29].

Among the most important molecules used, there is a new Schiff base ligand, N,N-bis(2-hydroxybenzilidene)-2,4,6-trimethyl benzene-1,3-diamine (H2 L) [1]. It binds with metal ions such as zinc ions (Zn2+), copper ions (Cu2+) and silver ions (Ag+) (see Scheme 1). Despite the existence of numerous applications for such molecules, the geometry and the exact nature of cation binding have not been fully investigated.

In the present work, based on an experimental study of Schiff’s base and its metal complexes [1], a density functional theory (DFT) computational study was performed to complete the experimental detection of Ag+ ions and Cu2+ ions through the fluorescence phenomenon by using the binuclear Zn2+ complex as a molecular switch.

Therefore, this study is designed to answer a question related to the difference in the fluorescence intensity of these metal complexes by explaining the mechanisms that lead to these fluorescence responses through a DFT computational study. Moreover, the classification of molecules according to the type it assumes as a fluorescence probe, i.e. a chemosensor or a chemodosimeter, is also tackled.

Finally, we aim to investigate the reason for the difference in the fluorescence intensity of the substrates by applying extensive theoretical studies of the ground and excited electronic states of the ligand conformers (H2L) and its Zn2+, Cu2+ and Ag+ metal ion complexes.

**Computational Details**

All calculations were performed using the G09 program package [30]. All the possible conformers of the ligand (H2L) were optimized using the B3LYP/6–311 + + G** [31–33] level of theory. Frequency calculations were performed to confirm global minima or transition states on the potential energy surfaces by having zero or one imaginary frequency, respectively. The ligand–metal complexes were optimized by using the B3LYP functional with a 6–311 + + G** basis set for all atoms except the metal ions, for which the LANL2DZ basis set was used. In addition, the Zn complex was subjected to further confirmation and validation using more functionals, namely, CAM-B3LYP, M06-2X and ωB97X. The binding energies (EBE) of the complexes were calculated by the following equation:

\[ E_{BE} = E_{BE} - (E_A + n \cdot E_B) \]

where EAB is the total energy of the geometry complex, EB is the corresponding total energy for the optimized ligand B, n is the number of ligands in the complex and EA is the total energy of the single point energy calculation for metal (A) using the same multiplicity as in the complex case [34]. The absorption and emission UV–VIS spectra of the E-cis isomer were simulated using the TDDFT [35] method at the B3LYP/6–311 + + G** level of theory, while the metal complexes were studied by the B3LYP/LANL2DZ/6–311 + + G** level of theory. These calculations were intended to investigate the electronic
properties, such as HOMO–LUMO energies, dipole moment, absorption–emission wavelengths and oscillator strengths.

The energy gap calculation is very important for investigating the molecular orbitals that result from chemical reactions or electronic excitation:

\[ \text{E}_{\text{gap}}(\text{eV}) = \text{E}_{\text{LUMO}}(\text{eV}) - \text{E}_{\text{HOMO}}(\text{eV}) \]

For both DFT and TDDFT calculations, gas-phase calculations were carried out at 298 K and 1 atm. The solvent effect was studied using a conductor-like polarizable continuum model (CPCM) \[36, 37\] with methanol as a solvent at 298 K.

Results and Discussion

Isomerization and Tautomerization of Ligands

Figure 1 depicts the atom numbering of the optimized structure of the gas-phase H<sub>2</sub>L ligand, which was adopted from the X-ray diffraction crystal structure [1]. It has the molecular formula C<sub>23</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>. Theoretically, the structures of the H<sub>2</sub>L conformers were investigated in the gas phase and methanol using the B3LYP/6–311+G** level of theory. The optimized geometries and minimum energies of all conformers are registered in Table 1. The six conformers of H<sub>2</sub>L were sorted out in descending order starting from E-cis with the lowest energy and hence being the most stable conformer. It is thus considered the reference substrate. It is immediately followed by E-trans. The energy difference between these two conformers is negligible (0.13 kcal/mol). Therefore, they could be considered to exist as a stable mixture. The H<sub>2</sub>L ligand could lead to a number of isomers and tautomers. Its isomers result from the rotation around single bonds, e.g., E-cis and E-trans, while the tautomers originate from the difference in functional groups, e.g., E-cis and K-cis. Additionally, the relative energies indicate that the energy difference between the most stable di-keto (KK) and di-enol (EE) forms is 9.90 kcal/mol. This amount of energy is certainly sufficient for proton transfer between these tautomers at room temperature. Moreover, the excited state E-cis* (-1149.9166 a.u.) is lower in energy compared to the K-cis* (-1149.8962 a.u.) tautomer. This means that E-cis is the most stable species in the excited state as well. Here, again, this is the second reason for the E-cis to be considered as the reference substrate. This finding provides an early clue for the fact that the E-cis does not follow the ESIPT mechanism. The effect of methanol on the structures of these H<sub>2</sub>L ligands was investigated using the B3LYP/6–311+G** level of theory. The solvation results were completely in line with those in the gas phase. The E-cis ligand in methanol is more stable than that in the gas phase and is still the most stable species.

Protonation and Deprotonation

The studied compounds possess two positions that can accept protons and one site that can donate a proton. The literature seems to lack a systematic study of the electronic structure, bonding characteristics and acid–base properties of this class of compounds. FT calculations were employed to investigate the sites of protonation of these compounds. Furthermore, the acid–base properties of ligands in Table S1 will be examined, and theoretical proton affinities and deprotonation enthalpies will be computed. Nevertheless, since most protonation processes occur in solution, the characteristics of protonation and deprotonation will vary with the properties of the solvent used.

All the possibilities of the protonation/deprotonation of E-cis were investigated. Table S1 displays geometry-optimized structures and minimum energies of the protonation/deprotonation forms in the gas phase and in methanol as a solvent. On the one hand, in the first
On the other hand, the reverse deprotonation process, where the proton is extracted endergonically from an oxygen atom producing (HL\(^{-}\)), requires an energy difference of 325.153 and 306.852 kcal/mol compared to those of the parent H\(_2\)L.
ligand in the gas phase and methanol, respectively. Likewise, in the second protonation process, the proton is added exergonically to the other nitrogen atom generating \((\text{H}_2\text{L}^2^+)\), with an energy difference of 429.782 and 547.377 kcal/mol compared to those of the \(\text{H}_2\text{L}\) ligand in gas-phase and methanol, respectively. Conversely, the reverse second deprotonation process, where the second proton is extracted endergonically from the other oxygen atom creating \((\text{L}^-2^-)\), needed energy differences of 750.439 and 615.901 kcal/mol compared to those of the neutral ligand \((\text{H}_2\text{L})\) in the gas phase and methanol, respectively. In summary, we could easily conclude that the protonation process of the E-cis tautomer is extremely energetically favorable, while its deprotonation process seems to be considerably unfavorable energetically.

**Absorption and Emission Spectra (UV–Vis) of Ligands**

Starting from the optimized ground state geometries, we investigated the absorptions to the vertical singlet excited states by using different TDDFT functionals, namely, B3LYP, CAM-B3LYP, M06-2X and ωB97X, with the 6–311+G** basis set. In Fig. S1, the simulations of UV–Vis spectra of the E-cis tautomer are shown, where (a) displays the electronic transitions using the optimized structure coming from the B3LYP/6–311+G** level of theory and (b) displays the electronic transitions applying the optimized structure coming from the different functionals. Furthermore, the details of the excitation energies and oscillator strengths, as well as the excited state compositions for the E-cis tautomer, are reported in Table S2. Experimentally, the electronic absorption spectrum of the E-cis tautomer shows intense bands at 314 and 258 nm corresponding to the \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions, respectively. It is clear that the B3LYP functional transition signal \((\text{H} \rightarrow \text{L} \text{ at a wavelength of } 314.5 \text{ nm and an oscillator strength of 0.033})\) is comparatively in excellent agreement with the experimental results [1]. It produced another stronger (oscillator strength of 0.148) electronic transition \((\text{H}-4 \rightarrow \text{L})\) at 257.5 nm, which is approximately superimposed on its experimental peer. For the other DFT functionals, their agreement with the experimental counterpart ordering is as follows: M06-2X < CAM-B3LYP < ωB97XD. As listed in Table S2, we generally observed that the values of column (b) obtained from these three functionals are close to the experimental values [1]. Additionally, the transition signals obtained from the CAM-B3LYP functional in columns (a) and (b) are 312.943 and 304.056 nm, respectively, while their peers from M06-2X are 251.521 and 265.737 nm, respectively. Comparatively, ωB97XD signals divert far from experimental signals [1]. These findings support the adoption of the B3LYP functional in subsequent calculations.

Figure 2 depicts the UV–Vis spectra of E-cis in the gas phase and methanol obtained by using the TDDFT/B3LYP/6–311+G** level of theory. The effect of using methanol as a solvent on the values of the calculated electronic \(n \rightarrow \pi^*\) transition yielded only a difference of ca. 3.5 nm compared to that of the gas-phase. In contrast, the electronic transition \(\pi \rightarrow \pi^*\) transition has a wavelength maximum nearly superimposable on both the experimental [1] and gas-phase values. Generally, the high oscillator strengths obtained when methanol is used as a solvent indicate more absorption efficiency in solution than in the gas phase.

Table 2 shows the visualization of the natural transition orbitals (NTOs) of the E-cis tautomer in the gas phase and methanol as a solvent obtained by using the TDDFT/B3LYP/6–311+G** level of theory. Here, the hole represents the space that the electron leaves in HOMOs due to electronic excitation. In contrast, the particle represents the space the electron occupies in LUMOs due to electronic excitation.

The estimation of energy gaps is quite important, especially for electronic excitation analysis, because the value of
the energy gap is taken as an indication of the probability of fluorescence emission.

Table 3 registers the HOMO, LUMO and energy gap values of the various H₂L conformers obtained by using the B3LYP/6–311 + + G** level of theory. We notice here that the E-cis and E-trans tautomers have the highest energy gap values. This does not mean that they have the most potent fluorescence emission, but it supports our conclusion for selecting both E-cis and E-trans as the most stable mixtures with the lowest energy.

To simulate the emission UV–Vis spectra of the E-cis tautomer in the gas phase and methanol, we used the TDDFT/B3LYP/6–311 + + G** level of theory on their optimized structures obtained by using the B3LYP/6–311 + + G** level of theory. Table 4 lists the electronic emission energies and oscillator strengths as well as the ground state compositions of the E-Cis tautomer. Experimentally, the electronic emission spectrum of the E-Cis tautomer does not show any noticeable fluorescence upon excitation at 350 nm. However, at 458 nm, some of the H₂L metal complexes showed an intense fluorescence band. The gas-phase π* → n emission transitions, which were assigned to L → H and L + 1 → H movements that gave wavelengths of 451.560 and 440.318 nm (2.746 and 2.816 eV with 0.55 and 0.49%), respectively, had zero oscillator strengths. In contrast, the positive effect of using methanol as a solvent is manifested in raising the fluorescence efficiency. Here, the π* → n emission signals are assigned to L → H and L + 1 → H transitions, which gave rise to wavelengths of 497.631 and 455.475 nm (2.491 and 2.722 eV; both 0.69%) with oscillator strengths of 0.083 and 0.107, respectively.

Table S2 shows the NTO visualization of E-Cis tautomer emission in the gas phase and methanol, which were obtained by using the TDDFT/B3LYP/6–311 + + G** level of theory. Electron excitation changes the ground state optimized structure of the E-cis tautomer. These variations were observed through the change of some bond types (from single to double bond and vice versa) and the bond angles. That is, electron transfer occurs after photoexcitation, called the photoinduced electron transfer (PET) mechanism.

### Table 3 The calculated HOMO, LUMO and energy gap of the various H₂L ligand forms obtained by using the B3LYP/6–311 + + G** level of theory

| Ligand Form | HOMO (eV) | LUMO (eV) | Energy Gap (eV) |
|-------------|-----------|-----------|----------------|
| E-cis       | -6.023    | -1.959    | 4.064          |
| E-trans     | -6.054    | -1.959    | 4.095          |
| K-cis       | -5.637    | -2.17     | 3.467          |
| K-trans     | -5.772    | -2.384    | 3.388          |
| K-cis-2     | -5.733    | -2.35     | 3.383          |
|             | -5.756    | -2.324    | 3.432          |

### Table 4 Electronic emission energy, corresponding oscillator strengths and the corresponding MO compositions of the E-cis tautomer in the gas phase and methanol obtained by using the TDDFT/B3LYP/6–311 + + G** level of theory. (Exp. 458 nm; Pandey et al. [1])

| E-cis | λ (nm) | E_{ex} (eV) | f | Composition | Coefficient |
|-------|--------|------------|---|-------------|-------------|
|       |        |            |   |             | Gas-Phase   |
|       | 451.560| 2.746      | 0.000| H → L     | 0.55        |
|       | 440.318| 2.816      | 0.000| H → L + 1 | 0.49        |
|       |        |            |   | Solvent (Methanol) |             |
|       | 497.631| 2.491      | 0.083| H → L     | 0.69        |
|       | 455.475| 2.722      | 0.107| H → L + 1 | 0.69        |
Excited State Intramolecular Proton Transfer (ESIPT)

To investigate the ESIPT mechanism using H₂L ligands, we compared the structural changes around the proton to be transferred in both the ground and excited states. Table S3 shows these structural changes for both the gas-phase and methanol-solvated E-cis and K-cis tautomers. The O47–H48 bond is shortened by 0.003 Å, while the H48–N20 bond is lengthened by 0.016 Å as a result of the formation of a single bond. Simultaneously, the bond angle δ(C3–N21–C23) is opened up by 4°. To understand the PET mechanism, we consider the central aromatic group, namely, 2,4,6-trimethyl benzene (TMB), as an acceptor and the azomethine group (AZM) as a free donor. Upon photexcitation, an electron is excited from a π-type bonding molecular orbital to a π*-type antibonding molecular orbital, i.e.,... This transition corresponds to the transition from the HOMO-n orbital (any orbital of π-type) of AZM to the LUMO orbital of TMB. Simultaneously, the lone pair on N21 of AZM as a HOMO orbital with higher energy than the HOMO-n orbitals allows one of the electrons of the lone pair to transfer from the HOMO orbital to a HOMO-n orbital. This process prevents the excited electron from returning to the HOMO-n orbital, which leads to fluorescence quenching [38, 39]. Methanol relatively reduces the effect of the PET process through the formation of a hydrogen bond between N21 of AZM and the hydrogen atom of the hydroxyl group of methanol (Fig. 4).

Figure 3 shows the geometric changes on one side of the E-cis tautomer. It is clear that both C1–C2 and C3-N21 bonds are shortened by ca. 0.02 and 0.09 Å, respectively, due to the formation of double bonds. On the other hand, the N21-C23 bond is lengthened by 0.14 Å as a result of the formation of a single bond. Simultaneously, the bond angle δ(C3–N21–C23) opened up by 4°. To understand the PET mechanism, we consider the central aromatic group, namely, 2,4,6-trimethyl benzene (TMB), as an acceptor and the azomethine group (AZM) as a free donor. Upon photexcitation, an electron is excited from a π-type bonding molecular orbital to a π*-type antibonding molecular orbital, i.e.,... This transition corresponds to the transition from the HOMO-n orbital (any orbital of π-type) of AZM to the LUMO orbital of TMB. Simultaneously, the lone pair on N21 of AZM as a HOMO orbital with higher energy than the HOMO-n orbitals allows one of the electrons of the lone pair to transfer from the HOMO orbital to a HOMO-n orbital. This process prevents the excited electron from returning to the HOMO-n orbital, which leads to fluorescence quenching [38, 39]. Methanol relatively reduces the effect of the PET process through the formation of a hydrogen bond between N21 of AZM and the hydrogen atom of the hydroxyl group of methanol (Fig. 4).

Geometry and Binding Energies of Complexes

An interaction between the parent ligand ion (L²−) and Zn²⁺ ions to form complex (1) with an L:M ratio of 2:2, respectively, were considered; that is, the spin multiplicities considered were 1 and 3 for Cu2+ complexes, resulting in Complex 9S and Complex 9 T, respectively. The different geometric structures of all the studied complexes of Zn²⁺, Cu²⁺ and Ag⁺ are listed in Table S4. They were obtained by using the B3LYP/LANL2DZ/6–311 + + G** level of theory. Their binding energies in both the gas phase and methanol were estimated using the aforementioned level of theory and registered in Table S4.

The first seven binuclear complexes are formed by the conjugation of two L²− ions with two metal ions (L:M, 2:2), where the filled four lone pairs on two nitrogen atoms (-CH = N-) and two oxygen atoms (-O−) interact with the four empty sp³ molecular orbitals of the metal ions to form distorted tetrahedral shapes. The objective of the present work is to investigate the effect of Cu2+ and Ag⁺ ions on the electronic structure, absorption and emission spectra of Complex 1. Upon the binding of two Cu2+ or two Ag⁺ metal ions with Complex 1, one ion chelates with two oxygen atoms of the ligand, and the other ion forms cation-π interactions with the benzene rings with an M:L:M ratio of 2:2:2, as shown in Table 5. It is also noticeable from the optimized structures of the two complexes of 1-2Cu²⁺ (Complex 9) and 1-2Ag⁺ (Complex 7) that one ion is up and the other is down.

For a better understanding of metal–ligand complexation, it is better to recall that the Zn2+ , Cu2+ and Ag⁺ electron configurations are [Ar]3d¹⁰ 4s⁰ 4p⁰, [Ar] 3d⁰ 4s⁰ 4p⁰, [Kr] 4d⁰ 5s⁰ 5p⁰, respectively. The empty s- and p-type orbitals are hybridized to form four empty sp³ orbitals with equal energies. They have the ability to form covalent coordination bonds with the four lone pairs of L²− ions.

The experimental and theoretical values of the bond lengths of complexes (1) and (2 T) are collected in Table S5 for comparison. In the case of complex 1 ([Zn₂L₂]), the four nitrogen atoms form a symmetric ligand L²− metal ion...
substrate with distances of 2.081 Å and 2.091 Å for [Zn-N1] and [Zn-N2], respectively, while the four oxygen atoms reach distances of 1.980 Å and 1.982 Å for [Zn-O1] and [Zn-O2], respectively, making up a distorted tetrahedral geometry (Td) about the metal centers with Zn-Zn separation of 6.722 Å. These findings are in good agreement with the experimental single crystal structure of this complex [1].

The Zn-N and Zn–O distances in methanol-solvated complex 1 are slightly elongated with [Zn-N1] of 2.134 Å, [Zn-N2] of 2.032 Å, [Zn-O1] of 2.031 Å, and [Zn-O1] 2.032 Å. These deviations explain the decreasing stability of complex 1 in methanol compared with its structure in the gas phase.

The bond lengths of Cu–O and Cu–N in [Cu2 L2 . H2 O] complex range between 1.972–1.947 Å and 2.051–2.065 Å, respectively. These range values agreed favorably with the expected range observed for copper complexes [41] and the values reported in X-ray analysis [1] for this particular complex. The crystal structure of 2 displayed the existence of one water molecule in the lattice. DFT calculations indicated that the H2O molecule forms hydrogen bonds, which increased the stability of the complex.

In this work, we primarily focus on the interaction between L2− ligands and Zn2+ ions leading to Complex 1. We then investigated the interaction of complex 1 with Ag+ and Cu2+ ions, yielding different complexes that might be of importance. The binding energies are calculated for all the studied complexes in both the gas phase, methanol and water as solvents. The results are listed in Table 5. It is clear from the results that the binding energies in the gas phase were generally more negative than those in the solvent. This is because the solvent molecules prevent effective interactions between the ligands and metal ions. The binding between the ligand and metal ions in water was generally more effective than that in methanol. This is because the former allows the formation of hydrogen bonds in these complexes.

According to the binding energy values, the order of the stability of the complexes in the gas phase is as follows: 9T > 9S > 8D > 8U > 7 > 2T > 2S > 3 > 4 > 6 > 1 > 5. The formation of the Cu2+ 2S complex requires more energy for pairing unpaired electrons, leading to diamagnetic properties. This is manifested through the amount of the binding energy of -1.521 a.u. for 2S and -1.572 a.u. for 2T, where the pairing energy is unrequired for the latter. Accordingly, we can

### Table 5

| Functional | λ (nm) | E<sub>ex</sub> (eV) | f | Assignment | Coefficient |
|------------|--------|--------------------|---|------------|-------------|
| B3LYP      | 396.358 | 3.128              | 0.099 | H→L+1     | 0.48        |
|            | 368.794 | 3.362              | 0.142 | H→L+2     | 0.49        |
|            | 277.520 | 4.468              | 0.000 | H→L+4     | 0.68        |
|            | 275.559 | 4.499              | 0.012 | H→L+4     | 0.53        |
| CAM-B3LYP  | 357.625 | 3.467              | 0.047 | H→L+3     | 0.51        |
|            | 350.230 | 3.540              | 0.548 | H→L+2     | 0.52        |
|            | 273.299 | 4.537              | 0.059 | H→L+2     | 0.52        |
|            | 248.089 | 4.998              | 0.049 | H→L+2     | 0.46        |
| M06-2X     | 351.481 | 3.527              | 0.560 | H→L+2     | 0.51        |
|            | 344.891 | 3.595              | 0.120 | H→L+2     | 0.56        |
|            | 278.261 | 4.456              | 0.018 | H→L+2     | 0.50        |
|            | 244.797 | 5.065              | 0.188 | H→L+2     | 0.36        |
| oB97XD     | 356.678 | 3.476              | 0.045 | H→L+3     | 0.51        |
|            | 343.239 | 3.612              | 0.117 | H→L+2     | 0.54        |
|            | 260.325 | 4.763              | 0.208 | H→L+2     | 0.40        |
|            | 179.738 | 6.898              | 0.200 | H→L+7     | 0.41        |

These bond lengths are in good agreement with the expected range observed for copper complexes [41] and the values reported in X-ray analysis [1].

According to the binding energy values, the order of the stability of the complexes in the gas phase is as follows: 9T > 9S > 8D > 8U > 7 > 2T > 2S > 3 > 4 > 6 > 1 > 5. The formation of the Cu2+ 2S complex requires more energy for pairing unpaired electrons, leading to diamagnetic properties. This is manifested through the amount of the binding energy of -1.521 a.u. for 2S and -1.572 a.u. for 2T, where the pairing energy is unrequired for the latter.

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|            | 179.738 | 6.898              | 0.200 | H→L+7     | 0.41        |

**Fig. 3** (a) The optimized structure of the E-cis tautomer using DFT calculations and the display of the PET mechanism occurring through photoexcitation. (b) The effect of the PET mechanism on the structure of the E-cis tautomer resulting from photoexcitation.
adopt $2 \mathbf{T}$ as a reference because it contains unpaired electrons that earn $2 \mathbf{T}$ high spin and paramagnetic properties that might affect, later on, the electronic emission process. In addition, complexes are formed through weak interactions between complex 1 and $\text{Ag}^+$ ions ([Zn$_2$L$_2$]. [Ag$^+$]$_2$ (7)) or Cu$^2+$ ions ([Zn$_2$L$_2$]. [Cu$^2+$], where the Cu$^2+$ ion is down (8D)) or ([Zn$_2$L$_2$]. [Cu$^2+$], where the Cu$^2+$ ion is up (8U)); the binding energies in the gas phase render their order of stability as follows: $8\mathbf{D} > 8\mathbf{U} > 7$, with a slight difference between 8U and 8D of ca. 0.015 a.u. On the other hand, the strongest complexes are formed when two Cu$^2+$ ions chelate in singlet (9S) or triplet (9T) states with complex 1, where one Cu$^2+$ ion interacts at the top through cation-$\pi$ bonding and the other one at the bottom through oxygen atom lone pairs. Finally, our theoretical study showed that 8D is the most stable complex, complementing the fact that it has been isolated and identified experimentally [1].

The Cu$^2+$ and $\text{Ag}^+$ ions are bonded to complex 1 through cation-$\pi$ interactions between trimethyl benzene (TMB) rings and/or through weak interactions with the lone pairs of the lower two oxygen atoms. The energies of HOMOs, LUMOs and energy gaps are listed in Table S6.

Ag$^+$ ions are considered electron acceptors due to the presence of four empty sp$^3$-hybridized orbitals, where the interaction with complex (1) causes charge transfer towards the silver ions. The results listed in Table S5 indicate that the energy gap of complex 1-2Ag$^+$ is quite close to that of complex 1. These results explain why Ag$^+$ ions keep enhancing the fluorescence bands [1].

On the other hand, the Cu$^2+$ ion is considered an electron donor due to the presence of the unpaired electron in the $t_{2g}^5$ degenerate orbitals, which interact with complex 1 through charge transfer towards the TMB rings and/or towards the lower two oxygen atoms. In the case of complexes 8D and 8U, this charge transfer results in an increase in the energy gap and hence subsequent blueshift effects on the absorption and emission spectra, leading to fluorescence enhancement. In contrast, Complex 9S is a low spin Cu$^2+$-complex (1) adduct with a chemical formula of [Zn$_2$L$_2$]. [Cu$^2+$]$_2$ shows a severe decrease in the energy gap (0.312 eV) that causes fluorescence quenching. This latter complex is different from the copper complex reported in the literature [1] { [Zn$_2$L$_2$]. [Cu$^2+$] }.

In conclusion, the ICT mechanism confirms that complex 1 acts as a fluorescent photoionized charge transfer (PCT) sensor for $\text{Ag}^+$ or Cu$^2+$ ions [1].

**Absorption and Emission Spectra (UV–Vis) of Complexes**

B3LYP, CAM-B3LYP, M06-2X and ωB97X functionals with a mixed basis set LANL2DZ/6–311++G** were applied to investigate the absorptions to the vertical singlet excited states. Details of the excitation energies and oscillator strengths, as well as the excited state molecular orbital compositions for complex 1, are reported in Table 7. Experimentally, the electronic absorption spectrum of complex 1 displays intense bands at 398 and 278 nm corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively [1]. TDDFT results indicate that the B3LYP functional signals were comparatively in excellent agreement with the experimental results [1]. The B3LYP functional gives an H$\rightarrow$L + 1 electronic transition at a wavelength of 396.36 nm (3.13 eV) and an oscillator strength of 0.099 with a percentage of 48%. The other H-2 $\rightarrow$ L + 4 electronic transition gives...
a wavelength of 275.56 nm (4.499 eV) and an oscillator strength of 0.012 with a percentage of 53%. Concerning the other functionals, the ordering according to their agreement with the experimental results is as follows: M06-2X > CAM-B3LYP > ωB97XD. In particular, the M06-2X functional gives a signal at 278.261 nm (4.456 eV) with an oscillator strength of 0.018 with a percentage of 50% due to the electronic transition H-3 → L, in addition to a π→π* electronic transition with a wavelength value in very close agreement with the experimental value [1].

Details of the excitation energies and oscillator strengths, as well as their assignments and coefficients for the E-cis ligand and complexes (1), (2S), (2T), (7), (8U), and (8D), are reported in Table S6. Experimentally, the electronic absorption spectra of these complexes display intense bands due to the n→π* and π→π* transitions. Weak absorptions of complexes (2T), (8D) and (8U) are observed in the UV range (340–440 nm), whereas compounds E-cis, (1), (2S) and (7) show strong absorption bands in the range between 240 and 300 nm. The π→π* electronic transitions of the complexes show redshifts compared to those of the E-cis ligand in excellent agreement with the measured values [1]. Furthermore, complex 2T displayed the H-5α → L +1α electronic transition with a maximum wavelength at 326.585 nm (3.796 eV) and an oscillator strength of 0.005 with a percentage of 45%, which nearly approximates that of complex 2S and the experimental value [1]. In addition, complex 8D exhibited a maximum wavelength quite close to that of the experimental value compared to that of 8T. In general, the weak absorptions in the visible spectra of complexes 2S, 2T, 2D and 2T indicate their poor efficacy in exhibiting fluorescence. Figure 5 depicts the simulated absorption spectra of complexes 1, 7 and 8D to verify the effect of the ICT mechanism. The π→π* electronic transition of complex 1 is redshifted (from 269 to 290 nm) in complex 7, while its n→π* transition is blueshifted (from 368 to 330 nm) in complex 8D. It is clear that the redshift effect is more pronounced than the blueshift impact. This is because the energy gap difference between complexes 1 and 7 (ca. 1.072 eV) is greater than that between complexes 1 and 8D (ca. 0.117 eV).

The studied lignad-metal complexes contain six benzene rings in addition to four oxygen and four nitrogen atoms. This chemical composition results in many n→π* and π→π* electronic transitions. The natural transition orbital (NTO) visualizations depicted in Table S8 display the origin (hole) and destination (particle) of the electrons of complexes 1, 7 and 8D upon photoexcitation in both the gas phase and methanol using the TDDFT/B3LYP/LANL2DZ/6–311 + +G** level of theory. It is clear from Table 6 that the values of the energy gaps of the E-cis ligand and its complexes in different functionals are different upon photoexcitation. It is interesting to note that the energy gaps estimated by the B3LYP, CAM-B3LYP, M06-2X and ωB97XD functionals for complex 2T compared to those of complex 1 decrease from 3.587, 6.062, 5.666 and 7.22 to 2.186, 4.74, 5.024 and 5.866 eV, respectively. On the other hand, the comparison of the energy gaps for complexes 7 and 8D using the same functionals increases from 0.331, 1.067, 0.816 and 2.166 eV to 2.495, 4.927, 4.536 and 6.155 eV, respectively. It is noteworthy that the energy gap values after photoexcitation give an initial impression of

![Fig. 5 Simulated absorption spectra of complexes 1, 7 and 8D obtained by using the B3LYP/LANL2DZ/6–311 + +G** level of theory](image-url)
the occurrence of explicit fluorescence of the target compounds when compared to each other. This conjecture is clear in Fig. 6, where a larger energy gap value of complex 7 indicated fluorescence enhancement and a lower energy gap value in complex 8D marked fluorescence quenching [1].

The emission light produced from the deactivation of the excited states as an opposite action of the absorption process is relatively time-consuming. Moreover, the normal termination of the emission calculations for the complexes that quenched the fluorescence was extremely difficult and tricky. Figure 7 depicts the emission spectrum of complex 1 in both the gas phase and solution (methanol) obtained by using the TDDFT/B3LYP/LANL2DZ/6–311 + + G** level of theory together with its experimental level for comparison purposes. It is noteworthy that the emission spectrum using methanol (451.43 nm) is in excellent agreement with the experimental (458 nm) spectrum, and it is extremely intense, while that simulated in the gas phase is relatively weak and diverges by ca. 57 nm from the observed value [1]. The simulated and experimental emission spectra of the E-cis ligand and complexes 1, 7 and 8D in methanol are pictured in Fig. 8. It is clear that both the E-cis ligand and complex 8D have extremely weak emission signals in excellent agreement with the experimental results [1], while the theoretical and experimental emission spectra of complexes 1 and 7 are comparatively very intense and close to each other. It is interesting to note that the intensity of the simulated emission spectrum of complex 7 is greater than that of complex 1, confirming the fluorescence enhancement upon the addition of Ag+ ions [1].

In contrast, the extremely small intensity of the simulated emission spectrum of complex 8D as a result of adding Cu2+ ions to complex 1 could be explained in terms of fluorescence quenching [1]. The order of the simulated intensity of fluorescence for these substrates is as follows: 7 > 1 > 8D ≈ E-cis in excellent agreement with experiment [1].

Table 7 registers the details of the electronic emission energies, oscillator strengths, and assignments and coefficients of MOs for E-cis and complexes 1, 7 and 8D in methanol as a solvent. The π* → π electronic emission transition of the E-cis ligand (L + 1 → H) showed a very weak band (f = 0.107) at 455.475 nm with a deviation of ca. 2.5 nm. The π* → n emission electronic transitions of E-cis (L → H) and complex 8D (L + 3β → H-2β) showed very weak bands at 497.6 and 496.2 nm, respectively. The oscillator strength of complex 8D is zero, indicating fluorescence quenching upon the addition of Cu2+ to complex 1. Conversely, the π* → π electronic emission transition of complexes 1 (L + 2 → H-1) and 7 (L + 2α → Hα) exhibited very intense bands at approximately 385 nm. They acquired oscillator strengths of 0.232 and 0.485, respectively, which indicated fluorescence enhancement by Ag+ ion chelation to complex 1. Moreover, we observed π* → n emission transitions of complexes 1 (L + 2 → H) and 7 (Lα → Hα) that yielded wavelengths of 411.01 and 406.88 nm and oscillator strengths of 0.032 and 0.048, respectively. Here, too, the fluorescence intensity improves clearly in complex 7 through the interaction of silver ions with complex 1, which squarely agreed with experiment [1].

As we previously mentioned, both the L2− ligand and its complexes contain six benzene rings in addition to four oxygen and four nitrogen atoms, a situation that renders the electronic structure of these substrates full of π* → π and π* → n transitions. Table 8 shows the positions of the origin and destination
of the excited electron in complexes 1, 7 and 8D upon photoexcitation, which results in fluorescence emission. In fact, since the fluorescence of complex 1 arises from an irreversible reaction between E-cis and Zn$^{2+}$ ions, E-cis can be classified as a fluorescent probe of a chemodosimeter type [2]. On the other hand, the fluorescence of complex 1 is enhanced or quenched by a reversible reaction with Ag$^+$ or Cu$^{2+}$ ions, respectively. These actions render complex 1 a fluorescent probe of a chemosensor type [41].

**Effect of Metal Ion Chelation**

E-cis is a chelating ligand that interacts irreversibly with metal ions, leading to different actions, such as enhancing or quenching fluorescence, depending on the nature of the metal ions. The chelation of the deprotonated form of E-cis (L$^2$−) with Zn$^{2+}$ ions reduces the energy of the HOMO orbital formed of the lone pair of N21 of the azo moiety of the ligand. Thus, the electrons excited from the HOMO to the LUMO of the TMB return to the HOMO, thus inhibiting the PET process and restoring fluorescence. This is called a chelation-enhanced fluorescence (CHEF) effect [42]. On the other hand, the chelation of the Cu$^{2+}$ ion leads to the inhibition of the PET process, similar to the previous mechanism, but quenches the fluorescence, called chelation quenched fluorescence [43]. This action could be attributed to the high spin and paramagnetic behaviour of complex 2 T.

Figure 9 illustrates a general summary of the most important

| Complex | Particle | Hole |
|---------|----------|------|
| 1       | (λ=411.009 nm)$\pi^* \rightarrow n$ |
| 7       | (λ=406.881 nm)$\pi^* \rightarrow n$ |
| 8D      | (λ=496.277 nm)$\pi^* \rightarrow n$ |
substrates and the ultimate results obtained in the present work.

**Conclusion**

This work aims to investigate the reasons that lead to the difference in the intensity of fluorescent behavior of the molecular designs that allows the detection of Zn$^{2+}$, Cu$^{2+}$, and Ag$^{+}$ metal ions using a computational study.

Geometric optimization was performed using the B3LYP functional, which was adopted as the best functional for the absorption and emission calculations. The use of methanol as a solvent proved useful in the DFT and TDDFT methods.

The E-cis isomer is the most stable conformer with a rotation barrier of 0.12 kcal/mol to give the E-trans counterpart. On the other hand, it is the most stable tautomer with a potential energy barrier of 6.65 kcal/mol to give the K-cis tautomer in the ground state only, a fact that could deny the occurrence of the ESIPT mechanism. Fluorescence quenching of E-cis through the occurrence of a PET mechanism was evidenced by the change in the electronic structure.

The irreversible interaction between E-cis and the Zn$^{2+}$ ion leads to the inhibition of the PET process and enhances fluorescence by the CHEF effect. Thus, the E-cis isomer could be adopted as a fluorescent probe (type a chemodosimeter) for Zn$^{2+}$ ions. The irreversible interaction between E-cis and the Cu$^{2+}$ ion leads to inhibition of the PET process and quenching of fluorescence by the CHQF effect. This could be attributed to the high spin and paramagnetic arrangement of complex 2 T. This means that E-cis is not a fluorescent probe for Cu$^{2+}$ ions.

The reversible interaction between complex 1 and the Ag$^{+}$ ion (electron acceptor) leads to the enhancement of fluorescence through the ICT mechanism. This is achieved by a decrease in the energy gap, which leads to a redshift of the absorption spectrum. Thus, complex (1) behaves as a fluorescent probe of type a chemosensor, i.e. a fluorescent PCT sensor for the Ag$^{+}$ ion. Additionally, the reversible interaction between complex 1 and the Cu$^{2+}$ ion (electron donor) leads to the quenching of fluorescence through the ICT mechanism. It originates from an increase in the energy gap value, which leads to a blueshift of the absorption spectrum. Thus, complex 1 could function as a fluorescent probe of type a chemosensor or, specifically, a fluorescent PCT sensor for Cu$^{2+}$ ions.

Finally, we conclude that complex 1 could act as an “On–Off-On” molecular switch by exchanging Cu$^{2+}$ and Ag$^{+}$ ions. This finding is in excellent agreement with the experimental study.
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Availability of Data and Material/ Data Availability The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics Approval Not Applicable.

Consent to Participate Not Applicable.

Consent for Publication Not Applicable.

Conflicts of Interest/Competing Interests Not Applicable.

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