Theoretical study of the electron-withdrawing and donating groups effects on luminescent properties of the europium complexes with substituted 1,10 phenanthroline

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Abstract. Effects of EDG and EWG on the luminescent properties of Eu(III)1,10-phenanthroline complexes have been studied theoretically using DFT/B3LYP and TDDFT method. The 6-31G basis set was used for the ligand atoms and Stuttgart_RSC_1997_ECP for europium. The groups were varied as 2-X-1,10-phenanthroline and 5-X-1,10-phenanthroline where X is CH3; CH=CH2; F; OH as EDG and CN; CF3; NO2; CHO as EWG. The results showed that the energy difference between singlet and triplet excited state of the ligand (ΔE ISC) increasing when using EDG and decreasing when using EWG. The different pattern occurs for energy difference between the triplet excited state of the ligand and the 5D0 level of europium (III) (ΔE ET), which increasing when using groups without a double bond (CH3; F; OH; CF3) and decreasing when using groups with a double bond (CH=CH2; CN; NO2; CHO). The highest energy transfer rate (W ET) was Eu(III)2-NO2-1,10-phenanthroline which was caused by interaction between NO2 with europium.

1. Introduction

Physical and chemical properties of lanthanide have made them an essential ingredient for the development of material technology. The physical and chemical properties such as optical, magnetic, and electrical properties contribute significantly to the enhancement of the quality of various materials. One type of material that has been widely utilizing lanthanide metal is optical material whose function involves radiation. The optical material utilizes the capability of lanthanide complex compound which can be luminescent, i.e. absorbing radiation and emitting it through fluorescence or phosphorescence.

The intensity, efficiency, and distribution of the emissions are better if the ligand used in the lanthanide complex is heterocyclic aromatic compounds, such as 1,10-phenanthroline. The conjugated system and high electron density of the compound play a role in maximizing the absorption of UV radiation and transfer of energy to the metal ion so that the 4f-4f5d transition of lanthanide ions as metal ion complex is more likely to occur [1]. This transition causes excitation and relaxation of electrons that emit infrared radiation to visible light. Materials emitting this radiation are very beneficial as fiber optic, biomedical assay, laser, light emitting diodes (LEDs), and others [2].

Other studies have demonstrated that the combination of 1,10-phenanthroline ligand with other organic compounds ligands, such as carbocyclic acid, phenylglyoxylic acid, acetylsalicylic acid, diphenyl sulfoxide, β-diketone, thenoyltrifluoroacetone, and others have a significant effect on the
luminescence properties of lanthanide complexes, both in intensity, lifetime, and distribution of emissions [3]. Similarly, the addition of a specific substituent to the ligand leads to 5-nitro-1,10-phenanthroline; 1,10-phenanthroline-5,6-dion; 1,10-phenanthroline-1-oxide [1]; 1,10-phenanthroline-NO [4]; and 4,7-diaza-1,10-phenanthroline [5] can increase the intensity of lanthanide complex emissions, particularly the Eu (III) metal complex.

The results of some of the above studies indicate that modification of 1,10-phenanthroline ligand using a particular substituent or combining it with several different ligands has a significant effect on the complex luminescence properties of Eu (III). However, this conclusion does not yet include all possible modification types so further research is needed with more specific modifications. One type of modification that can be learned is the use of Electron Donating Groups (EDG) and Electron Withdrawing Groups (EWG) as substituents in 1,10-phenanthroline.

The type, position, and variation of EDG/EWG substituents in heterocyclic aromatic ligands affect the optical properties of some complex compounds, either complex compounds of lanthanide or other metals ([6]). This conclusion is a reference for studying its effect on the complex luminescence properties of Eu (III)-1,10-phenanthroline. In addition to obtaining more specific conclusions according to the nature of EDG/EWG used, this study is also expected to produce basic guidelines for efforts to improve luminescence quality of lanthanide complexes.

The methods can be used to study the effects of EDG/EWG are experimental methods and computational methods. However, the large number of EDG/EWG and its varied modification types cause experimental methods, i.e. synthesizing and characterizing each complex compound are inefficient for that purpose. Therefore, an appropriate and efficient method for carrying out this research is the computational chemistry method.

One of computational chemistry method has been widely used to study the optical properties of lanthanide complexes is the Density Functional Theory (DFT). This theory with B3LYP function and Time Dependent-DFT (TD-DFT) approach have successfully studied the effect of substituents on the energy transfer probability of the first triplet-excited ($E_{T1}$) ligand 2-hydroxyisophthalamide to the Tb$^{3+}$ ion (Terbium (III)). Calculation error based on the experimental results reached 5% [6].

**Effective Core Potential** (ECP) approach can be used for the relativistic effects of the electrons at the Eu (III) 4f orbitals. The TD-DFT/B3LYP method taking into account the relativistic effect was applied to the Eu (III) complex with β-biketonates and α-phosphine oxides ligands. The parameters studied by this method are the energy difference between the first singlet-excited state and the triplet's first excited ($E_{ISC}$) and energy difference between the triplet's first excited triplet and the radiated energy created ($E_{ET}$) [7]. Other parameters that can be determined computationally are the distance of the ligand core to the metal nucleus ($R_L$) and energy transfer rate ($W_{ET}$) [8].

2. Method and Procedure

2.1. Computational Method

Molecular geometry was optimized using DFT/B3LYP method with *Stuttgart_RSC_1997_ECP* basis function for Eu (III) and 6-31G basis function for ligand atoms (H, N, C, and O). The energy of singlet excited electrons ($E_S$) and triplet excited ($E_T$) of the optimized molecule was determined using the TDDFT (CIS/Tamm-Dancoff) method where the excited state was localized to the ligand. Based on ECP theory, 4f orbitals of Eu (III) that interacting weakly with ligands are not treated as valence orbitals, but as pseudopotential core orbitals. Thus, the basis function used was the contracted valence basis function *Stuttgart_RSC_1997_ECP*. This method was based on methods in references [7]. For efficiency, the number of 1-10 substituted phenanthroline used as ligands was only one molecule. Thus, the coordination number Eu (III) used in each complex is two, i.e. as a bidentate complex as shown in Figure 1a-1e, where X = -CH$_3$, -CF$_3$, -F, -CHO, -CH=CH$_2$, -CN, -OH, or -NO$_2$.  

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2. Data Analysis

The values of \( \Delta E_{\text{ISC}} \) and \( \Delta E_{\text{ET}} \) were determined by \( \Delta E_{\text{ISC}} = E_{S_1} - E_{T_1} \) and \( \Delta E_{\text{ET}} = E_{T_1} - E_{S_{D_0}} \), where \( E_{S_1} \) is the first singlet energy, \( E_{T_1} \) is the first triplet energy, and \( E_{S_{D_0}} \) is the excited \( ^{5}D_{0} \) Eu (III) excitation energy (2.14649 eV). The \( W_{\text{ET}} \) value was determined by

\[
W_{\text{ET}} = \frac{2\pi}{\hbar} \frac{e^2 S_I}{(2J + 1)G} F \sum_{\lambda} \gamma_L \left\langle \alpha' J' \left\| \frac{1}{J} \right\| \alpha J \right\rangle^2 \]

where \( \lambda \) is an integer 2, 4, and 6; \( J \) is the total angular momentum quantum number of Ln (III); \( \left\langle \alpha' J' \left\| \frac{1}{J} \right\| \alpha J \right\rangle \) is the reduced matrix element operator tensor unit metal Ln (III); \( G \) is the degeneracy of the ligand initial state; \( S_l \) is the electric dipole strength associated with the transition \( \phi \rightarrow \phi' \) in the ligand; \( F \) is the Franck-Condon factor which determined by

\[
F = \frac{1}{\gamma_L} \left[ \frac{\ln 2}{\pi} \right]^{1/2} \exp \left[ -\frac{\pi (\Delta)^2}{h \gamma_L} \right] \]

where \( \Delta \) is the difference of the ligand triplet energy and the Ln (III) metal emission; \( \gamma_L \) is the width of the high half of the ligand spectrum excited triplet [9].

3. Results and discussion

3.1. Intersystem crossing energy (\( \Delta E_{\text{ISC}} \))

The comparison of intersystem crossing energy (\( \Delta E_{\text{ISC}} \)) for each substituent variation compared with 1,10-phenanthroline without substituent (H) is shown in Figure 2. The efficient value of \( \Delta E_{\text{ISC}} > 0.62 \) eV [7]. As shown in Figure 2, the EDG studied in this research (CH=CH₂; OH; F; CH₃) increase \( \Delta E_{\text{ISC}} \) value for all position (2-X-1,10-phenanthroline, 5-X-1,10-phenanthroline, and random-X-1,10-phenanthroline position). In contrast, EWG (CF₃, CN, NO₂, CHO) reduce \( \Delta E_{\text{ISC}} \) when compared with 1,10-phenanthroline without substituents (H). This pattern occurs because the EDG causes the electron molecule to be localized to the phenanthroline ring. As a result, the distance of the electrons becomes closer and the Coulomb's interactions become larger. When the intersystem crossing occurs, i.e. the change from singlet to triplet state, the electrons with the same spin will be far apart to achieve the stability of the molecule. The large Coulomb interactions cause the energy released so that the two electrons are far apart from each other. This causes the singlet and triplet excitation energy differences (\( \Delta E_{\text{ISC}} \)) to increase.

![Figure 1](https://example.com/figure1.png)

Figure 1. The molecular structure studied (a) \([\text{Eu}(\text{III})(2-X-1,10-	ext{phenanthroline})]^{3+}\); (b) \([\text{Eu}(\text{III})(5-X-1,10-	ext{phenanthroline})]^{3+}\); (c) \([\text{Eu}(\text{III})(5-X,6-X-1,10-	ext{phenanthroline})]^{3+}\); (d) \([\text{Eu}(\text{III})(2-X,9-X-1,10-	ext{phenanthroline})]^{3+}\); (e) \([\text{Eu}(\text{III})(2-X,5-X-1,10-	ext{phenanthroline})]^{3+}\).
Figure 2. Comparison of $\Delta E_{\text{ISC}}$ 1,10-phenanthroline, 2-X-1,10-phenanthroline, 5-X-1,10-phenanthroline, and random-X-1,10-phenanthroline position

For the EWG groups used, the NO$_2$ group relatively has smaller $\Delta E_{\text{ISC}}$ value for all position. This shows the ability of the NO$_2$ group as the electron attracting group is stronger than that of the other groups. As a result, the interaction of Coulomb between electrons in the phenanthroline ring is weaker as opposed to the effect of electron propulsion groups. This condition causes the energy liberated in the intersystem crossing process or the difference in singlet and triplet ($\Delta E_{\text{ISC}}$) excitation energy is smaller.

Different values of $\Delta E_{\text{ISC}}$ for 2-X-1,10-phenanthroline, 5-X-1,10-phenanthroline, and random-X-1,10-phenanthroline also results $\Delta E_{\text{ISC}}$ value that do not reach the efficient value, i.e. $> 0.62\, eV$ [7]. The substituted 1,10-phenanthroline ligand that does not meet the efficiency requirements of $\Delta E_{\text{ISC}}$ is a substituted ligand of an EWG, in particular a group having double bonds such as CHO and NO$_2$. This conclusion is consistent with the results of a study conducted on the complex of Tb (III) using a 2-hydroxyisophthalamide ligate substituted by CH$_3$, (C=O) NHCH$_3$, SO$_3^-$, NO$_2$, OCH$_3$, F, Cl, and Br groups, electrons that have double bonds lower $\Delta E_{\text{ISC}}$ ligands [6].

3.2. Energy transfer ($\Delta E_{\text{ET}}$)
The transfer energy ($\Delta E_{\text{ET}}$) of the 1,10-phenanthroline ligand to the $^5\text{D}_0$ energy level of europium ions for each substituent variation compared with 1,10-phenanthroline without substituents (H) is shown in Figure 3. The efficient value of $\Delta E_{\text{ET}} > 0.43\, eV$ [7]. As shown in Figure 3, the EDG and EWG studied in this research decrease $\Delta E_{\text{ET}}$ value for all position, except the F atomic group for 2-X-1,10-phenanthroline and 5-X-1,10-phenanthroline position. The significant group reducing of the $\Delta E_{\text{ET}}$ is a group having a double bond (CN; CH=CH$_2$; CHO; NO$_2$). This data can be explained using the Huckel approach, i.e. a group with double bonds lowers the energy of singlet excitation molecules. The singlet excited energy down causes triplet excited energy down. As a result, the difference between the energy of the substituted 1,10-phenanthroline triplet and the energy of the excited europium ion ($\Delta E_{\text{ET}}$) excitation level.

Another approach to explain the decreasing in singlet and triplet energy of 1,10-phenanthroline substituted double-bonded groups is the theory of particles in the box. This theory explains that the difference of the energy level of the electron system in the box is smaller for the larger width of the box. The width of the box referred to in the conjugated double bond system is the area of electron...
The region of the delocalization of the electron in a substituted 1,10-phenanthroline substituted group of molecules is wider. This causes the energy level of the system to be smaller, decreasing the energy of the singlet and triplets.

However, this approach fails to explain the behavior of the F atomic group. As known, the F atom has a free electron pair that can be delocalized. If the delocalization effect is maximal, the triplet energy of the molecule is smaller so $\Delta E_{ET}$ Value will be decrease. But, the results obtained that $\Delta E_{ET}$ increase as seen in Figure 3. This data can be explained using the electron density approach. Atom F as a propulsion of electrons by means of resonance causes higher electron density, resulting in higher orbital distance or excitation level in the molecule. This causes the energy needed to make the excited electrons larger. This approach corresponds to the explanation that the transition $n \rightarrow \pi^*$ indicates a hypsochromic shift when using an electron-driving group as a substituent [10].

Different values of $\Delta E_{ET}$ for 2-X-1,10-phenanthroline, 5-X-1,10-phenanthroline, and random-X-1,10-phenanthroline also results $\Delta E_{ET}$ value that do not reach the efficient value, i.e. $> 0.43$ eV [7]. Ligands that do not qualify for $\Delta E_{ET}$ efficiency are the group having a double bonds such as CH=CH, CN, CHO, and NO2. In contrast, substituents without double bonds such as CH3, CF3, OH, and F have a larger $\Delta E_{ET}$ value. Ligands eligible for the efficiency of $\Delta E_{ET}$ at the exclusivity level of the europium ion are 1,10-phenanthroline substituted CH3 and F groups both at 2-X,1,10-phenanthroline, 5-X,1,10-phenanthroline, or random-X-1,10-phenanthroline.

![Figure 3](image)

**Figure 3.** Comparison of $\Delta E_{ET}$ 1,10-phenanthroline, 2-X,1,10-phenanthroline, 5-X,1,10-phenanthroline, and random-X-1,10-phenanthroline position

3.3. Distance between the ligand and europium nuclei ($R_L$) and energy transfer rate ($W_{ET}$)

The $R_L$ value represents the distance between the core of substituted 1,10-phenanthroline as ligand molecule and the Eu (III) ion nucleus as the bidentate complex wherein each of the substituted 1,10-phenanthroline molecules is optimized first in the triplet-excited state. The result of $R_L$ calculation is shown in Figure 4.

Value of $R_L$ is a parameter that greatly influences the rate of energy transfer ($W_{ET}$) complex. Another parameter that greatly affects $W_{ET}$ is the energy of the triplet ($E_T$) ligand to be transferred. Theoretically, both parameters are inversely proportional to the $W_{ET}$ value so that the $W_{ET}$ value will
be very large if the $R_L$ and $E_T$ values are very small. However, the $R_L$ value is not related to the $E_T$ value so that the small value of one of these parameters does not significantly affect the $W_{ET}$ value. This explanation corresponds to the data of the $W_{ET}$ value for Eu (III) 2-X-1,10-phenanthroline, Eu (III) 5-X-1,10-phenanthroline, and Eu (III) random-X-1,10-phenanthroline as shown in Figure 5.

![Figure 4](image1.png)

**Figure 4.** The distance between the core of the ligand and Eu (III) ion nucleus ($R_L$) for 1,10-phenanthroline, 2-X-1,10-phenanthroline, 5-X-1,10-phenanthroline, and random-X-1,10-phenanthroline

![Figure 5](image2.png)

**Figure 5.** The energy exchange rate ($W_{ET}$) of the Eu (III) bidentate complex using a substituted 1,10-phenanthroline ligand

Another approach that can be used to describe the $W_{ET}$ profile in Figure 5 is the bonding orbitals between the donor atoms and the europium atoms. The data in the figure show that the $W_{ET}$ value of
the europium complex is very significant when using 2-NO$_2$-1,10-phenanthroline and 2-CHO-1,10-phenanthroline ligand. This can be explained by the second molecular orbital of the complex as shown in Figure 6.

Figure 6 (a) shows 2 bonding orbital in phase between the Eu (III) ions with the donor N atom of 1,10-phenanthroline and the O atom of the NO$_2$ group. In the complex, the O atom helps the transfer energy so that the $W_{ET}$ value of complex 2-NO$_2$-1,10-phenanthroline is very large. The same result happens in the 2-CHO-1,10-phenanthroline complex as shown in Figure 6 (b) i.e. an orbitals between Eu (III) ions with donor N atoms of 1,10-phenanthroline. However, the $W_{ET}$ value of the 2-CHO-1,10-phenanthroline complex is not as large as the $W_{ET}$ complex of 2-NO$_2$-1,10-phenanthroline because the CHO group does not aid in energy transfer.

In contrast, the Eu (III) 2-F-1,10-phenanthroline and Eu (III) 2-OH-1,10-phenanthroline complexes have small WET because no bonding orbitals exist between donor N atoms of 1,10-phenanthroline with ion Eu (III) as shown in Figure 7. The same approach can be used to describe the complex $W_{ET}$ profile of Eu (III) 5-X-1,10-phenanthroline. The data in Figure 5 shows relatively equal $W_{ET}$ values and each complex has a very small $W_{ET}$ value when compared to the previously described Eu (III) 2-NO$_2$-1,10-phenanthroline complex. This is because the molecular orbitals between the donor atoms and the Eu (III) ions are not formed so that the energy transfer process is not maximal as shown in Figure 8.
Figure 8. Complex molecular orbitals Eu (III) 5-X-1,10-phenanthroline when the triplet is excited triplet where (a) $X = \text{CH}=\text{CH}_2$ and (b) $X = \text{F}$.

Conclusions
The $W_{ET}$ obtained for the Eu (III) 2-X-1,10-phenanthroline and Eu (III) 5-X-1,10-phenanthroline complex corresponds to the $W_{ET}$ profile for the Eu (III) random-X-1,10 complex - phenanthroline. The data in Figure 5 shows a high $W_{ET}$ for Eu (III) 2,9-CHO-1,10-phenanthroline and low for Eu (III) 5,6-F-1,10-phenanthroline. The difference in value corresponds to the difference in the molecular orbital of each complex as shown in Figure 9.

Figure 9. Complex molecular orbitals of (a) Eu (III) 2,9-CHO-1,10-phenanthroline and (b) Eu (III) 5,6-F-1,10-phenanthroline when the excited triplet of ligand.

In the Figure 9, complex Eu (III) 2,9-CHO-1,10-phenanthroline has no bonding orbital between Eu (III) and N donor atoms. However, CHO group orbitals extending around ion (III) value of $W_{ET}$ Eu (III) 2,9-CHO-1,10-phenanthroline is higher. In contrast, the Eu (III) 5,6-F-1,10-phenanthroline complex forms an unfavorable orbitals (antibonding orbital) between Eu (III) ions with donor atom N. This orbital inhibits energy transfer so that the Eu(III)5,6-F-1,10-phenanthroline $W_{ET}$ value is very small.

4. Conclusions
The type, nature, position, and variation of EDG and EWG affect $\Delta E_{ISC}$, $\Delta E_{ET}$, $R_L$, and $W_{ET}$ complexes of Eu (III) substituted phenanthroline. Specifically, the EDG increases the $\Delta E_{ISC}$ value, the group with the double bond decreases the $\Delta E_{ET}$ value, and the group that can interact strongly with europium increases the $W_{ET}$ value.

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References
[1] Xu C 2010 Photophysical properties of lanthanide complexes with 5-nitro-1,10-phenanthroline Monatshefte für Chemie - Chemical Monthly 141 pp 631–5
[2] Binnemans K 2009 Lanthanide-Based Luminescent Hybrid Materials Chemical Reviews 109 pp 4283–374
[3] Bencini A and Lippolis V 2010 1,10-Phenanthroline: A versatile building block for the construction of ligands for various purposes Coordination Chemistry Reviews 254 pp 2096–180

[4] de Mello Donegá C, Junior S A and de Sá G F 1997 Synthesis, Luminescence and Quantum Yields of Eu(III) Mixed Complexes with 4, 4, 4-trifluoro-1-phenyl-1, 3-butanedione and 1, 10-phenanthroline-N-oxide Journal of alloys and compounds 250 pp 422–426

[5] Schmittel M and Lin H 2007 Luminescent Iridium Phenanthroline Crown Ether Complex for the Detection of Silver(I) Ions in Aqueous Media Inorganic Chemistry 46 pp 9139–45

[6] Samuel A P S, Xu J and Raymond K N 2009 Predicting Efficient Antenna Ligands for Tb(III) Emission Inorganic Chemistry 48 pp 687–98

[7] Aiga F, Iwanaga H and Amano A 2005 Density Functional Theory Investigation of Eu(III) Complexes with β-Diketonates and Phosphine Oxides: Model Complexes of Fluorescence Compounds for Ultraviolet LED Devices The Journal of Physical Chemistry A 109 pp 11312–6

[8] Malta O L and e Silva F G 1998 A Theoretical Approach to Intramolecular Energy Transfer and Emission Quantum Yields in Coordination Compounds of Rare Earth Ions Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 54 pp 1593–9

[9] Malta O L, Gonçalves e Silva F R and Longo R 1999 On the Dependence of The Luminescence Intensity of Rare-earth Compounds with Pressure: A Theoretical Study of Eu(TTF) 32H 2O in Polymeric Solution and Crystalline Phases Chemical Physics Letters 307 pp 518–26

[10] Rezchikova K I, Churakov A M, Burshtein K Y, Shlyapochnikov V A and Tartakovskii V A 1997 Benzo-1, 2, 3, 4-tetrazine 1, 3-dioxides as New Chromophore Systems Mendeleev communications 7 pp 174–5