



# Divalent Metal Complexes with the Pyrogallol-Based Organic Material: Optical and Charge Transport Properties

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## Abstract

The optical characteristics of the divalent heavy metal complexes of MEP ligand in gaseous phases, namely cadmium ( $Cd^{2+}$ ), mercuric ( $Hg^{2+}$ ), and lead ( $Pb^{2+}$ ), have been examined in this study work. DFT using the B3LYP hybrid functional was used to accomplish the calculations. For every one of these compounds, the charge transport characteristics, including charge transfer integrals, open circuit voltage, and light harvesting efficiency, are investigated.

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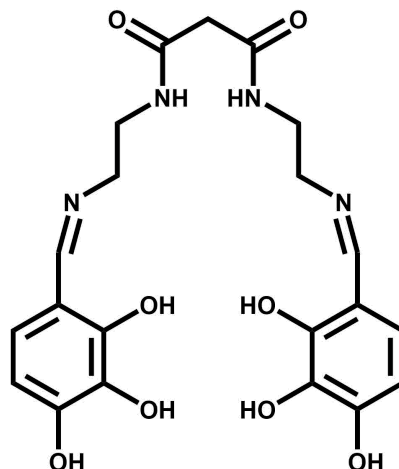
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## I. Introduction

Over the past years, organic materials—such as polymers, oligomers, and pi-conjugated molecules—have been increasingly popular in both the academic and industrial sectors due to their significantly simpler manufacturing procedures than those of inorganic materials [1]. Pi-conjugated organic compounds find wide-ranging uses in organic semiconductors, including photovoltaic devices, field-effect transistors, solar cells, and organic light-emitting diodes [2–5]. Nevertheless, a number of restrictions associated with these compounds, including low solubility and air instability [6–8], have piqued researchers' interest in learning more about these organic materials with pi-conjugation. Their potential use in optoelectronic and charge carrier applications is hampered by these drawbacks [6–8].

In order to get around these restrictions and enhance optoelectronic and charge carrier applications, researchers typically chemically alter and substitute the main chain, side chain, and terminal groups as well as add heteroatoms to the structure [9–11]. These structural changes are advantageous for investigating optoelectronic and charge carrier applications [12–13]. The effects of shifting the heteroatoms' (S and N) positions and the anthracene's central ring's heterocyclic ring configuration on the optical and charge transport characteristics of anthratetrazathiazole were studied by Tripathi and Prabhakar [14].

Considering the aforementioned information, we selected the organic molecule MEP, which is based on pyrogallol, as depicted in Figure 1. We also made a modest structural modification to the organic materials by forming divalent heavy metal complexes. This study involved a theoretical examination of the optoelectronic characteristics of pyrogallol-based compounds including the metals lead ( $Pb^{2+}$ ), mercuric ( $Hg^{2+}$ ), and cadmium ( $Cd^{2+}$ ). In an effort to shed light on the connection between molecular structure and optoelectronic properties, the impacts of the metals on the materials' electronic properties are explored. The goal of this study was to drive towards compounds that would be more effective as active optoelectronic materials. In order to research organic solar cells, theoretical understanding of the components' HOMO and LUMO energy levels is essential. As a result, the optical characteristics, charge transport integrals, and  $V_{oc}$  (open-circuit voltage) of the compounds under study are computed and reported.



**Figure 1. Schematic representation of the Pyrogallol Based Organic Material**

## II. Molecular Modelling

Using Gaussian 09 [15] software, all computations were carried out on an 12th generation computer powered by Intel. The optical properties of the molecules on the complexes' optimised geometry were calculated using the TD-DFT method. The B3LYP hybrid parameter was employed for metal complex calculations in the gaseous phase. At the same theoretical level, calculations were also done for the charge transport properties.

The charge transport integrals such as hole and electron [16-17] were calculated by using the following equations:

$$= (E_{\text{LUMO}+1} - E_{\text{LUMO}}) \quad (1)$$

$$= (E_{\text{HOMO}} - E_{\text{HOMO}-1}) \quad (2)$$

The photovoltaic properties such as light-harvesting efficiency (LHE) and open circuit voltage ( $V_{\text{oc}}$ ) were calculated by using:

$$V_{\text{oc}} = |E_{\text{HOMO}}(\text{Donor})| - |E_{\text{LUMO}}(\text{Acceptor})| - 0.3 \quad (3)$$

$$\text{LHE} = 1 - \quad (4)$$

The oscillating strength ( $f$ ) in the aforementioned equations is taken to correspond to the wavelength of the absorption maxima; the energy of the LUMO of the PBCM; the energy of the HOMO level of the proposed molecules is denoted by  $E_{\text{HOMO}}(\text{Donor})$ ; and the loss observed in organic solar cells is described by 0.3 [18].

## III. Results and Discussion

### 3.1 Optical properties analysis

Using DFT optimised geometry and the TD-DFT method, the optical properties of the designed complexes, including absorption wavelength, oscillating strength ( $f$ ), excitation transition energy ( $E_{\text{ex}}$ ), major transitions (MT), and their percentage contributions (%Ci), were calculated at B3LYP hybrid parameter. Table 1 and Figure 2 display the computed findings of these optical characteristics and absorption spectra. Furthermore, Table 1 lists the oscillation strength ( $f$ ) and excitation transition energy ( $E_{\text{ex}}$ ) with the highest absorption wavelength. Molecules MEP-Cd<sup>2+</sup>, MEP-Hg<sup>2+</sup> and MEP-Pb<sup>2+</sup> have maximum absorption wavelength values of 530.25, 413.44, and 617.85 nm, respectively. For Pyrogallol based complexes, the oscillation strength ( $f$ ) and excitation transition energy ( $E_{\text{ex}}$ ) vary from 0.0001-0.0715 and 2.0067-3.2958 eV, respectively. The complexes' greatest absorption wavelength falls between 376.19 and 617.85 nm in the visible spectrum.

**Table 1. Absorption wavelength, oscillating strength, excitation transition energy, major transitions with their percentage contributions of designed complexes**

Compounds	$f$	$E_{ex}$	MT	$\%C_i$	
MEP-Cd <sup>2+</sup>	530.25	0.0003	2.3382	H → L	0.70618
	446.76	0.0624	2.7752	H → L+1	0.69374
	418.92	0.0047	2.9596	H → L+2	0.69847
MEP-Hg <sup>2+</sup>	413.44	0.0042	2.9988	H → L	0.66221
	411.10	0.0009	3.0159	H-1 → L	0.65908
	376.19	0.0302	3.2958	H → L+1	0.68185
MEP-Pb <sup>2+</sup>	617.85	0.0001	2.0067	H → L	0.70527
	462.52	0.0715	2.6806	H → L+1	0.69209
	417.43	0.0019	2.9702	H-1 → L	0.70335

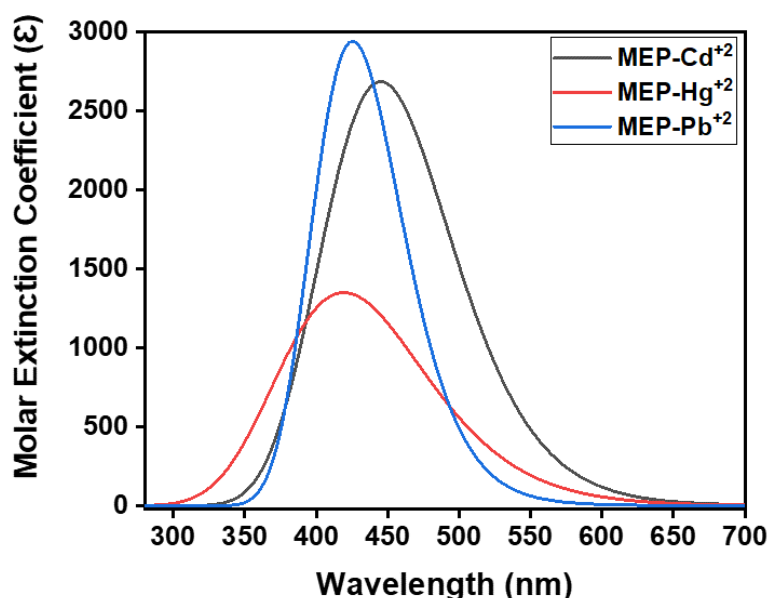


Figure 2. Absorption spectra of Pyrogallol Based Complexes

### 3.2 Charge transport properties analysis

The charge transport properties were obtained with the help of TD – DFT method by using equations 1 and 2 respectively. Table 2 and Figure 3 demonstrate the calculated values of hole/electron charge transfer integral for heavy metal complexes.

The high values of charge transfer integral enhance the conductivity and hole/electron transfer mobilities of organic semiconductors such as OLED etc. [19]. The values of hole charge transfer integral and electron charge transfer integral for the complexes are in range 0.004-0.026 eV, and 0.005-0.036 eV respectively. Furthermore, the trend of hole charge transfer integrals is as follows: MEP-Hg<sup>2+</sup> < MEP-Cd<sup>2+</sup> < MEP-Pb<sup>2+</sup> while order of electron charge transfers integral is as follows: MEP-Hg<sup>2+</sup> < MEP-Pb<sup>2+</sup> = MEP-Cd<sup>2+</sup>. The above order indicates MEP-Pb<sup>2+</sup> molecule have large value of hole charge transfer integral while MEP-Pb<sup>2+</sup> and MEP-Cd<sup>2+</sup> molecule have highest value of electron charge transfer integral, which can be used for hole/electron transport materials respectively.

Table 2. Charge transfer integral (Hole and Electron) and Open circuit voltage of Divalent heavy metal complexes

Compounds	Hole charge transfer integral ( $t_h$ )	Electron charge transfer integral ( $t_e$ )	Open circuit voltage ( $V_{oc}$ )
MEP-Cd <sup>2+</sup>	0.019	0.036	3.223
MEP-Hg <sup>2+</sup>	0.004	0.005	3.182
MEP-Pb <sup>2+</sup>	0.026	0.036	3.223

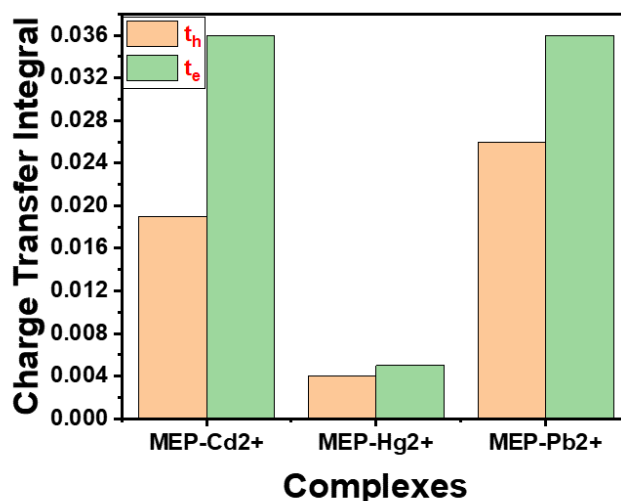


Figure 3. Graphical representation of Hole charge transfer integral ( $t_h$ ) and Electron charge transfer integral ( $t_e$ ) of complexes

### 3.3 Photovoltaic properties analysis

The open circuit voltage and light-harvesting efficiency of organic semiconductors, particularly organic photovoltaic devices like solar cells, can be used to assess their performance.

#### 3.3.1 Open circuit voltage analysis ( $V_{oc}$ )

In order to determine if effective charge transfer will take place between the acceptor, PBCM, and donor, or the complexes under study, the open circuit voltage is a crucial characteristic to assess. This assures efficient electron injection. Equation 3 was used to compute the open circuit voltage. In Figure 4 and Table 2, the open circuit voltage results are shown. The open circuit voltage values of complexes, MEP-Cd<sup>2+</sup>, MEP-Hg<sup>2+</sup> and MEP-Pb<sup>2+</sup> are: 3.223, 3.182 and 3.223 eV respectively. Complexes have open circuit voltages between 3.182 and 3.223 eV. The trend of open circuit voltage is as follows: MEP-Hg<sup>2+</sup> < MEP-Cd<sup>2+</sup> = MEP-Pb<sup>2+</sup>.

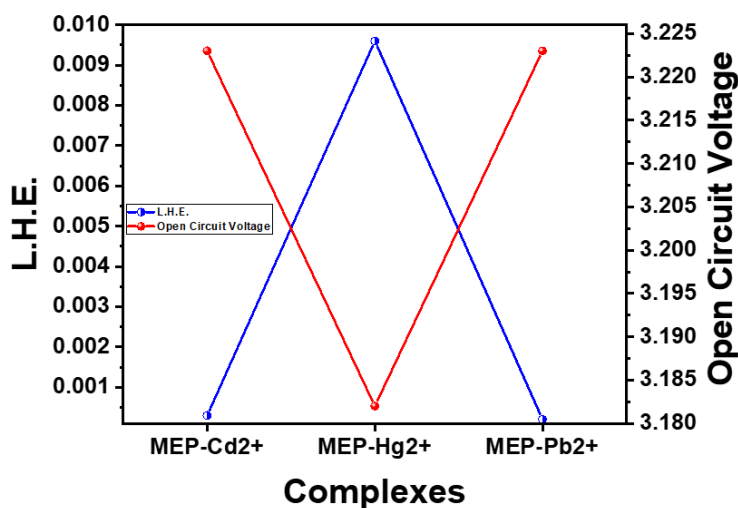


Figure 4. Light Harvesting Efficiency (L.H.E.) and Open circuit voltage ( $V_{oc}$ ) of Pyrogallol-based complexes

#### 3.3.2 Light-harvesting efficiency analysis

One crucial component that improves the efficiency of the solar cells' performance is their ability to harvest light. Improved performance of the solar cells is achieved through achieving the maximum photocurrent through higher light-harvesting efficiency. Equation 4 was used to compute the open circuit voltage whereas, table 3 and figure 4 represent the light-harvesting efficiency data. MEP-Cd<sup>2+</sup>, MEP-Hg<sup>2+</sup> and MEP-Pb<sup>2+</sup> had light-harvesting efficiency values of 0.0006, 0.0096, and 0.0002, respectively. Complexes have light-harvesting efficiency values between 0.0002 and 0.0096. The trend of improved solar cell performance and increased light-harvesting efficiency is as follows: MEP-Pb<sup>2+</sup> < MEP-Cd<sup>2+</sup> < MEP-Hg<sup>2+</sup>.

**Table 3. Absorption maximum wavelength, oscillating strength, excitation transition energy, light harvesting efficiency**

Compounds		<b>f</b>	<b>LHE</b>	<b>E<sub>ex</sub></b>
<b>MEP-Cd<sup>2+</sup></b>	<b>530.25</b>	<b>0.0003</b>	<b>0.0006</b>	<b>2.3382</b>
<b>MEP-Hg<sup>2+</sup></b>	<b>413.44</b>	<b>0.0042</b>	<b>0.0096</b>	<b>2.9988</b>
<b>MEP-Pb<sup>2+</sup></b>	<b>617.85</b>	<b>0.0001</b>	<b>0.0002</b>	<b>2.0067</b>

#### IV. Conclusions

In this work, we have examined how the charge transport, opto-electronic, and photovoltaic properties of the Pyrogallol-based ligand are affected by fluctuations in the heavy divalent metal ions inside it. Using the B3LYP hybrid functional, all of the computations in this work were completed with the aid of the DFT and TD-DFT methodologies. The complexes' absorption wavelength, as determined by this study's investigation, is between 387 and 457 nm, or within the visible spectrum. These molecules are advantageous for materials that transport holes and can be employed in p-type OLEDs or OFETs, according to the results of their charge transfer properties. The MEP-Hg<sup>2+</sup> complexes significantly boost open circuit voltage and light-harvesting efficiency, which enhance photovoltaic device performance. Consequently, our research contributes to the advancement of the novel class of organic semiconductor materials for use in electronic devices such OFETs, OLEDs, and photovoltaic solar cells.

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