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Research Paper

Optical and Charge Transport Properties of Divalent Metal Complexes with the Catechol Based Organic Material

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Abstract
In this research paper, we have discussed the optical properties of the divalent heavy metal {Cadmium (Cd^{2+}) mercuric (Hg^{2+}) and lead (Pb^{2+})} complexes of MEC ligand in gaseous phases. The calculations were performed by employing the DFT with the B3LYP hybrid paramter. The charge transport properties of the complexes such as light harvesting efficiency, open circuit voltage and charge transfer integrals are examined for each of these compounds.

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I. Introduction

Organic materials, such as pi-conjugated molecules, oligomers, and polymers have gained much popularity in academic and industrial sectors over the past decade because of their manufacturing processes are much less complex than inorganic materials [1].Organic materials with pi-conjugation have diverse applications in organic semiconductors [2-5] etc. However, these compounds have several limitations, such as air instability and limited solubility [6-8] which has stimulated the curiosity of researchers in studying these organic materials with pi-conjugation. These disadvantages hinder their potential utility in optoelectronic and charge carrier applications [6-8].

Generally, researchers overcome these limitations or improve optoelectronic and charge carrier applications by chemically modifying and substitution the main chain, side chain, and terminal groups and by introducing the heteroatom in the structure [9-11] which are favorable for exploring the optoelectronic and charge carrier applications [12-13].

Tripathi and Prabhakar investigated the influence of changes in the position of heteroatom (S and N) and central ring of anthracene with different heterocyclic rings on optical and charge transport properties in anthratetrathiazole [14].

Taking all the above facts into account, we chosen the catechol based organic molecule MEC as shown in figure 1 and slightly altering the structure of the organic materials byforming the divalent heavy metal complexes. In this work, theoretical investigation on the optical and charge transport properties of catechol-basedcomplexes with metalsviz., Cadmium (Cd^{2+}) mercuric (Hg^{2+}) and lead (Pb^{2+}) were performed. 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 find compounds that would be more effective as active optoelectronic materials. The study of organic solar cells requires a theoretical understanding of the components' HOMO and LUMO energy levels, so the optical properties and charge transport properties of the compounds are investigated and described.

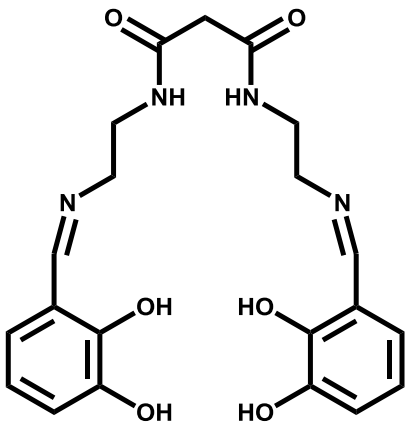

Figure 1.Graphicillustration of the Catechol Based Organic Material

II. Molecular Modelling

All the calculations were performed on 12th Gen computer powered byIntel using Gaussian 09 [15] software. TD-DFT method was used to calculate the optical properties of the molecules on the optimized geometry of the complexes. For computations of metal complexes in the gaseous phase, the B3LYP hybrid parameter was used. The calculations of charge transport properties were also performed at the same level of theory.

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

$$t_h = \frac{1}{2}(E_{LUMO+1} - E_{LUMO}) \quad (1)$$

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

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

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

$$LHE = 1 - 10^{-f} \quad (4)$$

In above formulas, f is oscillating strength (taken corresponding to absorption maxima wavelength), E_{LUMO}(Acceptor) is the energy of LUMO of PBCM, E_{HOMO}(Donor) is the energy of HOMO level of the proposed molecules, and 0.3 describes the loss found in organic solar cells [18].

III. Results and Discussion

3.1 Optical properties analysis

The photosensitive properties such as absorption wavelength, oscillating strength (f), excitation transition energy (E_{ex}), major transitions (MT) with their percentage contributions ($\%C_i$) for designed complexes were calculated with the help of TD – DFT method at B3LYP hybrid parameter by using DFT optimized geometry. The calculated results of these optical properties and absorption spectra are presented in Table 1 and Figure 2. Additionally, the oscillating strength (f) and excitation transition energy (E_{ex}) with maximum absorption wavelengthare tabulated in Table 1. The maximum absorption wavelength values of molecules, MEC-Cd^{2+}, MEC-Hg^{2+} and MEC-$Pb^{2+}$are:431.38, 437.48, and 457.47 nm respectively. The values of oscillating strength (f) and excitation transition energy (E_{ex}) of designed catechol based complexesare in range 0.001-0.0731, and 2.7102-3.2005 eV respectively. Themaximum absorption wavelengthof the complexeslies within the range of visible region from 387-457 nm.

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

Compounds	λ_{abs}	f	E_{ex}	MT	$\%C_i$
MEC-Cd^{2+}	431.38	0.0014	2.8741	H →L	99.63
	392.20	0.0201	3.1612	H-1 →L	67.41
	387.39	0.0731	3.2005	H-1 →L	29.92
	387.39	0.0731	3.2005	H →L+1	67.44
MEC-Hg^{2+}	437.48	0.0029	2.8341	H →L	99.38
	409.06	0.0414	3.0309	H-1 → L	91.38
	401.53	0.0389	3.0878	H → L+1	87.77
MEC-Pb^{2+}	457.47	0.0027	2.7102	H →L	97.97
	421.19	0.0347	2.9437	H-1 →L	97
	398.42	0.0251	3.1119	H →L+1	97.63

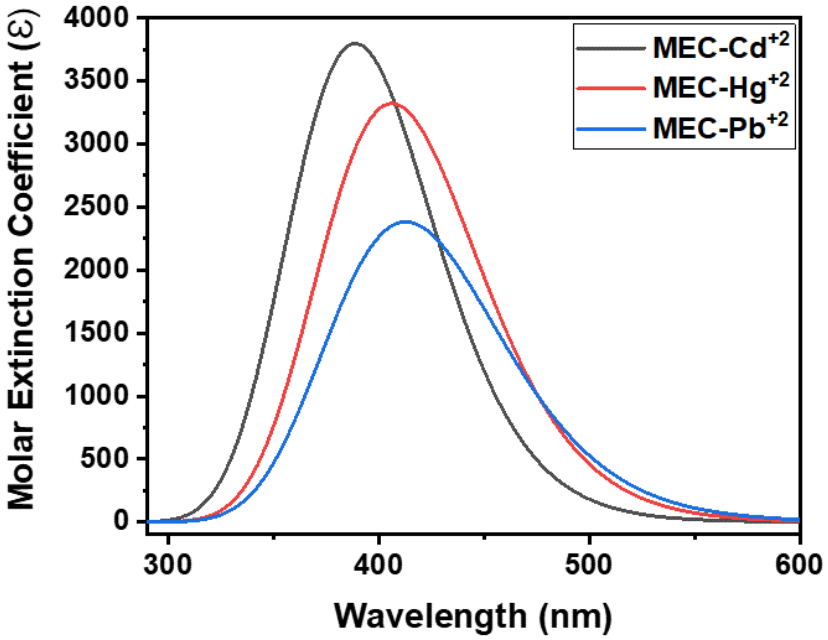

Figure 2.Electronic spectra ofCatechol Based Complexes

3.2 Charge transport properties analysis

The charge transport propertieswere obtained with the help of TD – DFT method using the DFT optimized geometry in the gaseous phase for complexes by using equations 1 and 2 respectively.Table 2 and Figure3 illustrate the calculated values ofhole/electron charge transfer integral forheavy metalcomplexes.

The high values of integrals enhance the conductivity and hole/electron transfer mobilities of organic semiconductors such as OLED etc. [19]. The values of integrals for the complexes are in range 0.012-0.016 eV, and 0.008-0.011 eV correspondingly. Furthermore, the order of hole charge transfer integralsis as follows: MEC-Hg^{2+}<MEC-Cd^{2+}<MEC-Pb^{2+} while order of electron charge transfers integral is as follows:MEC-Hg^{2+} = MEC-Pb^{2+}<MEC-Cd^{2+}**.** The above order indicatesMEC-Pb^{2+} molecule have large value of hole charge transfer integral whileMEC-Cd^{2+}molecule have highest value of electron charge transfer integral, which can be used for hole/electron transport materials respectively.

Table 2. Comparative data of charge transfer integrals and Open circuit voltageof Divalent heavy metal complexes

Compounds	Hole charge transfer integral (t_h)	Electron charge transfer integral (t_e)	Open circuit voltage (V_{oc})
MEC-Cd^{2+}	0.014	0.011	3.205
MEC-Hg^{2+}	0.012	0.008	3.202
MEC-Pb^{2+}	0.016	0.008	3.198

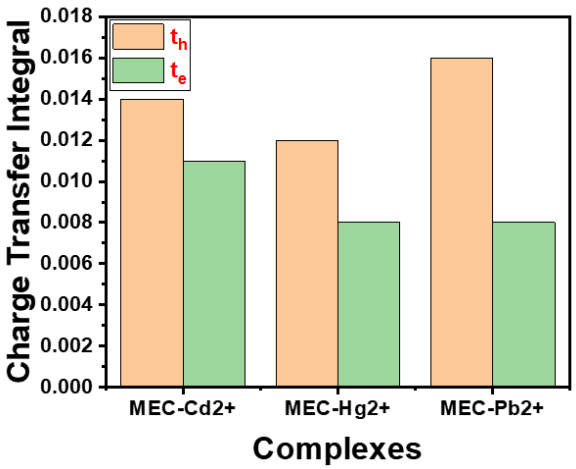

Figure 3.Graphical representation of charge transfer integrals (t_h and t_e) of complexes

3.3 Photovolatic properties analysis

The performance of organic semiconductors mainly organic photovoltaic devices such as solar cell can be examined using open circuit voltage and light-harvesting efficiency.

3.3.1 Open circuit voltage analysis (V_{oc})

The V_{oc} is a significant parameter to measure whether the effective charge transfer will occur between the donor i.e., studied complexes) and acceptor PBCMwhich ensures the efficient electron injection. Theopen circuit voltagewere calculated by using equation 3. The results of open circuit voltage are displayed in Figure 4 and Table 2. The open circuit voltage values of complexes, MEC-Cd^{2+}, MEC-Hg^{2+} and MEC-Pb^{2+} are:3.205, 3.202 and 3.198 eV respectively. The values of open circuit voltage of complexesare in range 3.198 – 3.205 eV.The trend of open circuit voltage is as follows: MEC-Pb^{2+}<MEC-Hg^{2+}<MEC-Cd^{2+}.

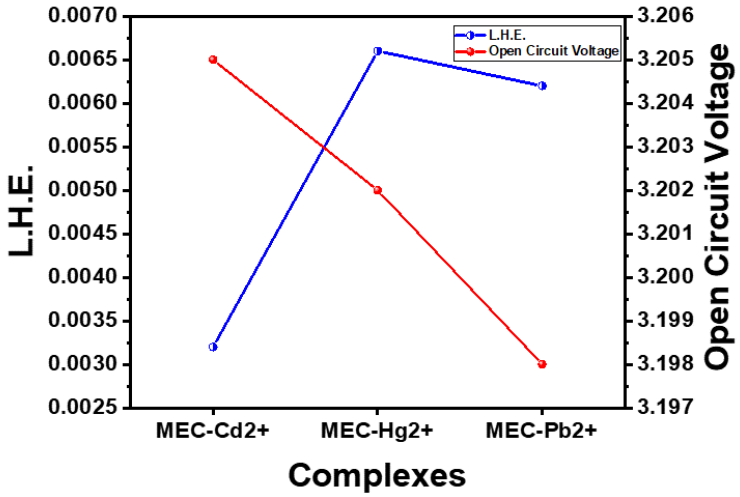

Figure 4. Light Harvesting Efficiency (L.H.E.) and Open circuit voltage (V_{oc}) of catechol-based complexes

3.3.2Light-harvesting efficiency analysis

The light-harvesting efficiency is essential property which enhances the performance of the solar cells. Higher light-harvesting efficiency leads to obtaining the maximum photocurrent which improves the performance of the solar cells. Theopen circuit voltagewere calculated by using equation 4. The results of light-harvesting efficiency are displayed in Figure 4 and Table 3. The light-harvesting efficiency values of, MEC-Cd^{2+}, MEC-Hg^{2+} and MEC-$Pb^{2+}$are:0.0032, 0.0066and 0.0062 respectively. The values of LHE for complexes are in range 0.0032-0.0066.The trend of enhanced light-harvesting efficiency and performance of solar cell improvement are as follows: MEC-Cd^{2+}<MEC-Hg^{2+}<MEC-Pb^{2+}**.**

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

Compounds	λ_{max}	f	LHE	E_{ex}
MEC-Cd^{2+}	**431.38**	**0.0014**	**0.0032**	**2.8741**
MEC-Hg^{2+}	**437.48**	**0.0029**	**0.0066**	**2.8341**
MEC-Pb^{2+}	**457.47**	**0.0027**	**0.0062**	**2.7102**

IV. Conclusions

In this study, we have investigated the influence of variation in the heavy divalent metal ions in the catechol-based ligand on theircharge transport, opto-electronic, photovoltaic properties. All the theoretical investigations were evaluated by using the Gaussian software and B3LYP hybrid functional with the help of DFT and TD-DFT methodology. According to analysis of this study, the absorption wavelength forthe complexesis in the range of 387-457 nmwhich lies within the visible region. The results of charge transfer propertiessuggests that these molecules are beneficial for hole transporting materials and can be used in p-type OLEDs or OFETs. The MEC-Hg^{2+} and MEC-Pb^{2+}complexes greatly increase in light-harvesting efficiency and open circuit voltage which improve the performance of photovoltaic devices. Therefore, our work is helpful for further deigning of the new type of organic semiconductor materials for applications in electrical devices such as photovoltaic, OLEDs and OFETs.

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