JOURNAL OF CRITICAL REVIEWS

ISSN-2394-5125 VOL 7, ISSUE 6, 2020

Synthesis, Characterization, Photophysical And Quantum Mechanical Study Of 2-[(*E*)-[(4-Bromo-2-Fluorophenyl) Imino] Methyl} Phenol As An Organic Light Emmiting Diode Compound

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ABSTRACT

To synthesis the OLED material, we must know the mechanism of excitation and emission of electron. Mechanism of excitation and emission is well understood with the help of quantum mechanical calculations. So in the present work, to understanding the theoretical information of compound from quantum mechanical calculation, we have synthesized the zinc complex of 2-[(E)-[(4-bromo-2-fluorophenyl) imino] methyl} phenol compound. The structure is confirmed by IR and H-NMR spectral characterization and the optical properties studied by UV-Visible and photo- luminous spectra. The interesting outcome of this work, the synthesis procedure gives the high yield, all theoretical data is match with experimental data and the molecule shows the high emission wavelength which gives very important property of OLED material. So this, 2-[(E)-[(4-bromo-2-fluorophenyl) imino] methyl} phenol is use as developing the OLED material.

Keyword: Zinc Complex, DFT/ PBE1PBE, Photophysics, Molecular orbital energy and OLED.

INTRODUCTION

Organic light-emitting diode (OLED) technology has been the forefront of both academic and industrial research in the past two decades after the breakthrough demonstration of phosphorescent organo-transition metal compounds as highly efficient emitters [1]. Significant progress has been made in producing OLEDs to the point where advanced products, e.g. portable device displays, are commercially viable. However, much work is still required in the field with respect to improving the efficiencies and lifetimes of OLEDs. In particular, the pursuit of low-cost, highly efficient, and stable blue-light emitting compounds has dominated research in the past few years [2,3]. A wide spectrum of approaches is actively being studied to achieve the aforementioned goal, ranging from the optimization of device design to synthesis of superior emitter compounds [4,5]. The scope of this work will survey the rational design and synthesis of new, promising blue-light emitters, as well as their application in both non-doped and host dopant OLED devices.

Organometallic blue fluorescent Zn(II) Schiff base complexes are synthesized and explored computationally in order to use them in organic electroluminescent materials. Characterization of these salicyldehyde-based–zinc complexes was accomplished by various physicochemical techniques to get insight into their applicability as an active layer in light-emitting diodes. The XRD spectra of this complex give formation of crystalline structure with tetrahydral geometry. The complex demonstrates good thermal stability and remarkable photoluminescence both in solution and in the solid state with maximum in the blue region. Quantum chemical calculations shows ligand to ligand type electronic transitions by means of time-dependent density functional theory calculations and results show that the origin of the luminescence for the target complexes/ The constructed light-emitting diodes demonstrate the excitation at 431nm and emission at 492 nm and external quantum efficiency of up to 2.64 %, which is a good value for sufficient energy band gap, for purely fluorescent organic light-emitting diodes.

Computational chemistry is used in a number of different ways. One particularly important way is to model a molecular system prior to synthesizing the target molecule in the laboratory. Although computational models may not be precisely accurate, but they are often good enough to rule out 90% of possible compounds as being unsuitable for their intended use. This is very useful information because synthesizing a single compound may require months of labour, raw materials cost and also generate toxic waste. A second use of computational chemistry is in understanding a problem more completely [6]. There are some properties of a molecule such as electronic charge distribution, dipoles and vibrations frequency that can be obtained computationally more easily than by experimental means. There are also insights into molecular bonding, which can be obtained from the results of computations, which cannot be obtained from any experimental method. In 2011, Jadhao N.U. and Rathod S.P. were done the quantum mechanical calculation for Schiff bases by DFT method which shows the appropriate result to experimental data and they shows the type of electronic state of UV-Visible spectrum and clear the transition type by the TD-DFT method [7].

We have been interested in preparing Zinc complex of Schiff bases in an effort to study the luminescence properties of these compounds. Study and design of fluorescence properties of the Zinc complex Schiff bases might open up new path

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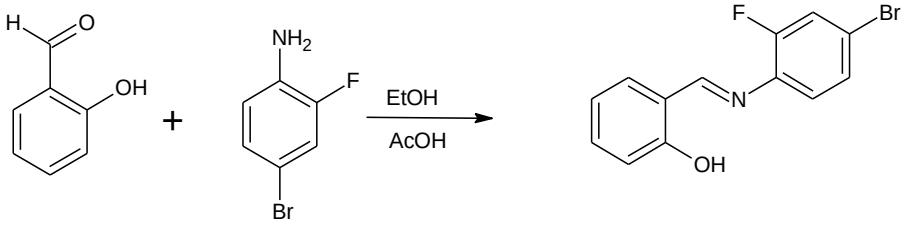
for further applications such as organic light emitting diodes (OLED), biosensors and probes. For the above mentioned reasons, the synthesis and characterization of Zinc complex Schiff base ligands and studies of their photophysical properties will be carried out. Computational calculations will be employed to study some molecular properties such as absorption, molecular orbital, molecular orbital energy gap and charge density for these compounds.

EXPERIMENTAL METHOD

Synthesis of 2-[(E)-[(4-bromo-2-fluorophenyl)imino]methyl}phenol

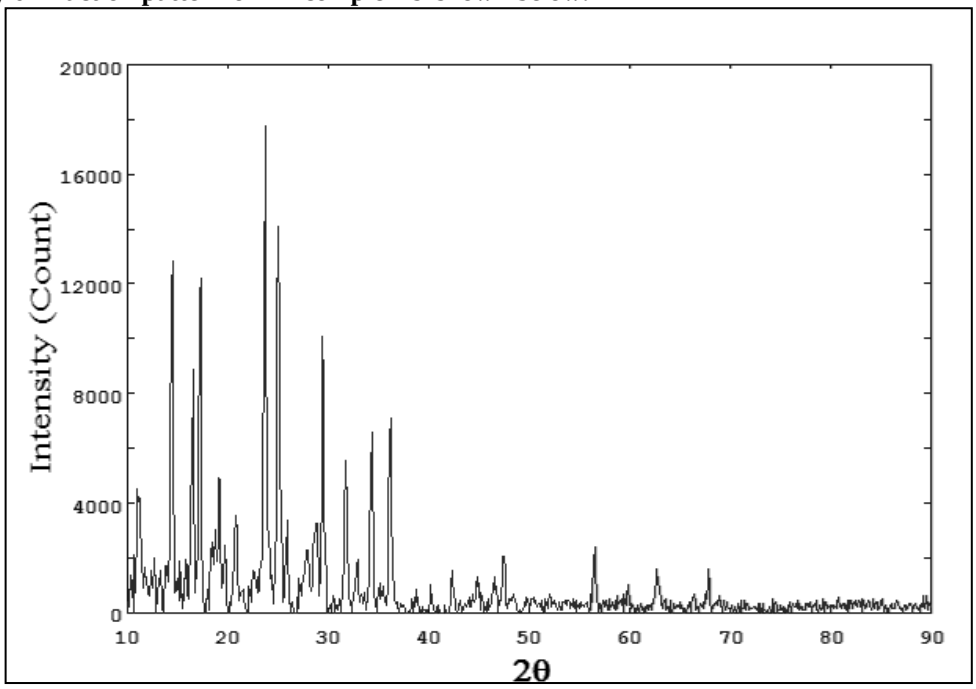


2-hydroxybenzaldehyde 4-bromo-2-fluoroaniline 2-{(*E*)-[(4-bromo-2-fluorophenyl)imino]methyl}phenol

2-hydroxybenzaldehyde (0.01Mol) was dissolved in 20 ml of absolute alcohol in 50 ml round bottom flask. To this, 4-bromo-2-fluroaniline (0.01 M) was added with constant stirring and finally catalytic amount of acetic acid. The reaction mixture is reflux with stirring for about 60 minutes, cool, diluted and washed with water. The product was filtered and recrystallized from absolute ethanol to get yellowish solid product. Yield is 80 % and M.P. is 68^0C

RESULT AND DISCUSSION:

1. The X-Ray diffraction pattern of Zn-complex is shown below:



XRD pattern of Zn-complex

Analysis of X-ray Diffraction Spectra

- Very strong and sharp peak with maximum relative intensity was observed at $2\theta=(23.706)^0$ and interplaner distance 3.75024Å.
- Below the value of interplaner distance 1.27695Å, the sharp peaks are not observed.
- Many well resolved lines were obtained in XRD pattern of this sample. The presence of large distinct lines confirmed the crystalline behavior of synthesized complex.

From the X-ray diffraction analysis, the powder Zn-complex has many strong, sharp diffraction peaks and some diffused background. This indicates the crystalline character of the compound. These spacing correspond to the chain distances of a well-organized molecular layer structure. The spectral data of X-ray diffraction pattern of Zn-complex is given in Table below

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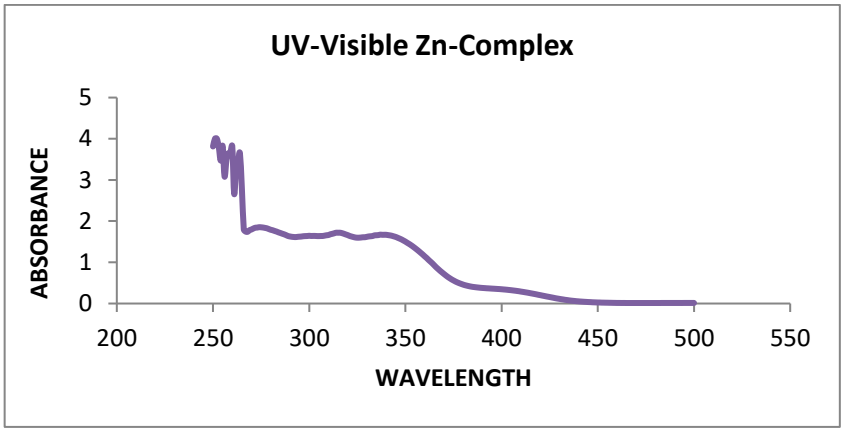
2. OPTICAL STUDIES OF ZINC-COMPLEXES

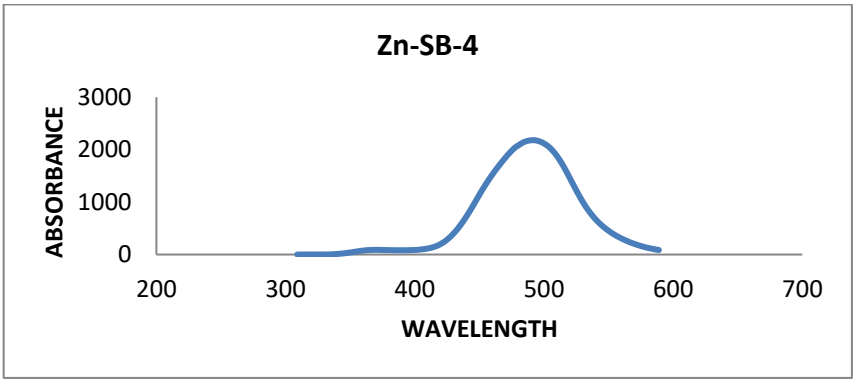


Absorption spectra of Zn-Complex in DMF

The Zn-complex was dissolved in DMF and exposed to UV light to check the emission. The solutions show emission of light by naked eye. However, the compound ZN-SB-4 shows a λ_{max} at around 260nm.

Photoluminescence Spectra

The excitation and photoluminescence (PL) spectra of Zn-complex in solution of acetonitrile (10 mM) form is as shown below.



Excitation and emission spectra of ZN-Complex

3.Thermal properties

Thermal characterization of the material has been done using thermo gravimetric analysis (TGA) technique and measure the change in weight of material as a function of temperature. In this technique a few milligram of substance in weight is heated at a constant rate of temperature under nitrogen atmosphere and note the change in weight at different temperature. Basically it gives the thermal stability of material.

Thermo gravimetric Analysis

Thermo Gravimetric Analysis (TGA) of synthesized Zn-complex was carried out in temperature range 0-600^{o} C as shown below.

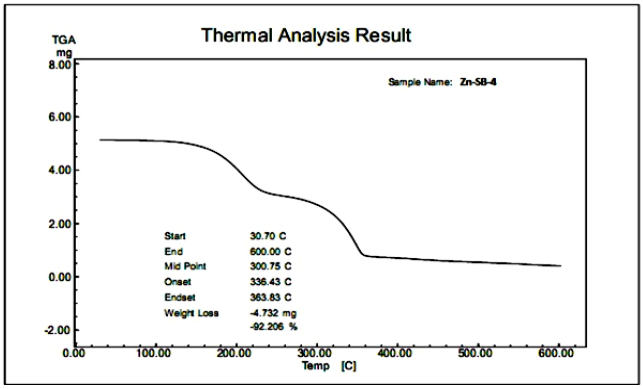


Figure 4.26: TGA thermogram of Zn-complex

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Analysis of TGA Thermogram

- No weight loss observed in first step of temperature range from 30.70 ^{0}C to 102 ^{0}C that is there is no temperature on a sample weight up to 102 ^{0}C.
- Total weight loss of about 92.206 % was observe at temperature 300.75^{0}C.

The TGA plot shows at temperature around 300.75^{o}C the material degrades completely. Hence the material is stable up to 300.75^{o}C.

Differential Scanning Calorimetry

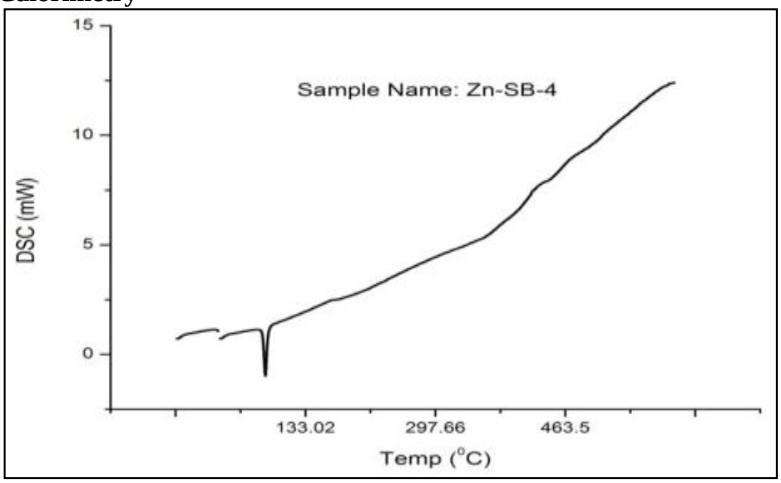

Figure 4.36: DSC scan of Zn-complex

Analysis of DSC Spectra

- Heat flow rate 20 ^{0}C/ min.
- Onset = 79.19^{0}C.
- Endset =85.89 ^{0}C.
- It show the melting point at 79.19 ^{0}C. (For metal and pure organic compound the extra polated onset temperature of endothermic event [nm].)
- It measure the heat flow associated with decomposition event and the decomposition temperature is found to be 198 ^{0}C.

4.Cyclic Voltametry

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. It offers a rapid location of redox potentials of the electroactive species. The voltammograms showed one or more cathodic peaks and anodic peaks at different scan rates, depending on the nature of the substituent and pH of the medium. Cyclic Voltammetry curve was recorded by multichannel Potentiostat. A Pt disc was used as working electrode. A Pt plate was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. 0.1 mol/L of tetra-butyl ammonium phosphate (TBAP) was used as supporting electrolyte. The concentration of SAZ in N, N'- Dimethylformamide (DMF) was 4X10 $^{-3\ mole}$/L. The scan rate was 100 mV/s.

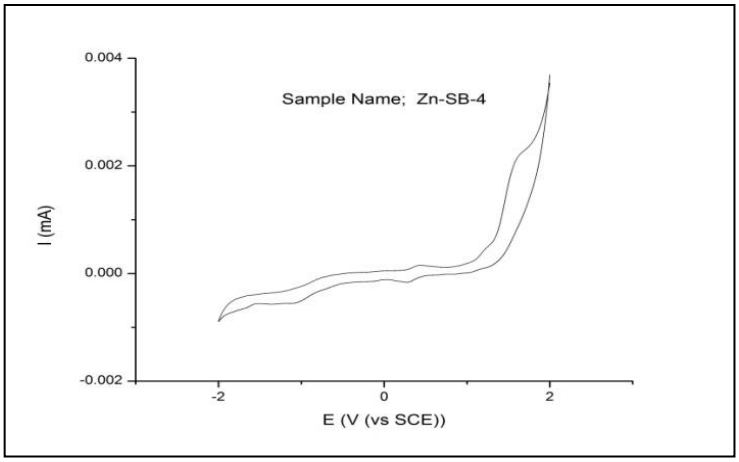

Figure 4.46: Cyclic voltametric curve of Zn-complex

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To confirm the HOMO and LUMO energy level of *Zn-complex*, the curve of cyclic voltametry of *Zn*-complex was measured as shown in figure 4.46.

- Onset oxidation potential Vs SCE is +1.46
- Endset reduction potentials Vs SCE is - 1.14
- The HOMO energy evaluated to be E_{HOMO} = - 5.96
- The LUMO energy evaluated to be E_{LUMO} = - 3.38
- The optical band gap is 2.58 eV.

5.MOLECULAR ORBITAL CACULATION

MOLECULAR OPTIMIZATION GEOMETRY

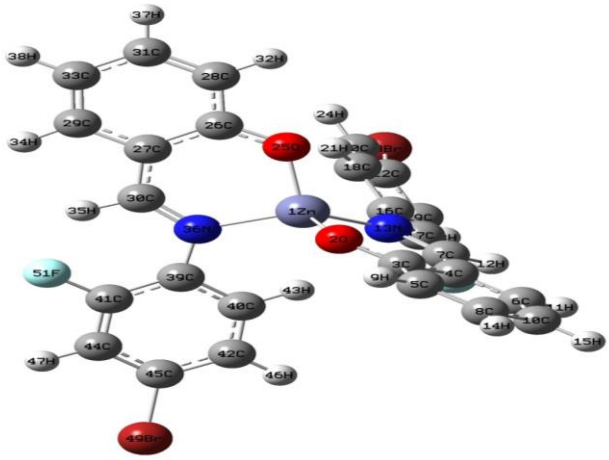
We started with geometry optimization of all ligands without symmetry constraints. Optimized structure converged to C_1 symmetrical species. The geometry was optimized in a singlet ground state by the DFT method with the PBE1function using 3-21G** basis set in gas phase.

Zn-complexes show the tetrahedral geometry of zinc (II).

In this zinc complex, the Schiff bases are show the planer structure which have less distortion in the compound.

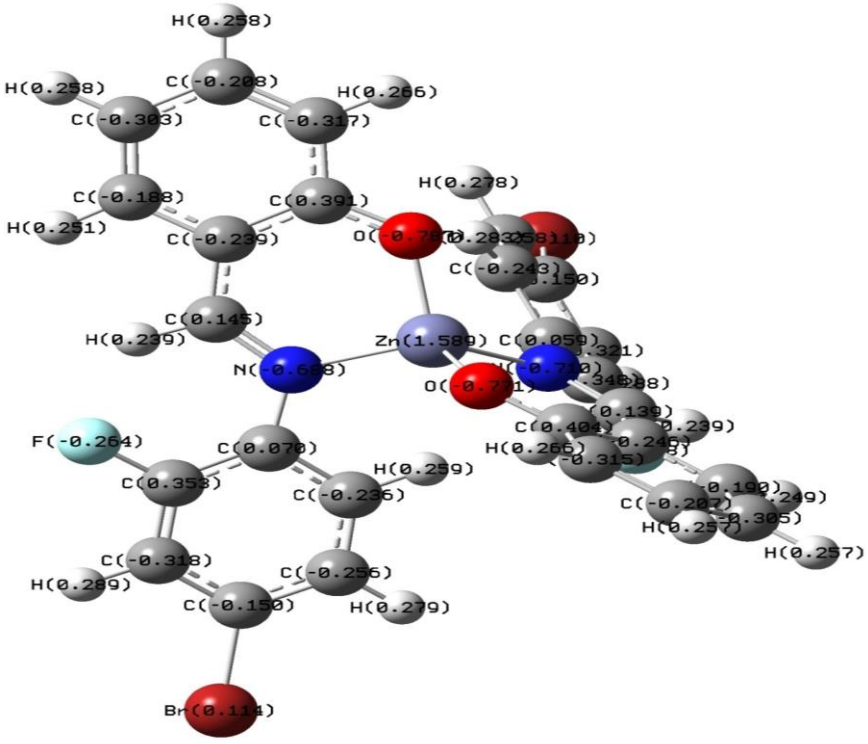
The tetrahedral geometry of zinc complex shows the effect on optical properties.

The optimized structures of Zn-complex shown below.



Optimized structure (in gas phase) of Zn-complex.

CHARGE DENSITY STRUCTURE



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Molecular orbital energy gap

In this section, the molecular orbital energy gap is determine, that is very important to study the photophysics of SB compound. The molecular orbital energy gap is calculated by E (LUMO) - E (HOMO) and energy of HOMO and LUMO of Zn-complex by TD-DFT method in gas phase.

Name of Compound	E (HOMO) (eV)	E (LUMO) (eV)	E(LUMO) - E (HOMO) (eV)
Zn-complex	-0.214	-0.075	0.139

Electronic absorption spectra in gas phase of Zn- complex

From molecular orbital energy gap, we can calculate the UV-Visible spectra of Zn-SB by TD-DFT method in gas phase.

Analysis of UV-Visible spectra of Zn-complex

The spectral values of Zn-complex is shown below:

❖ In the Zn-complex,

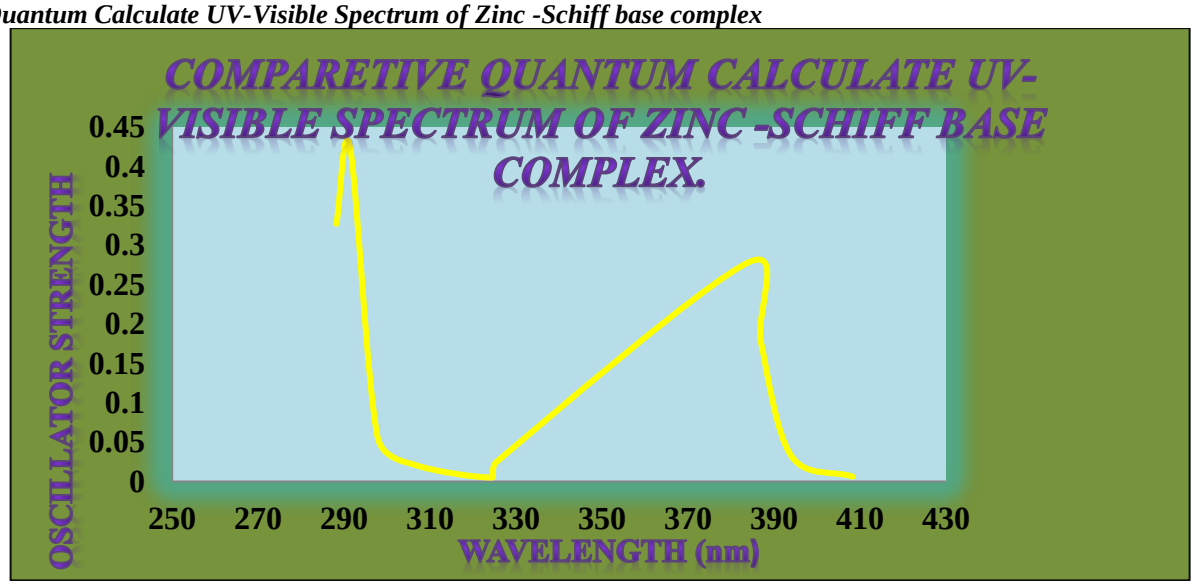
- λ_{max} = 291.40nm.
- Oscillator strength (*f*) = 0.4231.
- Excitation energy = 4.2547eV.
- From the HOMO and LUMO orbital, as shown in figure 4.80 and 4.81 respectively, the spectra is purely ligand to ligand charge transfer.

So, the TD-DFT is very useful tool for developing the HOMO and LUMO orbital and explained the type of UV-Visible spectra of Zn-SB-1 to 5 which is help to developing OLED material.

6.Excitation energy (eV), Wavelength (nm) and Oscillator strength for Zn-complex

SR.No.	Excitation energy (eV)	Wavelength (nm)	Oscillator strength
1.	3.0363	408.34	0.0061
2.	3.1468	394.00	0.0328
3.	3.2042	386.94	0.1781
4.	3.2270	384.21	0.2786
5.	3.8095	325.46	0.0249
6.	3.8210	324.48	0.0051
7.	4.0465	306.40	0.0212
8.	4.1638	297.77	0.0569
9.	**4.2547**	**291.40**	**0.4231**
10.	4.3021	288.20	0.3272

7. Quantum Calculate UV-Visible Spectrum of Zinc -Schiff base complex



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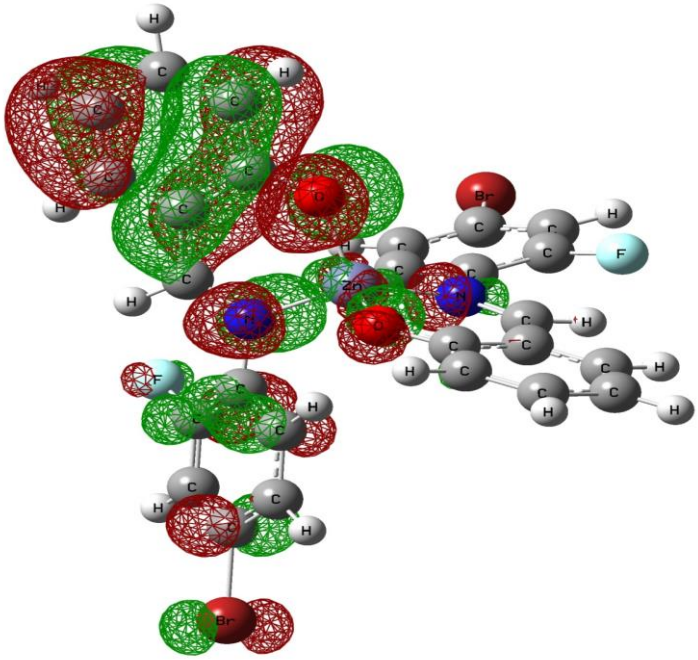
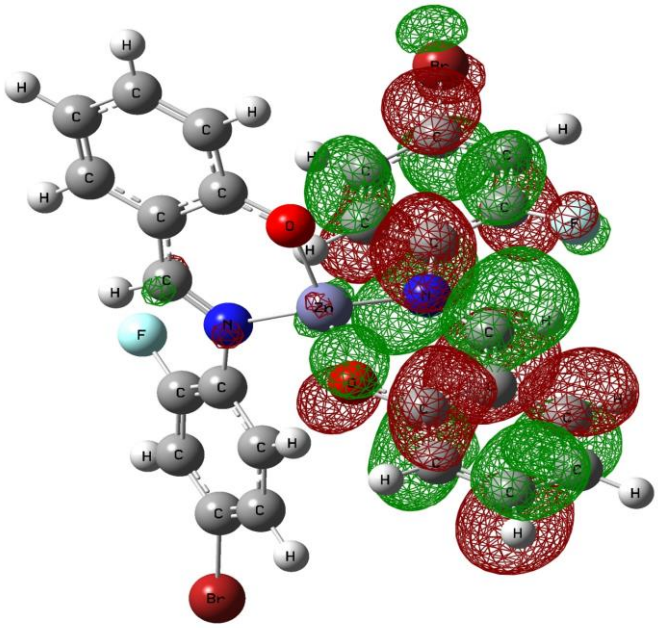
8.Molecular orbital structure of Zn-complex(HOMO):



Molecular orbital structure of Zn-complex(LUMO):



CONCLUSIONS

1. The photophysics of luminescent zinc metal ions coordinated by Schiff bases have received widespread interest in OLED.
2. Computational calculations are very good tool for Schiff bases and their zinc metal complex.
3. A computational calculation gives very important information for geometric optimization, spectroscopic properties and optical properties, molecular orbital by TD-DFT method.
4. TD-DFT gives important information of excitation spectra of synthesized Schiff bases and zinc complex like ligand to ligand type transition charged spectra.
5. These data help us to synthesize the Schiff base and their Zn complex.
6. All Schiff bases have been synthesized in nearly quantitative yield by condensation of various combinations of organic materials.
7. XRD spectra of all zinc complexes gives clear understanding of formation of crystalline structure.
8. A UV-Visible and PL spectrum gives the blue shift in zinc complex.

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9. DSC and TGA spectra of zinc complex show the good thermal behavior for preparing the OLED materials.
10. Cyclic voltametry of zinc complex show the sufficient energy band gap for preparing the blue light emitting organic phosphors.

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