Synthesis, Characterization And Photophysical 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 2-[(*E*)-[(4-bromo-2-fluorophenyl) imino) methyl) phenol compound. The structure is confirmed by IR and ^{1}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*)-(phenylimino) methyl] phenol is use as developing the OLED material.

Keyword: Schiff base, Photophysics, IR, Absorption spectra, 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.

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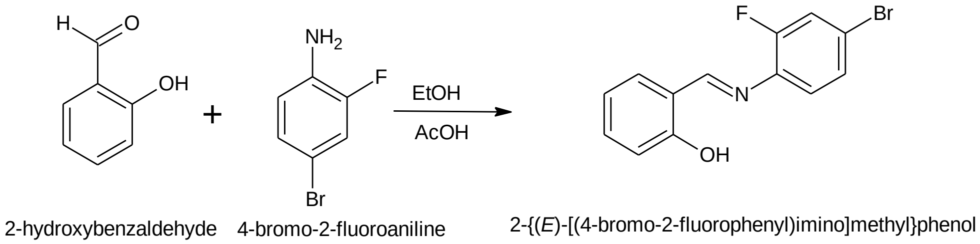
Computational chemistry is used in a number of different ways. One particularly important way is to model a molecular system prior to synthesizing the target molecule in the laboratory. Although computational models may not be precisely accurate, but they are often good enough to rule out 90% of possible 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 Schiff bases in an effort to study the luminescence properties of these compounds. Study and design of fluorescence properties of the Schiff bases might open up new path for further applications such as organic light emitting diodes (OLED), biosensors and probes. For the above mentioned reasons, the synthesis and characterization of a series of 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.

MATERIALS AND METHODS

All research chemicals were purchased from Sigma-Aldrich and S.D. Fine Chemicals India Pvt. Ltd. Reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates. UV spectra were recorded on Shimadzu 1800 UV–Visible spectrophotometer and IR spectra were recorded on Shimadzu 7600 FTIR spectrometer using KBr pellets. The ^{1}HNMR were recorded on Bruker WM-300 (at 300 MHz) using $CDCl_3$ as solvent. Chemical shifts are reported in δ ppm units with respect to TMS as internal standard. Purity of the compounds was checked on precoated TLC plates using silica gel G plates and iodine vapours as visualizing agent.

2.2.4. SYNTHESIS OF 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 Mol) 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 recrystallised from absolute ethanol to get yellowish solid product.

Yield is 80 % and M.P. is 68^{0}C

Properties and constitution of the compound

1) The compound give violet colouration with neutral ethanolic $FeCl_3$ solution and it was found to be soluble in dil. NaOH thereby indicating the presence of phenolic – OH group.
2) The analytical result of the compound indicates its molecular formula as $C_{13}H_9BrFNO$ and Formula Weight is 294.12.
3) Elemental analysis of the compound

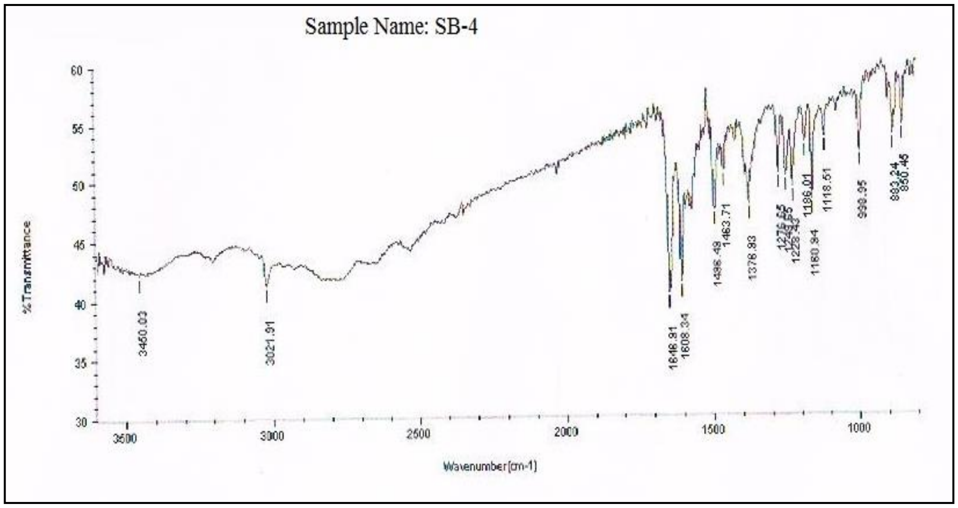
Elemental Analysis	% C	% H	% N

Found	52.98	3.00	4.62
Calculated	53.09	3.08	4.76

4) The spectral data of the compound are as follows :

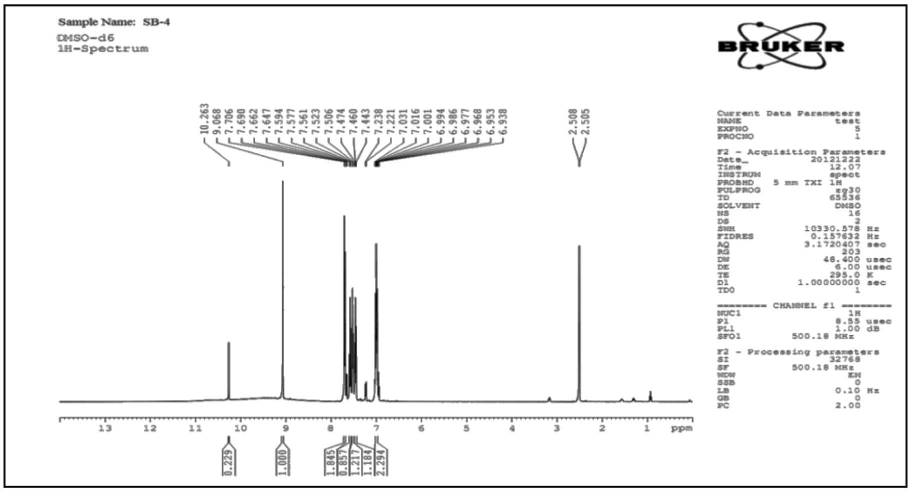
a) The IR spectrum of compound recorded in KBr was showed the following main absorption bands.

Frequency (cm^{-1})	Intensity	Correlation
3424.96	(v, b)	Strongly intramolecular H-bounded O-H stretching
1612.20	(s)	>C=N stretching



IR spectrum of compound

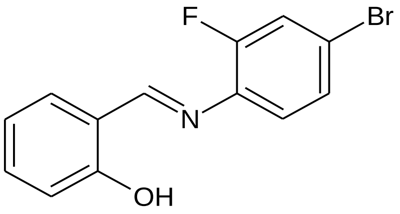
b) The PMR spectrum of the compound was recorded in DMSO with TMS as an internal standard showed the absorption peaks as listed below.



PMR spectrum of the compound

Chemical shift (δ)	Nature of Peak	No. of Protons	Types of protons
6.93-7.70	m	7H	Aromatic C-H
9.06	s	1H	Imine H
10.26	s	1H	Phenolic-OH

From the chemical properties, analytical results and spectral data the compound was assigned the structure as 2-{(*E*)-[(4-bromo-2-fluorophenyl)imino]methyl}phenol.



2-{(E)-[(4-bromo-2-fluorophenyl)imino]methyl}phenol.

. OPTICAL STUDIES OF LIGAND

Absorption spectra

The sample was dissolved in DMF and exposed to UV-Visible light to check the emission, the solutions show emission of light by naked eye. However, the compound SB-1 shows a λ_{max} at around 270 nm.

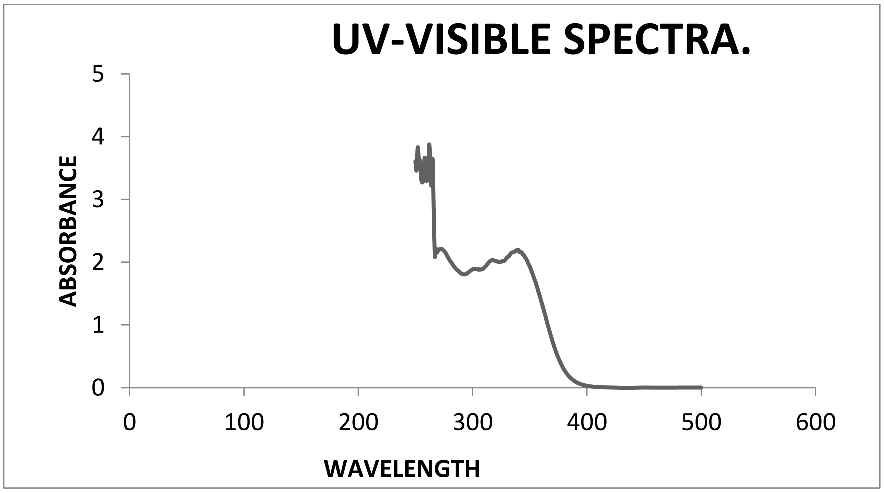
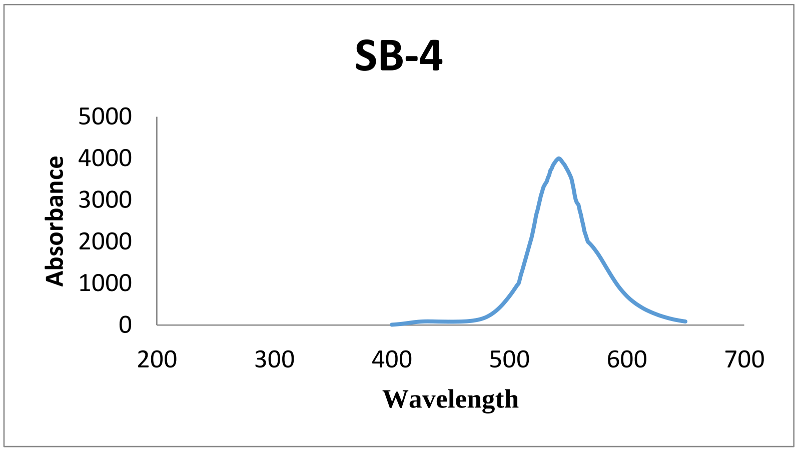


Figure 1: Absorption spectra of SB-1 in DMF.

The igands 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 SB-4(Series-4) shows a λ_{max} at around 343nm.

Photoluminescence Spectra

The excitation and photoluminescence (PL) spectra of SB-4 in solution of acetonitrile (10 mM) form is as shown in Figure 3.6.



Excitation and emission spectra

When the compound is excited at 431nm, it emits intense green light of intensity 4000 cdm^{-2} at wavelength 542nm.

. Molecular geometry optimization

We started with geometry optimization of this 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 But in this, the main dihedral angle (15C-14N-12C-1C) is 179.98^0 which is approximately match with planer dihedral angle although there is the strong distortion presented due to the electron cloud on two aromatic rings . The reason behind this planer structure is only presence of fluorine atom on 2-position of imino aromatic ring that is highly electronegative atom which attract the lone pair electron of hydroxyl group present on opposite ring so the attraction force is much greater than the repulsion force due to the electron cloud on two the aromatic rings

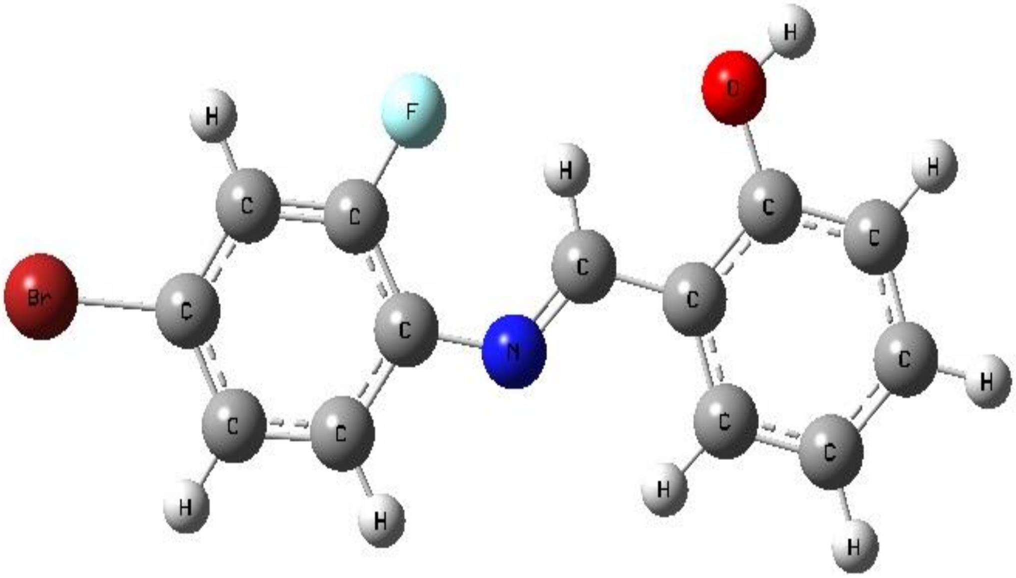


Figure: Electronic spectra

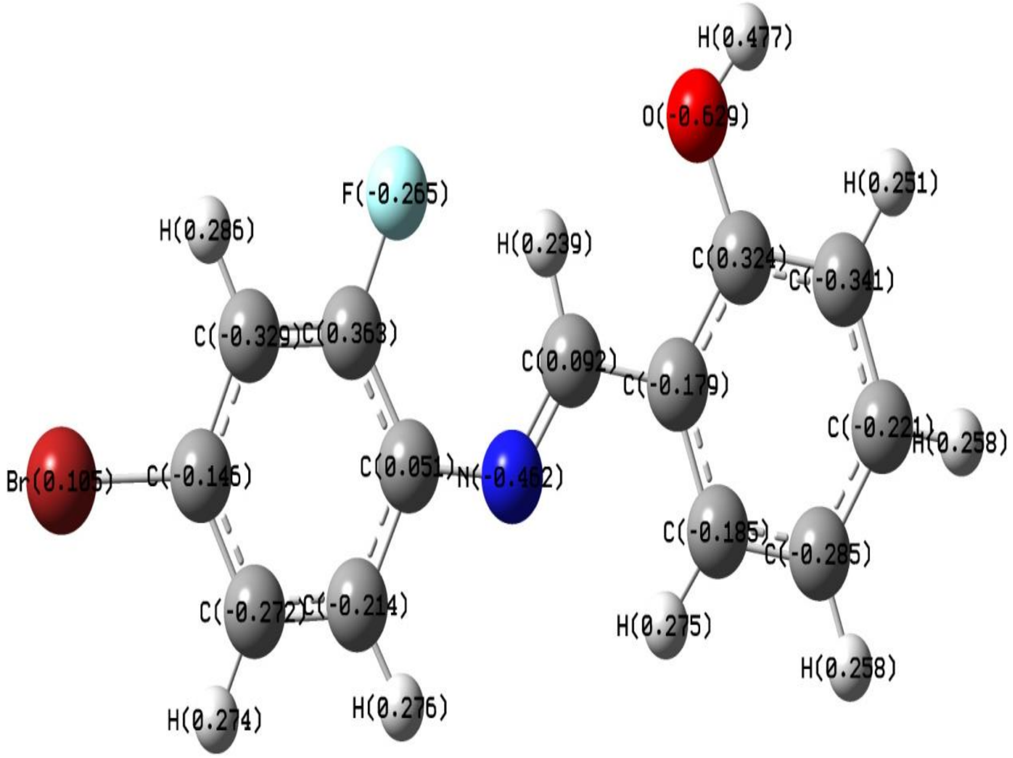


Figure: Charge Density

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 SB-1 to 5 and SB-6 to 10 shown in table 3.5 and 3.6 respectively by TD-DFT method in gas phase.

Molecular energy gap .

Name of Compound	E (HOMO) (eV)	E (LUMO) (eV)	E(LUMO) - E (HOMO) (eV)
SB-4	-0.225	-0.061	0.164

This molecular orbital energy gap gives the information about excitation energy in gas phase SB-1 molecule and that excitation energy was used for preparation of OLED material. So the TD-DFT is very useful tool for calculate the molecular orbital energy gap for developing OLED material.

absorption spectra in gas phase of ligands

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

Analysis of UV-Visible spectra

The spectral values of all compounds are shown in the table 3.7 and the graphical spectra of this data

- λ_{max} = 312.46 nm.
- Oscillator strength (*f*) = 0.8581.
- Excitation energy = 3.9680 eV.
- From the HOMO and LUMO orbital, as shown in figure 3.40 and 3.41 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 SB-1 to 5 which is help to developing OLED material.

Excitation energy (eV), Wavelength (nm) and Oscillator strength .

SB-4		
Excitation energy (eV)	Wavelength (nm)	Oscillator strength
3.7735	328.57	0.0005
3.9680	**312.46**	**0.8581**
4.4419	279.13	0.2592
4.8018	258.21	0.0049
5.1839	239.17	0.0237
5.5249	224.41	0.0678
5.5787	222.25	0.0002
5.6195	220.63	0.0000
5.6567	219.18	0.0127
5.7094	217.16	0.0000

CONCLUSION

From the present work, we concluded that, the quantum mechanical calculation is very much helpful to synthesized the organic material in respect to optimization, charge density and optical properties. So for preparation of novel molecules, firstly done quantum mechanical calculations. The synthesis procedure gives the maximum yield, for preparation of 2-[(*E*)-[(4-bromo-2-fluorophenyl]imino) methyl] phenol and the compound was confirmed by the help of chemical analysis, IR and ^{1}H-NMR spectral characterization. The 2-[(*E*)-[(4-bromo-2-fluorophenyl]imino) methyl] phenol compound shows the good optical properties with respect to reference OLED material. So this 2-[(*E*)-[(4bromo-2-fluorophynyl)imino) methyl] phenol is use as developing the OLED material.

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