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Synthesis and Optical Properties of Newly Synthesized 3,3'-((4-Methoxyphenyl) Methylene) Bis(4-Hydroxy-2H-Chromen-2-One) Molecule

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Abstract

In this report, a facile and efficient protocol has been followed for the synthesis of novel 3,3'-((4-methoxyphenyl)methylene) bis(4-hydroxy-2H-chromen-2-one) via a one pot reaction of aryl aldehydes with 4-hydroxycoumarin and in the presence of ethanol at 800C. The synthesized molecule is being further tested for structural confirmation with nuclear magnetic resonance and Fourier transform infrared spectroscopic technique. From the obtained result of ^{1}H NMR spectroscopy it has been confirmed that the synthesized molecule is stable with ten electron signal. The optical absorption measurement was carried out in order determine the optical property of the synthesized molecule such as the bandgap and molar extinction coefficient. Further the bond angles and bond lengths of the molecule was estimated theoretically using a software in order to confirm the structure with the experimental result. From over all outcomes the molecule exhibited a considerable result in order to derive the optical device application.

Keywords: *Coumarin, DFT, HOMO, LUMO, Organic Compound*

1.0 Introduction

In this technological world, the is a vast demand has been receiving from the scientific community in order to synthesis the organic molecules which is of free from the toxic reagents, alkali, acids, hazardous solvents and catalysts or to minimize the use of such materials or chemicals. This is due to the environmental and societal interest as we are aware of the impact of use of such toxic materials. In view of this, the green synthesis method is taking very important role during these decades in this method the use of toxic, alkali and hazardous solvents are reduced and skipped. Keeping all this under consideration, we have synthesized the titled compound 3,3'-((4-methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) molecule which is a fluorescent property exhibiting molecule using simple toxic chemical free technique and used for the further studies in order to investigate the optical properties of above said molecule[1,2].

Over the past few decades, extensive research has been carried out by the research community on organic and inorganic compounds treated with different groups of substituents such as aldehydes and ketones in order to develop eco-friendly biodegradable compounds to find out its wide application in cosmetics, industrial application. In this context, we have used aldehyde substituent the main benefit of using the substituent which is having a polar functional group (more reactive) will possess a stable end product and will lead to the state of better absorption and fluorescent property. The 4-hydroxycoumarin is chosed as a primary reactant molecule and it is a heterocyclic aromatic organic compound fused with the two benzene

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ring consisting of one single bonded oxygen and OH molecule respectively along with one double bond oxygen molecule. This 4-hydroxycoumarin is treated with the aryl aldehyde the double bounded oxygen is replaced with aryl aldehyde group to form the end product as a titled compound[2].

This group of organic molecules plays a vital role during the present years due to their vast application mainly in medical field, energy conversion, energy harvesting such as organic light emitting diodes, polymer light emitting diodes, photovoltaic cells, thin film transistors[3,4]. It is also important that the synthesized molecule must have a basic parameter in which it has an ability to determine or exhibit good performance in organic light emitting diode lighting systems and display technologies if they exhibit such properties it is good to use such kind of materials in display application. The solute solvent interaction also plays an important role in designing the semiconducting material. In view of this, in this manuscript we have planned to synthesis the organic compound such that it shows the good optical property, the structure of the compound is confirmed by the NMR technique and FTIR technique[3]. The optical bandgap is determined by the UV-Viss absorption spectroscopic method and the theoretical bandgap is estimated by Gaussian 09W code the results were discussed in detail in the result and discussion section.

2.0 Methods

2.1 Chemicals Used

The spectroscopic grade solvents *viz.,* ethanol, toluene, dimethyl formamide (DFM) were used to study the effect of solvent with the synthesized molecule. Along with the solvents, the 4-hydroxycoumarin and aryl aldehyde which were used to synthesis the compound. All these chemicals were procured from the local chemical supplier and are of laboratory reagent grade and are used without further purification.

2.2 Synthesis Protocol

The 4-hydroxycoumarin (3 mmol), aryl aldehyde (1 mmol) is taken in a round bottom flask then to this mixture 12 ml of acetic acid is added. All these three mixtures were heated on a burner at a temperature of 100°C, reaction takes to form a white precipitate as an end product with a yield of 78% the detailed procedure is explained in our previously published manuscript[2].

2.3 Experimental and Theoretical Technique

The synthesized organic compound was characterized to study the optical property (linear) the spectra was recorded using Perkin Lambda-35 UV-Vis spectrophotometer operating in the wavelength range 200 to 1100 nm at room temperature. The bond length and bond angles were estimated by Chem draw software. The theoretical optical absorption spectra were estimated by Gaussian 09W code keeping DFT B3LYP basis set[2]. This basis set is used because we got the considerable results with the above said basis set even though we have checked with other basis sets. The highest occupied molecular orbital and lowest unoccupied molecular orbital results were estimated using the same software with same basis set[3,4].

3.0 Results and Discussion

The synthesized molecule structure was confirmed from the NMR and FTIR spectroscopic technique. Figures 1 and 2 gives the NMR and FTIR spectra of the synthesized molecule. The NMR result confirms the synthesized molecule is stable and it has exhibited more than ten protons.

The optical absorption spectra of the 3,3'-((4-methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) molecule is presented in Figure 3. From the spectra we can infer that the optical density of the molecule is varied with changing in the solvents used as we mentioned in the chemical used section the ethanol, toluene and DMF solvents were used in the absorption spectra we found that the toluene solvent showed the maximum optical density

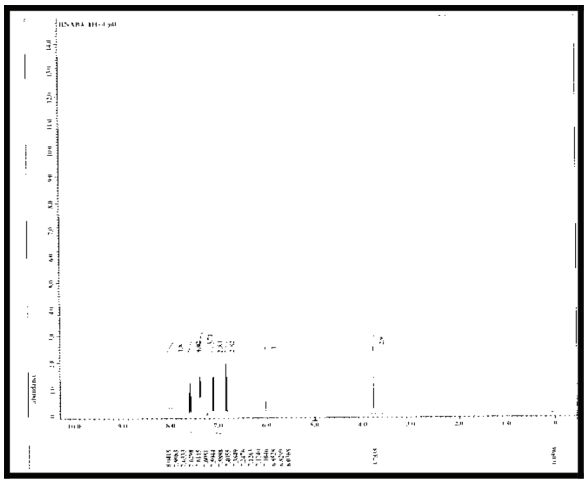


Figure 1. The NMR spectra of the studied molecule.

with respect to ethanol and DMS solvent. The DMS solvent showed low optical density value[5,6].

This variation of optical density with respect to wavelength is due to the dielectric constant and the refractive index these two parameters plays an important role in solute solvent interaction these measurements were done at the room temperature. The studied molecule interacts with the solvents having different polarities had showed intense S_o to S_1 state absorption band in the wavelength range 270 nm to 360 nm with ±2 nm experimental error. From the spectra it has been observed that the strong absorption peak is observed at 312 nm for all the solvent the intensity decreased from toluene to DMS solvent this is due to the intermolecular charge transfer and the transition assigned for this spectra as π to π* transition. And we can infer that no shift has been observed either red or blue shift[7].

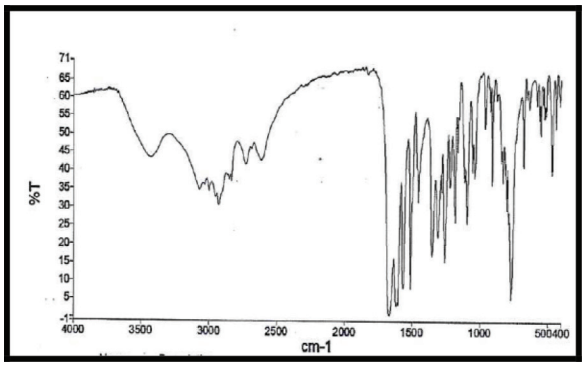


Figure 2. The FTIR spectra of the studied molecule.

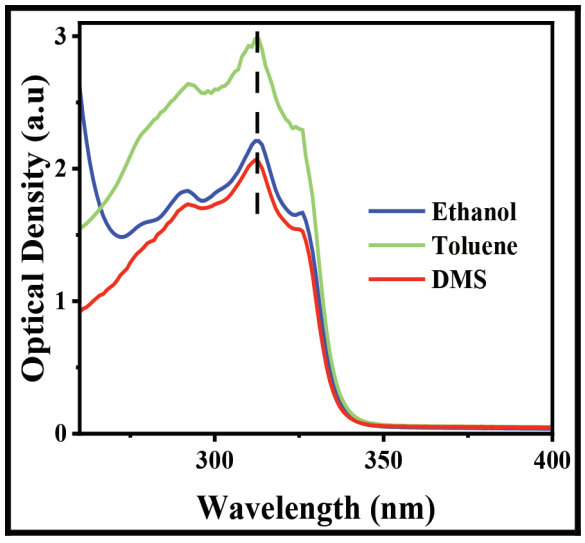


Figure 3. UV-Viss absorption spectra of studied molecule in all solvents.

The linear absorption coefficient as a function of photon energy is studied in order to estimate the optical bandgap energy of the molecule using Taue plot. The bandgap energy plot of synthesized 3,3'-((4-methoxyphenyl) methylene)bis(4-hydroxy-2H-chromen-2-one) molecule is presented in Figure 4.

The variation of bandgap energy is observed as we have changed the solvent. The solvent (ethanol, toluene, and DMF) having different dielectric constant and refractive index showed different energy bandgap values. For toluene solvent the bandgap is found to be 5.74 eV, for ethanol solvent the bandgap is found to be 5.57 eV and for ethanol solvent the bandgap energy is found to be 5.48 eV. This variation of bandgap energy is due to the solute solvent interaction and the electronic transition of electrons from different energy levels. Hence the Eg is varied from 5.48 eV to 5.74 eV thus it is found that the red shift in the bandgap was observed by increasing the solvent polarity and different solvent environments[8].

The experimentally calculated optical energy bandgap results are correlated with the theoretically estimated value for this theoretical calculation, Gaussian 09W code is used to determine the result. Initially the input file is created by using Gauss view software and the structure was drawn using the same software.

First we will optimize the molecule to get the optimized structure of the molecule to determine this the DFT B3LYP basis set is used (importance of basis set is mentioned in Section 2.3). then the optimized structure is used for the further calculations. The energy of the molecule is calculated and it is further analyzed for time dependent density functional study from that result

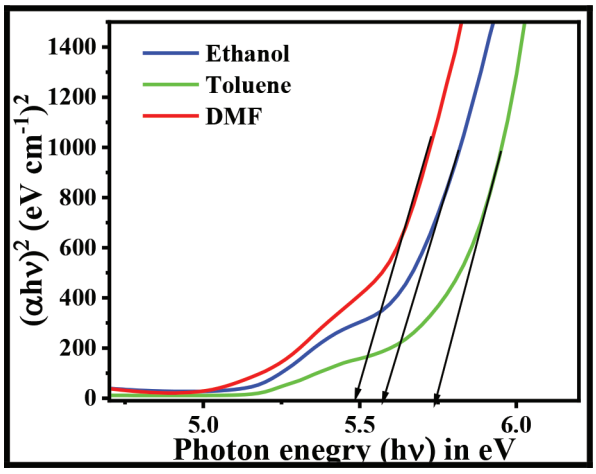


Figure 4. Tauc plot of the studied molecule in all solvents.

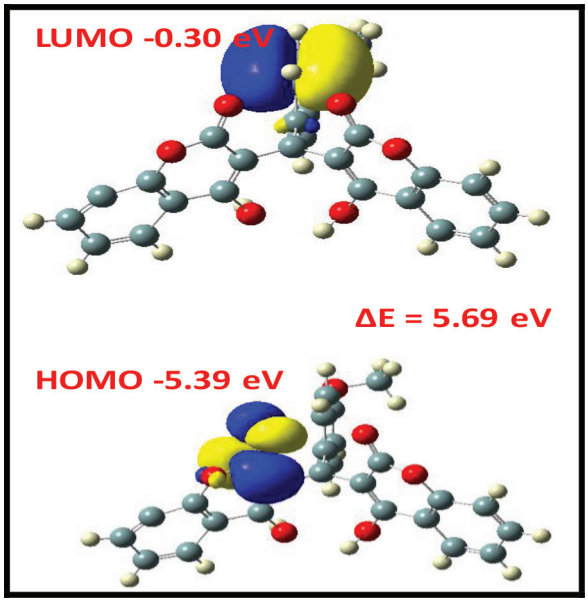


Figure 5. HOMO LUMO plot of studied molecule in ethanol solvent.

the energy bandgap value is determined. The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) was estimated from that energy result and the HOMO LUMO molecular orbital result are provided in the Figure 3. From the HOMO LUMO plots we can found that the energy bandgap value for toluene is found to be 5.69 eV with is in good agreement with the experimentally determined result in the HOMO LUMO plot the positive and negative (blue indicates positive site and yellow indicates negative site) site are localized at substituent group in HOMO region and LUMO is localized at the 4-hydroxycoumarin site[9].

We have calculated the bandgap energy value for all the three solvents we have got 5.69, 5.47 eV and 5.32 eV for toluene, ethanol and DMF solvents respectively and the HOMO LUMO plot for ethanol solvent is provided in this manuscript. From both this experimental and theoretical bandgap values we have observed wide bandgap values for the studied molecule and will be useful in semiconducting materials[6-9].

4.0 Conclusion

In this present work we have synthesized the 3,3'-((4-methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) molecule and determined the optical property of the molecule. Initially the structural confirmation was done by means of NMR and FTIR technique from these techniques we can confirm that the synthesized molecule is stable and the attachment of substitution group has been attached to the electron deficient moiety. The optical absorption studies were performed for the synthesized molecule it is clearly noticed that the absorption peak in toluene showed very strong absorption maxima at 312 nm, the absorption decreased and ended in DMS (in UV region) and is due to Intermolecular Charge Transfer (ICT) transitions, and this range also attributed to the π to π* transition. The theoretical and experimental bandgap energy was estimated from Tauc and using Gaussian 09W code. In theoretical calculation the HOMO and LUMO plots were determined from both the results obtained we can infer that the experimental and theoretical values are nearly matched to each other and varied from 5.78 to 5.32 eV and this compound is used for semiconducting material applications.

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