Synthesis and Photo Electrochemical Method for the Band gap Calculation of Novel Coumarin Derivative and its Fluorescence studies

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INTRODUCTION

Energy crisis is the main problem facing our world. The demand for energy increases as the population increases. The non-renewable energy sources are not fulfilling the energy requirements of the world and they produce environmental pollution also. As a result carbon dioxide level in the atmosphere increases. This cause global warming and acidification of oceans [1]. Hence an alternative source of energy is needed for the development of world. Solar energy is the best alternative renewable energy source since the solar radiation strikes on earth's surface in every year is much greater than all the non-renewable energy sources [7]

Organic solar cells is one of the major and interesting field of research, wherein the tuneable organic compounds with suitable modified organic compounds are used. It also has low manufacturing cost, flexibility and light weight properties [2]. Coumarin derivatives are being used in wide range of applications and the most significant one is in dye sensitised solar cell because they have good photoelectric conversion efficiency [10]. The band gap helps to find out the conducting ability of a sample. Band gap means the minimum energy required to excite an electron from the valance band to the conduction band.

Cyclic Voltammetry studies are used to find the redox properties of the compounds. Cyclic voltammetry is the most accurate method to characterise organic materials and hence to find out the band energy. The oxidation potential of organic compounds can be determined by cyclic volumetric analysis carried out by using three electrodes consisting of a platinum working electrode, a platinum, counter electrode and a calomel electrode as reference electrode with a scan rate of 25mV/sec. Cyclic voltammetry experiment was run in an acetonitrile solution containing tetra butyl ammonium hexafluorophosphate as supporting electrolyte [6]. The difference between the E_{HOMO} from CV and optical band gap from UV spectrum give E_{LUMO}. This E_{LUMO} value is compared with the values obtained from

Density functional theory (DFT) by computational studies. The capacitance of the substance is also calculated from CV. Capacitance is the ability of a system to store electrical charge when a potential difference exist between the conductors. High value of the capacitance means it store more charge.

The fluorescence spectra of the compound in (Dimethyl sulphoxide) DMSO -water mixture at different pH were determined and the optimum pH at which maximum fluorescence intensity was found out.

MATERIALS AND METHOD

Materials: All chemicals and solvents used for the synthesis are reagent grade and purchased from Alfa Aesar and Merck. Spectroscopic grade solvents were used for the spectroscopic analysis, cyclic voltammetry and fluorescence spectroscopy.

Methods

Synthesis of Ethyl-4-amino benzoate

0.01mole (1.37g) paraamino benzoic acid is dissolved in 12ml ethanol and 1ml con.H_2SO_4 is added to it. The mixture is refluxed until the reaction completes using a reflux water condenser [4].After the completion of the reaction, checked by TLC, it is cooled and poured into ice water and neutralised with sodium carbonate solution. The precipitate obtained is filtered, dried and recrystallized from alcohol and is confirmed by melting point.

Appearance: white solid, Melting point 92^0C, Yield 95%

Synthesis of 6-((4-(ethoxycarbonyl) phenyl)amino)-2-oxo-2H-chromene-3-carboxylic acid

A mixture of 0.001mole (0.269g) coumarin-3-carboxyllic acid, 0.00125mole (0.2604g) paraamino ethyl benzoate, 0.0001mole(22.4mg) palladium acetate, 0.0003mole (0.1866g) 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) and 0.003mole (0.4146g) anhydrous potassium carbonate (dried at 110^0C) in DMF were refluxed under nitrogen atmosphere [14] .The completion of the reaction was checked by TLC. After the completion of the reaction, the reaction mixture was filtered and dried under reduced pressure. The compound is purified by column chromatography using ethyl acetate and hexane as solvent. The scheme for the synthesis is shown in figure1

Appearance: Light yellow Solid, Melting point 298^0C, yield 40%.

The synthesised compound was characterised by UV Visible, ^{1}HNMR and FTIR spectroscopy. Electrochemical properties are studied by using cyclic voltammetry and the fluorescence studies at different pH were also found by using fluorescence spectroscopy.

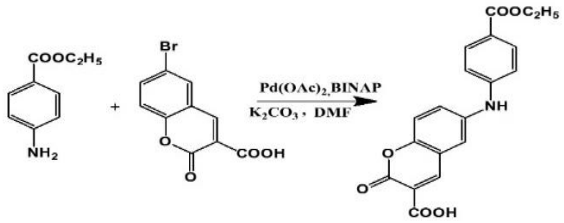

Fig.1. Scheme for the Synthesisof6-((4-(ethoxycarbonyl) phenyl)amino)-2-oxo-2H-chromene-3-carboxylic acid

RESULTS AND DISCUSSION

The UV visible spectrum of the compound, recorded ethanol, in Schimadzue UV visible spectrometer, is shown in figure 2. It shows a λ_{max} value of 333nm, 287nm and 274nm, indicates the presence of aromatic and carbonyl groups present in the compound. It has a λ_{onset} of 350nm

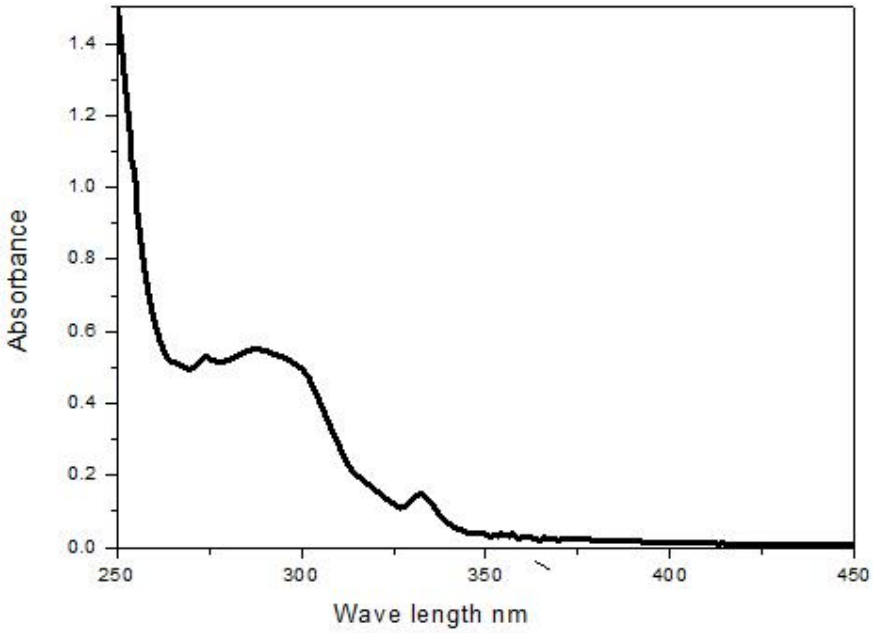

Fig.2 UV Visible spectrum

The FT-IR recorded as KBr pellets on FT IR spectrometer of the compound is shown in figure 3.The main peaks are 3400cm^{-1} (O-H stretching), 3304cm^{-1} (N-H stretching), 3051cm^{-1} (aromatic C-H stretching), 1642cm^{-1} (C=O stretching), 2998cm^{-1} (C-H stretching of CH_3), 2858cm^{-1} (C-H stretching of CH_2), 1590 cm^{-1} (C-N stretching) 1396cm^{-1}, 1504cm^{-1} (aromatic C-C or C-H stretching), 1118 cm^{-1} lactone C-O stretching.

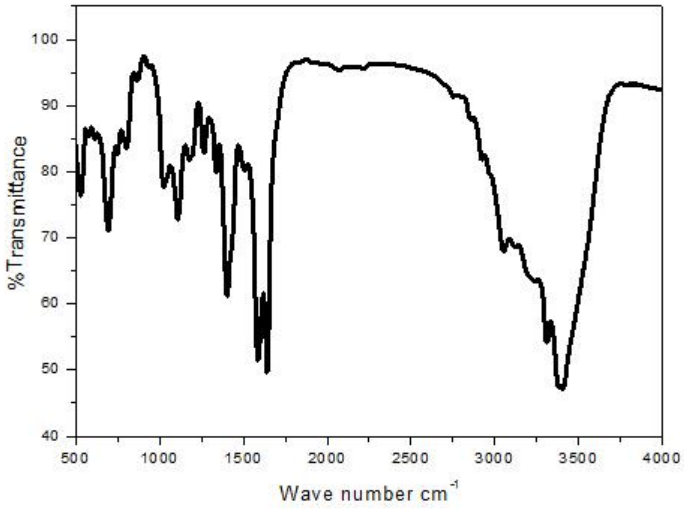

Fig. 3 FT-IR Spectrum

The ^{1}H NMR spectrum of the compound taken in Bruker spectrometer (500 MHz, $CDCl_3$) is shown as figure 4

The main peaks (δ ppm) observed in the spectrum are given below:

1.22 (3H, t) –CH_3 proton, 2.12 (2H, q)-CH_2 proton, 4.35 (N-H), the other peaks are due to the protons in the ring, 7.78 (2H, d d), 6.71 (1H, s), 7.61(2H, t), 7.33(4H, m),

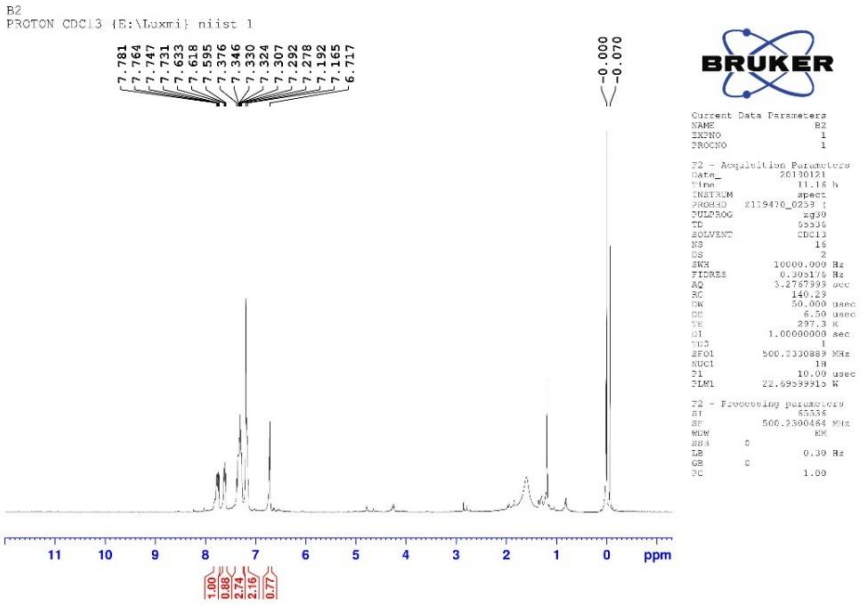

Fig.4 ^{1}HNMR Spectrum

Calculation of LUMO energy by using cyclic voltammetry and UV visible spectroscopy

The cyclic voltammetry curve of the compound is taken from Epsilon Cyclic voltammetry instrument and is shown in figure 5 and UV Visible spectrum in figure 2.The oxidation potential is determined by using platinum working electrode, platinum counter electrode and standard calomel electrode as reference electrode. Ferrocene is used as the external standard and tetrabutylammonium hexafluorophosphate in acetonitrile is used as the supporting electrolyte.

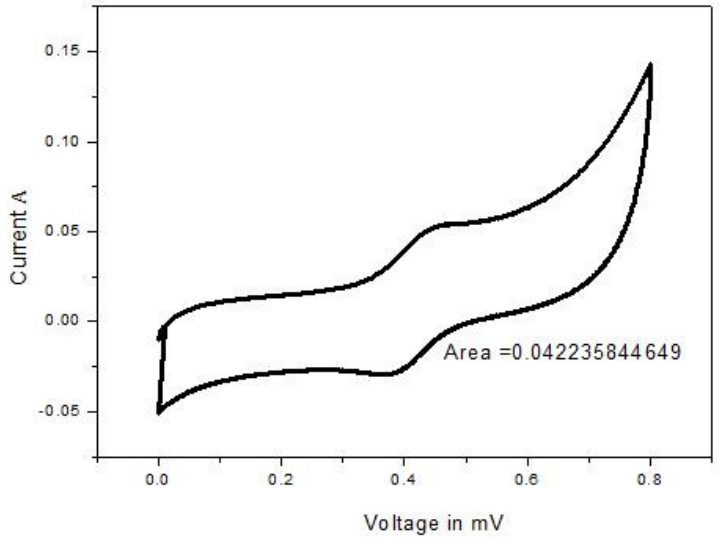

Fig.5 C-V Curve

E_{HOMO} value is obtained by using the equation E_{HOMO}= - (E_{ox}+4.8) [12]. The optical band gap is obtained from absorption spectrum by using the equation E_g =1240/λ_{onset} [9]. The E_{HOMO} and E_g are calculated according to the above equations and the values are shown in table 1.

Table.1 Calculation of E_{LUMO}

Compound	E_{ox} eV	E_{HOMO} eV	Optical Band gap $E_g$in eV	E_{LUMO} eV
B_2	0.798	-5.5980	3.1206	-2.4782

Calculation of band gap by DFT Method

The band gap of the compound is also calculated computationally by DFT method and the value obtained is compared with the experimental value. All theoretical calculations were performed using Gaussian 09 program .DFT method with hybrid B3LYP[8, 3] functional was used for geometry optimizations of the studied compounds. 6-31G (d) [13] basis set were employed for all atoms. The ground state and the lowest triplet-state geometries were fully optimized. Vibrational frequency calculations were performed at the same level of theory to prove that local minimum has been attained. The Electron distribution of HOMO/LUMO energy levels is shown in figure.6

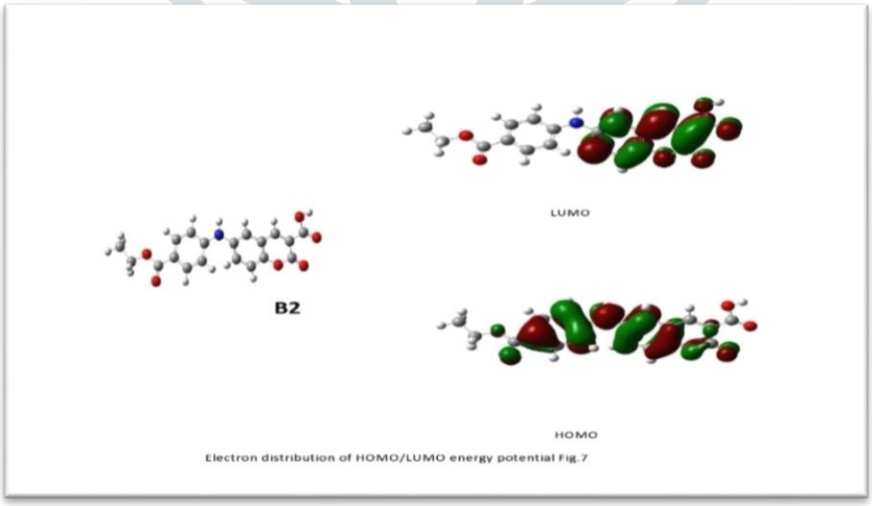

Fig.6 Electron distribution of HOMO/LUMO energy levels

The calculation of band gap is shown in table 2

Table 2 Band gap calculation

Compound	E_{HOMO}	E_{LUMO}	Band gap
B_2	-5.74133	-2.58753	3.1538013

The experimental band gap and theoretical band gap are comparable.

Calculation of capacitance

From the CV curve the capacitance of the sample is calculated using the known equation

Specific Capacitance C=Area/ 2 X voltage window X Amount of substance X Scan rate in volt/sec

$=4.2236 \text{ X } 10^{-8}/ 2 \text{ X } 0.8 \text{ X } 0.0167 \text{ X } 25 \text{ X } 10^{-3} = 0.62 \text{ X} 10^{-3} \text{F/g}$

The capacitance measurement is a method to find out the exciton behaviour of photovoltaic materials [15]. Exciton is a bound state of an electron and hole attracted by columbic force. The small value of capacitance indicates that the charge storage is less. But this can be used in small devices.

Fluorescence studies

The fluorescent spectra of the compound ($1X10^{-4}$M) in DMSO-water at different pH were determined using an Agilent technologies fluorescent spectrophotometer. The fluorescence spectra is shown in fig.7 .The intensity of fluorescence increases first with increase in pH and after a particular pH intensity decreases. The maximum intensity of fluorescence is shown at pH 9.

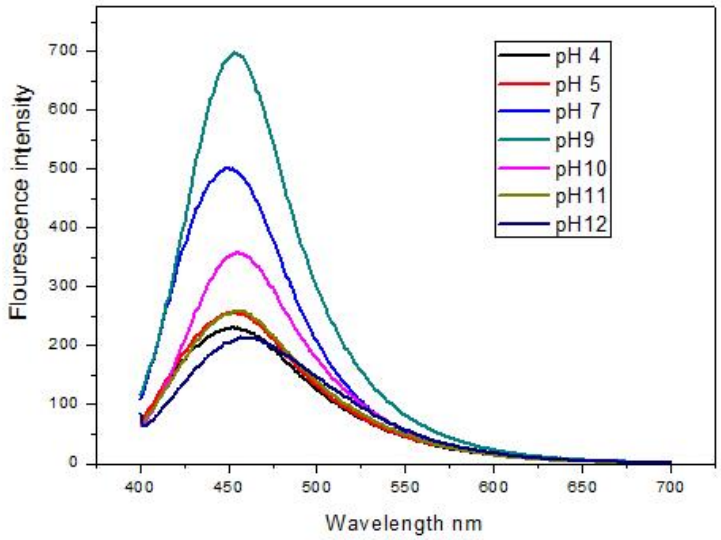

Fig.7 Fluorescence spectra at different pH

The band gap, E_{HOMO} and hence E_{LUMO} values were calculated experimentally by cyclic voltammetry and absorption spectra and are supported theoretically by DFT method. The values obtained shows that DFT method is suitable for the calculation of band gap. From the figure 2, the electron density is concentrated in Л conjugated rings in HOMO where as in LUMO electron density is concentrated in coumarin moiety. Experimentally obtained value is -2.4782eV and theoretical value is -2.58753eV.The TiO_2 has larger conduction band edge energy. Here the E_{LUMO} value is comparable to the conduction band energy of TiO_2 [5] .So this coumarin derivative can be used in dye sensitised solar cell. From cyclic voltammetry, the capacitance of the sample was determined. A small value of capacitance indicates that it can be used for the storage of charge in small devices. The fluorescence spectra at different pH shows that the intensity of fluorescence increases up to pH9, after that the intensity decreases. That is the compound shows different intensity in different pH. This feature of the compound is helpful in designing pH sensors [11]

CONCLUSION

The coumarin derivative is prepared by Buchwald Hartwig reaction and characterised by UV Visible, IR and NMR spectroscopy. From the absorption spectrum and cyclic voltammetry, the E_{LUMO} value is determined .The experimental result was supported by DFT studies. Band gap value and E_{HOMO} values indicates that the compound is appropriate to dye sensitised solar cells. The capacitance of the compound is also calculated from cyclic voltammetry. The capacitance value shows that the compound can be used in charge storage devices. From the fluorescence spectra it is observed that the intensity of fluorescence increases with increase in pH of the solution and after pH 9 the intensity decreases. This finding will useful for the design of chemical sensors for detecting the pH environment.

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