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Deep Blue Light Emission of (4,3-Oxo–HCMM) Coumarin Derivative for Organic LED Display Application

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Abstract. In the present technological world huge demand of white light emitting diodes has received much importance due to their vast applications in various sensors, lightning devices and display etc. The white light can be produced by mixing exact amount of green, blue and red light. Therefore, we made an attempt to produce a LED application making use of organic compounds. Hence, we synthesized 4-Hydroxy-3-[(4-Hydroxy-2-Oxo-2H-Chromen-3-yl) (4-Methoxyphenyl) Methyl]-2H-Chromen-2-One (4,3-Oxo–HCMM). In this present work we report, the 4,3-Oxo–HCMM possesses high color purity, good CIE chromaticity coordinate, and they would have potential organic light emitting devices (LED) application, this simple method to produce the blue light as blue component can play important role in WLED. Uv-Vis absorption spectra is used to determine the optical energy bandgap E_g , and from the photoluminescence spectra duality nature of wavelengths for 4,3-Oxo–HCMM molecule in different solvents is obtained due to solvation effect, this result shows a simple extraction of dye in different solvents which can be used to produce the desired wavelength.

INTRODUCTION

A great effort was put by many researchers in synthesis and design of new organic semiconductors (OS), while trying to find the synthesis process of low cost electronic compositions. A vast organic molecules was tested in this concern, including some p-extended coumarins. The effect of solvents should be understood in detail intending to understand and estimate the performance of electronic devices in different media. Hence, the Semiconductors (SCs) have interesting and significant optoelectronic properties for various technologies such as detectors, transistors, microelectronics, lasers¹⁻³, photovoltaics and diodes. Organic semiconductors (OSCs) have been widely used in energy conversion and medicine. For this, among various derivatives of coumarins, bis-coumarins have drawn much importance since they are well known to possess distinct photophysics, pharmacological and biological properties viz., antifungal, anti-HIV, antibiotic, antiviral, antibacterial, anticoagulant, anticlotting and anticancer and also proved several applications in different fields. Further, the biscoumarin derivatives has fascinated the scientific community due to the interesting applications of synthesized compounds (bis) such as blue and green OLEDs have met the requirements for practical applications². Therefore, we attempted to synthesis 4-Hydroxy-3-[(4-Hydroxy-2-Oxo-2H-Chromen-3-yl) (4-Methoxyphenyl) Methyl]-2H-Chromen-2-One (4,3-Oxo–HCMM) dye using acetic acid as a catalyst. Furthermore, the electronic spectra of 4,3-Oxo–HCMM derivative in solutions depending on the solvents parameters have showed excellent fluorescence properties. These derivatives also exhibit the phenomena such as inter molecular charge transfer (ICT) and excited state intermolecular proton transfer which were played a major role in view of excellent photophysical properties like large stoke shifts, significant photostability and intense luminescence⁴. However, in literature there is no considerable report on the fluorescence studies of 4,3-Oxo–HCMM bis coumarin compound. To this end, the present paper reports on the optical, fluorescence properties, Commission Internationale de l'Eclairage (CIE) and color purity of previously mentioned compound dissolved in different solvents.

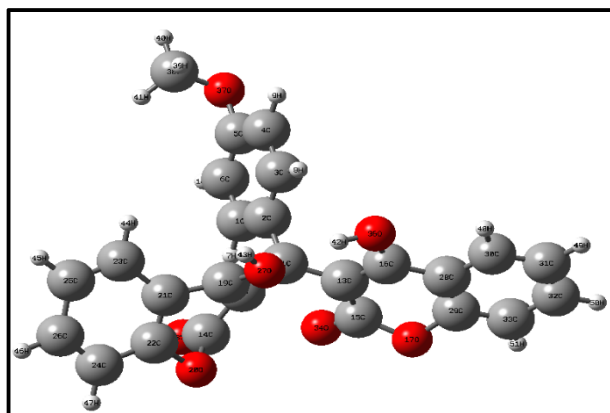
EXPERIMENTAL

Materials and Methods

All the solvents used in this present study (spectroscopic grade) such as 1,4 Dioxane, Hexadecane, Acetonitrile, Butyl acetate, Butanol and Octanol were purchased from the local chemical supplier having 99.9% purity were used without purification. The UV-Vis absorption spectra was collected from UV-1800 (Shimadzu) spectrophotometer and steady-state fluorescence experiment was carried out making use of Hitachi F-2700 Fluorescence Spectrofluorophotometer. The selected excitation wavelength is used for recording the fluorescence emission and obtained more resolution at the highest intensity. The experiment (all measurements) were carried out at 274 Kelvin with solution concentration of 10^{-6} – 10^{-7} M to overcome inner filter effect and self-aggregation effect.

Synthesis Procedure

The titledbiscoumarin derivative was synthesized by catalyst method choosing the acetic acid as a catalyst. The mixture of 4-hydroxycoumarin (4 mmol), aryl aldehydes (2mmol) and Acetic acid (10 mL) was taken in a 200mL beaker and refluxed for 2-3 hrs. By using thin layer chromatography (TLC) (Eluent: n-hexane and Ethyl acetate) the progress of the reaction was monitored. The vanishing of solvent in vacuum afforded the crude product which was recrystallized from ethanol to get 4-Hydroxy-3-[(4-Hydroxy-2-Oxo-2H-Chromen-3-yl) (4-Methoxyphenyl) Methyl]-2H-Chromen-2-One biscoumarins. The optimized structure of synthesized4,3-Oxo–HCMM is presented in Fig. 1.



to increase in the polarity of the solvents indicates $\pi \rightarrow \pi^*$ transitions are involved and also suggesting that the involvement of photo induced intermolecular charge transfer (ICT) state, apart from solvent polarity, the hydrogen bonding effect also plays a major role for the shift of emission bands. And also the observed phenomenon i.e., duality nature of wavelengths in 4,3-Oxo-HCMM molecule in different solvents is due to solvation effect, this results shows a simple extraction of dye in different solvents can be used to produce the desired wavelength⁴.

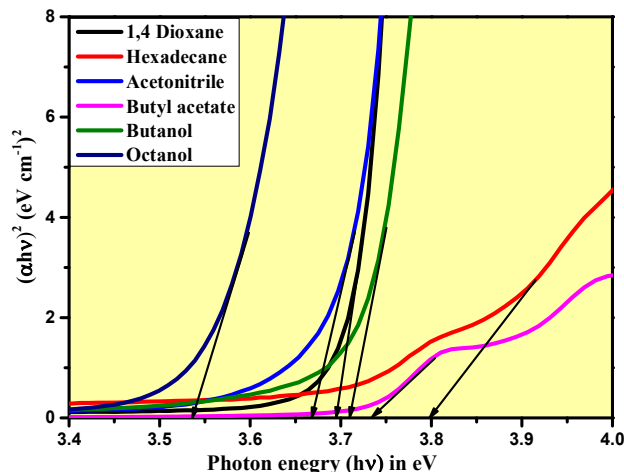


FIGURE3. Typical plot of $(\alpha h\nu)^2$ versus Photon energy for direct band gap measurements.

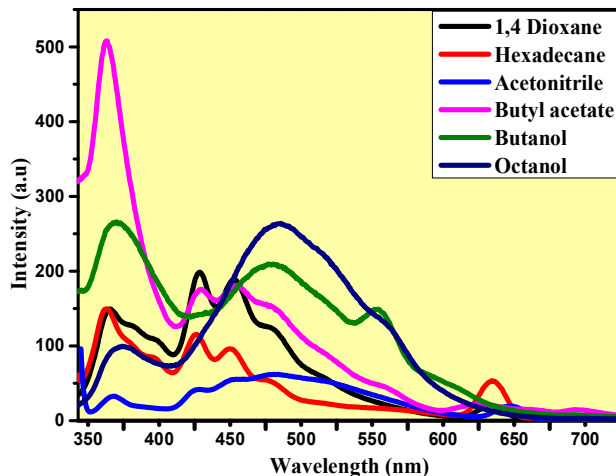


FIGURE4. The photoluminescence emission spectra 4,3-Oxo-HCMM.

In order to determine the color coordinate and color purity of 4,3-Oxo-HCMM derivative, The Commission Internationale de l'Éclairage (CIE) color coordinate values has been determined by using Osram Sylvania CIE coordinates software⁵. It is clear from the Fig. 5 that the CIE coordinates lies in deep blue region for 1,4-Dioxane, Hexadecane, Acetonitrile, Butyl acetate, Butanol and Octanol the corresponding x and y values are tabulated in Table 1. The color purity is an important property to estimate the possibility of the newly synthesized 4,3-Oxo-HCMM derivative for OLEDs and display applications⁶. The color purity of the 4,3-Oxo-HCMM is calculated using the following equation used below.

Solvents	λ_a (nm)	λ_e (nm)	Band gap E_g (eV)	CIE Coordinates		Color purity (%)
				x	y	
1,4-Dioxane	312	404	3.69	0.1778	0.1127	80.83
Hexadecane	280	339	3.80	0.2638	0.1808	30.34
Acetonitrile	310	455	3.66	0.1977	0.2237	57.25
Butyl acetate	310	388	3.73	0.1722	0.1257	79.05
Butanol	306	458	3.71	0.1761	0.2089	67.99
Octanol	308	458	3.53	0.1717	0.2219	66.11

Table 1. CIE color coordinates with color purity of 4,3-Oxo-HCMM in studied solvents.

Where, (X, Y) are CIE chromaticity coordinate values of studied compound, (X_a, Y_a) is the color coordinate of white illumination and (X_b, Y_b) is the CIE coordinate of the dominant emission wavelength. In this report the $(X_a, Y_a) = (0.310, 0.316)$, $(X_b, Y_b) = (0.14, 0.08)$, color purity and the (X, Y) values are presented in Table 1. From Table 1 it shows the color purity % at excitation wavelength of 320 nm for studied solvents.

$$\text{Color purity} = \frac{\sqrt{(X - X_a)^2 + (Y - Y_a)^2}}{\sqrt{(X_b - X_a)^2 + (Y_b - Y_a)^2}} \times 100\%$$

However, this results revealed that the observed the color coordinates of 4,3-Oxo-HCMM slightly vary with different solvents due to decrease in intensity as well as the area of the photoluminescence emission. Thus, the 4,3-Oxo-HCMM possesses high color purity and good CIE chromaticity coordinate also they would have potential

application organic light emitting devices, this simple method to produce the blue light as blue component can play important role. The calculated chromaticity coordinates for 4,3-Oxo-HCMM in chloroform are near to standard chromaticity (NTSC) for excellent blue color and thus are promising blue producers for WLED application⁷.

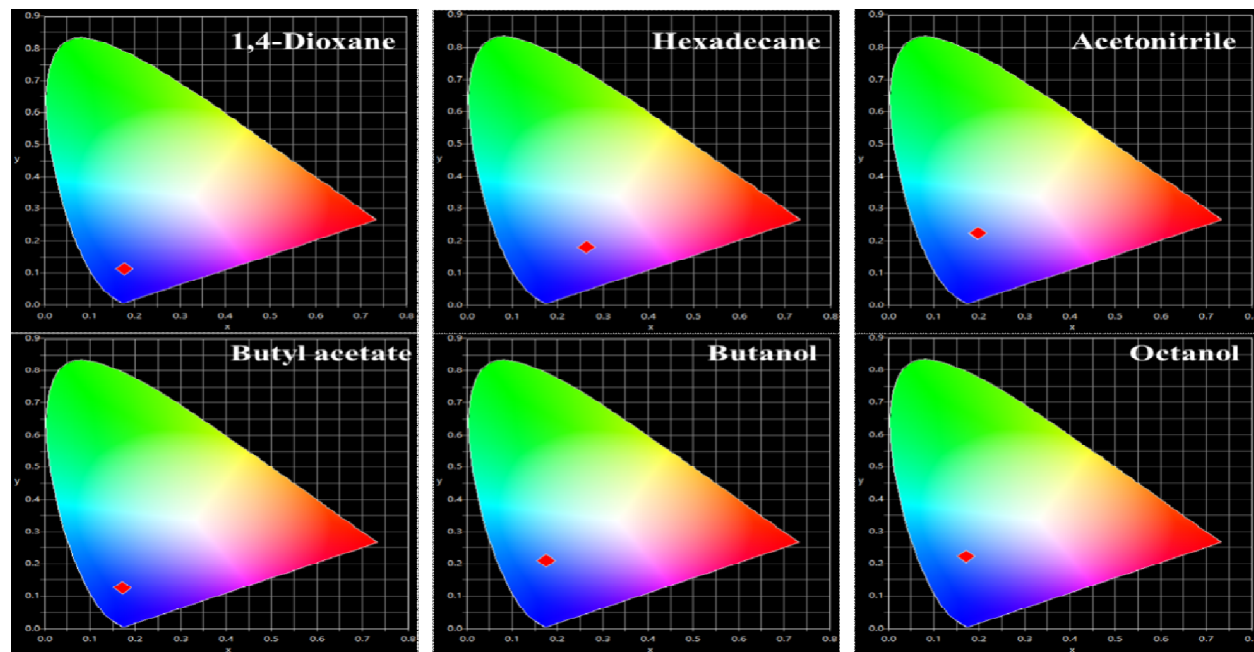


FIGURE 3. CIE Plots of 4,3-Oxo-HCMM in studied solvents.

CONCLUSION

The titled derivative 4-Hydroxy-3-[(4-Hydroxy-2-Oxo-2H-Chromen-3-yl) (4-Methoxyphenyl) Methyl]-2H-Chromen-2-One has been synthesized. Experimental bandgap energy E_g of the titled derivative was calculated using UV-Vis absorption spectra, from this we may conclude that the E_g is one of the important parameter for fabricating optoelectronic devices. The photoluminescence emission spectra showed a slight bathochromic shift (red shift) in the studied solvents, these red shifts are probably due to increase in the polarity of the solvents and suggesting that the involvement of photo induced intermolecular charge transfer (ICT) state, and those duality nature of wavelengths in 4,3-Oxo-HCMM molecule in different solvents is due to solvation effect, this results shows a simple extraction of dye in different solvents can be used to produce the desired wavelength. The 4,3-Oxo-HCMM possesses high color purity, good CIE chromaticity coordinate and they would have potential application in organic light emitting devices, this simple method is used to produce the blue light as blue component and can play important role. The calculated chromaticity coordinates for 4,3-Oxo-HCMM in 1,4-Dioxane are near to standard chromaticity for excellent blue color and thus are promising blue producers for WLED application.

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