

A DETAILED STUDY ON THE OPTICAL PROPERTIES OF 3-BENZOYL-7-HYDROXY COUMARIN COMPOUND IN DIFFERENT SOLVENTS AND CONCENTRATIONS

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A coumarin-derived compound, 3-benzoyl-7-hydroxy coumarin (BHYC), is synthesized to determine its optoelectronic properties, including absorbance band edge, optical band gap, transmittance, refractive index, electrical susceptibility, volume-surface energy loss functions and optical/electrical conductance parameters. The absorbance spectra of BHYC in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) solvents exhibit maximum peaks at 350 and 353 nm, respectively, in the near-ultraviolet region. The absorbance band edge values of BHYC in DMF and DMSO are 2.526 and 2.500 eV, respectively. The optical band gap of BHYC varies from 2.560 to 2.408 eV with increasing molarity. In contrast, the refractive index of BHYC increases from 2.47 to 2.95 with changing molarity. The obtained results show that 3-benzoyl-7-hydroxy coumarin exhibits a semiconductor behavior and it may be an important candidate for many optoelectronic devices, such as diodes, photodiodes and sensors.

Keywords: coumarin derivative; synthesis and characterization; optoelectronic parameters; dispersion parameters; solvent and concentration effects

ЕДНО ПОДРОБНО ИСПИТУВАЊЕ НА ОПТИЧКИТЕ СВОЈСТВА НА 3-БЕНЗОИЛ-7-ХИДРОКСИ КУМАРИН ВО РАЗЛИЧНИ РАСТВОРУВАЧИ И КОНЦЕНТРАЦИИ

Извршена е синтеза на дериват на кумарин, 3-бензоил-7-хидрокси кумарин (ВНУС), со цел да се определат оптичкоелектронските својства, вклучувајќи ги границата на апсорпционата лента, оптичкиот процеп на лентата, трансмитанцата, рефрактивниот индекс, електричната чувствителност, функциите на губењето на енергијата на волуменска површина и оптичките/електричните параметри на кондукција. Апсорпционите спектри на ВНУС во диметилформаид (DMF) и во диметилсулфоксид (DMSO) манифестираат максимуми, соодветно, на 350 и 353 nm, во блиската ултравиолетова област. Вредностите на граничните апсорпциски ленти на ВНУС во DMF и во DMSO, соодветно, се 2,526 и 2,500 eV. Оптичкиот процеп на лентата варира од 2,560 до 2,408 eV со зголемување на моларноста. Наспроти тоа, рефрактивниот индекс со промена на моларноста расте од 2,47 до 2,95. Добиените резултати покажуваат дека 3-бензоил-7-хидрокси кумарин манифестира полупроводнички својства и може да биде важен кандидат за оптоелектронски инструменти, како што се диоди, фотодиоди и сензори.

Клучни зборови: дериват на кумарин; синтеза и карактеризација; оптоелектронски параметри; параметри на дисперзија; влијание на растворувачи и на концентрација

1. INTRODUCTION

Natural and synthetic coumarins are important classes of oxygenated heterocyclic compounds [1]. These heterocyclic molecules of both natural and synthetic origin have attracted considerable attention from organic and medicinal chemists for many years due to their unique features. The applications of these molecules vary in a wide range depending on their biological, physical and chemical properties. These compounds show significant biological or pharmacological activities, including antibiotic, antibacterial, antitumor, antiviral, anticoagulants, antipsoriatic, anti-HIV, anti-inflammatory and enzyme inhibitor properties [1–6]. In addition, these kinds of molecules have intensively π -conjugated bond systems like other aromatic heterocycles. This feature makes them important in terms of their photophysical and spectroscopical properties [7]. Based on these compounds, some applications, such as organic light-emitting diodes, electroluminescence and fluorescence materials, nonlinear optical materials, photoalignment of liquid crystalline molecules, charge-transfer agents, two photon absorption materials, organic-inorganic hybrid materials and laser dyes, have been realized in various industrial and technological platforms [8–16].

The π -electron system present in the structure of these molecules also causes them to be active in the UV-visible absorption range [7]. Some studies have determined the optical properties of coumarins based on their UV sensitivities [17–22]. However, sufficient studies on the optical properties of coumarins, such as absorbance band edge, optical band gap, transmittance, refractive index, electrical susceptibility, volume-surface energy loss functions and optical/electrical conductance parameters, in various solvents and concentrations are not yet available in the literature according our current knowledge. In light of this literature deficiency, we synthesize a coumarin-derived compound, 3-benzoyl-7-hydroxy coumarin (BHYC), to determine its optoelectronic properties. While there are a few papers on the synthesis of 3-benzoyl-7-hydroxy coumarin, none of them are related to its optical properties. For example, in one study reported on this compound, Raju and co-workers synthesized a series of 3,4- and 3,6-disubstituted chromenones (coumarins), including 3-benzoyl-7-hydroxy coumarin, and reported their α -glucosidase inhibitory antihyperglycemic activities [1]. In another study, Secci *et al.* synthesized sev-

eral coumarin derivatives substituted with carbonyl, acyl and carboxyhydrazido groups at the 3-position of molecules (including 3-benzoyl-7-hydroxy coumarin), which were tested in vitro for their human monoamine oxidase A and B (hMAO-A and hMAO-B) inhibitory activity [23]. In another study, Heravi and co-workers developed a new strategy for the synthesis of 3-acyl coumarins with various functional groups and substitutions, including also 3-benzoyl-7-hydroxy coumarin using a mesoporous molecular sieve, MCM-41, as a novel and efficient catalyst [24]. However, they only reported the synthesis of coumarins and did not investigate any of their properties.

As discussed above, there are a number of studies involving the synthesis, characterization and investigation of various properties of many coumarin derivatives with different functional groups, with the exception of 3-benzoyl-7-hydroxy coumarin. However, the majority of these studies focused on fluorescence emissions or biological activities. Therefore, we aim to synthesize a coumarin-derived compound, BHYC, with intensive conjugated π -electrons to investigate its optoelectronic parameters in various solvents and concentration systems. The obtained results show that 3-benzoyl-7-hydroxy coumarin exhibits a semiconductor behavior and it may be an important candidate for many optoelectronic devices, such as diodes, photodiodes and sensors.

2. EXPERIMENTAL

2.1. Instrumental techniques

A Bruker 300 MHz Ultrashield TM instrument was used to characterize BHYC by nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy at room temperature using a deuterated DMSO solvent and tetramethylsilane (TMS) as an internal standard. The infrared characterization was obtained with a Perkin Elmer Spectrum 100 FTIR spectrometer with an ATR accessory. The UV measurements of the BHYC solutions were recorded with a Shimadzu UV-1800 spectrophotometer.

2.2. Materials

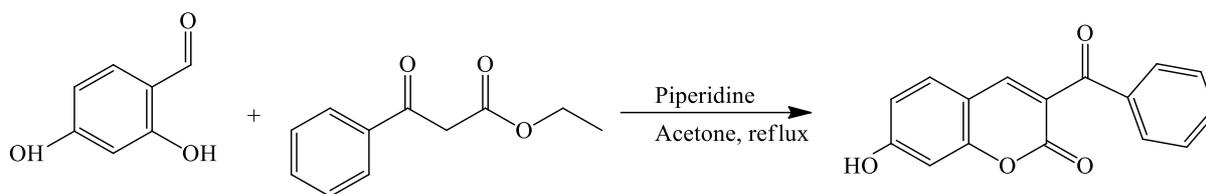
As analytical reagents, 2,4-dihydroxybenzaldehyde, ethyl benzoylacetate and piperidine were purchased from Sigma-Aldrich. The used solvents, *N,N*-dimethylformamide (DMF), dime-

thyl sulfoxide (DMSO), acetone, methanol and ethanol were also obtained from Sigma-Aldrich.

2.3. Synthesis of 3-benzoyl-7-hydroxy coumarin (BHYC)

In general, 3-substituted carbonyl coumarins may be synthesized by the Knoevenagel condensation of salicylaldehydes and β -ketoesters with catalytic amounts of piperidine in the presence of various solvents, such as acetonitrile, ethanol and so on. We herein synthesized the 3-benzoyl-7-hydroxy coumarin compound according to the

pathway reported in previous studies [1, 23]. Briefly, BHYC was synthesized as follows: 2,4-dihydroxybenzaldehyde (2.762 g), ethyl benzoylacetate (3.844 g), three drops of piperidine and 50 ml of acetone were dissolved in a three-necked reaction balloon. Then, the mixture was refluxed and stirred on a magnetic stirrer for 2 h. After this, the organic raw mixture was precipitated in excess methanol and the rose-colored product (BHYC) was separated and dried. Finally, it was purified by recrystallization twice in ethanol. The synthesis of BHYC is shown in Scheme 1.



Scheme 1. Synthesis of BHYC

2.4. Preparation of BHYC solutions

To determine the effect of concentration on the optical parameters of BHYC, a series of BHYC/DMSO solutions at different concentrations of 10, 15, 58, 186 and 270 μM was prepared. In addition, to determine the solvent effect on the optical parameters, the BHYC solutions in DMSO and DMF solvents were kept at 12 μM and the optical measurements for both solvent systems were performed. The required amounts of BHYC for all concentrations were obtained with an AND-GR-200 Series analytical balance.

3. RESULTS AND DISCUSSION

The FTIR spectrum of BHYC is illustrated in Figure 1, where the vibration at 3171 cm^{-1} is characteristic for $-\text{OH}$ stretching. The absorption bands at $3062\text{--}2930$ and $2900\text{--}2825\text{ cm}^{-1}$ were attributed to aromatic and aliphatic C-H stretching, respectively. Stretching for benzoyl and lactone carbonyls was observed at frequencies of 1710 and 1682 cm^{-1} , respectively. The absorptions at 1650 and 1609 cm^{-1} were recorded for the lactone $\text{C}=\text{C}$ stretching in the coumarin group and the aromatic $\text{C}=\text{C}$ stretching vibrations, respectively.

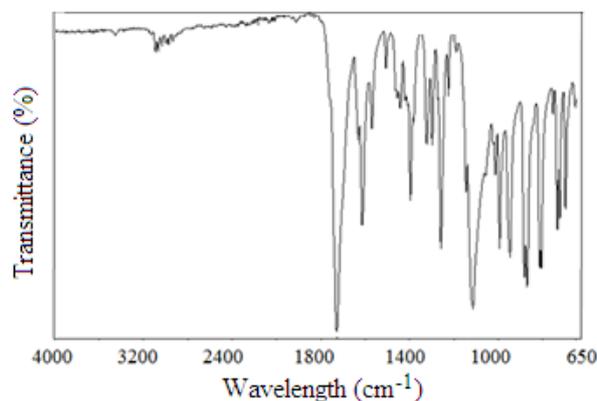


Fig. 1. FTIR spectrum of BHYC

The spectral characterization of BHYC was also performed by $^1\text{H-NMR}$ spectroscopy. The $^1\text{H-NMR}$ spectrum of BHYC is shown in Fig. 2. The singlet signal observed at 10.98 ppm is attributed to the O-H proton in the coumarin ring. The signal at 8.35 ppm is attributed to the coumarin lactone $=\text{CH}-$ proton. The chemical shifts observed between 7.88 and 6.79 ppm are characteristic for aromatic $=\text{CH}-$ protons in benzoyl and coumarin rings, respectively. Another two resonances at 3.3 and 2.5 ppm are also reasoned from the DMSO solvent.

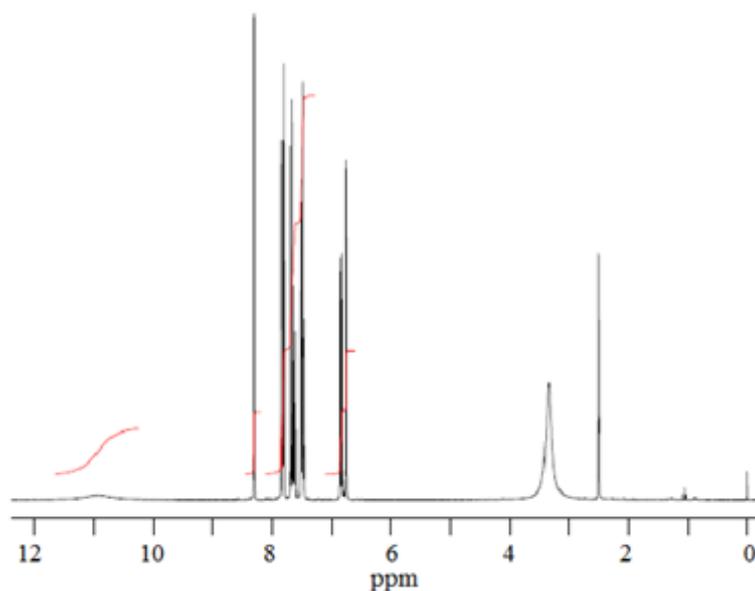


Fig. 2. ¹H-NMR spectrum of BHYC

3.1. UV spectral characteristics and absorbance band edges of BHYC solutions

Generally, an absorbance spectrum gives the absorption properties of a material and is significant to obtain its crucial optical parameters. We obtained the absorbance and transmittance spectra of the BHYC solutions for various concentrations of 10, 15, 58, 186 and 270 μM in DMSO solvent and also for various solvents, such as DMF and DMSO, at a fixed concentration of 12 μM .

Figures 3(a,b) indicate the absorbance and transmittance spectra of the BHYC solutions for 10, 15, 58, 186 and 270 μM molarities, respectively. As seen in Figs. 3(a,b), the transmittance values of the BHYC solutions decrease with increasing molarity, while the absorbance values of the BHYC solutions increase with increasing molarity. The absorbance and transmittance spectra of the BHYC are not observed at higher molarities than $\sim 186 \mu\text{M}$. The obtained results show that the UV spectra of the BHYC solutions change significantly with molarity.

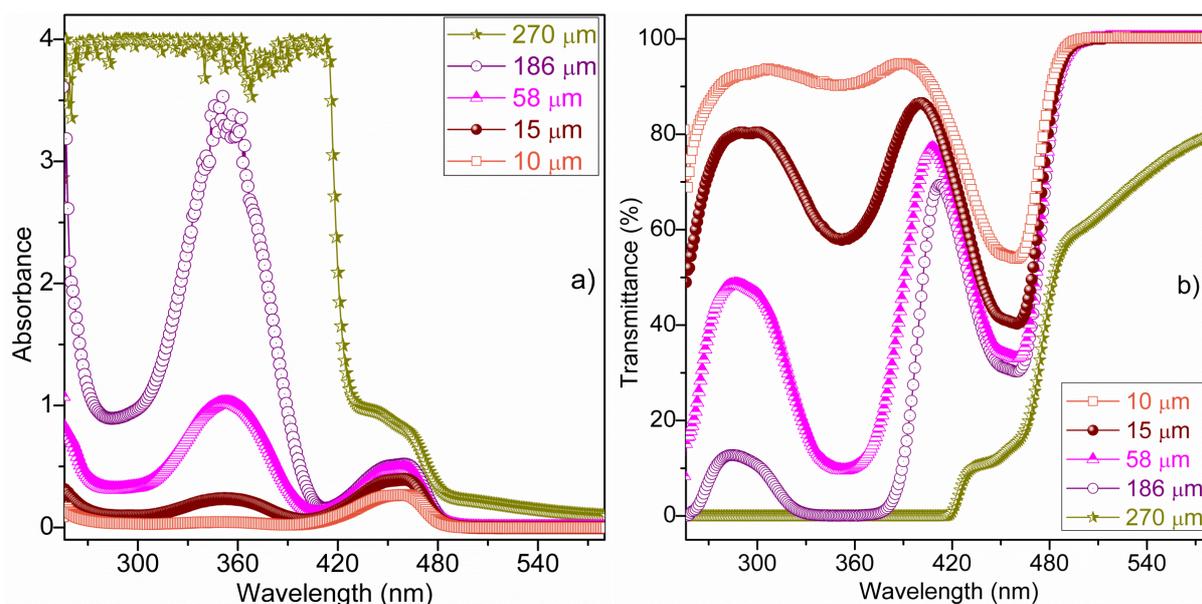


Fig. 3. a) Absorbance and b) transmittance spectra of BHYC solutions for 10, 15, 58, 186 and 270 μM molarities

We then investigated the UV spectra of BHYC for the DMF and DMSO solvents. Figures 4(a,b) show the absorbance and transmittance spectra of BHYC for the DMF and DMSO solvents, respectively. As seen in Fig. 4a, the absorbance spectra of the BHYC for DMF exhibit the maximum peak at 350 nm, which is in the near-ultraviolet (NUV) region and exhibits a small peak at 456 nm, which is in the visible (V) region. In contrast, the transmittance spectra of BHYC for DMF exhibit a medium peak at 281 nm, which is in the NUV region and exhibits a high peak at 414 nm, which is in the V region. As seen in Figure 4b,

the absorbance spectra of BHYC for DMSO exhibit a maximum peak in the NUV region (at 353 nm) and a medium peak in the V region (at 460 nm). However, the transmittance spectra of BHYC for DMSO exhibit a medium peak in the NUV region (at 287 nm) and a high peak in the V region (at 408 nm). These results suggest that the curves of the UV spectra for DMF and DMSO are similar, whereas their peak positions, i.e., wavelengths, are different from each other. The DMF and DMSO solvents have dramatic effects on the UV spectra of BHYC.

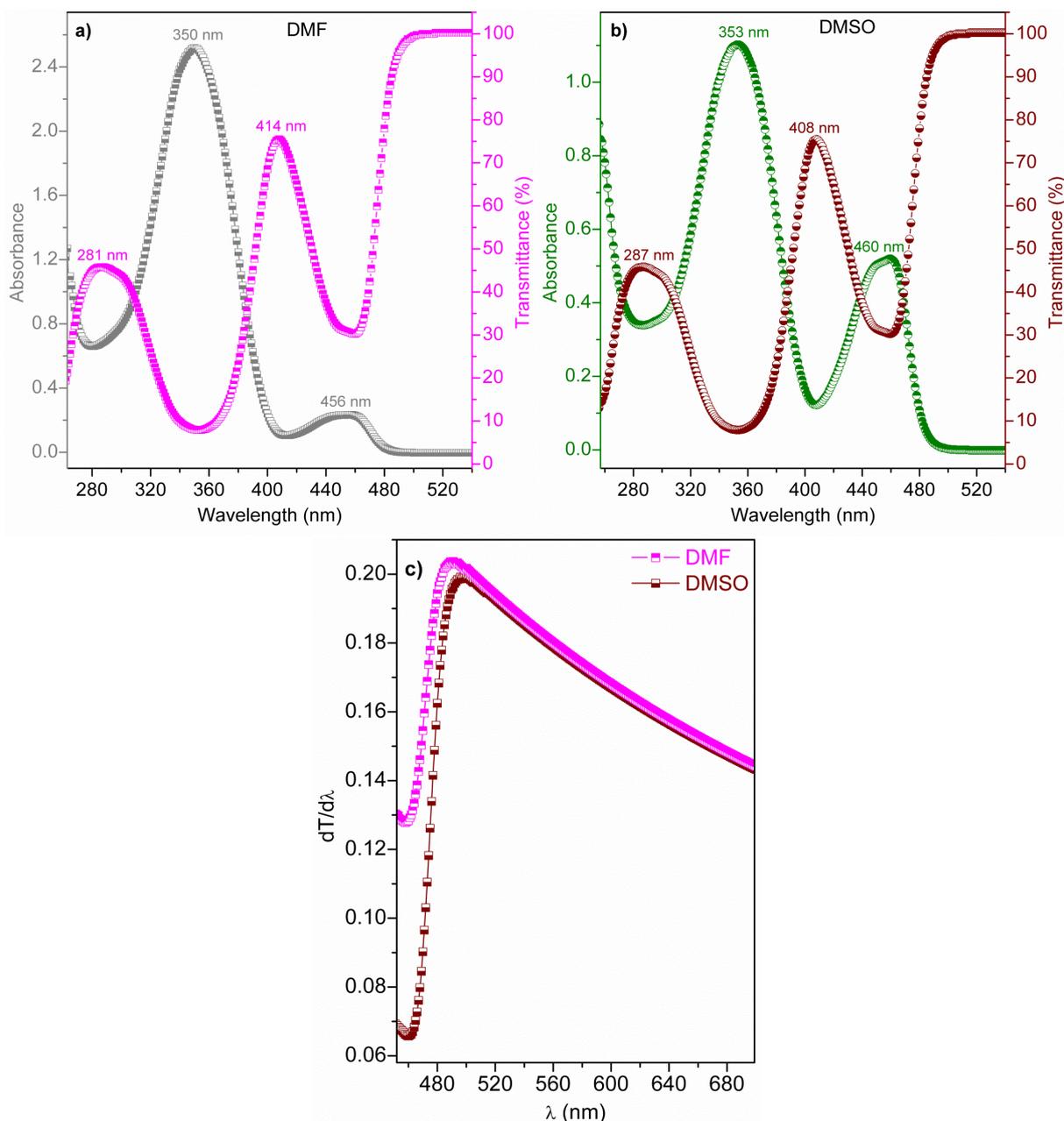


Fig. 4. Absorbance and transmittance spectra of BHYC for a) DMF and b) DMSO and c) their $dT/d\lambda$ curves vs. wavelength (λ)

The absorbance band edge ($E_{\text{Abs-be}}$) gives useful information regarding the absorption properties and estimates the optical band structure of a material. For this, we have obtained the $E_{\text{Abs-be}}$ values of BHYC for the DMF and DMSO solvents using the maximum peak values (491 and 496 nm, respectively) of Figure 4c, which gives the $dT/d\lambda$ curves vs. wavelength (λ). The ($E_{\text{Abs-be}}$) values of BHYC for DMF and DMSO are found to be 2.526 and 2.500 eV, respectively. These results show that the absorbance band edge of BHYC for DMF is higher than the absorbance band edge of BHYC for DMSO.

3.2. Optical band gaps and refractive indices of BHYC solutions

The optical band gap (E_g) and refractive index (n) play a role in investigating the optoelectronic properties of the optoelectronic materials and devices. The E_g values of the BHYC for 10,

15, 58, 186 and 270 μM , and for DMF and DMSO, are obtained from the $(\alpha E)^2$ curves vs. photon energy (E) [25] (α is absorption coefficient) using the Tauc model [26], as seen in Figures 5(a,b) for different molarities and solvents, respectively.

The optical band gap values of BHYC are calculated to be 2.560, 2.549, 2.543, 2.539 and 2.408 eV at concentrations of 10, 15, 58, 186 and 270 μM , respectively. As seen by these values, the E_g value for 270 μM is the lowest (2.408 eV) while the E_g for 10 μM is the highest value (2.560 eV). According to these results, we can say that the E_g values of BHYC may be controlled with molarity and the lowest optical band gaps may also be obtained with a higher molarity. Furthermore, the E_g value calculated for the DMSO solvent (2.552 eV) is lower than the E_g value for the DMF solvent (2.591 eV). The optical band gaps are consistent with the absorbance band edges of BHYC.

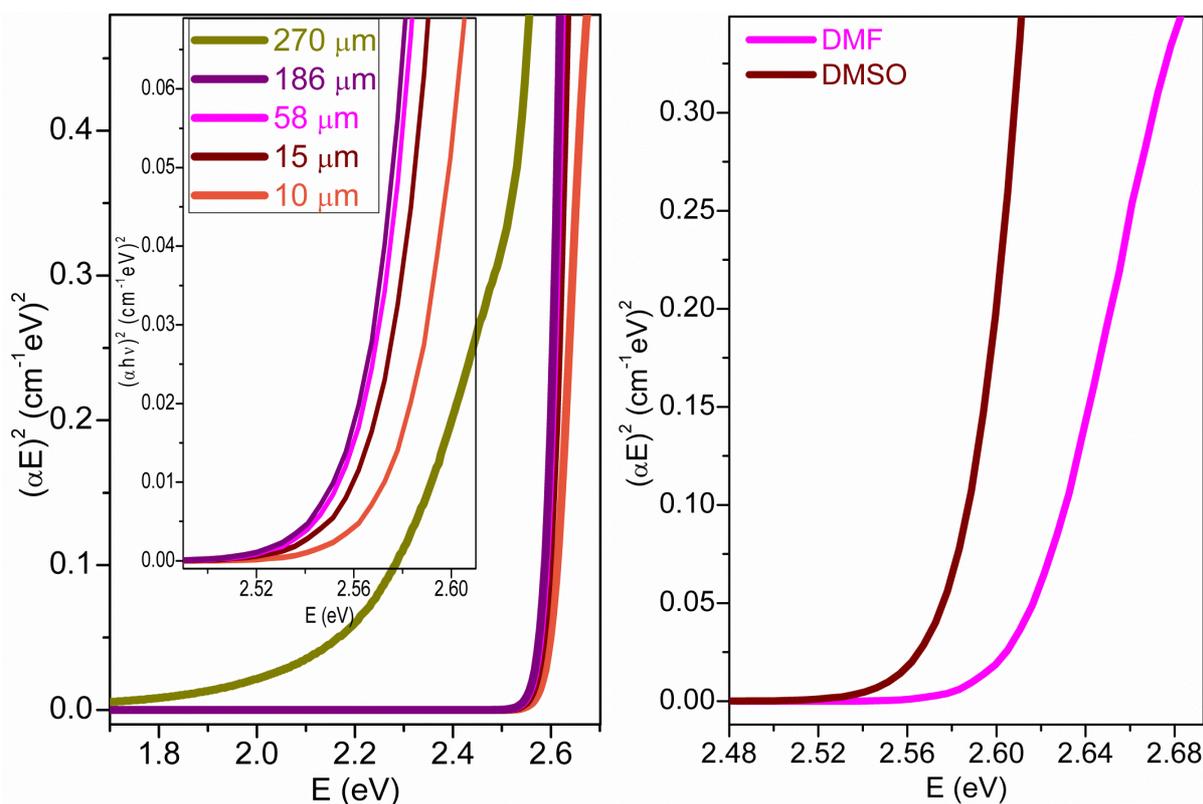


Fig. 5. $(\alpha E)^2$ curves vs. photon energy (E) of BHYC for different molarities (a) and solvents (b)

Depending on the optical band gaps of BHYC, we calculated the refractive indices for the Kumar-Singh, Herve-Vandamme, Reddy, Ravindra and Moss relations [27–30]. The n value of BHYC varies from 2.47 to 2.95 by changing the molarity. The n curves of BHYC for different molarities and solvents are shown in Figures 6(a,b), respectively.

As seen in Figure 6a, the n values obtained from the Reddy relation are the highest, while the n values obtained from the Moss and Herve-Vandamme relations are the lowest. A similar result is obtained for DMF and DMSO, as seen in Figure 6b. The refractive indices of BHYC for DMF are lower than the refractive indices of BHYC for DMSO.

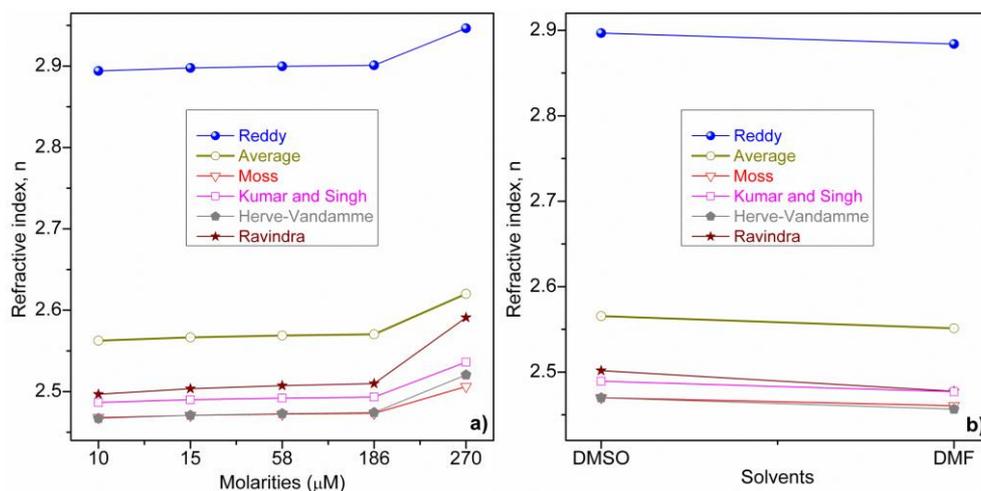


Fig. 6. Refractive index (n) curves of BHYC for different molarities (a) and solvents (b)

3.3. Electrical susceptibility, volume-surface energy loss functions and optical/electrical conductance parameters of BHYC for different solvents

Electrical susceptibility (χ_c) depends on the carrier transitions and is determined from the optical constants by the following equation [25, 31]:

$$\chi_c = \frac{1}{4\pi} (n^2 - k^2 - \varepsilon_0) \quad (1)$$

where $k = \alpha\lambda/4\pi$ and ε_0 is the dielectric constant in the absence of any contribution from free carriers. The χ_c values of BHYC for DMF and DMSO are calculated from Eq. (1). Figure 7 indicates the χ_c curves vs. λ of BHYC. As seen in Figure 7, the χ_c exhibits the maximum peaks at ~ 305 – 385 nm and the χ_c values of BHYC for DMF are much higher than the χ_c values of BHYC for DMSO.

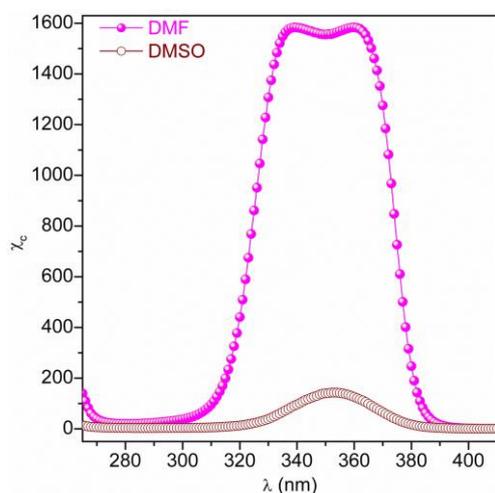


Fig. 7. Electrical susceptibility (χ_c) curves vs. λ of BHYC for DMF and DMSO solvents

Volume and surface energy loss functions (VELF and SELF), which are dispersion parameters, depend on the real ($\varepsilon_1 = n^2 - k^2$) and imaginary ($\varepsilon_2 = 2nk$) parts of the dielectric constant. The VELF and SELF can be obtained by [32, 33]:

$$\text{VELF} = \frac{\varepsilon_2^2}{(\varepsilon_1^2 - \varepsilon_2^2)} \quad (2)$$

and

$$\text{SELF} = \frac{\varepsilon_2^2}{((\varepsilon_1 + 1)^2 + \varepsilon_2^2)} \quad (3)$$

The VELF and SELF values of BHYC for DMF and DMSO are calculated from Eqs. (2) and (3), respectively. The VELF and SELF curves vs. E of BHYC for DMF and DMSO are shown in Figure 8. The scatter ones belong to VELF, while the dot ones belong to SELF. As seen in Figure 8, the VELF values of the BHYC are close to SELF values of the BHYC, and the VELF values of the BHYC for DMSO are higher than the VELF values of the BHYC for DMF solvent.

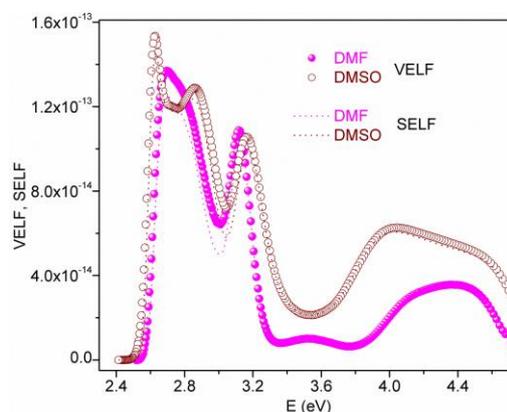


Fig. 8. VELF and SELF curves vs. E of BHYC for DMF and DMSO solvents

The conductance of a material is important for the efficiencies of electronic and optoelectronic devices. For this, we investigated the optical conductance (σ_{opt}) and electrical conductance (σ_{elect}) values of the BHYC for DMF and DMSO using the following equations [34]:

$$\sigma_{opt} = \frac{\alpha nc}{4\pi} \quad (4)$$

and

$$\sigma_{elect} = \frac{2\lambda\sigma_{opt}}{\alpha} \quad (5)$$

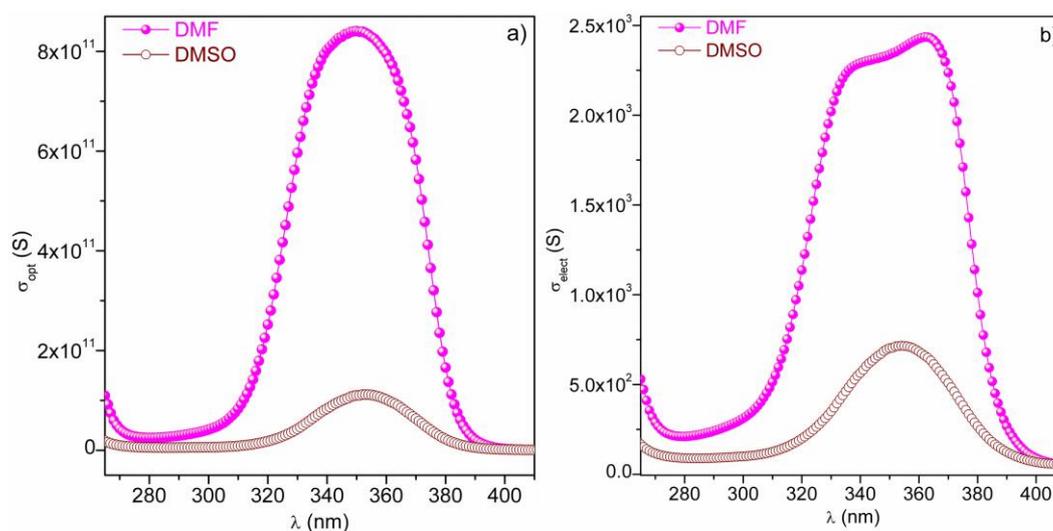


Fig. 9. (a) Optical conductance (σ_{opt}) and (b) electrical conductance (σ_{elect}) curves vs. λ of BHYC for DMF and DMSO solvents

4. CONCLUSIONS

The absorbance spectra of BHYC in DMF and DMSO solvents exhibited the maximum peaks at 350 and 353 nm in the near-ultraviolet region, respectively. The absorbance band edge values of BHYC for DMF and DMSO were found to be 2.526 and 2.500 eV, respectively. The optical band gap of BHYC varied from 2.560 to 2.408 eV with increasing molarity. In contrast, the refractive index of BHYC shifted from 2.47 to 2.95 with increasing molarity. We obtained and compared the electrical susceptibility, volume-surface energy loss functions and optical/electrical conductance parameters of BHYC for DMF and DMSO solvents. The obtained results show that 3-benzoyl-7-hydroxy coumarin exhibits a semiconductor behavior and it may be an important candidate for many optoelectronic devices, such as diodes, photodiodes and sensors.

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where c is the velocity of light. The σ_{opt} and σ_{elect} values obtained from Eqs. (4) and (5) are emphasized in Figures 9 (a, b), which show the σ_{opt} and σ_{elect} curves vs. λ of BHYC, respectively. As seen in Figures 9 (a, b), the σ_{opt} and σ_{elect} exhibit the maximum peaks at ~305–385 nm, and the σ_{opt} and σ_{elect} values of the BHYC for DMSO are much lower than the σ_{opt} and σ_{elect} values of BHYC for DMF.

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