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Synthesis and Optical Properties of a Biphenyl Compound

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Abstract

In this work the synthesis of a biphenyl compound (BPHD) [2,2(biphenyl-4-4-diylbis (azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol], was characterized by FTIR spectroscopy and CHN analysis. Then optical absorption of single crystals were measured. Thin films were deposited by spin-coating. Transmittance measurements in the wavelength range (190 - 900) nm were used to calculate the refractive index (n), the absorption index (k), the optical band gap E_g^{opt}, optical conductivity σ_{opt}, and electric conductivity σ_{ele}.

Keywords: Synthesis, biphenyl derivative, optical properties

Introduction

New kinds of organic materials for photovoltaic devices has been explored because of increasing demand of logging energy. Solar panels produced hitherto on an industrial scale are based on inorganic crystals like silicon. However, manufacturing of such devices is still expensive and has a negative effect on the natural environment. For these reasons organic materials for photovoltaic devices are investigated. Organic materials are very promising candidates in photovoltaic devices due to economic reasons and a high demand for the products [1]. One of the first solar cells which could be considered as organic origin was characterized by Tang [2]. A thin-film, 2-layer organic photovoltaic cell was fabricated from copper phthalocyanine and a perylene tetracarboxylic derivative [2]. However, no product of conducted research has been used in a commercial application.

Detailed investigation of linear and non-linear optical coefficients enable the fabrication of materials for use in specific apllications such as optoelectronic devices [3,4]. Knowledge of optical constants of the materials (optical band gap and extinction coefficient) is vital to scrutinize the atomic structure, electronic band structure and electrical properties. The refractive index is an important optical parameter for the design of windows and optical fibers [5]. The refractive index provides the information about the chemical bonding and electronic structure of the material. An accurate measurement of the optical constant can be easily performed on semiorganic crystals [6].

The study of the optical absorption in the solids provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations while the higher energy part of the spectrum gives knowledge about the electronic states in the atom [7].

Materials and methods

Salicylaldehyde and Diphenyl diamine were obtained from Fluka Co. Methanol and ethanol solvents were obtained from Merck co. The chemical structure of the BPHD is shown in **Figure 1**.

In a round bottom flask (20 m mol) salicylaldehyde was placed and then diphenyl diamine (10 m mol) was added in ethanol (30 mL) and refuxed for 1 h. The pale yellow precipitate which formed was removed by filtration, washed with methanol and purified by recrystallization and dried in a vacuum oven at 60 °C. Its melting point was 190 °C.

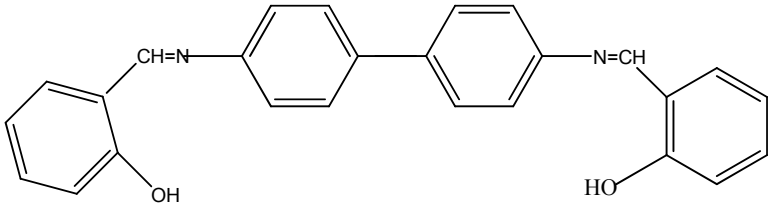

Figure 1 The chemical structure of the BPHD.

Results and discussion

The FT-IR spectrum was obtained with an FT-IR-model 8400s spectrophotometer by Shimadzu, under ambient conditions and is illustrated in **Figure 2**. The FTIR spectra of BPHD has fairly strong absorption in the region 1000 - 1600 cm^{-1} and the bands in this region have contribution mainly from C=N (1569.95) cm^{-1} stretching, C-N (1282.57 cm^{-1}) stretching, C-O (1184.21 cm^{-1}) stretching, C=C (1618.17 cm^{-1}) aromatic stretching and C-H (2920.03 cm^{-1}) stretching aromatic bonds. A broad band was observed at 3382.91 cm^{-1} stretching and is related to the O-H group.

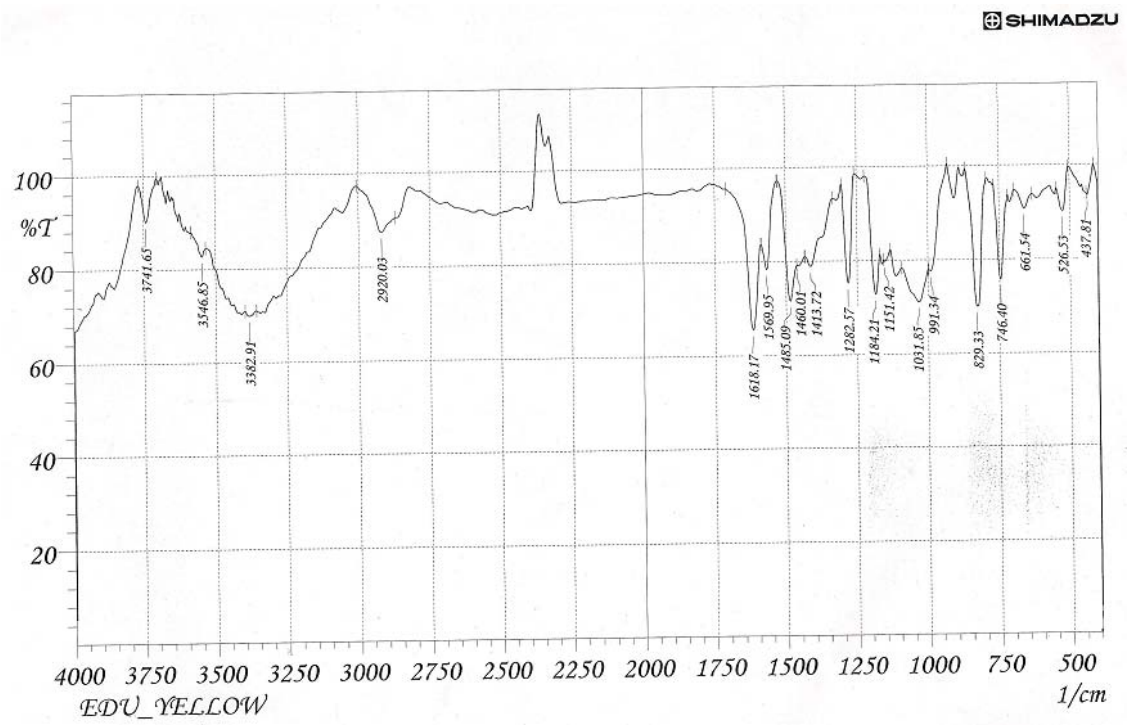

Figure 2 IR spectrum of BPHD.

Elemental analysis of the BPHD was carried out using a EuroVector EA 3000A instrument, and which is shown in **Table 1**.

Table 1 Elemental analysis of functionalized BPHD.

C%		N%		H%	
Theoretical	Calculated	Theoretical	Calculated	Theoretical	Calculated
86.63	86.91	7.48	7.13	5.88	5.36

The optical properties of BPHD were measured. The transmission (T) and absorbance (A) were recorded using a CE-7200 spectrophotometer at the range (300 - 900 nm). **Figures 3** and **4** show the spectral distribution of transmittance (T) and reflectance (R) for the BPHD film. The optical absorption coefficient (α) can be calculated from the transmission data using this relation [8];

$$\alpha = 2.303\log(1/T)/d \quad (1)$$

where d is the thickness of the sample.

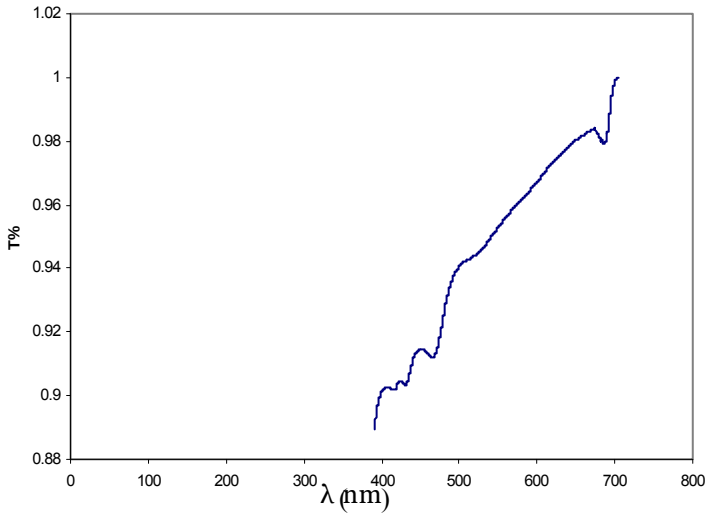

Figure 3 The transmission of BPHD.

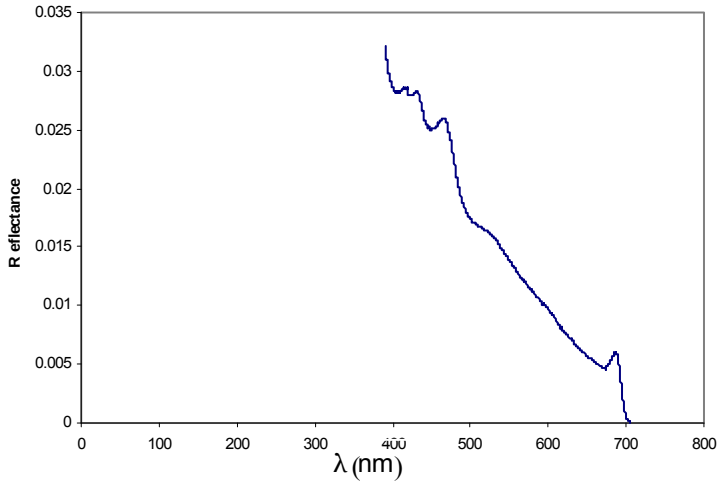

Figure 4 The reflectance of BPHD.

The BPHD thin film dispersion spectrum of the refractive index n, and the extinction coefficient, K, versus the wavelength is shown in **Figures 5** and **6**. We can observe that the refractive index, and the extinction coefficient, K, decrease as the wavelength increases.

The extinction coefficient (K) can be obtained from the relationship [8];

$$K=\alpha\lambda/4\pi \quad (2)$$

where λ is the wavelength.

The linear refractive index is given by [9];

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (3)$$

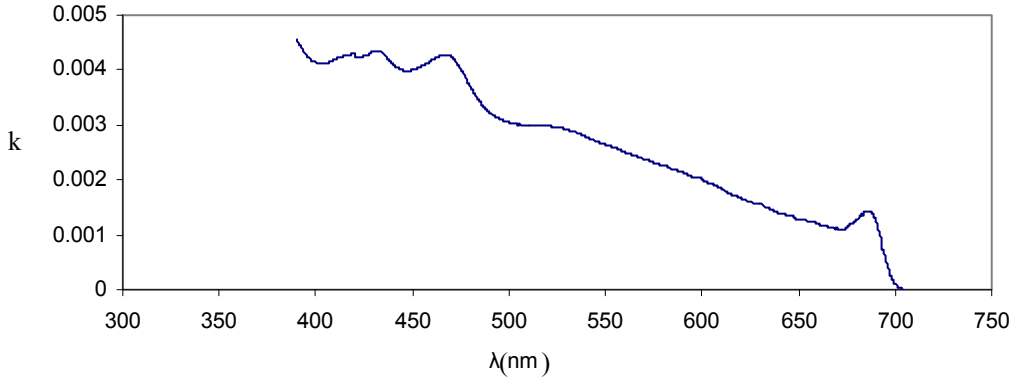

Figure 5 Dependence of the mean values of the absorption index k on the wavelength λ for BPHD.

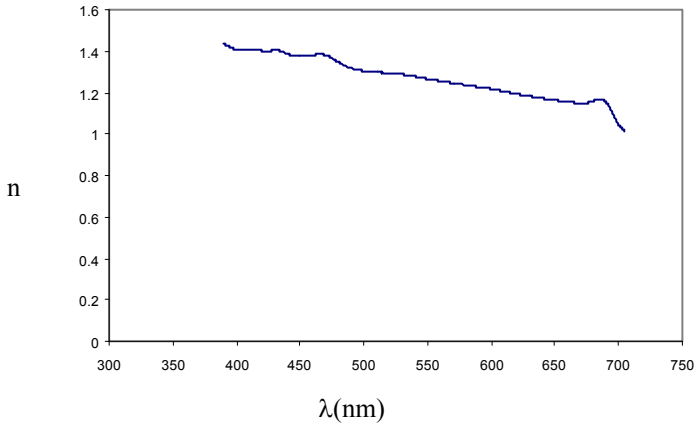

Figure 6 Dependence of the mean values of the refractive index n on the wavelength λ for BPHD.

The dispersion curve of the refractive index is fairly flat in the long wavelength region, showing the typical shape of dispersion curve near an electronic interband transition. The low value of extinction coefficient is in the order of 10^{-2} in visible, which is a qualitative indication of excellent surface smoothness of the BPHD thin film [10].

The relationship between absorption coefficient and indirect energy gap can be written as [11-13].

$$\alpha = \alpha o * [h\nu - E_g \pm E_p]^r / h\nu \qquad \text{for } h\nu > E_g \tag{4}$$

$$\alpha = 0 \qquad \text{for } h\nu \leq E_g \tag{5}$$

were E_g and E_P are respectively indirect energy gap, and the energy of the absorbed (+) or emitted (-) phonons. r has 2 values; 2 for allowed indirect transition and 3 for forbidden indirect transition.

The plot of αhν versus photon energy are shown in **Figure 7**. There are 2 straight line portions that are clearly seen in this curve. The lower energy line corresponds to the phonon absorption processes, and photon energy intercept at E_g+E_P. The other line corresponds to the phonon emission processes and photon energy intercept at E_g-E_P. The value of the indirect band gap energy E_g is about 1.915 eV and the phonon energy E_P is about 0.165 eV.

The calculated Ep is too high to be considered as lattice phonons and it may be suggested that tail states or defects in the energy gap is present. This result is in agreement with other works [14]. The usual method to determine the value of E_g involves a plotting of $\alpha h\nu^2$ versus hν and is shown in **Figure 7**.

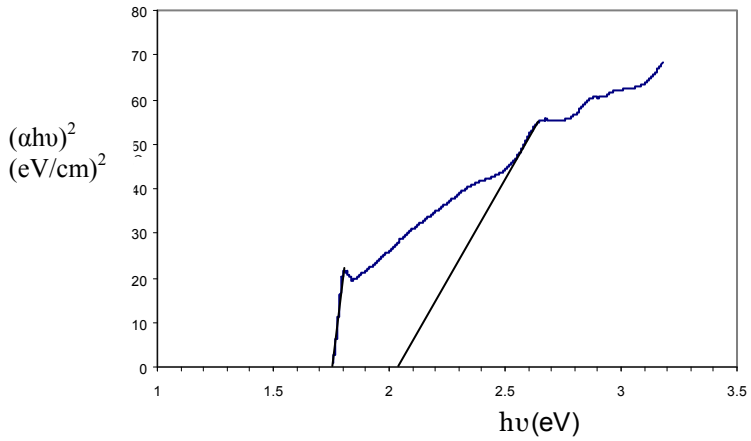

Figure 7 Dependence of $(\alpha h\upsilon)^2$ on the photon energy hυ for BPHD.

The absorption coefficient α can be used to calculate the optical conductivity σ_{opt} as follows [15];

$$\sigma_{opt} = \alpha nc / 4\pi \quad (6)$$

where c is the velocity of light.

Figure 8 shows the variation of optical conductivity σ_{opt} as a function of photon energy hν. The increased optical conductivity at high photon energies is due to the high absorbance of biphenyl derivatives thin film and also may be due to the electron excited by photon energy [16].

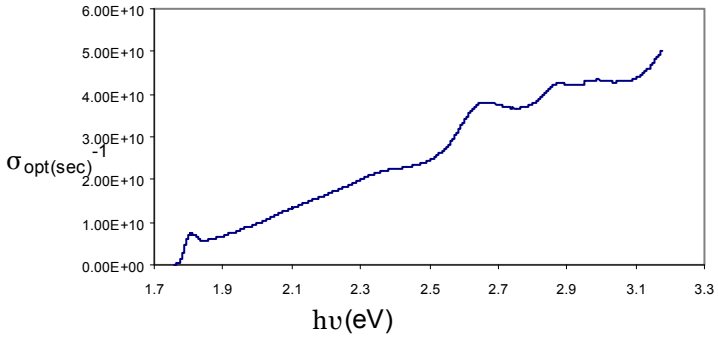

Figure 8 The relationship between σ_{opt} and photon energy (hυ) of BPHD.

The electrical conductivity σ_{ele} can be estimated by the optical method using the relationship;

$$\sigma_{ele} = 2\lambda\, \sigma_{opt}/\alpha \quad (7)$$

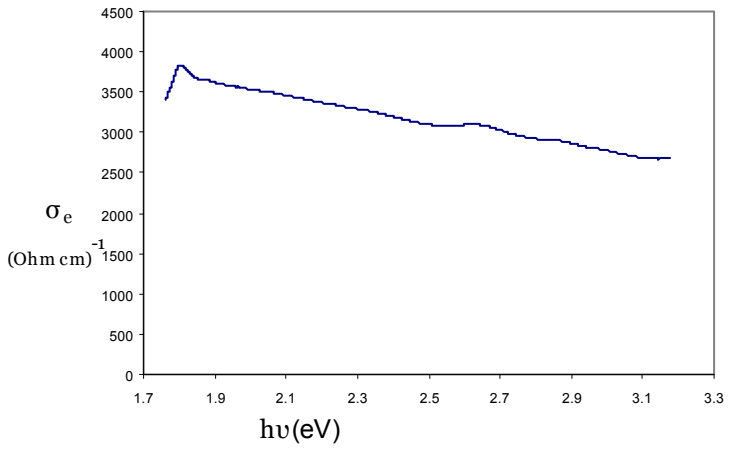

Figure 9 The relationship between σ_e and photon energy (hυ) of BPHD.

Conclusions

We have synthesized and characterized a new biphenyl derivative BPHD Schiff base which can be used as optical properties materials. Optical transmission and reflector spectrums are used to calculate the optical, electric and dielectric properties i.e. absorption coefficient, refractive index, extinction coefficient, optical and electrical conductivity, optical band gap for the BPHD thin film. The optical conductivity $\sigma_{Opt.}$ increased with increasing photon energy. The BPHD thin film exhibited more transmittance at high wavelength. The high transmission, low absorbance, low reflectance and low refractive index of the BPHD thin film in the UV-Visible region make the materials a prominent one for antireflection coating in solar thermal devices.

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