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The Influence of Doping of Fullerene Derivative (PCBM) on the Optical Properties of Vanadyl Phthalocyanine (VOPc)

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***Abstract*—**This paper presents a spectroscopic study on doping of Vanadyl pathalocyanine (VOPc) by [6,6]-phenyl C61 butyric acid methyl ester (PCBM). The films are characterized by UV/Vis/NIR spectroscopy. A drastic increase in the absorption coefficient has been observed with increasing dopant concentration. Optical properties of VOPc:PCBM films deposited by spin coating technique were studied in detail. Optical band gap decreased with the PCBM incorporation in the VOPc film. Optical band gap calculated from the absorption spectra decreased from 3.32 eV to 3.26 eV with a variation of 0–75 % of PCBM concentration in the VOPC films.

***Keywords*—**Optical properties, spin-coating, optical properties, optical energy gap

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I. Introduction

RECENTLY PCBM, a fullerene derivative, is used as both the electron transporting and electron accepting material in most of the devices [1, 2]. The absorption spectra of PCBM pristine films studied in [3, 4] show that the transition from the lowest singlet excited state occurs at around 700 nm (1.7 eV) [5]. The PCBM is reported to be highly soluble in organic solvents and make homogeneous bulk-heterojunction [6]. The tuning of band gap to a desirable value in semiconductor material for different applications is an important tool in optoelectronics [7-10]. The optical band gap Eg is useful in determining the light absorption edge.

Metallophthalocyanines (MPCs) have acquired great interest because of their high thermal and photochemical stabilities [11] and large absorption coefficient in the visible region [12]. There has been growing interest in widening the absorption band of phthalocyanines into the near infrared region for the potential application in optical data storage and security printing [13]. Various MPCs such as magnesium phthalocyanine, copper phthalocyanine, tin phthalocyanine etc. have been investigated for their optical properties [14-16]. For the past few decades, MPCs are known for their potential use in inks, photoconductors, solar cells, and a variety of sensors. The structural and electrical properties of VOPc and VOPc based devices have been explored [17]. Temperature-dependent electrical properties of VOPc based heterojunction under dark conditions have been explored [18]. Previous investigation on VOPc thin films has reported a relatively high mobility (~1 cm^2/Vs) [19]. Due to this particular feature VOPc is considered as a potential candidate for the development of future electronic devices.

The present study focuses on the spectroscopic studies of a bulk-heterojunction system composed of VOPc) and PCBM blend. The blend of VOPc and PCBM, with three different concentrations, has been successfully obtained in chloroform. The thin films have been fabricated by casting process. The optical band gaps of the thin films have also been investigated.

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II. Experimental Details

The VOPc and PCBM were purchased from Sigma-Aldrich and used as obtained. The chemical structures of VOPc and PCBM are shown in Fig. 1. The blends of VOPc and PCBM with three different concentrations of 25 %, 50 % and 75 % were prepared in chloroform. In order to obtain homogeneous solution, the prepared blends were stirred for about 48 hours.

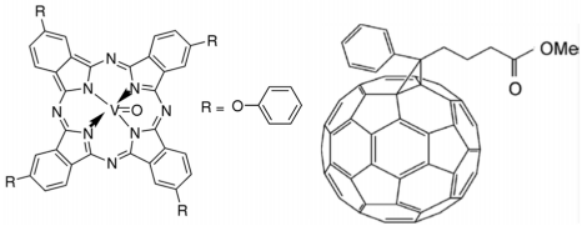


Fig. 1 Molecular structure of Vanadyl Phthalocyanine (VOPc) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM)

Commercially available glass slides were used as substrates. Prior to the preparation of thin films from the VOPc:PCBM blends, the glass slides were thoroughly cleaned in four different steps with soap solution, de-ionized water, acetone and ethanol, sequentially. The whole cleaning process was carried out in an ultrasonic supported bath for about 20 minutes. Finally the substrates were dried by blowing nitrogen. The thin films were spun-cast on the cleaned substrates at a spin rate of 1500 rpm using a WS-400B-6NPP-Lite spin coater. All thickness measurements were carried out on the films coated on glass substrates by employing a KLA

Tencor P-6 surface profilometer. The horizontal and vertical resolutions were maintained at around 337µm and 327 µm respectively. The absorption spectra of the samples were taken at room temperature using Jasco V-570 UV/Vis/NIR spectrometer. .

III. Results And Discussion

The absorption spectrum of the as-deposited VOPc thin film is presented in the inset of Fig. 2. The Soret band or B-band, which lies in the ultra violet region, consists of two prominent peaks and one shoulder in the range of 270 to 410 nm. The strong peaks (high energy peaks) occur at 290 and 346, while the shoulder exists at 410 nm. The intense Soret-band or B-band arises due to the electronic transition from $\pi - \pi^*$ (b_{2u} to e_g) orbitals.

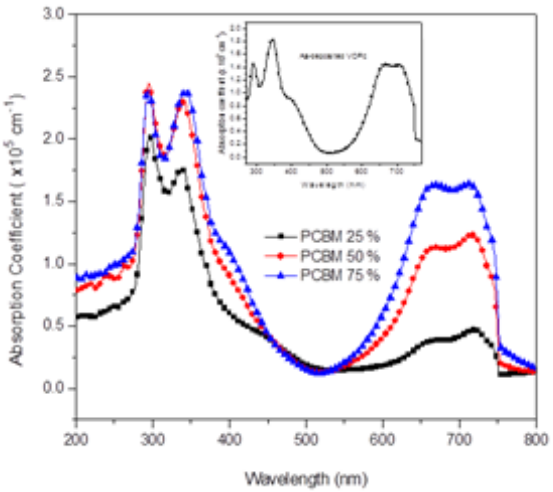


Fig. 2 Optical absorption spectrum of VOPc:PCBM blend for different dopant concentrations. Inset shows a spectrum for undoped VOPc

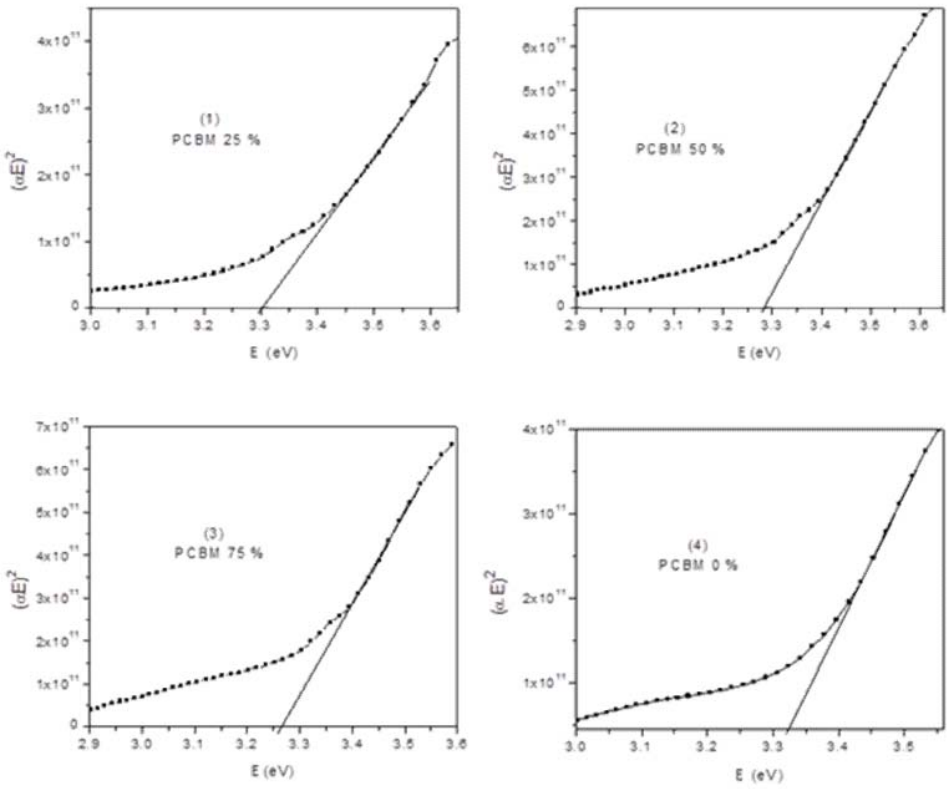


Fig. 3 The variation of the absorption coefficient (α) as a function of photon energy for different dopant concentrations (1) 25 %; (2) 50 %; (3) 75 % and (4) 0 %

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Another well known band of metal-phthalocyanines, namely Q-band, appears in the visible spectral region between 630 nm and 750 nm. A close observation of the absorption spectra unveils the fact that the Q-band splits out in two peaks due to the Davydoff splitting. The characterized peaks for VOPc occur at 660 nm and 715 nm. It is generally accepted that π – π* (a_{1u} to e_g) excitation takes place between bonding and antibonding molecular orbitals in the Q-band region [20]. The high energy peak is associated with the first π – π* transition on the macrocycle [20]. However, the low energy peak has been attributed to a second π – π* transition, excitonic vibration [20] or vibrational interval [21].

The effect of doping concentration of PCBM on absorption spectra is also shown in Fig. 2. It can be observed the doping concentration has a considerable effect on the absorption coefficient of the investigated films. The absorption coefficient of the samples seems to increase with increasing concentration of PCBM. The intensity of the bands in the absorption spectrum strongly depend on the concentration of the dopant, which could be ascribed to the doping and to the charge transfer complexes between the VOPc and PCBM. The VOPc acts as electron donor while PCBM acts as electron acceptor. This feature makes the VOPc:PCBM blend suitable for photovoltaic applications, where the efficiency strongly depends on the dissociation of the exciton and on charge separation [22].

The optical energy gaps Eg, evaluated using absorption spectroscopy, for the as-deposited VOPc and the PCBM doped VOPc films are shown in Fig. 3. The information about direct and indirect inter-band transitions can be acquired through one-electron theory [23]. The absorption edge data of phthalocyanines have been analyzed by this theory [24]. The relation between absorption coefficient and photon energy is given as below [23]:

$$\alpha h\nu = \alpha_0 (h\nu - E)^r \qquad (1)$$

Where E is the energy gap, r is the factor used to evaluate the type of transitions. The value of r equals 1/2 for direct allowed, 2 for indirect allowed and 3/2 for forbidden band-band transitions. The Eq. (1) is manipulated and used to plot a graph between photon energy and $d\ln(\alpha h\nu)/dh\nu$ in order to obtain the value of 'r'. The transition determining factor 'r' is calculated to be equal to 1/2 showing direct inter band allowed transition, which is consistent with band to band transition in other phthalocyanines [25-27].

The energy gap for undoped VOPc and VOPc:PCBM blend of different concentrations are determined from the plot of $(\alpha h\nu)^2$ and photon energy. Extrapolating the linear portion of the plot to the x-axis at 0, the optical gap was evaluated from the intercept as shown in Fig. 3. The optical band gap of the film decreases from 3.32 to 3.26 eV for various doping concentrations of VOPc:PCBM blend films.

The energy gap for undoped VOPc is 3.32 eV while the optical energy gap for the doped VOPc with PCBM concentration of 25 %, 50 % and 75 % are 3.30 eV, 3.28 eV and 3.26 eV respectively. It is evident from the statistics that the optical energy gap decreases with increasing doping levels of PCBM. The decrease in the energy band gap may be ascribed to the intermolecular interactions between VOPc and PCBM. It may also be inferred that the conjugated chain lengths may also enhance. Another possible reason for this decrease in the optical band gap may be attributed to the fact that the increasing PCBM concentration induces a considerable structural changes in the films. The characteristics of the energy gap states can be determined by the empty π states in the conduction band and filled π states in the valence band [28].

Fig. 4 shows that a red shift occurs as a result of the doping concentration of PCBM in the absorption spectra of VOPc:PCBM blend films. The red shift in the blend films can be attributed to the decrease in the energy gap with doping contents [10]. With the help of this doping process the energy gap has successfully been reduced from 3.32 eV to 3.26 eV.

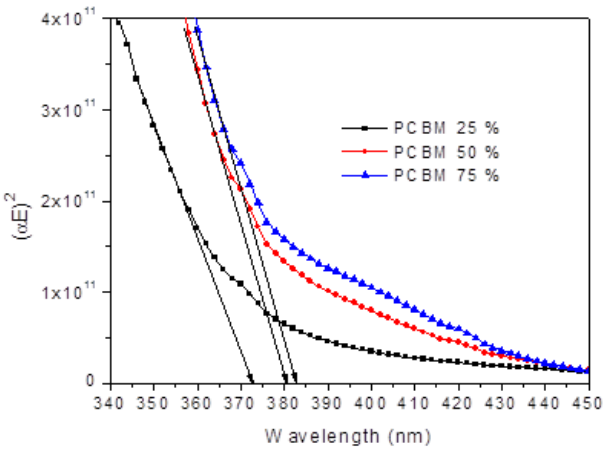


Fig. 4 The variation of the absorption coefficient (α) as a function of photon energy for different dopant concentrations (1) 25 %; (2) 50 % and (3) 75 % indicating red-shift along the absorption edge

IV. CONCLUSIONS

The films of undoped VOPc and VOPc doped with PCBM for three different concentrations 25 %, 50 % and 75 % have been fabricated on commercially available glass slides by spin coating process. The optical properties have been investigated by UV/Vis spectroscopy. The absorption spectrum has been employed to determine the energy gap for doped and undoped samples. The spectroscopic studies reveal that the energy gap decreases from 3.32 eV to 3.26 eV with increasing doping

levels. The red shift appears in the absorption spectrum which can be attributed to the reduction in optical band gap.

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