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The effect of heat treatment on the optical properties of organic semiconductor (NiPc/C_{60}) thin films

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Abstract

Thin films of the blended solution of (NiPc/C_{60}) on glass substrates were prepared by spin-coated method for three different ratios (100/1, 100/10 and 100/100). The effects of annealing temperature and C_{60} concentration on the optical properties of the samples were studied using the UV-Vis absorption spectroscopy and FTIR spectra. The optical absorption spectrum consists of two main bands, Q and B band, with maxima at about (602-632) nm and (700-730) nm for Q_1 and Q_2 respectively, and (340-375) nm for B band. The optical energy gap were determined from optical absorption spectra, The variation of optical energy gap with annealing temperature was nonsystematic and this may be due to the improvement in crystal structure for thin films. While the energy gap decreased by increasing the concentration of C_{60} approaches from the energy gap of this compound.

Key words
Organic semiconductors, NiPc: C_{60}, optical properties and heat treatment.

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تأثير المعاملة الحرارية على الخواص البصرية لأغشية اشباه الموصلات العضوية الرقيقة (NiPc / C_{60})

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الخلاصة

تم تحضير الأغشية الرقيقة للمزيج من (NiPc / C60) على ركائز الزجاج بواسطة طريقة الطلاء البرمي لثلاث نسب مختلفة (100/1، 100/10 و 100/100). تمت دراسة تأثير درجة حرارة التلدين و تركيز C_{60} على الخواص البصرية للعينات باستخدام مطيافية الامتصاص UV-Vis و أطياف FTIR. يتكون طيف الامتصاص البصري من نطاقين رئيسيين، النطاقين Q و B، مع حد أقصى يبلغ حوالي (632-602) nm و (730-700) nm لـ Q_1 و Q_2 على التوالي، و (375-340) nm للنطاق B. تم تحديد فجوة الطاقة الضوئية من أطياف الامتصاص الضوئي، وكان تباين فجوة الطاقة الضوئية مع درجة حرارة التلدين غير نظامية، وقد يرجع ذلك إلى تحسن البنية البلورية للأغشية الرقيقة. في حين أن فجوة الطاقة انخفضت عن طريق زيادة تركيز C_{60} تقترب من فجوة الطاقة في هذا المركب.

Introduction

"Organic semiconductors" be present organic materials showing the typical behavior of semiconductors, i.e. that is insulators whose conductivity can be increased by heating, doping, illumination or further processes are increasing the charge carrier density [1]. Organic materials have chemical and mechanical properties that fundamentally distinguish them from inorganic ones, at present, organic semiconductors have create wide commercial application in organic light-emitting diodes (OLEDs) and other electronic devices [2], owing to ease of processing at low temperature, architectural flexibility, material variety, lighter weight, and environmental safety. Finally, the possibility for synthetic modification of organic components provides for fine-tuning of electronic, optical, and magnetic properties [3].

One of the main advantages of using a solution based process is its versatility in coating methods. Most of the literature denotes to spin-coating methods; however, techniques such as inkjet printing, spray coating, doctor code and Meyer bars have involved the attention of research groups, because of the opportunity to integrate low-cost devices into a large area and flexible substrates [4–6].

Metal phthalocyanines (MPc) is a group of small molecules with Q-band absorption in the red range near to IR, with high optical and chemical stability [7]. Properties such as electron conductivity and the absorption range variation by altering the central metal [8].

The fullerenes (C_{60}) is made up of 60 spherical carbon sp^2 hybridized in solid ball shape [9] and institute an attractive class of molecular building blocks for the synthesis and manufacture of advanced nanomaterials and devices [10,11]. In particular, buckminsterfullerene C_{60} has found a wide range of applications in various fields of modern nanoscale science and technology, due to its extremely small size (0.498 nm in radius), highly symmetrical molecular form, and very rich electronic properties in both the ground and excited states [12]. The molecular structure of NiPc and C_{60} is shown in Fig.1.

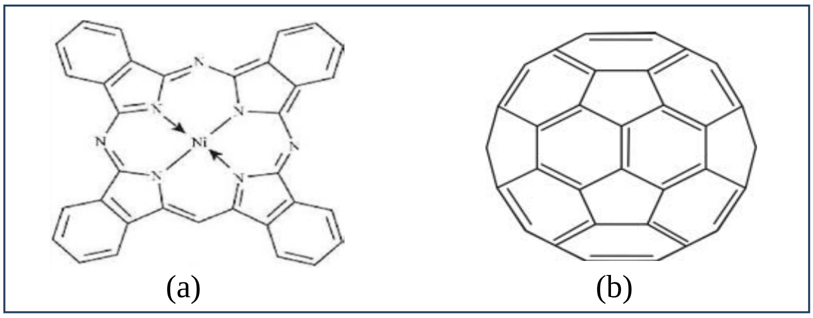

Fig. 1: The molecular structure of (a) NiPc and (b) C_{60} [13, 14].

Today, the most commonly used architecture is the so-called heterojunction blend, where the two components are intimately mixed in one layer. The blend gives a larger interfacial area between the donor and the acceptor material compared to the bi-layer architecture that is good for both the formation of the charge-transfer state (CT state) and charge separation [15].

Organic donor and acceptor materials are promising candidates to create donor/acceptor interface bilayered (hetrojunction) and blended (bulk-hetrojunction) [16]. Various active layer have been explored since the introduction of organic semiconductor devices. The first is based on a single layer with a very low efficiency. The introduction of a bi-layer improved the device performance.

Experimental work

Nickel phthalocyanine (NiPc) and Fullerene (C_{60}) were purchased from sigma-Aldrich and used without additional purification. Before deposition the blend, glass substrates were cut to the size of 2.5cm×2.5cm and cleaned in an ultrasonic bath for 10 min, to avoid contaminants from the glass surface, using different steps with distilled water, liquid soap, a solution of ethanol and acetone, respectively. The substrates were dried in nitrogen gas.

Three weight ratios of (NiPc/C_{60}) used to prepared the blends and thin films which are (100/1, 100/10 and 100/100), respectively by mixing 15mg/ml of NiPc in chloroform and (0.15, 1.5 and 15) mg/ml of C_{60} in toluene. The blend solutions of NiPc and C_{60} for each ratio were putted on a hot plate stirrer for 40 hours with temperature of 50 ^{o}C, then the two blended solutions is filtered using (0.2) μm filter and mixed together and leaved 20 hours again on stirrer to get homogenous solution.

Now the blended solution becomes ready to spin-coated on pre-cleaned glass substrate using spin coater type CHEMAT SCIETIFIC SKW-4A2 for 2000 rpm for 1.5min. The prepared samples leaved in air for one day then putted in an oven at 70 ^{o}C for 15 min to remove the residual solvent may be stay inside the film as Nano bubbles. The bulk heterojunction blend (NiPc/C_{60}) thin films were annealed in a vacuum oven at different temperatures (373, 423 and 473) K for one hour to study the influence of heat treatment temperatures on optical properties.

The optical properties of as-deposited and annealed thin films were studied by using a double beam JASCO V-570 UV–VIS spectrophotometer whereas the glass substrate was used as a reference in the wavelength of absorption spectrum ranged from (320–800) nm. FTIR spectroscopy over the range of (400-4000) cm^{-1} with resolution 4 cm^{-1} in the transmittance mode was measured by (Fourier Transform Infrared Spectrophotometer FTIR-8400 SHIMADZU). The spectra was obtained at room temperature and recorded in the transmittance mode by using Thermo Scientific^{TM} Nicolet^{TM}iS^{TM}10 FTIR Spectrometer.

Results and discussion

The optical energy gap was determined by using the Tauc formula for allowed direct transition, by plotting $(\alpha h\nu)^2$ against the photon energy which is calculated from Eq.(1):

$$\alpha h\upsilon = B\,(h\upsilon - Eg)^{r} \qquad (1)$$

where B is constant in inverse proportional to amorphousity, r =1/2, 3/2, 2, 3 for allowed direct, forbidden direct, allowed indirect, forbidden indirect transitions respectively.

The absorption spectra of (NiPc/C_{60}) thin films at room temperature, 373, 423 and 473 K with three different ratios are shown in the Fig.2, it shows the variations of absorption spectra of (NiPc/C_{60}) films as a function of wave length in the range of 300–800 nm for three different ratios. This absorption spectrum shows two peaks which are *B* and Q bands, The Q band containing two peaks Q_1 and Q_2 which are in good agreement with Ato et al. [17] and Benten et al. [18].

The Q_1 band at around 620 nm is owing to the move between the bonding and antibonding (π–π*) at the dimer part of the phthalocyanine molecule, while a shoulder peak follows with low absorption intensity of Q_2 band due to the transition between the bonding and antibonding (π–π*) at the monomer part. This shoulder peak corresponds to the absorption in the monomer portion of the molecule from the second π-π* transition or as excitation peak or as a vibrational interval [19]. The central metal atom (Nickel) of the phthalocyanine molecule is associated with the *d*-band. So, within the UV region of the spectrum, peak absorption is strong at around 340nm is attributed to partially occupied $d–\pi^*$ transitions causes B band to appear.

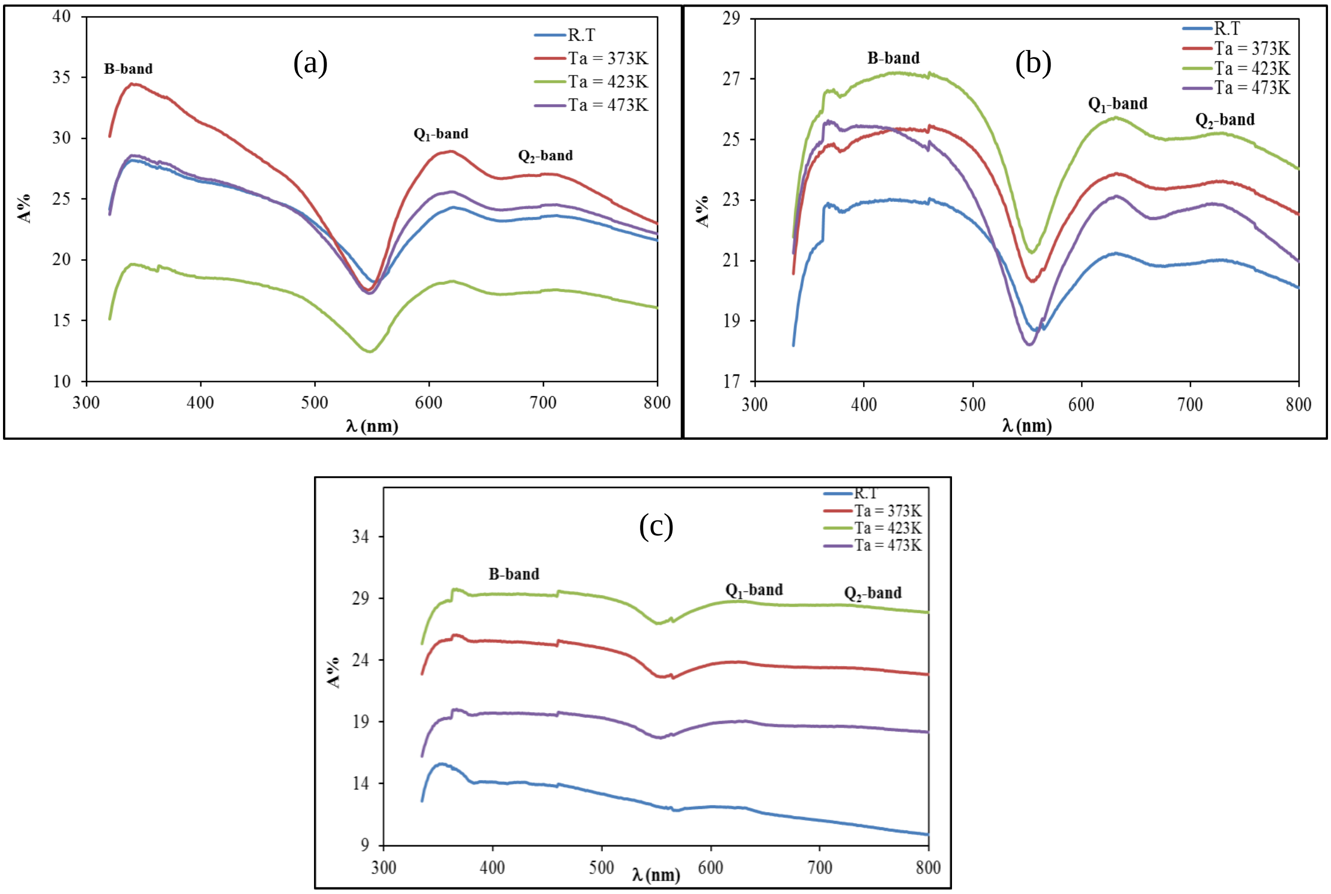

Fig.2: Absorbance spectrum of as-deposited and annealed Thin Films of NiPc/C_{60} blends with three different ratios of C_{60} to NiPc (a) (100/1), (b) (100/10), and (c) (100/100).

Fig. (2a), shows that the light absorption increases by increasing of temperature to 373 K and then drops at 423 K. At 473 K, the light absorption increases again.

Figs. (2b) and (2c), show that the light absorption increases by increasing of temperature to 373 K and continues to increase when the temperature reaches to 423 K, and finally, when the temperature reaches to 473 K, the light absorption decreases.

The tensile stress resulting from the restriction imposed by the annealing temperature affects the electronic structure and thus produces new absorption spectra. Anderson et al.[20] has been reported that the central metal atom of the phthalocyanines effects the optical absorption spectrum. It is observed that Q band peak is shifting to a longer wavelength above 373 K and shifting to a shorter wavelength side below 373 K.

It is estimated that the interaction energies between nearest neighbors are 0.87 eV (CuPc–CuPc) [21], 1.5 eV (C60–C60) [22, 23], and 0.44 eV (CuPc–C60) [24], respectively. Due to the similarity of CuPc and NiPc in terms of molecular structure, optical properties, and energy levels, comparable properties are assumed for NiPc. These high energies suggest a preferential aggregation of like molecules. Given sufficient thermal energy for diffusion, the formation of interconnected NiPc and C_{60} networks can occur. This network would allow for easier extraction of charge carriers generated from dissociated excitons and leads to less charge recombination in the BHJ.

The features visible in the spectra are related to NiPc with the clearly separated peaks. But there is an effect in UV region due to the adding of C_{60} because of the correlation between HOMO and LUMO of both NiPc and C_{60} in UV region, depending on the ratio of C_{60} in the blend.

The optical energy gap values (E_g^{opt}) for (NiPc/C_{60}) films were determined using Tauc equation which is used to find the optical transition type by drawing the relations $(\alpha h\nu)^2$, $(\alpha h\nu)^3$, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{3/2}$ vs. photon energy (hν) and choice the optimal linear part. The first relation was found to lead to a linear dependence, which describes the allowed direct transition. E_g^{opt} is then determined by the extrapolation of the portion at (α=0) as exposed in Figs. 3 and 4.

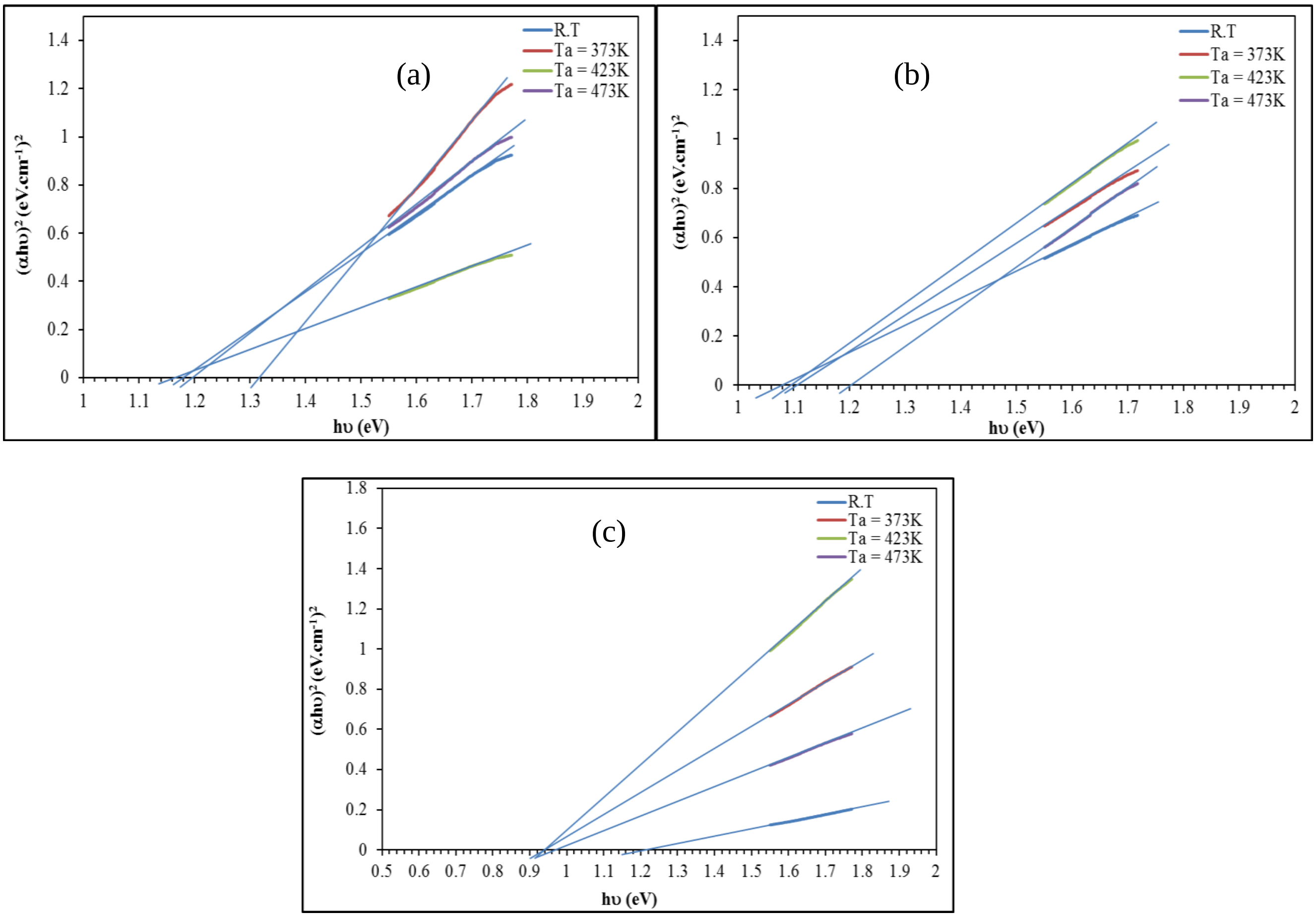

Fig. 3:** $(\alpha h\nu)^2$ **versus photon energy of incident radiation for as-deposited and annealed thin films (Q-band) of NiPc/C_{60} blends with three different ratios of C_{60} to NiPc (a) (100/1), (b) (100/10), and (c) (100/100).

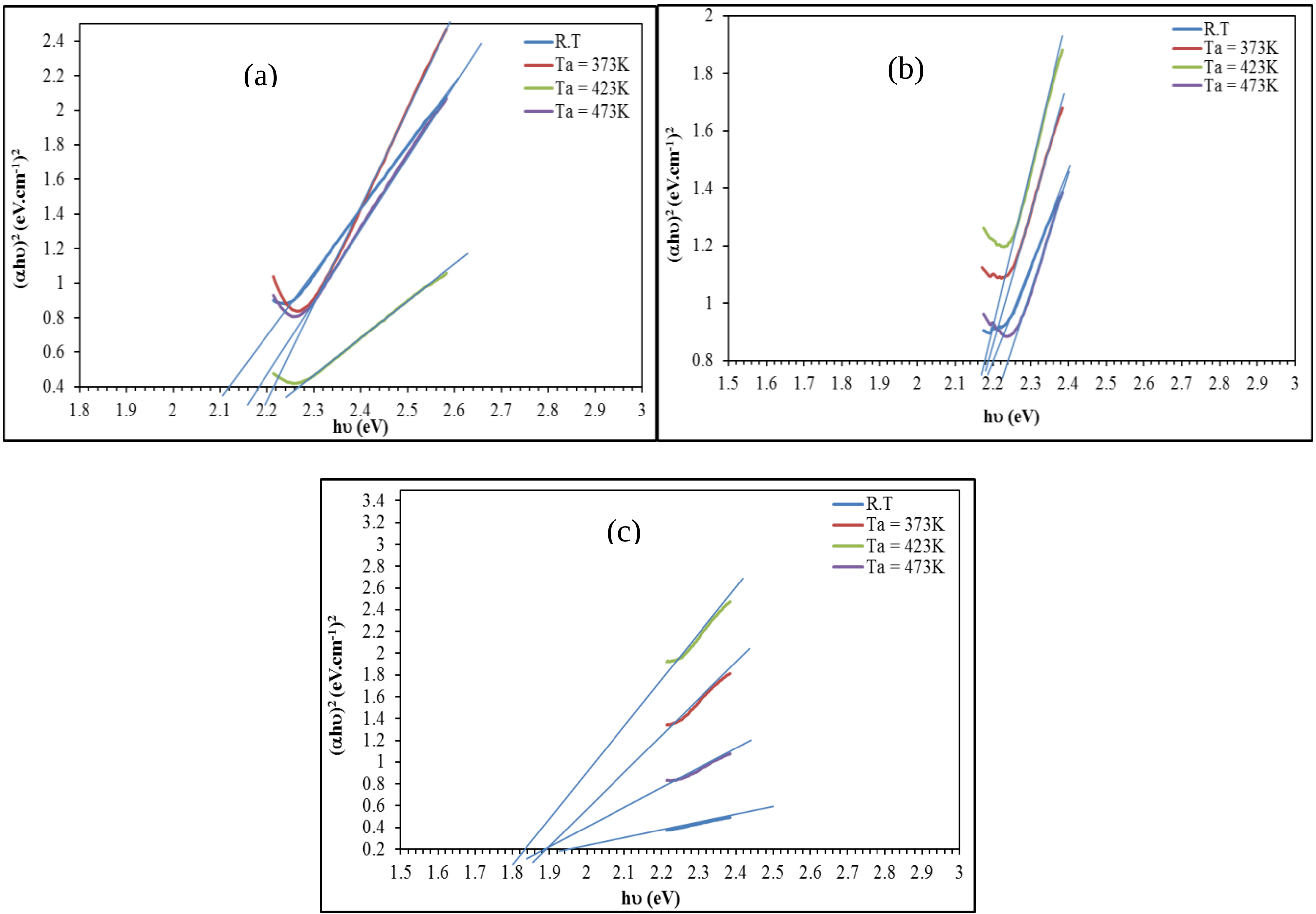

Fig.4: $(\alpha h\upsilon)^2$ versus photon energy of incident radiation for as-deposited and annealed thin films (B-band) of NiPc/C_{60} blends with three different ratios of C_{60} to NiPc (a) (100/1), (b) (100/10), and (c) (100/100).

The optical energy gap was found to increase after heat treatment increase to 373 K, due to the reduced localized state within the energy gap, i.e, between the HOMO and LUMO bands, the crystallization of molecule of the material and reduction of crystal defects due to crystal growth of the films atoms. and then shows a decrease after heat treatment increase to 423K, the reason behind the decreasing the rate of energy gap is the appearance of localized states in the area between the HOMO and LUMO that make the required photon energy for direct electronic transitions reduced, making the transmission of electrons from the HOMO to LUMO easier [25]. Finally after annealing temperature increase to 473 K the energy gap increase again due to structure change to nanofiber [26].

The interaction energies between nearest neighbors of NiPc and C_{60} in the UV region caused the new gap named transport gap [27, 28], therefore the values of energy gap of B-band was in the range 1.84eV to 2.27eV for three blended ratios. In fact, these values of transport gap are less than the values of energy gaps of NiPc and C_{60} when measured separately [26, 29].

From Table 1(a), for the ratio (100/1) one can note that the optical energy gap for Q-band increased from 1.18eV to 1.32 eV when the film annealed at 373 K, whereas, its values decreased to 1.17 eV with increasing annealing temperature to 423 K, and finally, when the temperature reaches to 473 K, energy gap increased to 1.20 eV. The same behavior observed in B-band, the optical energy gap values was (2.12, 2.22, 2.18, 2.27) eV at R.T, 373, 423, 473 K, respectively. Other ratios of the blended (NiPc/C_{60}) thin films showed in Tables 1 (b) and (c) indicate that the energy gaps follow the same behavior in terms of increasing and decreasing, and variation nonsystematic with increasing the annealing temperature.

Table 2 shows that the energy gap decreases with increasing of concentration of C_{60} ratio.

Table 1: Bands position and optical energy gaps of as-deposited and annealed thin films of NiPc/C_{60} blends with three different ratios of C_{60} to NiPc (a) (100/1), (b) (100/10), and (c) (100/100).

(a)

Annealing temperature (K)	B- band	Q-band		Eg (eV)	
	peak position (nm)	Q_1 peak position (nm)	Q_2 peak position (nm)	Q band	B band
RT	340	621	711	1.18	2.12
373	339	618	701	1.32	2.22
423	339	621	711	1.17	2.18
473	339	618	711	1.20	2.27

(b)

Annealing temperature (K)	B- band	Q-band		Eg (eV)	
	peak position (nm)	Q_1 peak position (nm)	Q_2 peak position (nm)	Q band	B band
RT	367	631	729	1.08	2.19
373	372	632	727	1.11	2.20
423	372	631	730	1.10	2.18
473	367	632	720	1.20	2.24

(c)

Annealing temperature (K)	B- band	Q-band		Eg (eV)	
	peak position (nm)	Q_1 peak position (nm)	Q_2 peak position (nm)	Q band	B band
RT	353	602		0.94	1.90
373	367	626	715	1.22	1.98
423	367	626	718	0.94	1.84
473	367	632	716	0.98	1.90

Table 2: Variation of optical energy gaps of (NiPc/C_{60}) thin films with different C_{60} to NiPc ratios (a) R.T, (b) Ta=373 K, (c) 423 K and (d) 473 K .

(a)

C_{60} wt% concentration	Eg (eV)	
	Q band	B band
1	1.18	2.12
10	1.08	2.19
100	0.94	1.90

(b)

C60 wt% concentration	Eg (eV)	
	Q band	B band
1	1.20	2.27
10	1.20	2.24
100	0.98	1.90

(c)

C60 wt% concentration	Eg (eV)	
	Q band	B band
1	1.17	2.18
10	1.10	2.18
100	0.94	1.84

(d)

C60 wt% concentration	Eg (eV)	
	Q band	B band
1	1.32	2.22
10	1.11	2.20
100	1.22	1.98

Conclusions

1. Thin films of (NiPc:C_{60}) were prepared for three different ratios on glass substrates successfully from the blend of organic semiconductors (NiPc:C_{60}) has been prepared with three different ratios of C_{60} (100:1) , (100:10) and (100:100) by dissolving this compounds in appropriate organic solutions.
2. The optical energy gap is variation nonsystematic by increasing of annealing temperature, and this can be owing to the development in crystal structure for thin films, while the energy gap decreased with the increased concentration of the C_{60} approach of the energy gap in this compound.

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