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## Tuning the Optical Band Gap of DH6T by Alq3 Dopant (Penalaan Jurang Tenaga Optik DH6T dengan Menggunakan Bahan Pendop Alq3)

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### ABSTRACT

*Dihexyl-sexithiophene (DH6T) was doped with tris (8-hydroxyquinolinat) aluminum (Alq3) to prepare blends of DH6T/Alq3 by dissolving the mixture in the chloroform/hexane co-solvent. Solid films with different thickness deposited on quartz substrates were obtained from the blends via casting process. Optical absorption spectroscopy has been performed to measure the optical band gap of pure and doped DH6T as well as variations in the band gap with dopant concentration (weight %). This variation in optical band gap with dopant concentration was determined quantitatively with fitted and extrapolated techniques and observed qualitatively from the red shift appeared along the optical absorption spectra. The results showed that within a specific dopant content, the optical energy gap,  $E_g$  of DH6T decreases from 2.69 eV to 1.8 eV with increasing dopant concentration to 23.1%.*

*Keywords: Band gap tuning; dihexyl-sexithiophene; doping; optical properties*

### ABSTRAK

*Diheksil-seksitiofena (DH6T) telah didopkan dengan tris (8-hidroksiquinolinat) aluminium (Alq3) bagi menyediakan adunan DH6T/Alq3 dengan melarutkan campuran-bahan dalam pelarut-bersama klorofom/heksana. Filem nipis yang berbeza ketebalan diperolehi melalui proses tuangan daripada campuran-bahan. Spektroskopi serapan optik dijalankan untuk mengukur jurang tenaga optik bagi DH6T yang tulen dan DH6T yang didopkan serta mengukur perubahan jurang tenaga dengan perubahan ketumpatan bahan pendop (% berat). Perubahan dalam jurang tenaga optik dengan ketumpatan pendop ini ditentukan secara kualitatif melalui teknik pepadanan dan ekstrapolasi serta pemerhatian secara kualitatif daripada anjakan merah bagi spetrum serapan optik. Keputusan menunjukkan bahawa jurang tenaga optik  $E_g$  DH6T pada kandungan bahan pendop tertentu telah berkurang daripada 2.69 eV kepada 1.8 eV bila ketumpatan meningkat kepada 23.1%.*

*Kata kunci: Diheksil-seksitiofena; penalaan jurang tenaga; pendopan, sifat optik*

### INTRODUCTION

The most studied and synthesized thiophenes were oligothiophenes, either unsubstituted from terthiophene (3T) to octithiophene (8T) or substituted by alkyl chains as a pendent group in the  $\beta$  position or as end groups in the  $\alpha$ ,  $\omega$  position (Horowitz et al. 1997; Liu et al. 2005; Marks et al. 1998; Muccini 1998; Sotgiu et al. 2002; Tavazzi et al. 2001; Wu & Conwell 1997; Yakuphanoglu 2007). Among all the organic semiconducting materials sexithiophene (6T) films show the highest mobility (Chen et al. 2006). With improving solubility of sexithiophenes, the addition of hexyl side chains to  $\alpha$ -sexithiophene (6T) has provided us with dihexyl-sexithiophene organic semiconductor, DH6T (Sato et al. 1998), which is characterized by reasonable field-effect mobility reaching as high as 1 cm<sup>2</sup>/Vs (Murphy et al. 2004).

Studying the electrical (Yakuphanoglu 2007) and optical properties of DH6T are strong key points to give us information about its optoelectronic behaviours. Furthermore, the optical band gap ( $E_g$ ) is a necessary parameter needed to be considered in the optoelectronic

applications. The value of  $E_g$  defines the fundamental light absorption edge. Light with enough energy can promote electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) level. Therefore, tuning this optical band gap (Bhat & Deepak 2005; Hwang et al. 2001; Lopez et al. 2004; Michinobu et al. 2008; Yang & Holdcroft 1997) into the desirable value for applications is of great importance.

The current paper aims to tune the optical band gap of DH6T by tris (8-hydroxyquinolinat) aluminum (Alq3) dopant with different weight percentage, as it was seen that Alq3 is a viable means for tuning the band gap,  $E_g$  of dihexyl-sexithiophene material.

### EXPERIMENTAL DETAILS

The materials, dihexyl-sexithiophene (DH6T) and tris (8-hydroxyquinolinat) aluminum (Alq3) were purchased from Sigma-Aldrich in powder form. The linear molecular formula of DH6T and Alq3 are C<sub>36</sub>H<sub>38</sub>S<sub>6</sub> and Al(C<sub>9</sub>H<sub>6</sub>NO)<sub>3</sub>, respectively. To obtain films of DH6T:Alq3, a suitable

organic solvent is necessary to dissolve the coexistence materials, and at the same time, allows the solution to be dried effectively in a desirable period through evaporation. For this purpose, among seven pre-tried solvents (results not shown here), chloroform and hexane as a co-solvent was selected. The DH6T:Alq3 mixtures with different dopant contents (weight %) were dissolved in 2 mL of chloroform/hexane (1:1) co-solvent with concentration of 5 mg/mL. The prepared blends were stirred on magnetic stirrers at 550 rpm for about 48 h.

Films of DH6T:Alq3 were coated onto pre-cleaned quartz substrates by casting technique. The quartz slides were cleaned ultrasonically with Decon® Neutracon foam solution for 15 min. Then, the slides were rinsed with acetone, ethanol and distilled water in succession and separate procedures each after an other for 10 min in an ultrasonic bath, respectively. Finally, the quartz slides were dried thoroughly using nitrogen gas.

The optical absorption spectra of the films were recorded at room temperature using Jasco V-570 UV-Vis-NIR spectrophotometer in the wavelength range from 250 to 1500 nm. The thicknesses of the films were determined using KLA Tencor P-6 surface profiler by scratching the film in three different regions across its surface, then taking average of the measurements. This was carried out after which the spectra measurement for each film has been recorded.

## RESULTS AND DISCUSSION

The optical energy gaps ( $E_g$ ) for the undoped and doped DH6T have been determined via the optical absorption spectroscopy. The absorption of light by the DH6T:Alq3 films produce various amounts of photons inside the films, where photons with enough energy can promote electrons from HOMO to LUMO energy level and cross the optical band gap,  $E_g$ . The absorption coefficient,  $\alpha$  for the films was calculated using the relation  $\alpha = 2.303 A/t$  where,  $A$  is the absorbance of the film and  $t$  its thickness. The square of absorption coefficient and photons energy  $(\alpha E)^2$  is calculated and related to the energy gap,  $E_g$  and photon energy,  $h\nu$  according to the following equation (Varghese et al. 2002):

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^n.$$

where,  $n = 1/2$  for direct and  $n = 2$  for indirect allowed transitions. The value of  $n$  has been deduced for our DH6T:Alq3 films by fitting the correlated photonic energies with the absorption coefficient using MATLAB curve fitting. It was found that at approximately  $n = 0.5$ , the best-fitted curve with respect to the recorded practical data has been obtained. This indicates the presence of direct allowed band transition within the absorption edge, where a larger linear extrapolated area can also be seen along the curves utilizing absorption coefficient against photons energy. The graphs of  $(\alpha E)^2$  against  $h\nu$  for different dopant content were plotted, as shown in Figure 1.

Extrapolation of these plots to  $(E\alpha)^2 = 0$  gives the energy gap. Energy gaps of 2.69 eV for undoped DH6T whilst 1.88 eV, 1.8 eV and 1.94 eV for the doped DH6T with Alq3 dopant contents of 9.1%, 23.1% and 33.3% were determined, respectively. It is evident that there is a non-monotonic change in the optical band gap, which results in increase of  $E_g$  at 33.3% dopant content in comparison with other doping states. The decrease in  $E_g$  for the films from 0% to 23.1% (w%) is attributed to the presence of intermolecular interactions between the DH6T chains and Alq3 ligands. This in turn, due to aggregation of Alq3 molecules among the DH6T host, led to increase in the conjugated chain lengths responsible for the absorption of photons energy. However, one can notice that at Alq3 content of 9.1%, the  $E_g = 1.88$  eV decreased strongly compared to that of the undoped film with  $E_g = 2.69$  eV. Furthermore at 23.1% dopant content, the  $E_g$  decreased to 1.8 eV which indicates lesser decrease in  $E_g$  comparing with that of 9.1% dopant content in which  $E_g = 1.88$  eV. This may be ascribed to the existence of nearly saturated interaction between the chains and molecular ligands. Therefore, from this lesser decrease in  $E_g$ , we perceive that the minimum value of energy gap may lie between dopant concentration of 9.1% and 23.1% if more intentionally doping and theoretical formula to fit with the experimental observations is considered.

Figure 2 shows this non-monotonic change in  $E_g$  and the red shift occurrence along the absorption spectra from 0% to 23.1%. This is in contrast to the lower dopant content, at 33.3% in which a blue shift has been observed. This may be because of the appearance of predominating Alq3 ligands over the DH6T chains, as Alq3 corresponds to relatively high  $E_g$  of about 2.8 eV (Dalasinski et al. 2006). Finally, with this sort of doping process (solution processing), the band gap of DH6T has successfully been tuned from 2.69 eV to 1.8 eV.

## CONCLUSIONS

Films of pure and doped DH6T with Alq3 have been prepared and coated on quartz substrates by solution casting technique from the blends of DH6T:Alq3 dissolved in chloroform/hexane co-solvent. By utilizing the optical absorption spectra of the films, optical band gap of DH6T has been tuned from 2.69 eV to 1.8 eV. It was evident that there is a non-monotonic change in the optical band gap of DH6T, such that there is a red shift and decrease in  $E_g$  within dopant contents from 0% to 23.1%. This was attributed to the aggregation of Alq3 molecules among the DH6T host to produce larger conjugated chains for absorbing lower photonic energy. However, having a blue shift and increasing  $E_g$  at 33.3% and above was seen, the minimum  $E_g$  may lie between 2.69 eV to 1.8 eV within dopant contents of 9.1% to 23.1% if there is more research work carried out within this dopant concentration region.

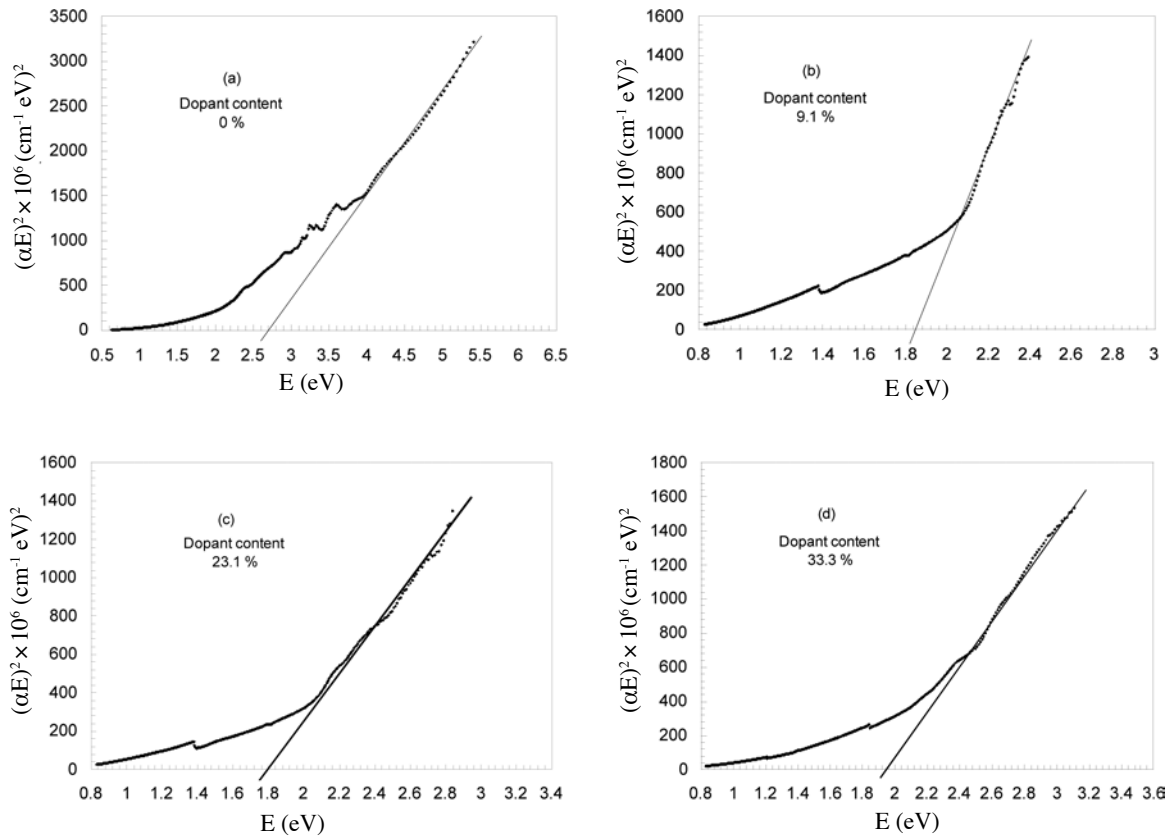


FIGURE 1. Plots of  $(\alpha E)^2$  against photon energy  $E$  for different dopant contents (a) 0% (b) 9.1% (c) 23.1% (d) 33.3%

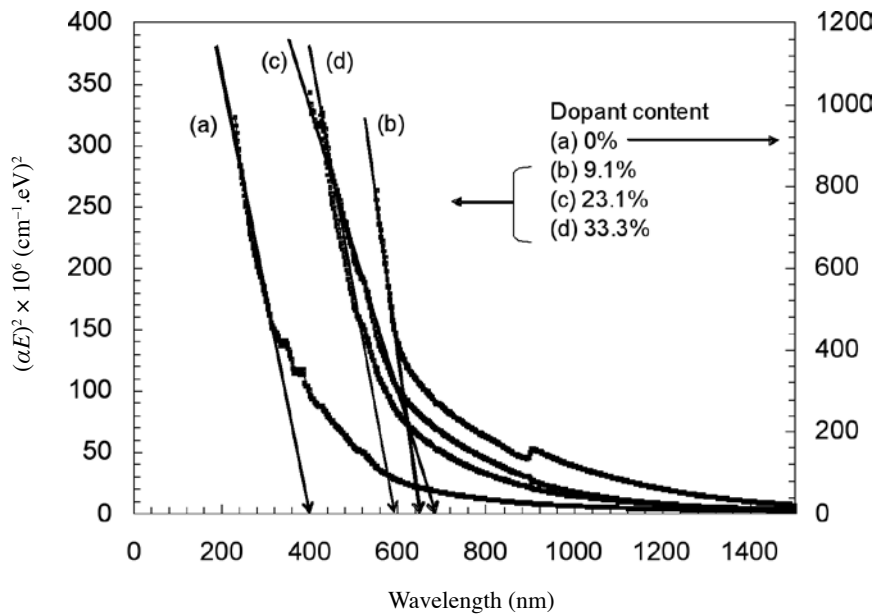


FIGURE 2. Plots of  $(\alpha E)^2$  versus wavelength for different dopant contents indicate red shift existence along the absorption edge

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