

Investigation of the Effect of Solvents on the Structure and Optical Properties of the Organic Semiconductor Anthracene

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Abstract:

In this work, thin films of anthracene were prepared with various solvents (dichlorobenzene, acetone, and toluene) on glass substrates by spin coating. Our paper explores the structural and optical measurement techniques that shed light on these films. Two distinct peaks were identified in the XRD examination of the anthracene powder; these peaks moved to the higher 2θ in response to various solvent treatments. Atomic force microscopy (AFM) demonstrates unequivocally that, in contrast to other solvents, samples made with dichlorobenzene solvent do not exhibit anthracene aggregates. The energy band gap and the trap levels found in the forbidden energy gap govern the optical characteristics of anthracene thin films. Surprisingly, the kind of solvent used has a significant impact on these qualities; they are not independent.

Key word: (thin films, Anthracene, solvents, properties, band gap).

1. Introduction

Organic semiconductors are a ravishing class of materials, with a wide range of properties [1-7]. The increasing demands of enhancing Si-based electronics with materials that offer easier processing methods completed with functionalization by chemical manipulation motivate the interest in organic electronics[8].

Aromatic materials are fascinating organic compounds that feature unique ring structures in their structure. The benzene ring is the simplest types of aromatic compounds consisting of six carbon atoms and six hydrogen atoms. In the aromatic series, benzene is recognized as the origin compound [9]. Compounds known as isomers share the same chemical formula but have different structural characteristics. Isomers, then, have different atomic orders but the same number of atoms in each element. Despite having the same chemical formula, each molecule's physical characteristics might vary. The process of changing one molecule into another with similar atoms is known as isomerism. This might happen on its own or maybe a reaction is needed to make this happen. Anthracene is one example of an isomeric aromatic compound [10].

Despite being the first organic chemical studied in the 1950s and 1960s for organic semiconductor conductivity, anthracene remains a promising molecule [11-13]. The

anthracene One of the most studied spectrally active chemicals is anthracene due to its remarkable solubility in a variety of solvents and physical properties, including its vibrant electronic spectrum during both absorption and emission [14].

An significant class of chemicals, anthracene and its derivatives have been the subject of much research in many fields. Certain anthracene derivatives, which are used in the construction of electrical and photonic devices, show promising features in the field of materials science [15]. Anthracene is a solid polycyclic aromatic hydrocarbon consisting of three benzene rings fused. Thus anthracene, now approaching its centenary still provides abundant material for scientific research and practical application [16]. In addition to, anthracene single crystals can act as the organic semiconductor materials, which could be acquired by vapor crystallization [17], zone refining [18], or by solvent process [19,20]. Anthracene, like most aromatic compounds, it tends to use herringbone packing to increase the intermolecular van der Waals forces, maximize the stacking density, and lower the energy state [21].

By estimating the contribution of each type of universal interaction (dispersive, inductive, and polarization) to the total spectral shift recorded by passing the spectrally active substance from its gaseous phase into a homogeneous solution achieved in solvents with different physical properties, the effect of solvents on the electronic spectra of some anthracene derivatives was studied [22–24].

In order to streamline the film manufacturing process, we looked at the promising material anthracene in this work to understand the function of various solvents in the anthracene matrix. We present a thorough analysis of the impact of solvents on the optical characteristics and composition of anthracene.

2. Material experimental details

Anthracene dissolved in the solvents (dichlorobenzene, acetone, toluene) purchased from Sigma-Aldrich company, has chemical formula $C_{14}H_{10}$ and molecular weight ($M_w=178.23$ g/mol).

Anthracene thin films were deposited on glass substrates, each of $(2.5 \times 2.5 \text{ cm}^2)$ area, were used as substrates. Spin casting was utilized to make anthracene thin films. Using this procedure, many milligrams of anthracene are dissolved in the solvents to create a solution with the right concentration. It was conveyed in many drips using a pipette on a clean, high-quality glass substrate. The substrate must be positioned horizontally to guarantee that the thin layer of solution covers the entire surface. It must then be covered to slow down the rate of evaporation and achieve a homogeneous thickness of thin and crystalline models. Avoid materials that melt in the solvent since they can alter the manufactured material's purity by melting other materials. Place them in a tiny, closed glass tube and place it on a magnetic stirrer set to 70 degrees Celsius for 50 hours.

Composition measurements for as-deposited anthracene thin films were done using X-ray analytical X'pert Pro Made in Netherlands, size = 0.05° . Time per steps = 1s, $\Delta = 1.54 \text{ nm}$. The scanning angle 2θ was varied in the range of $(3^\circ - 60^\circ)$ with speed 5.00

(degree /min) with preset time = 0.24 (sec). Using Core AFM 2023 and Nanosurf AG Switzerland, surface morphological measures for as-deposited Anthracene thin films were investigated. AFM micrographs may offer information regarding 2D pictures for all analyzed materials. The Japanese firm Shimadzu used a UV-visible spectrophotometer to test the combination dispersions in order to determine how the solvents affected the absorption film. The ultraviolet-visible absorption spectra were recorded in the wavelength range 200–400 nm at room temperature. Anthracene thin films with a thickness of 100 nm were tested using photoluminescence measurements taken by a Renishaw 2000 system operating at excitation wavelengths of 300 nm. The thin films were made with several solvents (dichlorobenzene, acetone, and toluene) to demonstrate the energy gap.

3. Results and discussion

3.1 structure measurements

The powdered anthracene thin film's X-ray diffraction patterns are displayed in Figure (1). Figure (1) depicts the X-ray diffraction spectrum of anthracene. It has three minor peaks and two sharp peaks at approximately 11.35° and 19.35° , respectively, corresponding to the (100) and (200) planes. It indicates that the nature of the film's structure is polycrystalline..

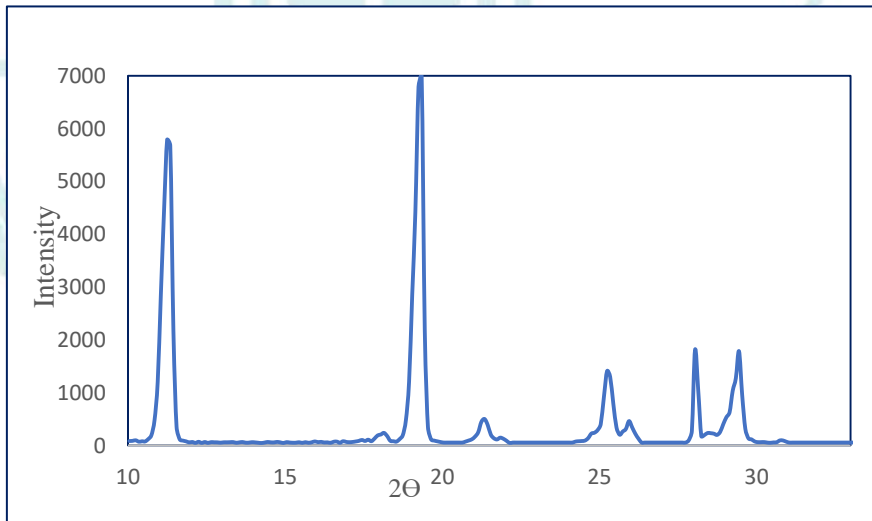
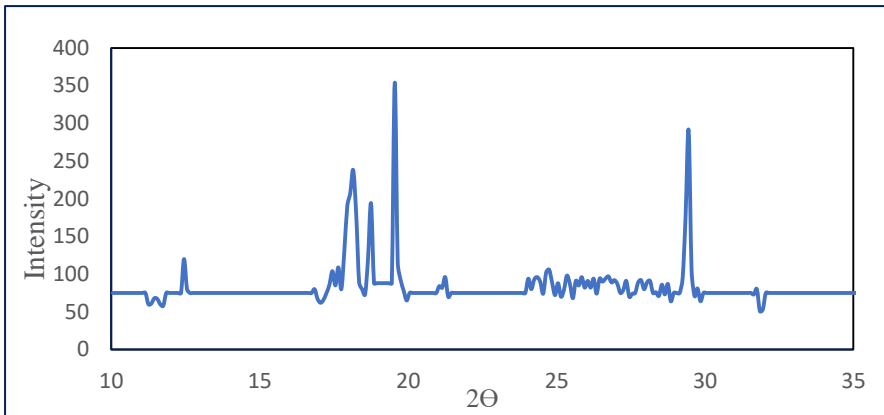


Figure (1): XRD thin-film pattern powdered anthracene

Figure (2) displays the patterns of X-ray diffraction. Using the spin coating technique, a solution approach is used to create the thin film of anthracene using the solvent



dichlorobenzene.

Figure (2): XRD pattern of anthracene thin films made using dichlorobenzene as a solvent

Figure (2) shows the X-ray diffraction spectrum of anthracene in thin films that have been formed; it has two sharp and two tiny peaks. It indicates that the nature of the film's structure is polycrystalline. The findings indicate that this solvent caused the peak to move to the higher 2θ .

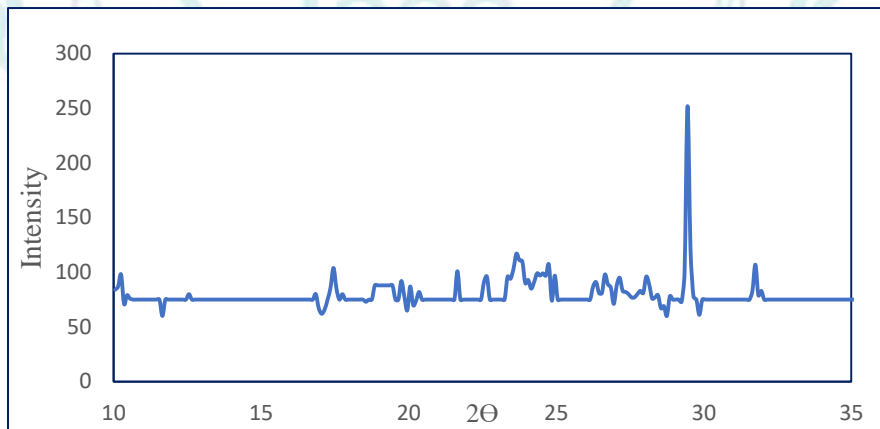


Figure (3): The XRD pattern of anthracene thin films made using acetone as a solvent

Additionally, deposited anthracene thin films have one strong shift to the higher 2θ with this solvent and a few tiny peaks in their X-ray diffraction spectra, as seen in figure (3). It indicates that the nature of the film's structure is polycrystalline. The nature of the thin-film anthracene crystal structure on the glass substrate is revealed by the investigation X-ray (XRD) data. They have both a monoclinic and a polycrystalline multi-crystalline structure.

The thin film of anthracene generated with a solvent toluene is created by a solution method employing the spin coating technique, as shown by the X-ray diffraction patterns in Figure (4). The X-ray diffraction spectrum of anthracene revealed many tiny peaks and one strong peak that was moved to the higher 2θ when compared to anthracene powder. It indicates that the nature of the film's structure is polycrystalline.

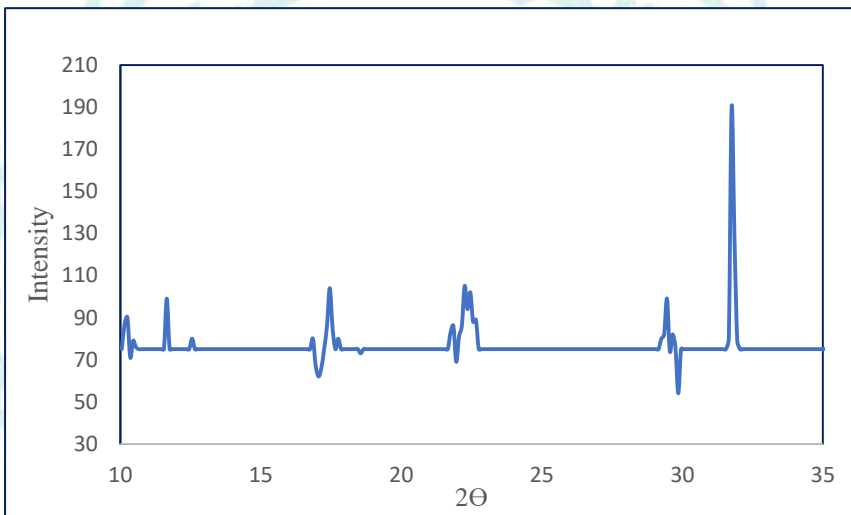
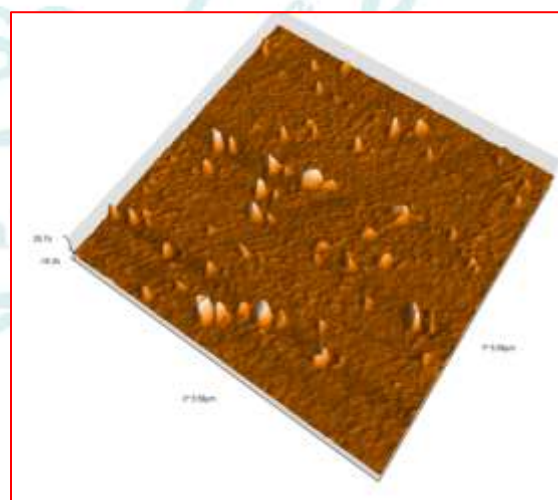
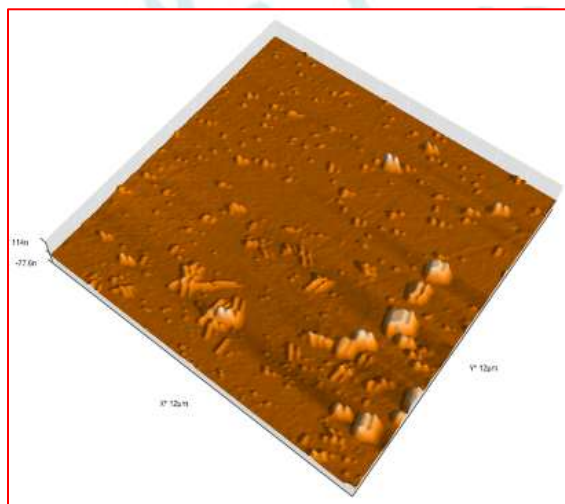
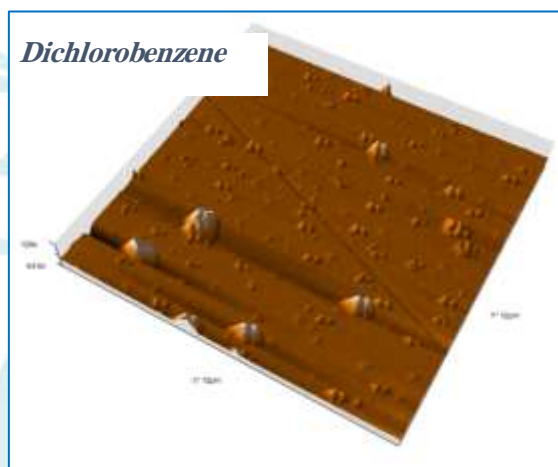
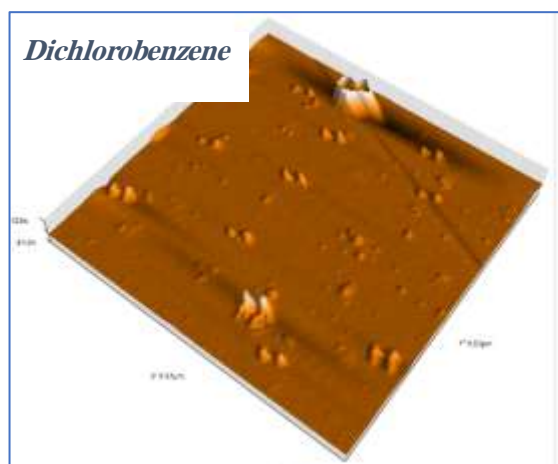


Figure (4): XRD thin-film pattern of anthracene made with toluene as a solvent

We observe that the positions of the peaks and the kind of solvent used alter the crystal structure of anthracene when utilizing various solvents. Anthracene powder has two distinct peaks, one of which moved to the higher 2θ when exposed to different solvents.

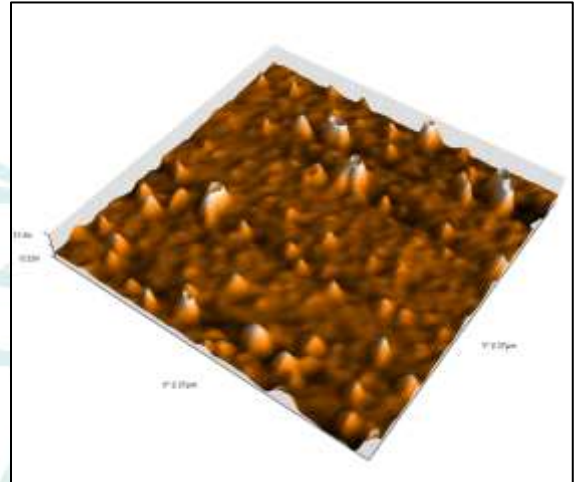
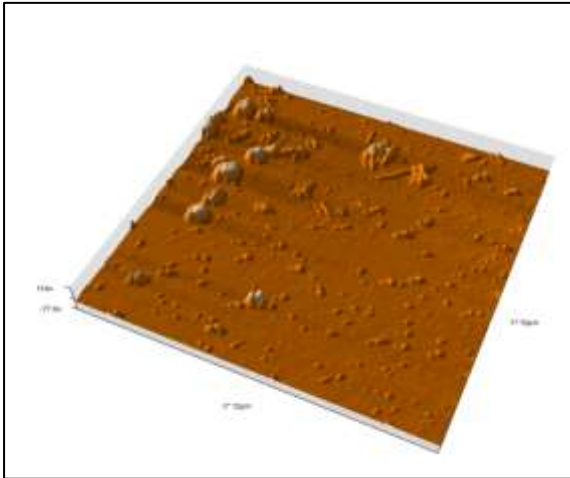
In this work, the surface morphology of anthracene thin films made at room temperature was observed using two-dimensional AFM profiles, which were obtained from AFM pictures. It's evident from the AFM photos in Figures (5). Because the blended polymer mixture is appropriately soluble, an organic solvent may have an impact on the polymer active layer. AFM examination of the surface morphology was done to determine the impact of various solvents on the active layer. Due to different solvents, even if the active layers are created at the same spin speed, there is a noticeable difference in surface morphology in their AFM pictures. Different active layers of anthracene produced using

solvents such as dichlorobenzene, acetone, and toluene, respectively, are shown in AFM pictures (2D view) in Figure (5). These photos show that samples made with dichlorobenzene solvent do not include any anthracene aggregates. This might be because AC is more soluble in dichlorobenzene than it is in acetone and toluene.



Acetone

Acetone



Toluene

Toluene

Figure (5): AFM images of the anthracene films prepared by using solvents of dichlorobenzene, acetone, and toluene

3.2 Optical Measurements

Figure (6) presents the absorption spectra of anthracene thin films that were produced using various solvents and had a thickness of 100 nm. It is evident that the absorption edge of anthracene spectra is impacted by the use of various solvents.

The transmittance spectra for anthracene thin films generated in various solvents are displayed in Figure (7), where they exhibit the opposite behavior as the absorbance spectra. Conversely, the fluctuation of the absorption coefficient with wavelength for the four produced materials is shown in Fig. (8).

The distinctive peaks seen between 325 and 425 nm are associated with the anthracene core's $\pi-\pi^*$ ($S_0 \rightarrow S_1$) transitions. The values of E_g^{opt} has been determined using Tauc equation to find transition type by plotting $(\alpha h\nu)^r$ where $r=2$ versus photon energy ($h\nu$) and select the optimum linear part intersect the $h\nu$ axis as shown in Fig. (9). The energy

gap also affected depending on the absorption edge by dissolve the Anthracene with dichlorobenzene, acetone, and toluene and their values were (3.9, 3.84 and 3.86)eV respectively.

The change in refractive index with solvent as a function of wave length is shown in Fig. (10). As seen in Fig. (11) the extinction coefficient explains the energy loss associated with the absorption coefficient.

Figures (12) and (13) Display the wavelength-dependent changes in the real (ϵ_1) and imaginary (ϵ_2) components of the dielectric constant for anthracene thin films made with various solvents. With the change in heat treatment, the behavior of ϵ_1 and ϵ_2 is the same as that of n and k , respectively. The imaginary component of the dielectric constant mostly depends on the (k) values, which are connected to the fluctuations of the absorption coefficient, whereas the variations of ϵ_1 primarily depend on the value of (n^2) due to the lower values of (k^2) compared with (n^2).

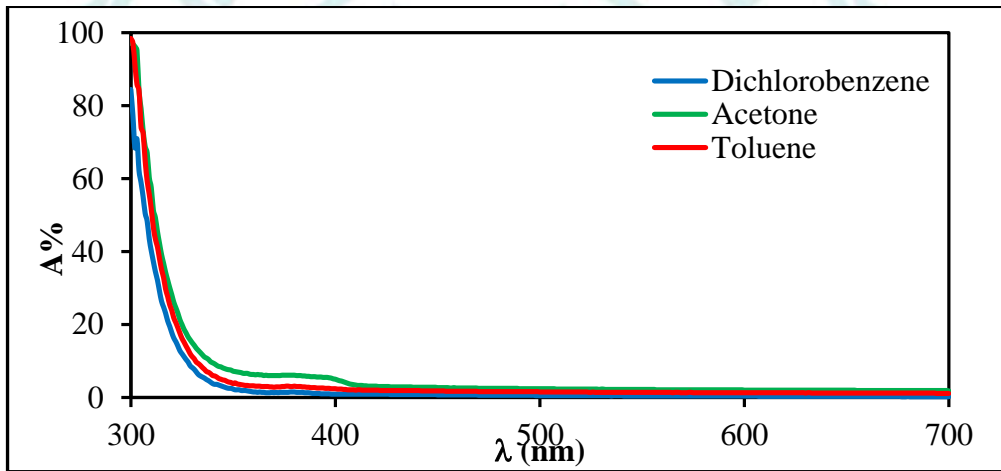


Figure (6): The absorbance of anthracene thin films prepared with different solvents as a function of wavelength

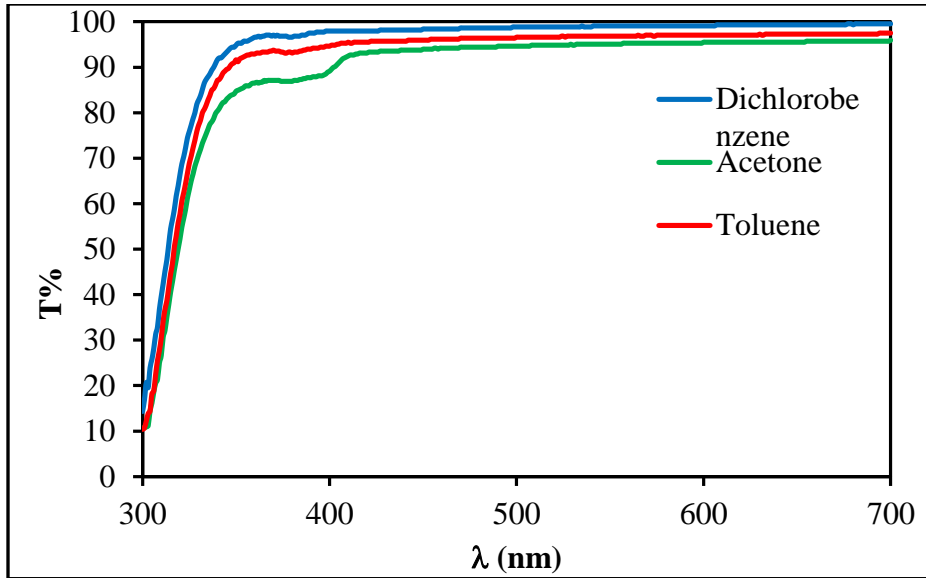


Figure (7): The transmittance of anthracene thin films prepared with different solvents as a function of wavelength

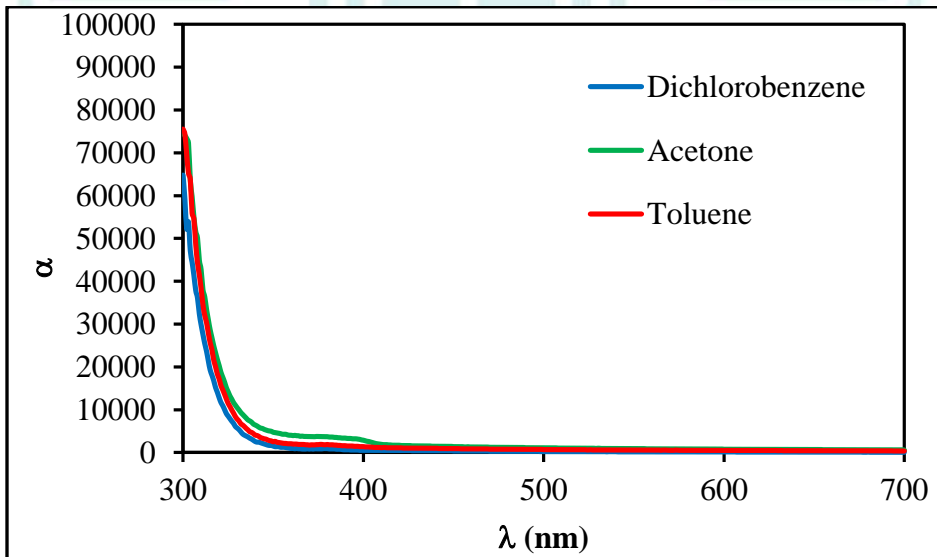


Figure (8): The absorption coefficient of anthracene thin films prepared with different solvents as a function of wavelength

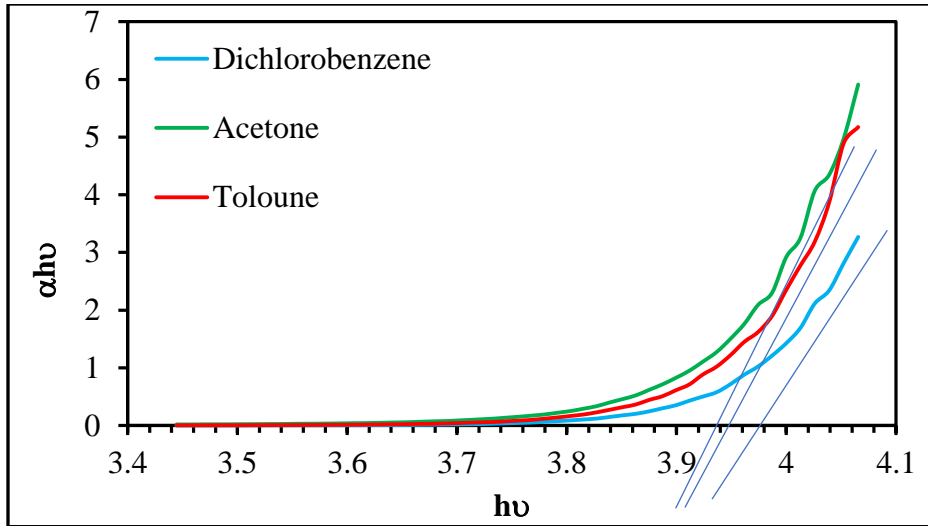


Figure (9): $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of anthracene thin films prepared with different solvents

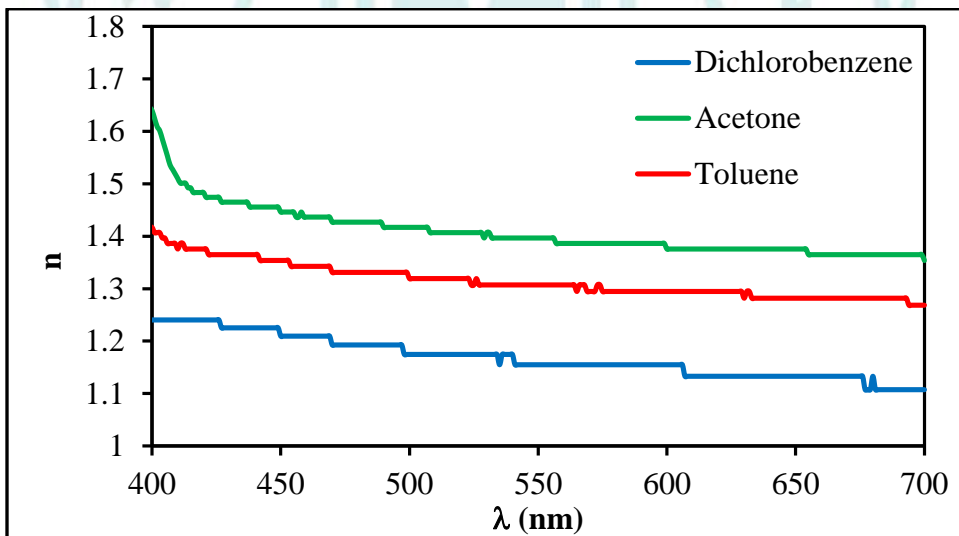


Figure (10): The refractive index of anthracene thin films prepared with different solvents as a function of wavelength

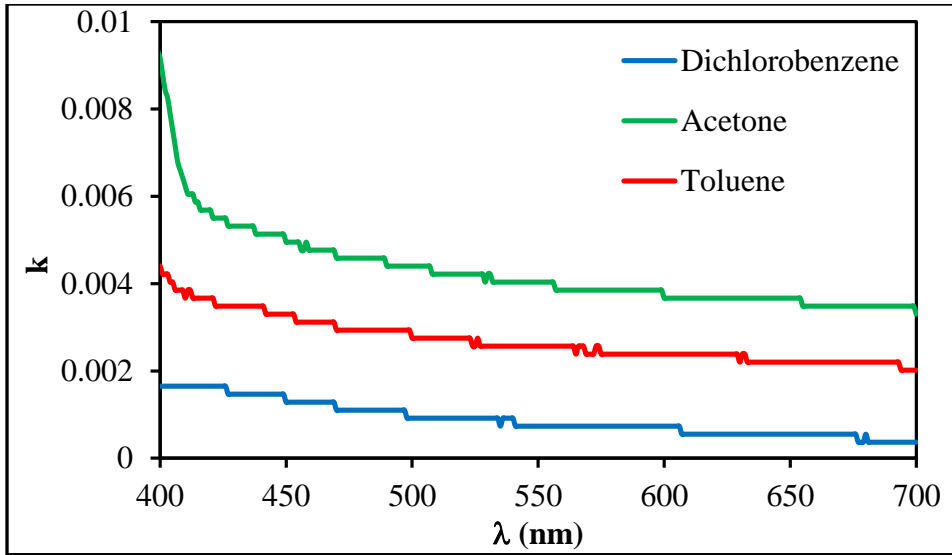


Figure (11): The extinction coefficient of anthracene thin films prepared with different solvents as a function of wavelength

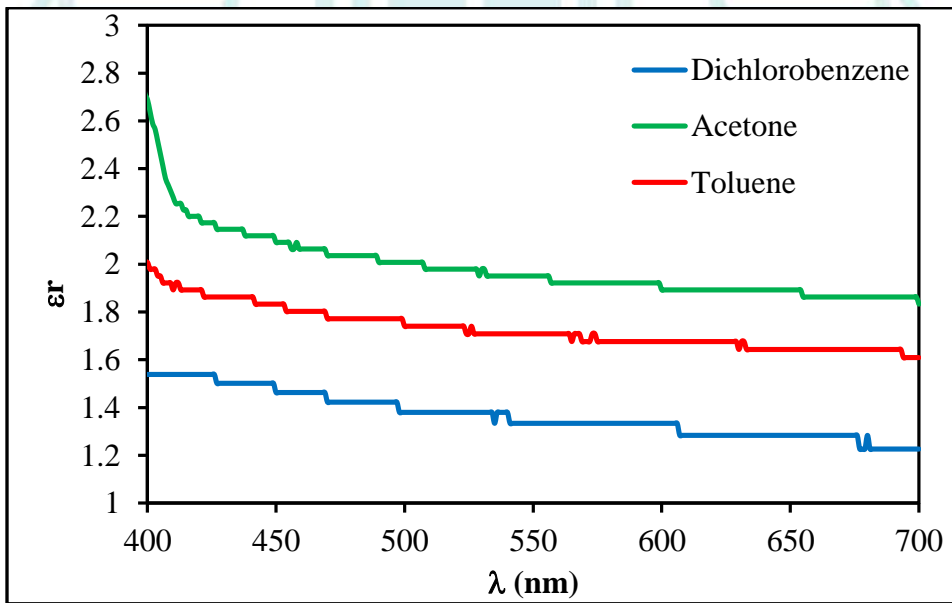


Figure (12): The real part of the dielectric constant of anthracene thin films prepared with different solvents as a function of wavelength

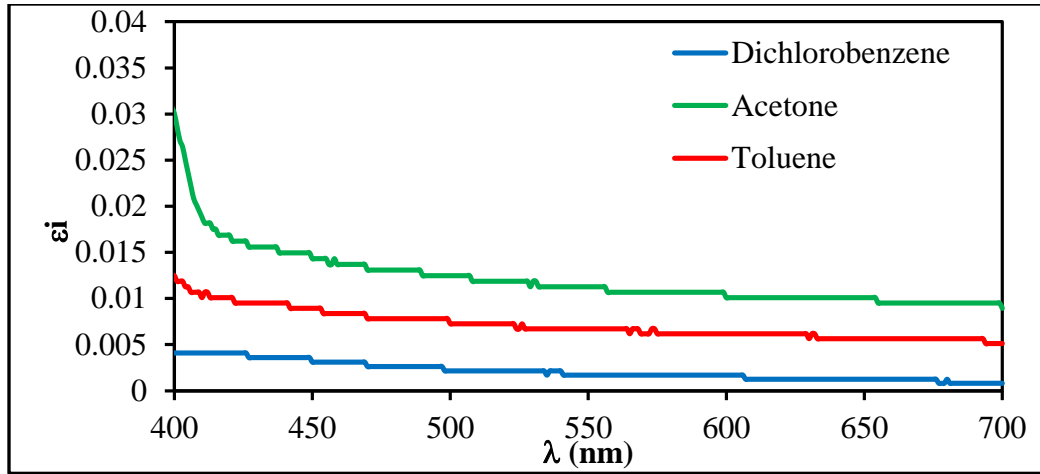


Figure (13): The imaginary part of the dielectric constant of anthracene thin films prepared with different solvents as a function of wavelength

The photoluminescence (PL) spectroscopy was conducted on anthracene compounds in dichlorobenzene, acetone, and toluene to study the effect of different solvents on the absorption edge of anthracene. The optical energy gap have been determined using PL spectra and their values were (3.76, 3.73 and 3.71)eV respectively. These results confirm the results obtained by UV-Vis measurement.

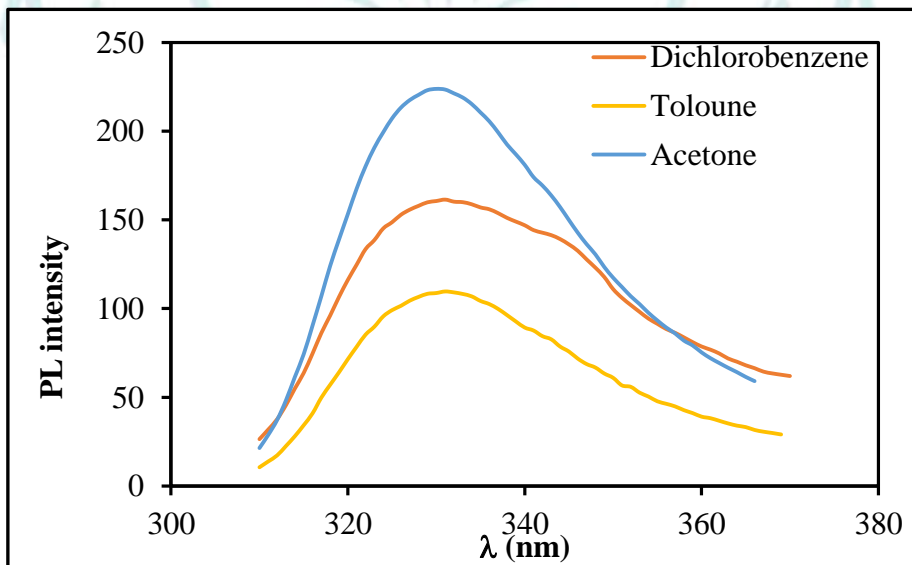


Figure (14): The Photoluminescence spectra of anthracene thin films prepared with different solvents as a function of wavelength

4. Conclusion

In the current study, the anthracene thin film was effectively created utilizing the spin coating approach with several solvents. We looked at anthracene in powder and thin-film forms using XRD analysis. The films have a polycrystalline structure, as shown by the results. We looked at anthracene in powder and thin-film forms using XRD analysis. The films have a polycrystalline structure, as shown by the results. It has been discovered that the solvent type affects the energy band gap and the trap levels located in the forbidden energy gap, which govern the optical characteristics of anthracene thin films. When molecules of anthracene rearrange, they interact in a Vander Waals-type way, which changes the energy band gaps HOMO and LUMO. Different solvents are causing molecular rearrangements.

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