

## Enhanced Absorption Edge of Anchusa-Italica-Doped Pentacene towards Optoelectronic Applications

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**Abstract.** The dye-doped polymer is commonly used in the field of optoelectronics, given its effectiveness in optimising the device's performance. This study is devoted to the synthesis and characterisation of Anchusa-Italica-doped Pentacene thin-film. Scanning electronic microscopy structural analysis, Fourier transform spectroscopy, and UV-visible transmittance spectra with a range of 300-900 nm were also carried out. The fundamental optical properties such as the absorption coefficient, optical energy gap, absorption and refractive indices were calculated based on the methods already used in the literature as Tauc's relationship. The morphology of the samples indicated that dye structure was affected in the doped pentacene. The Fourier transform infrared technique (FT-IR) resulting spectrum of the doped samples also showed a significant absorption peak corresponding to C-H as an index of impurities. The calculated band-gap energy of the impurity sample was reduced and was the lowest compared to both the pure dye and polymer samples. The optical absorption and transmittance spectra revealed that it was positioned in the desirable ranges for optoelectronic applications. An anomaly in the absorption index was also observed through excitation of the resonance mode with transparent indication. This effect was deduced from the calculation of the refractive index. The results presented in this paper significantly contribute to the developments in the field of optoelectronic devices based on dye/polymer organic materials.

### Introduction

Nowadays, the need for green renewable energy is becoming imperative due to its contribution to resolving environmental and human health problems. The use of natural dye extracted from plants for optoelectronics applications is one of the subjects that have contributed towards reducing global environmental pollution [1-3]. Natural dyes are widely available, easy to extract and considered as green technology [4-6]. The features mentioned above provide fascinating attributes for applications in several domains. Many previous works have reported on the technology of natural dye extraction, including applications in textile dyeing [7-9], functional finishing [10-12], food coloration [13-15], cosmetics [16,17], histological staining [18-20], dye-sensitised solar cells [21-23], PH indicators [24-26] and several optoelectronic applications [27-29]. Some investigations of natural dyes have acquired significant results through employing pigments extracted from plants. In the literature, many articles have tended to focus on biomaterials dyes, like anthocyanins, cyanidins, tannins, chlorophyll and their derivatives (carotenoids, betalains, chalcones, etc.) [30,31]. One of the primary sources of natural dyes is flowers given their composition, which includes anthocyanin. The anthocyanin is responsible for most cyanic colours extending from the scarlets, reds and violets to the dark blue of the flavonoids of the flowers, fruits and also leaves [32]. The significant interest in natural dyes, for photosensitisers, for example, is due to their high absorption efficiency, light gain efficiency, low cost, easy preparation and eco-friendliness. Given these important factors, the exploration of new natural sources of dyes is motivating and attracting most researchers in this field.

In solar cell applications, efficient generation of electron-hole pair (exciton) is required to create a thin functional layer having a large bandgap with sufficient energy. Such bandgap can be achieved in a dye-doped polymer interface, such as dye-doped pentacene [33-35]. The latter has enhanced electronic coupling between the dye electrolyte and the semiconducting electrode, providing a broad spectrum of absorption. No electron recombination should be allowed to occur across the electrode/electrolyte interface [36]. Together, these factors can strengthen the power conversion efficiency of optoelectronic devices. The organic dye acts as the prototype model, whereas the pentacene represents the electron acceptor molecule [37]. Accordingly, the pentacene (see Figure 1), which is derived from the acene family has been the main focus of researchers for many years [38]. This is mainly due to the natural control of the electron transition and absorption characteristics, linked to the conjugated p-electron system as well as what is called synthetic protocols of the reactions in the acene core with large groups [39].

Depending on the structural features of the pentacene, natural dyes, like *Anchusa Italica*, which may be considered as a good candidate, have not been used previously in the literature. *Anchusa Italica* belongs to the genus *Borage* of the family *Boraginaceae* and is an essential popular medicinal plant found in the Mediterranean and tropical regions [40,41]. This plant contains alkaloids, tannins, saponins, triterpenes, and the major components of natural dyes: the polyphenols such as anthocyanins and flavonoids [42]. Consequently, due to the  $\pi \rightarrow \pi^*$  conjugated electronic structure of natural dye and the semiconducting behaviour of polymers, many works have exploited the dye and/or polymer in different applications [43-46]. Mixing dye-doped polymers present an extremely efficient material combination that have been employed widely as [47-49] and considered promising candidates in photo-physical properties [50-54]. Research on the preparation of new materials, which observe and develop semiconducting and optoelectronic materials, is effectively important.

This study aims to obtain a desirable optical material combination of dye and polymer and improve their optical properties. We begin by extracting valuable natural dye from *Anchusa Italica* flowers, which is used later as filler together with pentacene. The optical properties of the resulting natural dye-doped polymer, in both solution and powder forms, were systematically characterised. The results presented in this work should significantly contribute towards the development of applications that use organic/inorganic electronic and optoelectronic devices.

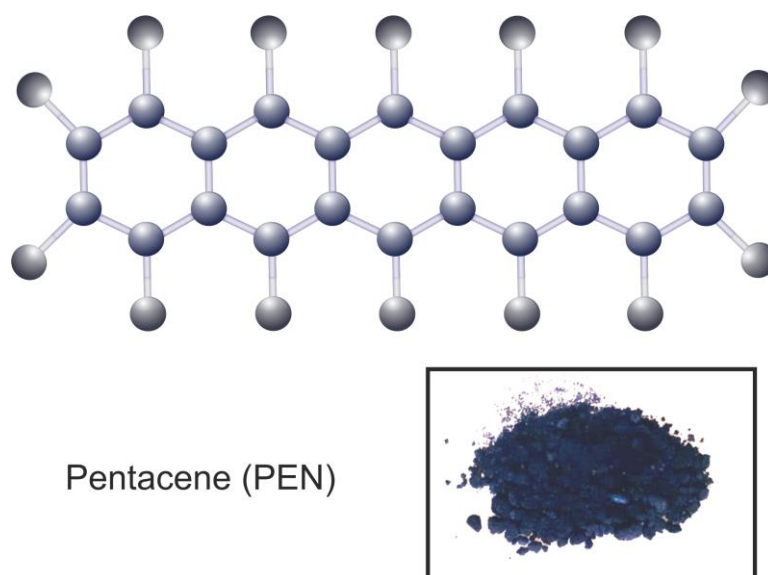


Fig. 1: Chemical structure of pentacene  $C_{22}H_{14}$  molecule and its production in powder form.

## Materials and Methods

**Natural dye extraction.** The *Anchusa Italica* (*A. Italica*) flowers for this research were purchased from local pharmacies and verified laboratories in Iraq. The petal layers were initially washed under

running tap water to eliminate any dust particles. These petals were then dried in the shade at room temperature for up to two weeks and then crushed with mortar. The aqueous extract ore was used through which the powdered plant was soaked in distilled water in a closed glass container. About 6 g of the powdered petals of the flower were dissolved in 100 ml of distilled water and placed in a water bath, ensuring that the impregnation was continuous for around 10-15 minutes (see Figure 2). Afterwards, the extracts were filtered using medium fast filter paper with 55 g/m<sup>2</sup> and 0.33 mm thickness and left to cool down completely. The extracted dye was kept in suitable glass containers at a temperature of 4 °C for use in later experiments. The concentration was determined to be 7% without the need for the molecular weight of the plant [55].

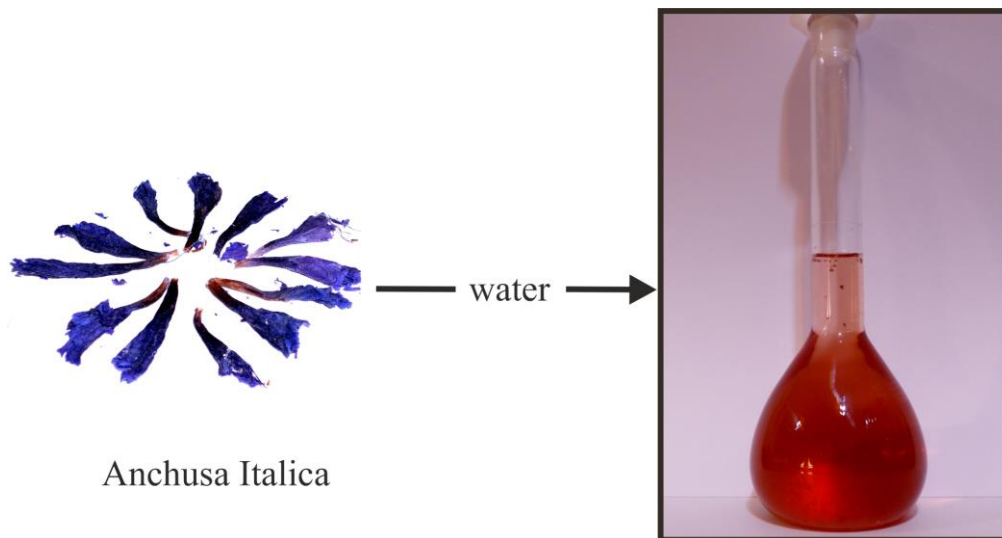


Fig. 2: A. Italica flower and its extracted dye.

**Preparation of pentacene solution.** Pentacene (C<sub>22</sub>H<sub>14</sub>) was obtained from Sigma-Aldrich Chemical Co. Ltd. The same method, as described above, was followed, with the only difference in that chloroform was used as a solvent. A given weight of pentacene (PEN) solution was placed in a glass container with a tightly fitting lid before placing under a magnetic stirrer to completely dissolve the contents before being left for 24 hours to ensure optimum homogeneity was attained. Next, the solution was filtered using medium fast filter paper with 55 g/m<sup>2</sup> and 0.33 mm thickness. The table below shows the used substances, their concentration and the stirring time.

Table 1: The solvents used in the preparation.

Substance	Solvent	Substance concentration (M)	Stirring time (min)
Pure Pentacene	Chloroform	0.64	20
Pure Dye	Distilled water	0.07	30

The molar ratio M is determined using the following relation:

$$M = \frac{W(\text{gm})}{W_m \left( \frac{\text{gm}}{\text{mol}} \right)} \times \frac{1000}{\text{Volume}(\text{ml})} \quad (1)$$

where W and W<sub>m</sub> represent the weight and the molecular weight respectively.

**Preparation of thin-film.** As the PEN is the host material, the dye-doped PEN films were prepared using the following physical mixing process. A volumetric ratio of polymer (V = 0.19 ml) and dye

( $V = 0.01\text{ml}$ ) solutions were mixed to obtain 5% of the doping ratio upon which time the final product was placed into a glass container for 24 hours to ensure homogeneity. The solution was then filtered and placed on a clean glass slide to create thin-films by applying a spin-coating method for several rotations (1000 rpm/min). The samples were next dried at ambient room temperature for 24 hours to ensure their suitability. The A. Italica-doped PEN films were uniform and pure enough to be used with a thickness of about 190 nm.

**Stretching mode analysis.** The infrared spectrum of the pure *Anchusa Italica* dye and A. Italica-doped-PEN powders were obtained and recorded as KBr disk using the Fourier Transform Infrared Technique (FT-IR). The results of the IR spectroscopy in the mid IR range ( $4000\text{--}400\text{ cm}^{-1}$ ) are shown in Figure 3. The examination of the transmitted light reveals the amount of energy absorbed at each frequency. The different absorption peaks presented in Figure 3(a) resulting from the interaction between electromagnetic radiation and matter detected in the molecule is the O–H group which has stronger bonds and light atoms vibrating at a high stretching frequency at  $3386\text{ cm}^{-1}$ . Also, the group responsible for absorption described by the anti-peak at  $2927\text{ cm}^{-1}$ , represents the saturated C–H stretch. These absorption peaks of the O–H and C–H groups are attributed to acids, flavonoids, fatty, saponins and tannins. The high absorption band seen at  $1631\text{ cm}^{-1}$  is due to the conjugated dyeing C=C stretch vibration.

Furthermore, the carbonyl bond of C=O, depicting weak stretching vibration is located at  $1735\text{ cm}^{-1}$  which is due to the variation of polar dipole-dipole interaction. The latter is conferred to hexahydrofarnesyl acetone, diisobutyl phthalate, flavonoid and tannins. Another noticeable band of C–O stretch is found at two different frequencies: the strong signal at  $1061\text{ cm}^{-1}$  due to the  $\text{sp}^3$  orbital and a weak peak located around  $1253\text{ cm}^{-1}$  due to  $\text{sp}^2$  orbital. The weak signal located at  $1416\text{ cm}^{-1}$  is attributed to the  $\text{CH}_2$  bend.

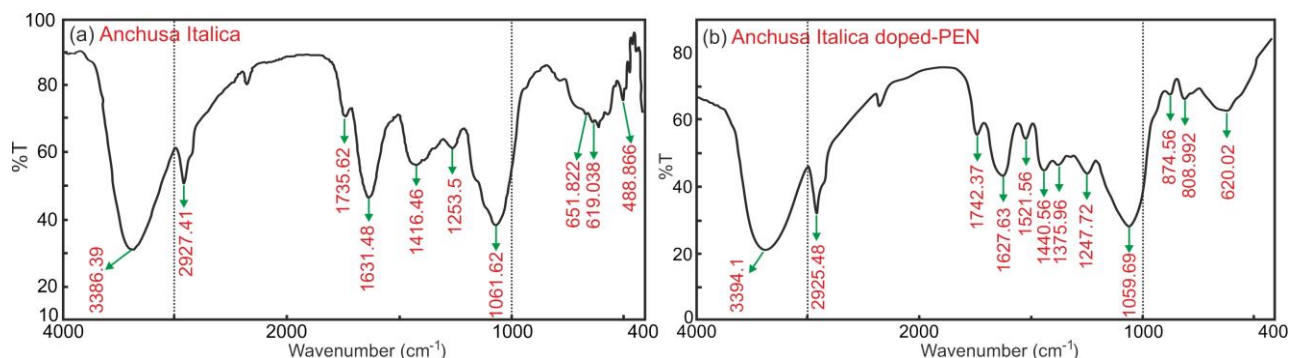


Fig. 3: The FT-IR spectra of thin-films, pure A. Italica (a) and A. Italica-doped PEN (b).

Regarding the IR-transmission spectrum of pure PEN, more details regarding the interpretation for the reader can be seen by referring to [56]. The FT-IR spectrum of the A. Italica-doped PEN is presented in Figure 3(b) in which this spectrum displays a unique band around  $3394\text{ cm}^{-1}$  [ $\nu$  (O–H)], in which the spectrum at  $2925\text{ cm}^{-1}$  is attributed to C–H aliphatic whereas the participation of C=O group is localised at  $1742\text{ cm}^{-1}$ . The range between  $1627$  and  $1247\text{ cm}^{-1}$  exhibits active bands which are due to the functional group of C=C aromatic and olefinic groups at  $1627\text{ cm}^{-1}$ . The absorption peak at  $1059\text{ cm}^{-1}$  is attributed to the bending vibration of the C–O group. Furthermore, two bending vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  can be observed at  $1440\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$ , respectively. The essential changes in the IR spectrum of the doped sample can be seen in the  $1000\text{--}2000\text{ nm}$  range. The critical IR transmittance bands of the compounds are presented in Table 2.

Table 2: The main IR transmittance bands recorded for the powder compounds.

Compound	$\nu(\text{O-H})$ str.	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C=O})$ str.	$\nu(\text{C=C})$ str.	$\nu(\text{C-O})$ str.	$\nu(\text{C-H})$ aliphatic bend
A. Italica	3386	2927 (m)	1735 (w)	1631 (s)	1061 (s)	1416 (w)
A. Italica-doped PEN	3394 (br)	2925 (m)	1742 (w)	1627 (s)	1059 (s)	1440 (w)

br = broad, m= medium, s= strong, w= weak

The characterisation of surface micrographs is essential for optoelectronic devices. The surface analysis of both PEN and A. Italica-doped PEN films were investigated by Scanning Electron Microscopy (SEM). As shown in the SEM image of the PEN surface (Figure 4(a, b, c and d)), many grains, distributed throughout the sample surface, exhibit a large size (50 nm); thus indicating a polycrystalline, amorphous structure with a high density (as shown in Figure 4(b), which is a close-up of figure 4(a)). On closer examination of the Figure 4 results, several cracks can be seen in the surface morphology of the PEN film (as per the red arrow shown in Figure 4(a)). Meanwhile, aggregates of many grains are also observable in Figure 4(c), as A. Italica-doped PEN film, which appears to have less roughness regarding surface morphology (as shown in the magnified image of Figure 4(d)). This filler shows that the dye has a well-enhanced structure and the cracks presented in Figure 4(a) have saturated and filled completely (see Figure 4(c & d)). Furthermore, this observation is in good agreement with the FT-IR results.

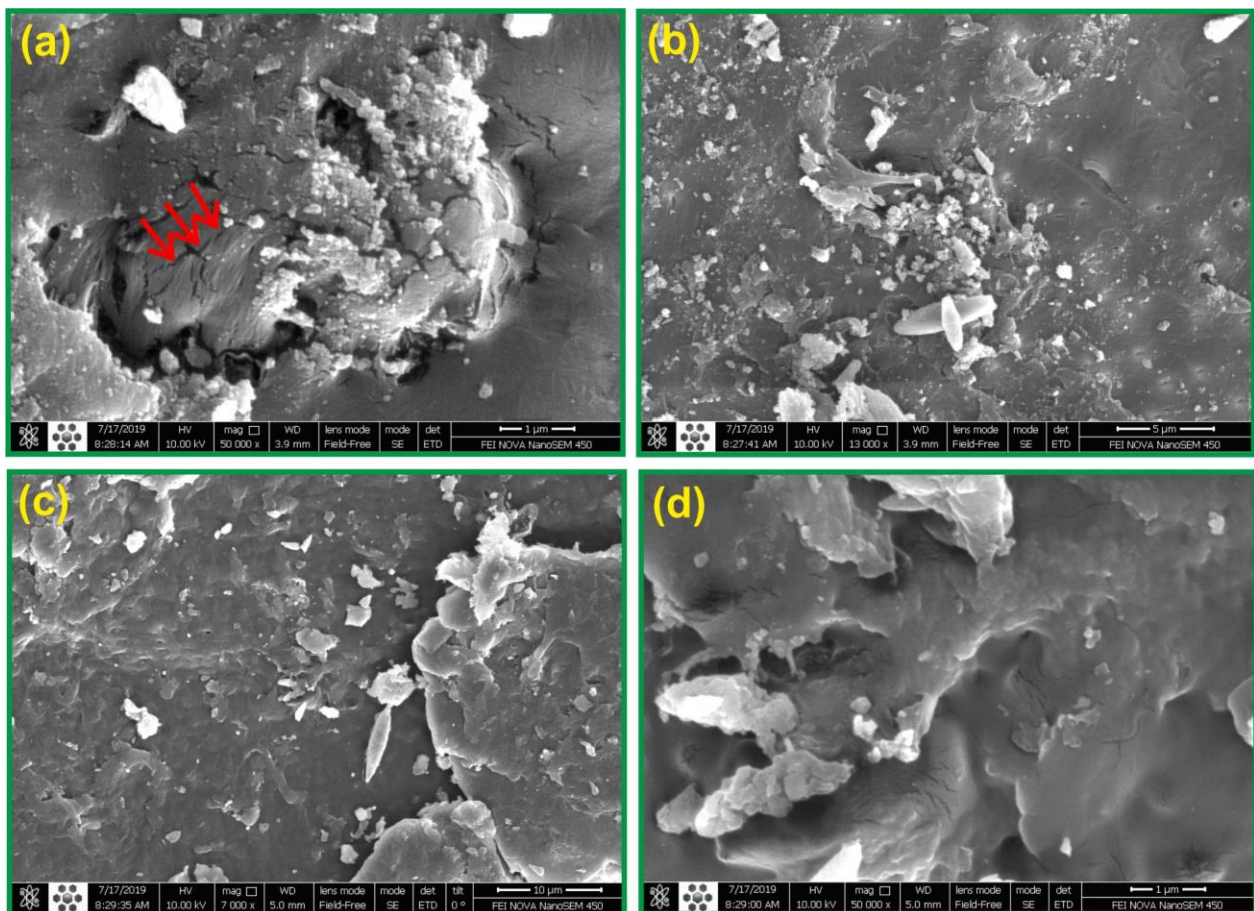


Fig. 4: SEM images of the studied pure PEN film (a), a zoom-in made over the same slice of PEN film in a (b). A. Italica-doped PEN (c), a zoom in made over the slice in c (d).

## Results and Discussion

For optoelectronic applications, linear optical properties of direct and indirect bandgaps are fundamental and are characterised by the study of the electronic structure of an organic compound. Due to the unusual linear optical parameters, a more detailed study on thin-film samples must be performed, such as absorptions, transmittances, reflectance, optical absorption coefficient, optical energy gap, excitation factors, and different other parameters.

**Optical absorption and transmission.** The optical absorbance spectrum is affected by several factors: the chemical composition, the absorbed photon energy, the thickness and the topography of thin-film. In our study, several UV-visible spectroscopies were performed using a double beam UV-visible spectrophotometer (CE-7200) at room temperature. Absorption spectra were recorded for the pure A. *Italica* dye, Pentacene and A. *Italica*-doped PEN thin-films in the 300-900 nm band. From the results presented in Figure 5(a), it can be seen that the absorbance spectrum of the pure pentacene is strongly affected by the doping with A. *Italica* dye. The absorbance is maximised in the 350-550 nm bandwidth, having a maximum value between 350 nm and 400 nm. This result demonstrates a significant amount of absorption, which is desirable in optoelectronic devices. Moreover, the absorption of A. *Italica*-doped PEN thin-film significantly decreased in the broad 350-600 nm bandwidth. Indeed, it is well-known that photon energy in the UV and visible spectra by the materials as organic molecules contain the single (mono) bond ( $\sigma$ ), twin or triple bond  $\pi$ , and nonbonding n-orbitals electrons.

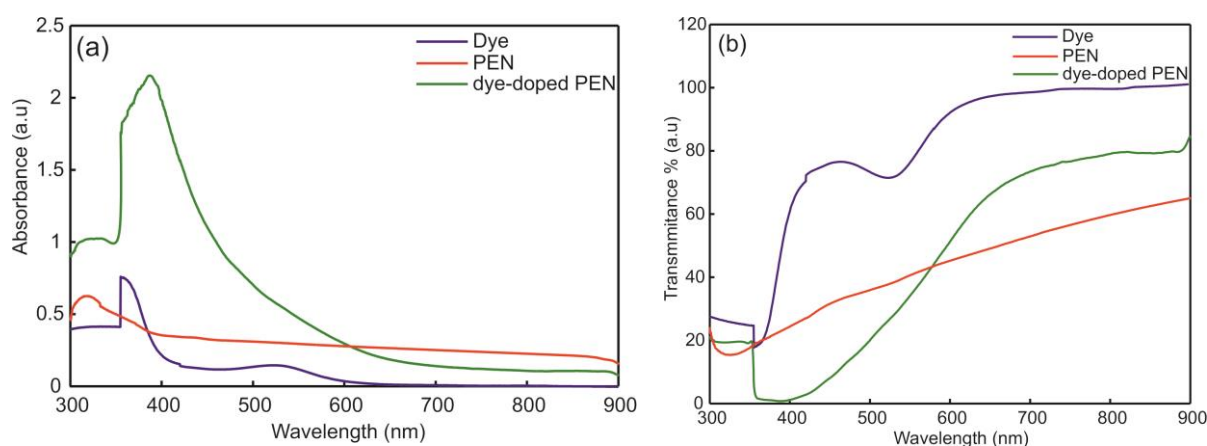


Fig. 5: The absorption (a) and transmittance (b) spectra of the pure A. *Italica* dye (blue line), Pure Pentacene (red line) and A. *Italica*-doped PEN (green line).

Furthermore, these bonds can absorb the energy to be excited from the ground state to higher energy states [57]. The absorption peaks in the spectra in the 400-600 nm band, generally correspond to the electronic transitions, including  $\pi \rightarrow \pi^*$  due to low energy requirements (see Figure 5(a)) [58] [59].

The optical response of the dye-doped polymer represents the so-called K-band, which directly links to the conjugated groups having saturated bonds with other unsaturated bonds. As can be observed, A. *Italica* shows a small peak at 540 nm. The emergence of this peak can be interpreted as  $n \rightarrow \pi^*$  excitation in the unsaturated compounds containing a nonbonding pair of electrons. In general, the  $n \rightarrow \pi^*$  transition, which is known as the R-band, arises as a result of unsaturated chemical groups (chromophore groups) existing in a molecule [60]. Nevertheless, when chromophore links with an Auxochrome (O-H group for example), a high absorption peak in the sample spectrum can eventuate and shift towards the longer wavelength (see the green curve in Figure 5(b)). On the other hand, the transmission spectra measured and presented in Figure 5(b) emphasises that the optical responses are compatible with the absorption spectra presented in Figure 5(a).

**Optical absorption coefficient and Optical energy gap.** In the region of the absorption band, it is necessary to determine the absorption coefficient  $\alpha$ , given its significance in the changes occurring

in the electronic structure of the doped material [61]. For this purpose, the absorption coefficient can be estimated from the following expression [62]:

$$\alpha = \frac{1}{d} \ln \left[ \frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2} \right] \quad (2)$$

where  $T$  and  $R$  are the transmittance and reflection, respectively, and  $d$  represents the thickness of the samples. The absorption coefficient  $\alpha$  has been measured for the pure A. Italica dye; Pentacene and A. Italica-doped PEN thin-film in the 300-900 nm bandwidth (see Figure 6(a)). The results show a significant difference in height between the peaks for which the dye-doped PEN thin-film is the most prominent.

Once again, these distinct peaks presented in Figure 6(a) of the A. Italica-doped PEN are due to  $\pi$ - $\pi^*$  excitation between bonding and antibonding molecular orbitals [63] [64]. The calculated absorption coefficient often leads to addressing the so-called optical energy gap or absorption edge. The optical energy gap  $E_g$  is one of the most important physical parameters in semiconductors and dielectric materials that contribute to enriching the photovoltaic and photodetectors applications. As such, it is necessary to address a brief description of the HOMO-LOMO gap concept. The latter represents the minimum energy creation of a discrete, uncorrelated free electron and hole. Its behaviour is linked with the transport of isolated particles in the solid-state. The values of the energy bandgap in this study were deduced from the intercept of  $(\alpha h\nu)^\gamma$  versus  $h\nu$  with the x-axis (i.e.  $(\alpha h\nu)^\gamma = 0$ ) (see Figure 6(b)). The latter expression is a result of using the Tauc's relationship, which is given by [65]:

$$\alpha = \frac{A\{(h\nu - E_g)\}^\gamma}{h\nu} \quad (3)$$

where  $A$  is a transition probability dependent constant, and  $\gamma$  represents the distribution of the density of states index, which takes different values depending on the transition type (direct takes 1/2 and 3/2 for allowed and forbidden respectively whereas indirect takes 2 and 3 for allowed and forbidden respectively).

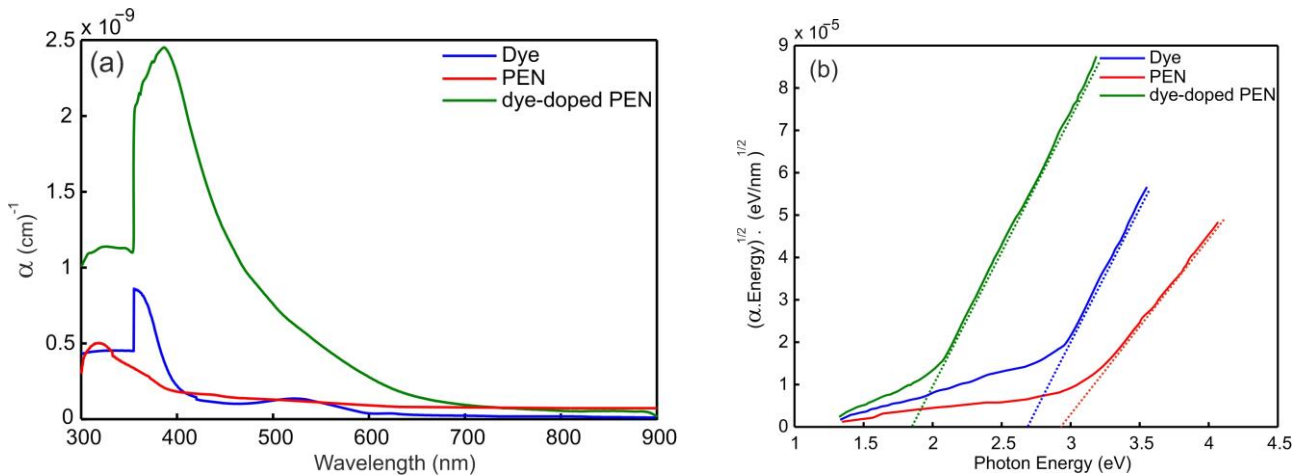


Fig. 6:(a) The absorption coefficient  $\alpha$  through the A. Italica (blue curve), pure PEN (red curve) and A. Italica-doped PEN samples. (b) The calculated optical energy gap of samples from the  $(\alpha h\nu)^{1/2}$  variation versus  $h\nu$ .

In Figure 6(b), the bandgap energies of the samples are calculated according to the relation as mentioned previously (see Eq. 2) after replacing the index  $\gamma$  with 2. This latter value is adopted because the absorption coefficient  $\alpha$  is less than  $10^4$ , which indicates that the transitions between the electronic states were indirect. Figure 6(a) shows that doping the Pentacene with the organic dye led to a reduction in the energy gap. The results presented in Figure 6(b), indicate the creation of new localised atomic energy levels below the natural conduction band of the Pentacene. These new levels are prepared to more readily receive the electrons and generate tails called “Urbach tails” in the optical

energy gap. Indeed, the presence of the nitrogen and oxygen in the dye structure and hence in the dye-doped PEN structure [which is evident in IR analysis (see Figure 3)], have significantly contributed to enhancing the structure with more molecule's dipoles. Therefore, this explains that the thin-film samples become more productive and hence polarised. As a result, the photoconduction of the doped Pentacene is increased, which is an important result and a highly desired property

**Absorption and Refractive indices.** The study of the optical factors  $n$  and  $k$  play a crucial role in the optical response for their connection to the interband transition of electrons from valence bands to the conduction band. As it is well-known,  $n$  is called the refractive index and represents the phase velocity of the wave in each material, and the extinction coefficient  $k$  is the quantity of the falling photon energy by matter electrons. Moreover, it is the intrinsic property of a chemical component that reflects how strongly the component attenuates light at a given wavelength. These two quantities can be linked together to form a complex frequency-dependent equation, where  $n$  and  $k$  represent the real and imaginary parts, respectively. The study of the refractive index  $n$  is attractive for different applications such as solar cells [66], fluorescence [67], chemical sensors [68], spectral filters [69], optical trapping [70], biomedical detection [71], and second harmonic generation [72].

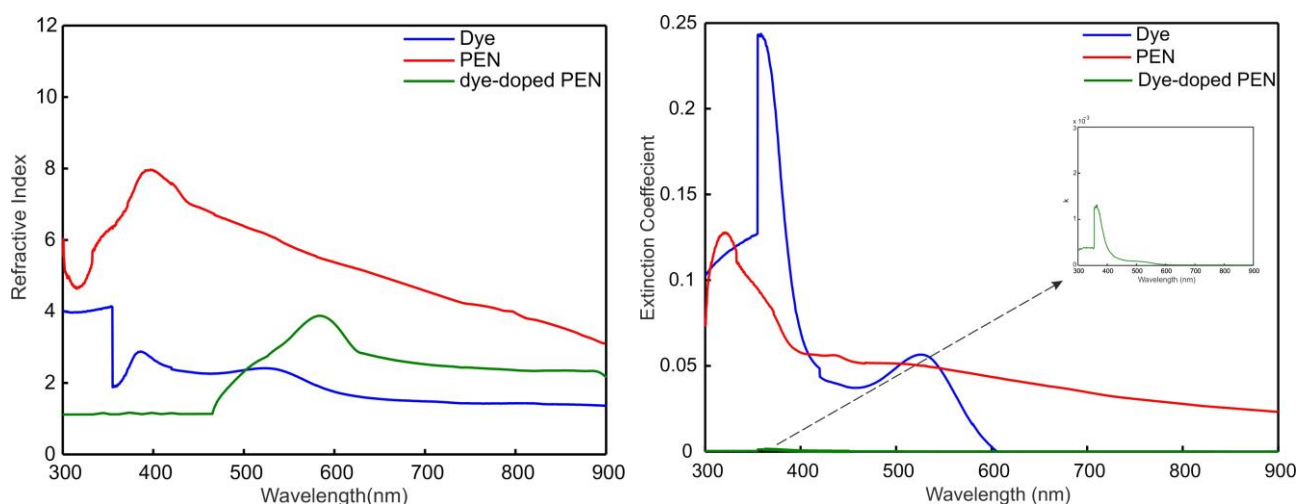


Fig. 7: Refractive index (a) and the extinction coefficient (b) of thin films. Inset of (b) presents a zoom made over the extinction peak in the whole range.

In determining the doping effects in PEN on index  $n$ , the plot of this index as a function of wavelength is presented in Figure 7. The results show that the refractive index  $n$  decreased over the whole bandwidth when the pentacene is doped with the organic Dye. Besides that, an anomalous dispersion appears in the bandwidth 300-600 nm. On the other hand, this seems reasonable for the spectral range of 500-900 nm, as depicted in Figure 7(a). The anomaly in the real part of the refractive index is due to the excitation of the resonance mode, which represents the coupling of collective oscillation of the conduction electrons in a thin-film with incident light. The significant absorbance represented in the optical response can most likely be attributed to the resonance excited through the thin-film of the doped-sample and ensured by the real part of the refractive index.

Regarding the extinction coefficient  $k$ , this was later measured for the pure A. Italica dye; PEN and A. Italica-doped PEN thin-film in the same range as the  $n$  index (see Figure 7(b)). One can observe from the figure that the absorption index  $k$  of the doped PEN exhibits a significant drop in its value lying just below both the pure (dye and PEN). Consequently, this reflects a very low attenuation of the light while passing through the doped polymer film, which means that it has become increasingly transparent (see the inset of Figure 7(b)).



## Conclusions

In this work, the first use of *A. Italica* dye-doped with pentacene as host material was presented. The combination of natural dye and polymer has always been successful in improving optical properties, with regards to device performance optimization. Natural dye was extracted in a simple way from *A. Italica* flowers via distilled water only. The PEN powder was synthesized via an in-situ polymerization method.

A profile of the surface (via SEM examination and FT-IR analysis of the doped sample) was undertaken in addition to investigating the spectrophotometric properties of the doped thin-film samples. The stretching mode analysis shows peak intensities at  $1631\text{ cm}^{-1}$  and  $1333\text{ cm}^{-1}$  of the doped sample, which corresponds to the stretching modes of the conjugated dyeing C=C and the variation of polar dipole-dipole interaction C=O, respectively. The vibration of the latter is a credible presence of hexahydrofarnesyl acetone, diisobutyl phthalate, flavonoid and tannins. The broad absorption peak of mix dye/polymer in the visible range refers to low energy requirements arising from the electronic transition  $\pi \rightarrow \pi^*$ .

The SEM analysis of the physical aspect of the synthesised *A. Italica*-doped-PEN revealed a surface morphology with less roughness and impurity. Accordingly, the experimental results have shown that absorption maxima of the doped sample exhibited a shift towards the low energy region. These results importantly indicate that natural dye added to PEN plays an essential role in decreasing the energy bandgap of thin-film from 2.8 to 1.7 eV.

Moreover, the absorption spectra were studied through the concept of the refractive index. Here, it was found that the absorption peaks of the samples resulted from a reduction in the real part of the refractive index in the 300-400 nm range. Overall, the results presented in this paper, are motivated to obtain new optical materials and the optimization of optoelectronic properties; which can definitely be exploited in potential applications in different but related fields; particularly in optoelectronic devices.

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