Structural and photo-physical properties of spin-coated poly (3-hexylthiophene) thin films

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Abstract

Regioregular poly(3-hexylthiophenes) (P3HTs) and its blends were studied regarding their structural and photo-physical properties using fullerene as an electron acceptor material. Photo-physical and structural characteristics of the polymer blends were studied using UV-Vis spectroscopy, photoluminescence (PL), Fourier transform infrared absorption (FT-IR) spectroscopy and Raman spectroscopy analysis. Films based on the polymer blends with C_{60} showed photo-induced absorption characteristic for charged excitations. The absorption spectra of the rr-P3HT exhibit a shift to higher energies (blue shift) of the $\pi-\pi^*$ inter-band transition upon mixing with C_{60}. A distinctive photoluminescence quenching effect is observed indicating photo-induced electron transfer. The complete reduction of PL of P3HT after mixing with C_{60} in a 1:1 weight ratio indicates an effective charge transfer from P3HT to C_{60}.

***Keywords*:** Fullerenes; Polymers; Thin films; Photoluminescence spectroscopy

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1. INTRODUCTION

The use of polymeric materials in the fabrication of low cost photovoltaic devices or plastic electronics has been extensively studied due to its low-cost synthesis and easy manufacture of thin film devices by vacuum evaporation/sublimation or solution cast or printing technologies. Organic semiconductor thin films also show high absorption coefficients [1] exceeding 10^5 cm^{-1}, which makes them good chromophores for optoelectronic applications. It has been shown by Roncali [2] that the electronic band gap of organic semiconductors can be engineered by chemical synthesis for simple colour changing of light emitting diodes (LEDs). Despite the good properties mentioned above great progress in both power conversion efficiency and stability is needed for practical device applications.

In order for a major breakthrough to take place, a significant improvement in the device efficiency-to-cost ratio is essential. There are several factors that influence the efficiency of OPVs, e.g. the structure of the polymer, the morphology of the film, the interfaces [3] between the layers (organic/metal, organic/organic) and the choice of electron acceptor and the ratio between this and the polymer [4]. Intensive research in organic photovoltaics has led to a wide variety of different structure designs and different types of hole and electron acceptor materials [5 – 7]. With regard to improving the efficiency, low band gap polymers which harvest the red part of the solar spectrum are being examined [8]. Studies on the stability of organic photovoltaic cells have typically focussed on optimisation of the stability of encapsulated devices under continuous light illumination [8-11]. Lifetimes of up to 2000 h continuous operation have been reported

for devices protected from oxygen and water ingress **[11]**. In this article, we report on the structural and photophysical properties of P3HT thin films using spectroscopy investigations to study the photoinduced charge generation in photoexcited P3HT films and its blends with fullerene as an electron acceptor material.

2. EXPERIMENTAL DETAILS

The bilayer or blended structures were prepared according to the following procedure.   Regioregular poly(3-Hexylthiophene) (P3HT), M_n ~ 64000 g/mol, and fullerene (C_{60}) were purchased from Sigma Aldrich and were used as received without further purification. The regioregularity of the regioregular material was specified as > 98 %. The ratio of the number-average molecular weight M_n of the polymer and the molecular weight of the monomer is known as the degree of polarization (DP). Since the molecular weight of a hexylthiophene unit is 170 g/mol and the molecular weight of the rr-P3HT is about 64000 g/mol the degree of polymerization can be calculated as about 376.47. The chemical structures of rr--P3HT and C_{60} are shown in Figure 1.

The ITO coated on 1 mm glass substrates, with a resistance ≤ 20 Ω/square, was first cleaned thoroughly with solvents and dried in dry nitrogen. A thin layer of poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) solution was spin coated onto the ITO structure. The spinning rate and time of spin-coating were between 2000 and 3000 rpm and 30 s. The PEDOT layer was subsequently annealed in ambient at 100 °C for 15 min on a hotplate. The active layer containing regioregular poly(3-

hexylthiophene) (rr-3HT) was dissolved in 1 ml of chloroform solution and spin coated on top of the PEDOT:PSS layer. For the blended samples; rrP3HT (~ 5 mg or a weight percentage of 50 %) and C_{60} with different concentrations (~5 mg and 20 mg) was dissolved in 1 ml of chloroform solution to obtain ratios of 1:1 and 1:4. This corresponds to a C_{60} weight percentage of 50 % and 80 %, respectively. The solution was stirred overnight on a hotplate at 50 $°C$. The precursor solution prepared for this study had a molar concentration of 0.15 M. The solution were spin coated on top of the PEDOT:PSS layer. The spinning rate and time of spin-coating were 2500 rpm and 30 s.

UV–vis spectra were recorded on a Perkin Elmer λ 20 spectrometer from 900 to 300 nm. The photoluminescence (PL) spectra were measured by exciting the samples with 350 nm line of deuterium lamp. It should be noted that for some photoluminescence measurements, the PEDOT:PSS layer was omitted in order to avoid masking of P3HT features which overlap with those of PEDOT. The emission was detected with Jobin Yvon PMT detector. The structure of pure P3HT with different concentrations of C_{60} was characterized by Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer FT-IR spectrometer and Raman spectroscopy using a Horiba Jobin Yvon HR800 micro-Raman spectrometer. The Raman spectroscopy measurements were conducted at room temperature with a 514 nm excitation laser with a spectral resolution of 0.4 cm^{-1}. It should also be noted that for some FTIR and Raman spectroscopy measurements that the blends were spin-coated on a Si (100) substrate.

3. RESULTS AND DISCUSSION

The PL technique has been widely used to investigate the energy level of materials and to provide fundamental information on the properties of the energy levels lying within the band gap. The PL of P3HT and its blend with fullerene (C_{60}) was measured to check if there is interaction of the two components in the excited state. Saricifti et al. [12] reported that the PL quenching of an appropriate donor polymer by a suitable acceptor gives an indication of an effective donor–acceptor charge transfer for composites of p-conducting polymers and fullerene derivatives. Figure 2 compares the PL spectra of P3HT film with that of blends of P3HT with different fullerene ratios. The PL spectra of P3HT and its blends were obtained by using an excitation wavelength of 350 nm in the range from 400 to 900 nm. An incomplete quenching is observed for the PL spectra of P3HT and the blend of P3HT:C_{60} with a weight ratio of 1:4. The PL spectra of the blend of P3HT:C_{60} with a 1:4 wt. ratio also shows a blue shift (shift to higher energies or lower wavelengths) compared to the spectra of a P3HT film, suggesting that the polymer chains are twisted and not π-stacked on each other.

At this point, it is unclear whether the incomplete quenching resulted from the reduced exciton mobility on the polymer chains or from the pore size (not measured) simply being too large given the small exciton diffusion length that has been observed in thiophene-based polymers [13]. The larger intensity of PL emission from the P3HT film can also be attributed to the surface oxidation defects of the exposed film. The degree of PL quenching is also related to oxygen adsorbed on surface-active sites or possible

structural order of the polymer film on the silicon substrate [14]. Al-Ibrahim et al. [15] reported that materials with high absorption coefficient are necessary for application in polymer solar cells, because the film thickness of the photoactive layer should not be normally over some hundreds of nanometers (typical are 100–300 nm). This limitation is predicted by the much lower charge mobility compared with inorganic semiconductors. The P3HT shows PL, which is completely quenched when it is mixed with a 1:1 wt. ratio of C_{60}. Therefore, the excitons created during the PL have a finite lifetime and during the diffusion process (charge transfer process) they decay or dissociate through several mechanism. In order to achieve efficient photovoltaic conversion, the excitons have to dissociate into free electrons and holes, before they decay radiatively, thermally or vibronically. The most common way to achieve exciton dissociation into free electrons and holes is through a photo-induced charge transfer process.

We conclude that the change of the photoluminescence intensity originates from a phase separation and thus changes in the morphology of the active layer. The fullerene surplus at higher concentrations (P3HT:C_{60} film with a 1:4 wt. ratio) is not homogeneously dispersed within the polymer matrix, but diffuses away and creates phase separated clusters, agglomerates or C_{60} islands. The complete quenching of the P3HT:C_{60} film with a 1:1 wt. ratio indicates that due to the finer phase separation in the chloroform blend, all of the C_{60} is in close enough contact with the polymer to undergo a charge transfer. In solar cells a significant amount of light absorption is in the C_{60} phase, the amount of generated charge carriers and therefore the photocurrent is reduced in the coarsely phase separated blend (1:4 wt. ratio). Charges become trapped on C_{60} islands and act as recombination sites for any opposite charge that then approaches.

However, a finer phase separation and smaller grain size does not warrant increased photocurrent, since the photo-generated charge carriers will have to overcome much more interfaces during their travel in a fine mixture. Chrivase et al. [16] reported that atomic force microscopy measurements on a P3HT:PCBM composite disclose some variation in morphology due to the crystallization of PCBM. The concentration of the PCBM clusters and their size (up to 500 nm) were found to be correlated with the amount of PCBM in the blend. They also showed that PCBM concentrations above 50 %, leads to a partial damage of the absorber–metal interface due to the formation of voluminous PCBM clusters.

To obtain the electronic states in photo-excited P3HT, the PL curve of P3HT and the three PL emission peaks by Gaussian fitting are illustrated in Figure 3. The PL spectra of P3HT (Figure 2 and 3) show resolved vibronic structures at 645 nm, 700 nm, and 780 nm. It can be found that the Gaussian curves: 1, 2 and 3 fitted the PL curve perfectly. The data of the Gaussian fitting multi-peaks are shown in Table 1, in which calculated energies are indicated as well. The PL emission peaks located at around 645 nm (1.92 eV) was assigned to the pure electronic transition and the peak at around 700 nm (1.76) to the first vibronic band [17]. The PL emission in the higher wavelength region indicates ordering in the P3HT lamella structure within the spherulites [18, 19]. However, more precise work is necessary to confirm this.

The UV-Vis absorption spectra of fullerene, the P3HT film as well as different blends of P3HT:C_{60} spin coated on an ITO coated glass substrate are presented in Figure 4. In the spectra, absorption caused by P3HT is visible between 450 and 700

nm. For the P3HT film the solid-state absorption spectra showed two peaks at 507 nm and 538 nm and one shoulder at 586 nm. These first two bands can be attributed to the $\pi-\pi^*$ transition, whereas the shoulder around 586 nm is due to the inter-chain interactions. Similar results and absorption values were obtained by Chen et al. **[20]** for regioregular P3HT. The maximum absorption wavelength for the film with P3HT:C_{60} (1:1 wt. ratio) was at ~ 501 nm showing a blue-shift. The peak absorption wavelength changed significantly for film with P3HT:C_{60} using a 1:4 wt. ratio. The characteristic peak absorption wavelength (λ_{max}) for film with P3HT:C_{60} (1:4 wt. %) are broad at a wavelength of ~ 501 nm. Since the concentration of P3HT was always kept the same in the solutions used for spin-coating, that is, the total amount of P3HT may be the same for all films, the quenching of the absorption for the film with the presence of C_{60} can be attributed to the interaction between the polymer and C_{60}. One possible effect of the presence of C_{60} molecules is the lowering of the interaction among the P3HT chains. However, the longer-wave absorption bands of P3HT and its blends at ~ 538 and ~586 nm remain nearly uninfluenced. This is an indication that these changes are not generated by ground state doping of the polythiophenes by C_{60}.

The structure and charge transfer between P3HT and C_{60} was further studied by FTIR spectroscopy as shown in Figure 5. The FTIR absorption bands for rr-P3HT are given in Table 2. The peaks of 2852, 2923 and 2950 cm^{-1} were assigned to CH_2 out of phase mode, CH_2 in phase mode and CH_3 asymmetry stretching mode, respectively. The peak at 1457 cm^{-1} represents the symmetric ring stretching mode. The ratio between the intensity of the antisymmetric C=C stretching peak (mode at 1509 cm^{-1})

and the intensity of the symmetric stretching peak (mode at 1456 cm^{-1}) can be used to probe the average conjugation length (i.e., the length over which backbone planarity is maintained without interruption and which defines the chromophore) of P3HT [21, 22]. Therefore using this relation (I_{1510}/I_{1456}) we observed that the conjugation length of P3HT chains actually shows a decrease from 0.50 for P3HT to 0.45 over the range of the different blends studied, showing a decrease in the ordering of the films. Furukawa et al. [21] reported that the average conjugation length will increase if the relative intensity of the FTIR peak at 1510 cm^{-1} (asymmetric C=C stretching) increases. The vibrations of some compounds are sensitive to the charge on the compounds. It has been shown by Ouyang et al. [23, 24] that both the C=C and C-S stretching vibrations may shift when the amount of charge present on the compound changes. The C=C stretching vibrations are really complicated since both P3HT and C_{60} have C=C stretching vibrations, and therefore, it is difficult to explain the charge-transfer effect by analyzing the C=C vibrations. Also it is not easy to find C-S peak in the IR spectra of P3HT [23].

However, the thiophene ring associated with P3HT shows an out of plane deformation of C-H, and the band at 819 cm^{-1} is assigned to this C-H deformation vibration of P3HT. This change in the vibration energy can be used to study the charge-transfer effect in P3HT [25]. However, no changes are observed for the C-H band at 819 cm^{-1} for the different P3HT:C_{60} ratios. A new band appears at around 1182 cm^{-1} and 2360 cm^{-1} as for the 1:1 P3HT: C_{60} film. These bands become intense with the increase of the amount of C_{60}. These bands at 1182 cm^{-1} and 2360 cm^{-1} are not from C_{60}. Hence, this change in vibration energy might be due to the charge transfer that

occurs between sulphur atom in P3HT molecule and C_{60}. Some charge is transferred from the sulphur atoms, to the conjugated chains of the C_{60} molecules, and this result in a slight positive charge being present on the sulphur atoms.

Figure 6 shows the Raman spectroscopy of the P3HT films as well as different blends of P3HT:C_{60} films deposited on a Si substrate. The spectrum of the poly(3-hexylthiophene) film deposited on Si features all the vibrational frequencies expected for the conjugated polymer [26]. The data were stacked to avoid overlaying of the different peaks. The Raman peaks at 715 cm^{-1}, 1380 cm^{-1} and 1450 cm^{-1} are assigned to the P3HT C-S-C ring deformation, C-C skeletal stretching deformation and C=C ring stretching deformation, respectively [27 - 29]. It is observed that the peak position corresponding to the symmetric C=C stretching deformation, is shift to a higher wavenumber (cm^{-1}), if the polymer is blended with C_{60}. A downward shift in the wavenumber generally indicates an increase in the crystallinity of P3HT polymer and the extension of the effective conjugation length along the polymer backbone [30]. The intensity and the full-width at half maximum (FWHM) of P3HT and its blends of the C=C stretching deformation are often used as an indication of the ordering in the material. The high intensity in the pure P3HT/Si film indicates a highly order/crystalline material. When the P3HT is blended with C_{60}, a decrease in the intensity of the C=C stretching deformation are observed. This might be due to a strong disordering of P3HT chains caused by an addition of C_{60} fullerene. This causes the C_{60} molecules to diffuse or migrate forming larger clusters which lead to a phase separation of P3HT and C_{60}.

As a result, the polymer film prepared with a C_{60}-fullerene has the favourable molecular morphologies for the transport of charge carriers and is also responsible in the improvement of cell efficiencies. No Raman features attributable to C_{60}, such as the A_{1g} 1469 cm^{-1} mode of fullerenes could be resolved. Klimov *et al*. [31] showed that the Raman modes of P3HT in the blends are not influenced by the contributions of the C_{60} fluorescence.

4. CONCLUSION

The interaction between P3HT and C_{60} in solid-state thin films was studied by UV–Vis absorption, photoluminescence, FTIR and Raman spectroscopy analysis. In this study the spectroscopic investigations show that the films of P3HT and blends with different ratios of P3HT:C_{60} exhibit an efficient photo-induced charge transfer. The blended P3HT:C_{60} film with a 1:4 wt. ratio was found to be incompletely quenched whereas the blended P3HT:C_{60} film with a 1:1 wt. ratio was completely quenched. The complete reduction of PL of P3HT after mixing with C_{60} in a 1:1 wt. ratio indicates an effective charge transfer from P3HT to C_{60}. The absorption spectra of regioregular P3HT show distinctive changes upon blending the polymers with C_{60}. The peak wave length of the $\pi-\pi^*$ inter-band transition of the P3HT blended with different fullerene ratios is shifted towards shorter wavelength. The detected shift to lower wavelength for blends may be due to differences in the molecular weights of the three polythiophenes or is a special feature of the applied solvent inducing unfavourable chain conformations and/or

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a disadvantageous interchain packaging. The FTIR spectroscopy showed no changes in peak assigned to C-H deformation vibration associated with the thiophene ring. The peaks at around 1180 cm^{-1} and 2360 cm^{-1} proved the occurrence of a charge-transfer process.

5. ACKNOWLEDGMENTS

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TABLE AND FIGURE CAPTIONS

Table 1:   PL bands, wavelength and calculated energies (eV) for P3HT

Table 2:   FTIR band positions (cm^{-1}) and their assignments of P3HT films

Figure 1:   Chemical structures of P3HT and C$_{60}$.

Figure 2:   Photoluminescence spectra of films of P3HT, P3HT:C$_{60}$ (1:1 wt. ratio) and P3HT:C$_{60}$ (1:4 wt. ratio) dissolved in chloroform

Figure 3:   PL spectra of a film of P3HT deposited on a Si substrate and their Gaussian band fits.

Figure 4:   UV–Vis absorption spectra for (a) fullerene (C$_{60}$) and (b) P3HT films compared with different blends of C$_{60}$.

Figure 5:   FTIR spectra for thin films of P3HTand P3HT: C$_{60}$ in 1:1 and 1:4 wt. ratios.

Figure 6:   Raman spectra of (a) P3HT, (b) P3HT:C$_{60}$ (1:1 wt. ratio) and (c) P3HT: C$_{60}$ (1:4 wt. ratio) films spun on a Si substrate.
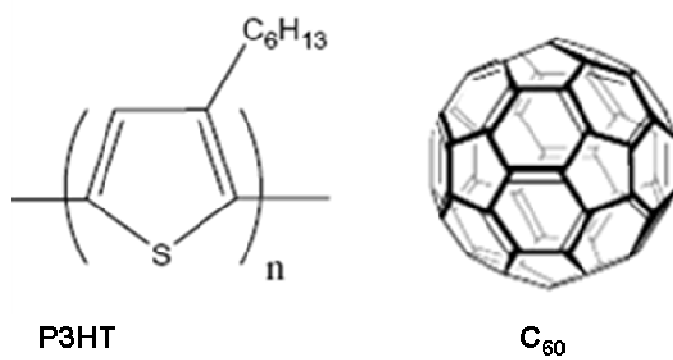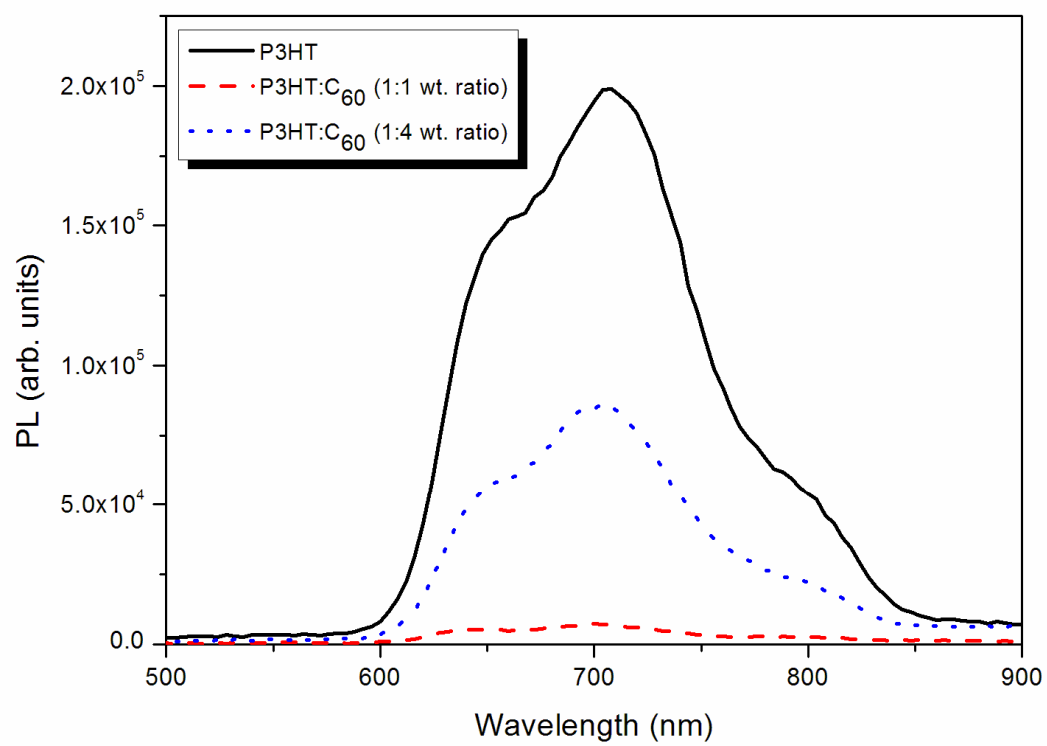
Figure 1
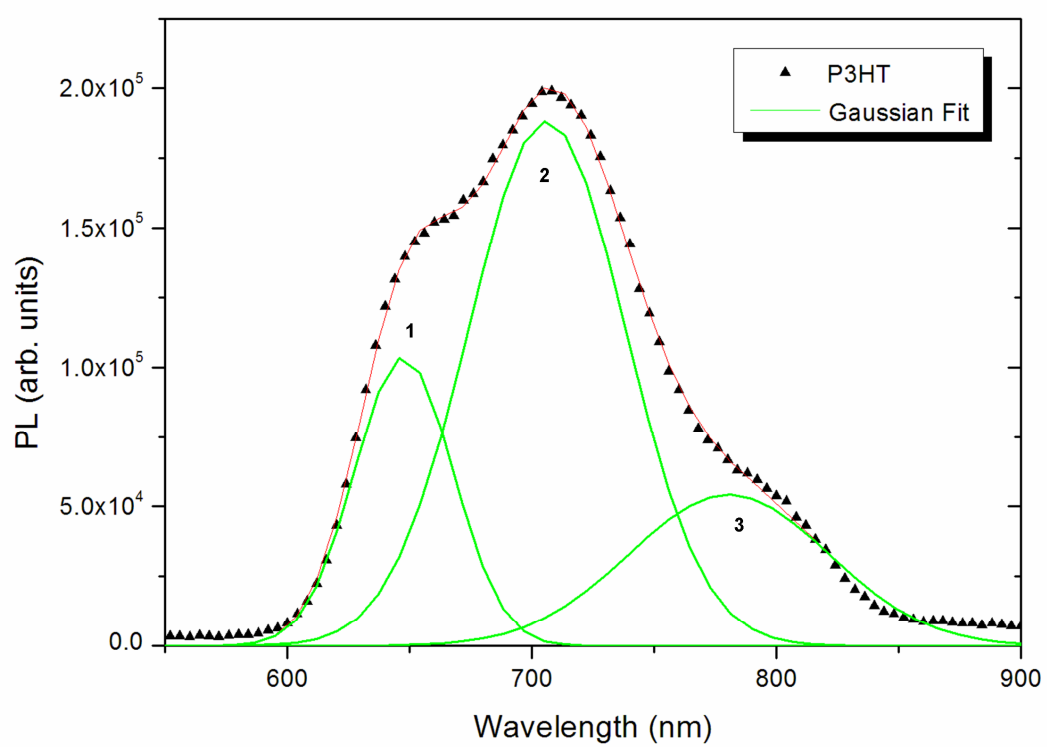

P3HT C_{60}

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Figure 2

Figure 2

Figure 3

Figure 4
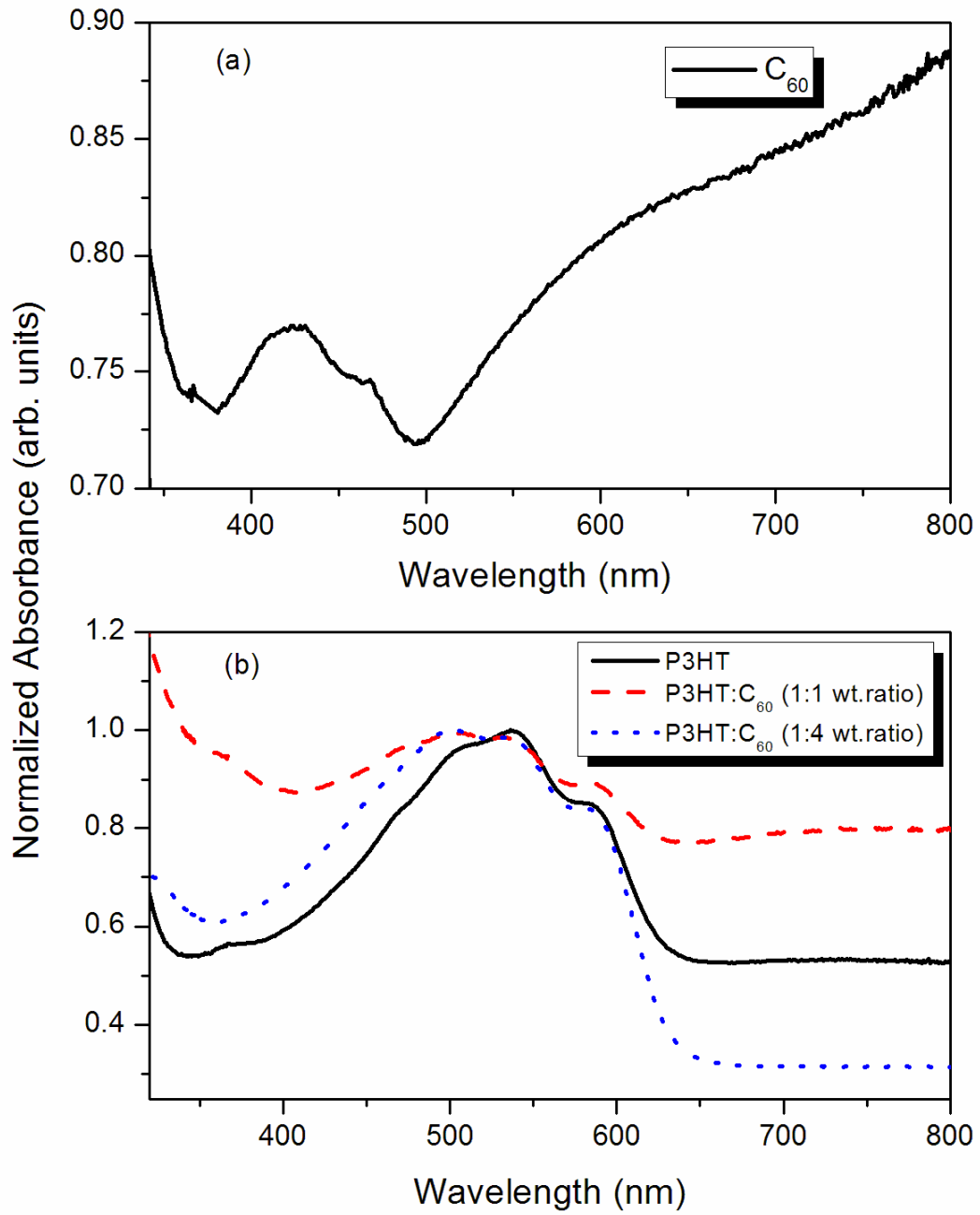
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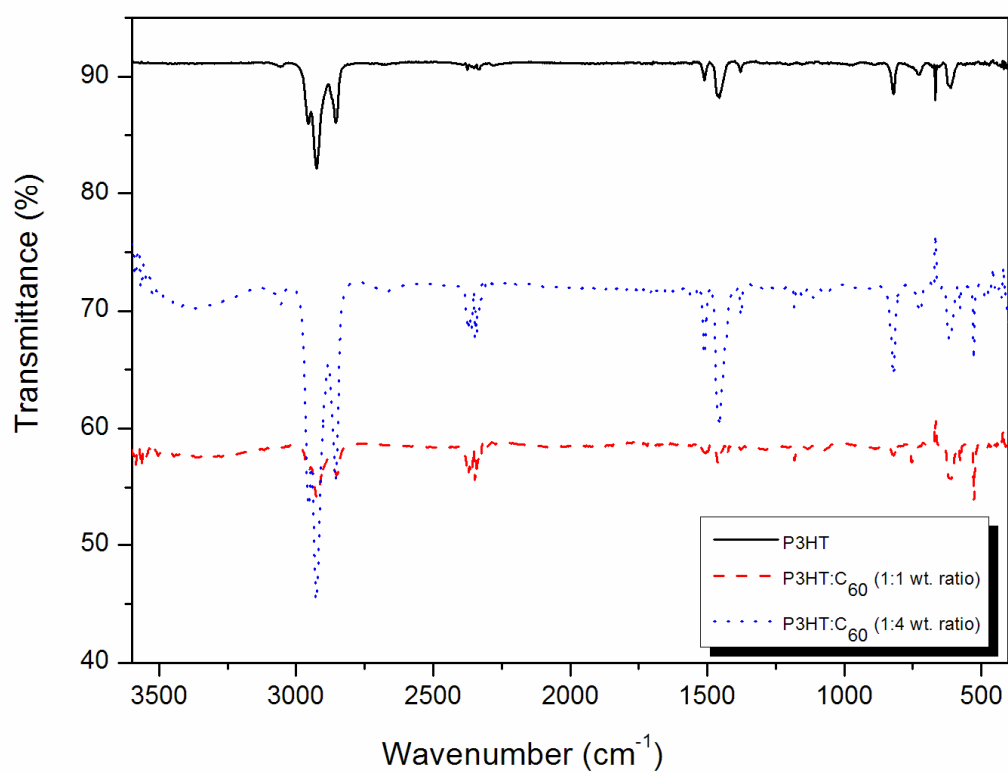
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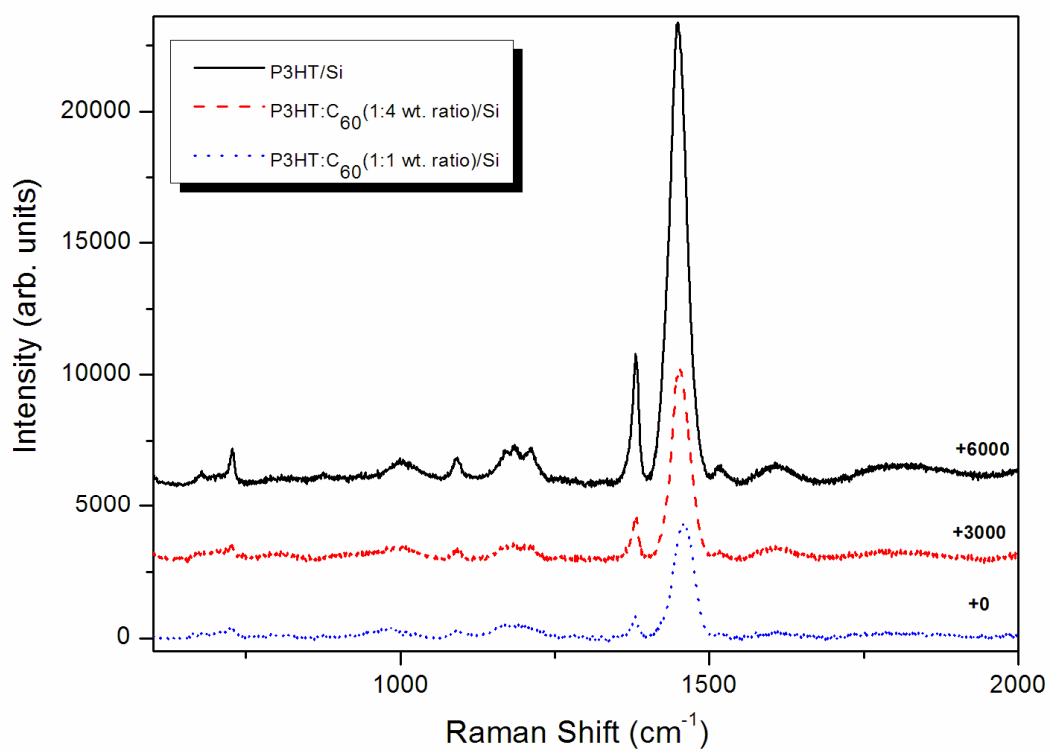
Table 1

Peak	Wavelength (nm)	Experimental (eV)	Width (nm)	Area (a.u)
1	647.50	1.92	40.223	5.2239E6
2	706.05	1.76	63.927	1.5086E7
3	780.44	1.59	82.021	5.5765E6

Table 2

rr-P3HT wavenumber (cm^{-1})	Assignments
721	Methyl rock
819	C-H out of plane mode
1182	-
1377	Methyl deformation
1507	Anti symmetric C=C stretching mode
1457	Symmetric C-C stretching mode
2360	-
2856, 2925, 2955	Aliphatic C-H stretching mode