

Synthesis and Characterization of poly(3-hexylthiophene)

Abdullah A. Hussein¹, Abdullwahab A. Sultan², Mohammed T. Obeid¹, Asheaq T. Abdulnabi²
and Mohammed T. Ali²

¹Department of Material Science, Polymer Research Centre, University of Basrah, Iraq

² Southern Technical College, Basrah, Iraq

Abstract

Poly(3-hexylthiophene) (P3HT) thin film has been synthesized from chlorobenzene solvent by spin coating method on glass substrates. P3HT was characterized by the measurement of Fourier transform infrared spectrophotometer (FTIR), Raman spectroscopy, X-ray diffraction (XRD), and atomic force microscopy (AFM). The optical properties of the films were studied by using VIS-UV spectrophotometer and photoluminescence (PL), the absorbance spectrum have been recorded at wavelength within the range (300-800) nm. The optical absorption (A) was analyzed to determine the optical constants such as absorption coefficient (α), refractive index (n), and extinction coefficient (k). Analysis of the absorption coefficient was also carried out to determine the energy gap and nature of transitions.

Keywords: *Poly(3-hexylthiophene)*, *Spin coating method*, *Optical properties*.

1. Introduction

In the context of technological applications, among many conjugated polymers, poly(3-alkylthiophenes) have been found to be a special class of polymers with good solubility, processability and environmental stability. Generally this class of materials exhibits an optical band gap in the range of 1.7–2.1 eV [1, 2]. P3HT is the most widely used conjugated polymer for organic optoelectronics applications due to of their high solubility in organic solvents, high mobility, high crystallinity, acts as the light absorbing, hole transporting material excellent thermal stability (42% weight loss at 900°C), and high electrical conductivity (3.4×10^{-4} to 1.0×10^{-1} S.cm⁻¹ when doped with iodine). Considerable effort has been made to improve the intrinsic characteristics of P3HT (p-type materials) to enable their use in organic solar cells and organic field-effect transistors and acts as the light absorbing and hole transporting material [2, 3]. When P3HT was used as the donor material in organic solar cells bulk heterojunction,

the power conversion efficiency (PCE) was about 8% owing to nanoscale phase separation induced by annealing [3].

2. Experimental

2.1 Instruments

The FT-IR spectra were acquired in reflection mode at room temperature using an evacuated (type PerkinElmer Inc.- Spectrum 100 FT-IR Spectrometer). Potassium bromide (KBr) disk was used as beam splitter in wave-number region 4000-400 cm⁻¹. The refractive index and extinction coefficient of sample was performed using M2000V (J.A. Woollam Co., Inc.) spectroscopic ellipsometer is operating in the wavelength range 350-850 nm. X-Ray Diffraction was performed using (multi-purpose X-ray diffractometer is a Philips X'Pert MPD system). The UV-vis absorption spectra of P3HT was recorded in range 300 – 800 nm wavelength by using Varian Cary 5000UV– VIS– NIR spectrometer and Raman spectroscopy using a Horiba Jobin Yvon HR800 micro-Raman spectrometer. Atomic Force Microscopy (AFM) measurements are implemented on a BRUKER Nano-Scope IV Multi-Mode Adapter AFM with the tapping mode.

2.2 Synthesis of P3HT

Synthesis of P3HT was achieved by a route, using Iron Chloride (FeCl₃) as catalyst [23]. FeCl₃ (2 gm, 12.3 mmol) was added to dry Chloroform CHCl₃(~12 mL) and stirred for 15 min at room temperature. The monomer 3-Hexylthiophene(3HT) (0.5 gm, 3mmol) in dry CHCl₃(~12 mL) was then added drop-wise to the FeCl₃solution and the reaction mixture was stirred overnight under Ar at room temperature. The polymerization reaction was then terminated by pouring the reaction mixture into excess Methanol MeOH (~50mL). The crude polymer precipitate was filtered using a PTFE membrane filter (1µm, Millipore) and washed with ethanol (200mL), a distilled water:acetone mixture (1:1 v:v, 250:250mL:mL) and finally with acetone (250mL). The dark brown solid product obtained was dried under vacuum for 72h to afford P3HT (0.45 gm, 90%). The P3HT solution were

deposited on a thoroughly cleaned glass substrates in a nitrogen atmosphere of a glove box, to obtain thin films by spin coating method.

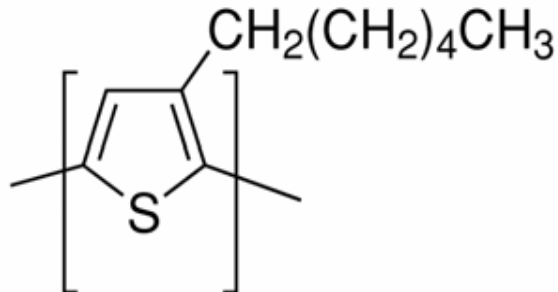


Fig. 1 The polymer poly (3-hexylthiophene) (P3HT).

3. Result and Discussion

Figure (2) shows the measured Fourier transform infrared (FTIR) spectrum of P3HT film. From figure (2), it can be seen that, the absorption peaks at 3419 and 2443–2923 cm^{-1} are assigned to the CH_2 out-of-phase stretching, CH_2 in-phase stretching and the CH_3 asymmetric stretching vibrations on the thiophene ring, respectively. The peak at 1652–1291 cm^{-1} represent the $\text{C}=\text{C}$ asymmetric stretching vibration and the $\text{C}-\text{C}$ symmetric stretching modes, respectively. The peak at 1073 cm^{-1} to the CH_2 stretching vibration. The peak at 668 cm^{-1} was the characteristic peak for the absorption of sulfate atom (S-atom) on the polythiophene ring.

The optical absorption spectra of P3HT film deposited onto glass substrate after annealing at 125 $^{\circ}\text{C}$ for 15 min in the wavelength between 300 to 800 nm, are shown in Figure (1). The UV-visible spectrum of the P3HT film showed two peaks at $\lambda=520$ and 554 nm and one shoulder at $\lambda=610$ nm. The three bands are also called vibronic absorption shoulders. These three bands can be attributed to the $\pi-\pi^*$ transition in crystalline $\pi-\pi$ stacking structure of polymer P3HT chains (conjugated polymer), [4]. The higher the P3HT order the more inter-digitation and stacking occurs, the more pronounced are the vibronic shoulders.

The absorption coefficient, α was calculated by using Beer-Lambert's law: ($\alpha = 2.303A/d$) where, A is the absorbance. Figure (3) shows the absorption coefficient spectra of P3HT film. The spectra reveal all the films exhibit low absorption in the visible and

NIR region but high absorbance in the UV range. High absorption characteristics in the UV range are due to melanin wide band gap properties.

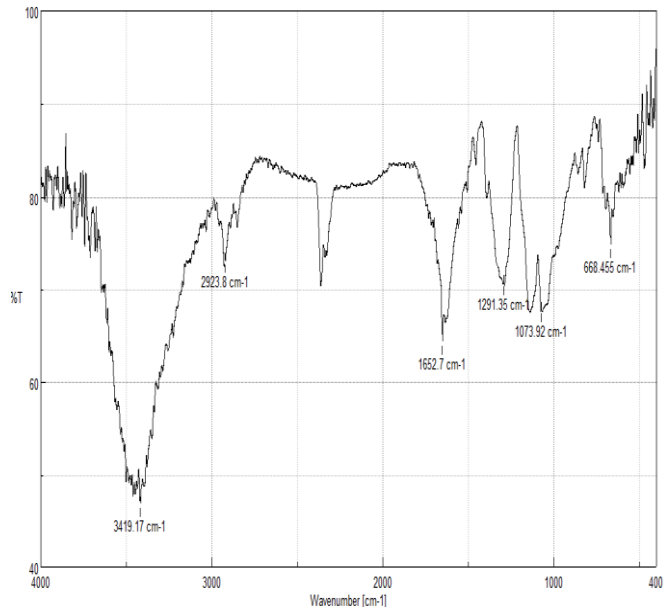


Fig. 2 Fourier transform infrared (FTIR) absorption of P3HT film.

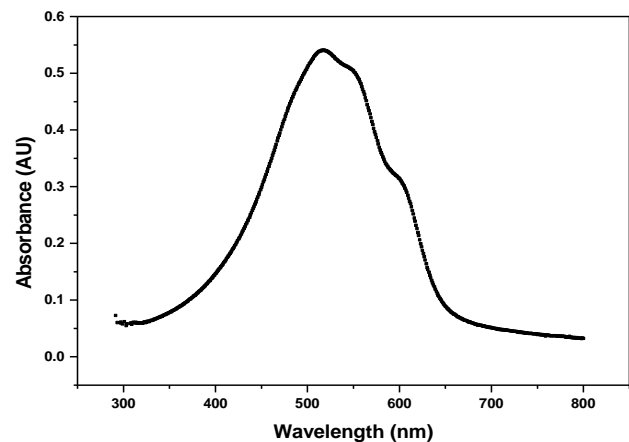


Fig. 3 UV-vis absorption spectra of P3HT film.

The band-gap energy E_g which is associated with HOMO to LUMO electron transitions between the π and π^* molecular orbitals [5], were estimated using Tauc's approach $\alpha h\nu = A(h\nu - E_g)^{1/2}$ of direct band-gap energy (where, $h\nu$ is the incident photon energy) by extrapolating the linear curve to the photon energy

axis, we found that the band gap energy of P3HT as a function of film thickness are ~1.9 eV, which were close to the reported values of synthetic P3HT [6-8]. The energy gap values depend in general on the films crystal structure, and the arrangement and distribution of the atoms in the crystal lattice. Also it is affected by crystal regularity. The energy gap (E_g) can be calculated from the classical relation for near edge optical absorption in semiconductors [9, 10]; the relation is drawn between $(\alpha h\nu)^2$ and photon energy ($h\nu$), as shown in Figures (4 & 5) for P3HT. The determined band gap values is obtained by extrapolating the linear region of the plot $(\alpha h\nu)^2 = 0$. The allowed direct transition optical gap is found 1.92. This downshift is attributed to the thiophene ring in the polymer P3HT [10].

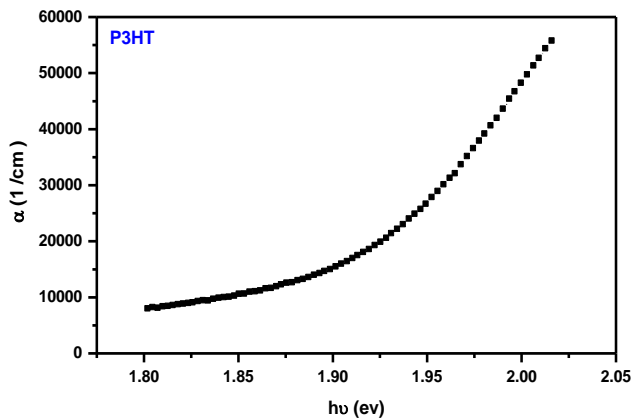


Fig. 4 The relationship between absorption coefficients (α) versus Photon energy of P3HT.

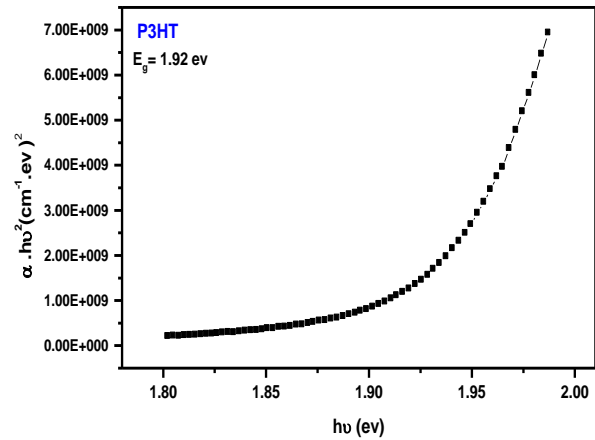


Fig. 5 The relationship between $(\alpha h\nu)^2$ versus photon Energy for P3HT.

The refractive index ($n=1+ R^{1/2}/1-R^{1/2}$) and extinction coefficient ($K=\alpha\lambda/4\pi$) of P3HT film measured by an ellipsometer are shown in Figure (6). The parameters (n and K) were obtained from measurements on Si substrate and then used as fixed parameters for further fitting. It can be observed that, the refractive index value 1.83 at wavelength 560 nm and the extinction coefficient 0.23 at wavelength 490 nm. Slight deviation in optical constants for thin films might be attributed to the formation of organic aggregation.

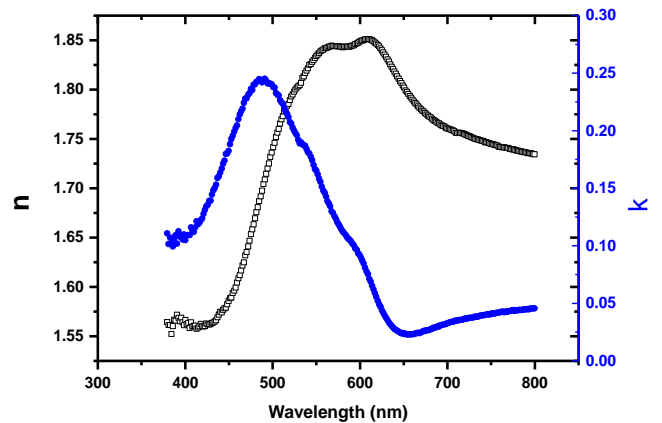


Fig. 6 Refractive index n and Extinction coefficient k of P3HT film.

Figure (7) displays the Photoluminescence spectra of P3HT film under excitation by using an excitation

wavelength of 430 nm in the range from 400 to 800 nm. It can be seen that the P3HT solutions had the maximum photoluminescence peak at 594 nm. The high intensity of photoluminescence emission from the polymer P3HT film can be due to the surface oxidation defects of the exposed film. The degree of photoluminescence quenching is related to possible structural order of the polymer film on the substrate or on the oxygen adsorbed on surface active sites [11, 13].

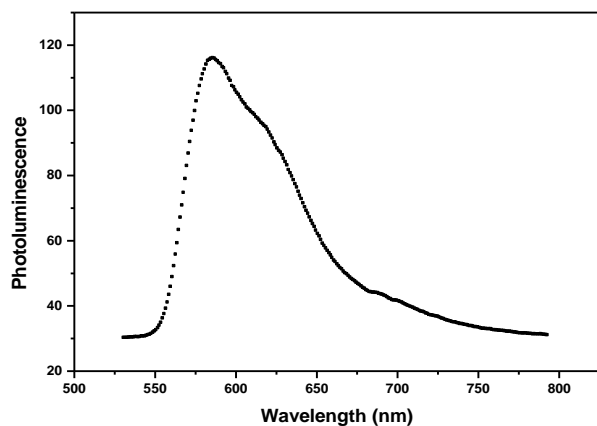


Fig. 7 Photoluminescence spectra of P3HT solution.

Among the several conjugated polymers, P3HT which is known to be one of region-regular polymers which have various characteristics according to self-organization [14]. The highly regular chain structure of P3HT facilitates their self-organization into two-dimensional sheets by means of inter-chain stacking and shows highly crystalline property [15]. The degree of self-organization can be varied by controlling the film growth rate or by controlling the time to solidify from a wet film [16,17]. The slow growth will assist the formation of self-organized ordered structure and give high crystallinity in the P3HT. The presence of P3HT polymer was observed by XRD analysis. Figure (8) shows the X-ray diffractograms of polymer. P3HT film has a peak at $2\theta \sim 5.4^\circ$ with a full width at half maximum (FWHM) of ~ 0.25 (degree) corresponding to d_{100} -spacing, attributed to an inter-chain lamella peak. These peaks are possibly related to crystalline orientations of the thiophene units with respect to the substrate, which is similar with the literature reports [18, 19].

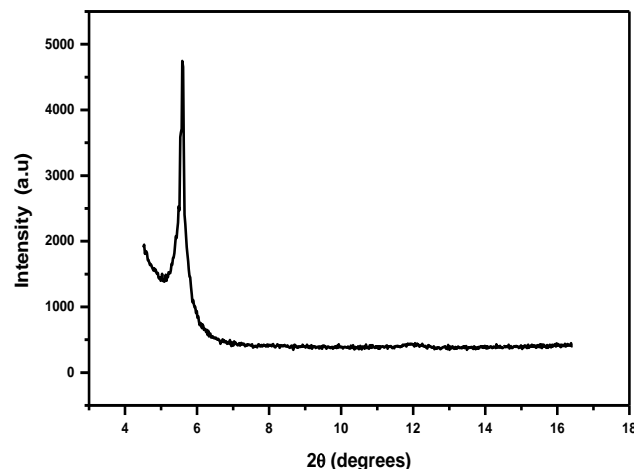


Fig. 8 X-ray diffraction of P3HT film.

Figure (9) displays Raman spectroscopy of P3HT film in the range $200-2000 \text{ cm}^{-1}$. There are several Raman modes in the range $600-1600 \text{ cm}^{-1}$ [198, 199]: the main in-plane ring skeleton modes at 1452 cm^{-1} (symmetric C=C stretching mode) and at 1380 cm^{-1} (C-C intra-ring stretching mode), the inter-ring C-C stretching mode at 1208 cm^{-1} , the C-H bending mode with the C-C inter-ring stretch mode at 1180 cm^{-1} , and the C-S-C deformation mode at 728 cm^{-1} . We focus on the two main in-plane ring skeleton modes at ~ 1450 and $\sim 1380 \text{ cm}^{-1}$ in figure (9) because they are supposed to be sensitive to π -electron delocalization (conjugation length) of P3HT molecules [20] as well as to crystallinity extent [21, 22].

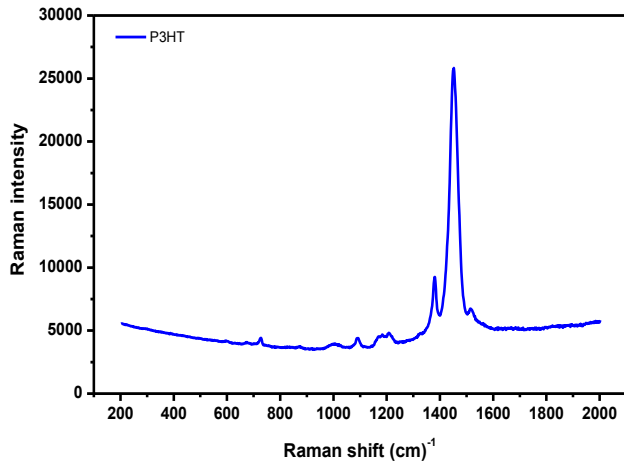


Fig. 9 Raman shift of P3HT film.

Figure (10) shows image of Atomic Force Microscopy (AFM) topography measurements (surface morphologies) of P3HT film. From analyzing and the extracted data, It can be seen that, the (R.M.S) surface roughness for P3HT film was found to be 4.37 nm, mean roughness of film (R_a) is 4.12 nm, and the maximum height of the film (R_{max}) is 35.8 nm.

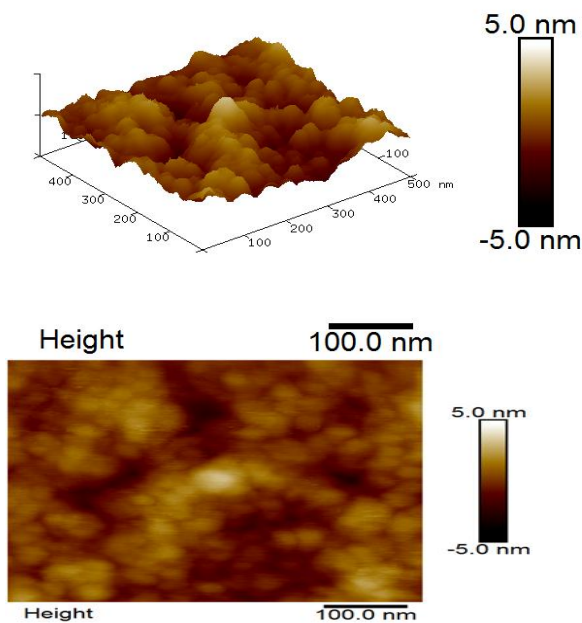


Fig. 10 AFM images of the P3HT film .

4. Conclusions

We have successfully synthesis P3HT solution by using Iron Chloride ($FeCl_3$) as catalyst, and prepared the film by using spin coating method. The optical parameters such as absorbance, refractive index and extinction coefficient as well as FTIR spectrum, PL spectra, Raman shift, surface morphology of the P3HT film have been investigated. XRD results showed film have (100) preferred orientation. The optical band gap values of P3HT was found 1.9 eV.

Acknowledgements

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References

- [1] D. Chirvase, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov, J.C. Hummelen, Electrical and Optical design and characterisation of regioregular poly(3-hexylthiophene-2,5diyl)/fullerene-based heterojunction polymer solar cells, *Synthetic Metals* 138, 299–304, (2003).
- [2] El. Jeffries, M., and R. D. McCullough, , *Conjugated polymers theory, synthesis, properties, and characterization, in regioregular polythiophenes*, T.A.S.a.J.R. Reynolds, Editor., CRC Press, Taylor & Francis Group, (2007).
- [3] Reyes, M., Kim, K., and Carroll, D., High-efficiency photovoltaic devices based on annealed poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1- phenyl- (6,6) C61 blends. *Applied Physics Letters*, 2005. 87(083506).
- [4] T. A. Chen, X. Wu, R.B. Rieke, Regio controlled Synthesis of Poly(3-alkylthiophenes) Mediated by Rieke Zinc: Their Characterization and Solid-State Properties, *J. Am. Chem. Soc.* 117 233, (1995).
- [5] M. A. Green, "Third generation photovoltaics: solar cells for 2020 and beyond", *Physica E-Low-Dimensional Systems & Nanostructures*, 14 (1-2), 65-70, (2002).
- [6] C. J. Keavney and M. B. Spitzer, Indium-Phosphide Solar-Cells Made By Ion-Implantation, *Applied Physics Letters* 52 (17), 1439-1440 (1988).

- [7] D. E. Carlson and C. R. Wronski, Amorphous silicon solar cell, *Applied Physics Letters* 28 (11), 671-673, (1976).
- [8] Y. Ohtake, K. Kushiya, M. Ichikawa, A. Yamada and M. Konagai, Polycrystalline Cu(InGa)Se-2 thin-film solar cells with ZnSe buffer layers, *Japanese Journal of Applied Physics Part 1- Regular Papers Short Notes & Review Papers* 34 (11), 5949-5955, (1995).
- [9] V. Shrotriya, J. Ouyang, and R. Tseng, Absorption spectra modification in poly(3-hexylthiophene):methanofullerene blend thin films, *Chemical Physics Letters* 411, 138-143, (2005).
- [10] O. Ourida and B. Mohammed, Influence of the Blend Concentration of P3HT in the Performances of BHJ Solar Cells, *Science Academy Transactions on Renewable Energy Systems Engineering and Technology (SATRESET)*, 1, 3, (2011).
- [11] U. Zhokhavets, T. Erb, H. Hoppe, G. Gobsch, and S. Sariciftci N, Effect of annealing of poly(3-hexylthiophene)/fullerene bulk hetero-junction composites on structural and optical properties, *Thin Solid Films* 496(2):679-682, (2006).
- [12] G. Li, V. Shrotriya, Y. Yao, J. Huang, and Y. Yang, Manipulating regioregular poly(3-hexylthiophene): [6]-phenyl-C61-butyric acid methyl ester blends-route towards high efficiency polymer solar cells, *J Mater Chem* 17(30):3126-3140, (2007).
- [13] H. Shen, P. Bienstman, and B. Maes, Plasmonic absorption enhancement in organic solar cells with thin active layers, *J Appl Phys* 106(7):073109, (2009).
- 1.1 [14] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig and D. M. de Leeuw, Two-dimensional charge transport in self-organized, high-mobility conjugated polymers, *Nature*, 401, 685-688 (1999).
- [15] B. Grevin, P. Rannou, R. Payerne, and A. Pron, J.P. Travers, Multi-scale scanning tunneling microscopy imaging of self-organized regioregular poly (3-hexylthiophene) films, *J. Chem. Phys.* 118, 7097, (2003).
- [16] G. LI, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty O, K. Emery, and Y. Yang, High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends, *nature materials*, 4, (2005).
- [17] M. Al-Ibrahim, and O. Ambacher, Effects of solvent and annealing on the improved performance of solar cells based on poly (3-hexylthiophene): fullerene, *Appl. Phys. Lett.* 86, 201120, (2005).
- [18] B. Kippelen, and J.L. Bredas, Organic photovoltaics, *Energy Environ. Sci.*, 2, 251, (2009).
- [19] M. Grätzel, Photoelectrochemical cells, *Nature*, 414, 338, (2001).
- [20] Y. Gao, and J. K. Gery, *J. Am. Chem. Soc.*, Resonance Chemical Imaging of Polythiophene/Fullerene Photovoltaic Thin Films: Mapping Morphology-Dependent Aggregated and Unaggregated C=C Species, *J. Am Chem Soc.* 131, 9654-9662, (2009).
- [21] S. Wood, O. Garnett, N. Tokmoldin, W. C. Tsoi, Saif A. Haque and J. Kim, *In situ* formation of organic-inorganic hybrid nanostructures for photovoltaic applications, *Faraday Discuss*, 174, 267-279, (2014).
- [22] G. Louarn, M. Trznadel, J.P. Buisson, J. Laska, A. Pron, M. Lapkowski, and S.J. Lefrant, Raman spectroscopic studies of regioregular poly (3-alkylthiophenes), *Phys. Chem.* 100, 12532, (1996).