



Highly Dendritic Polythiophene/silver (PT/Ag) Nanocomposite for Solar Energy Applications



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POLYTHIOPHENE/SILVER (PT/Ag) nanocomposite has been synthesized and characterized. Morphological studies have been made to elucidate the structure of the formed nanocomposite. The morphological studies revealed that the formed nanocomposite is highly dendritic forming tree like structure. A bulk heterojunction solar cell (BHJSC) has been built using the prepared nanocomposite as photo active layer. The solar cell parameters such as open circuit voltage Voc, short circuit current Isc and fill factor FF have been determined via current- voltage I-V characteristic. The maximum power conversion efficiency (PCE) obtained from I-V characteristic was 14.2 % which is much higher than that obtained from other commercial polythiophene based solar cells (SC). The enhanced PCE was attributed to the superior highly dendritic structure of the formed nanocomposite which provides charge transfer (CT) pathways and facilitates separation of the formed excitons into free electrons and holes. As far as we know none of these characteristics have been reached before in the open literature for PT based solar cells.

Keywords: Nanocomposite, charge transfer, bulk heterojunction solar cell and power conversion efficiency.

Introduction

Energy specialists expect that the world would need 30 Terra Watt (TW) of energy resources by the year 2050 to conserve profitable growth. Numerous scientists have confidence in that the sun can offer a fully advanced solution for the energy crisis. Thus, solar cells (SCs) can be considered as a conventional renewable energy resource when their manufacturing cost is decreased to reasonably priced level similar with other accessible energy resources. One of the renewable energy technologies is photovoltaics (PVs), the technology that directly converts daylight into electricity. PV is one of the fastest growing of all the renewable energy technologies; in fact, it is one of the fastest growing industries at present.

The first generation PV was based on Si wafers. These PVs are now marketed and produce power conversion efficiencies PCEs between 12% and 33% depending on the manufacturing procedures and wafer quality [1]. Since silicon based photovoltaics are cost expensive, scientists are giving much attention in producing cost effective organic polymer based solar cells [2-4]. These devices are characterized by simpler manufacturing procedures, specifically spin coating, than their inorganic counterparts. There are two essential architectures of photoactive layer, namely bilayer structure and bulk heterojunction (BHJ) structure. The bilayer heterojunction solar cell is formed by separately depositing donor and acceptor materials, leading to formation of two layers with a sharp, well-defined interface [5]. A solution-processed bulk heterojunction BHJSC is

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the most fruitful device architecture for organic based SC. Power conversion efficiencies PCEs in organic based SCs are highly enhanced up to 3-8% for the bulk heterojunction solar cells (BHJSCs) [6-8]. Record values of PCE up to 12% have been also reached [9]. Numerous approaches have been explored to increase the PCE for OSCs such as synthesis of new materials, architectures, buffer layers and deposition methods [10, 11]. Conjugated polymers are one class of materials with highly-extended π -electron systems in their main chains and are considered of great interest due to their unique electronic properties and their potential technological applications especially in solar cell applications [12-14].

They can provide a diversity of easy and cheap processing techniques for forming thin film devices [15]. Composites of conducting polymers with inorganic nanoparticles, combining the diverse properties of components and are considered as an extraordinary advanced materials [16-18]. Boron bonded to conjugated polymers was able to act as an electron donor, or act as hole blocking layer in BHJSCs applications [19-22]. Amongst the most significant conducting polymers is polythiophene (PT) which is commonly used in various electronic devices [22-24] and photovoltaics PVs [25-27]. Polythiophene (PT) is frequently used as donor material in organic PVs [28, 29]. The extensive conjugation in conducting polymers can enrich the HOMO level and lower the LUMO level down, leading to a reduction in their bandgap [30,22]. This reduction in bandgap produces an absorption shift towards the NIR which is favorite for organic based SCs development, due to the broadened absorption. Several poly(p-phenylenevinylene)-, fluorene-, carbazole- and thiophene-based conjugated polymers (among others) have been working as active layers in organic based SCs [31-33]. Currently, polythiophene derivatives, such as poly(3-hexylthiophene) (P3HT), are amongst the most predominantly used electron donors in combination with the highly soluble fullerene molecules (PCBM) as electron acceptors for OSCs under the bulk heterojunction BHJ architecture [34].

In the light of the previous information, we introduce here a novel BHJSC based on the PT/Ag nanocomposite as photo active layer exploiting its superior highly dendritic structure and hence an attempt has been made to improve the PCE of the custom organic based solar cells. The solar cell parameters such as short circuit current,

open circuit voltage and fill factor have been determined. The Power conversion efficiency PCE has been also determined.

Experimental

Materials

Silver nitrate is product of MERCK, Germany. Thiophene monomer (99.5%) (PT) and dodecyl benzene sulfonic acid (DBSA, surfactant) and all other chemicals used are products of Sigma-Aldrich Company, USA.

Preparation of PT/Ag nanocomposite:

PT/Ag colloidal dispersion has been prepared according to Elhalawany *et al* [18] as follows: 5.9×10^{-3} mole of thiophene monomer and 1 ml acetic acid have been homogenized for 5 minutes using high shearing effect homogenizer at 10,000 rpm in presence of DBSA surfactant to form the miniemulsion. Finally 10 ml of 5.8×10^{-2} M AgNO_3 solution has been added to the formed miniemulsion under continuous vigorous stirring at 10,000 rpm for further 15 min till a stable orange brownish colloidal dispersion has been appeared. The formed stable colloidal dispersion has been then centrifuged, washed several times by water methanol mixture, filtered and finally dried in an electric oven at 70 °C for 4 h.

Characterization of the prepared materials

Fourier transform infrared (FT-IR) spectra:

FT-IR analysis for the prepared nanocomposite has been carried out in Infra-Red unit, Central service labs, National Research Center (NRC) using FT-IR-6100, Japan. **Scanning electron microscope (SEM):** The morphological structure of the prepared nanocomposite has been investigated via SEM /EDX (JEOL JXA- 840 A Electron PROBE), microanalyzer microscope, Japan at Central Service Labs (NRC), Cairo, Egypt.

Solar cell measurements:

Sample preparation:

First the purified powdered nanocomposite has been dissolved in methylene chloride to form the corresponding nanocomposite solution. A thin film of 50 nm of the solution processed PT/Ag nanocomposite has been prepared by spin casting onto ITO conducting glass electrode through spin-coating method at 3000 RPM for 60 s. Then dried at 100°C for 10 min. afterward, the film was kept at 60°C for 24 h in vacuum oven. The formed film has been placed on a plate at room temperature for a period of 60 min for complete annealing. Silver (Ag) electrode of about 90 nm

in thickness was thermally evaporated onto the back (the unpolished side) of the ITO electrode. This was carried out under vacuum of 10^{-5} – 10^{-6} mbar and evaporation rate of 5 nm/sec. The solar cell device dimension for this measurement was 1 cm².

Source Meter SMU Instrument:

The solar cell parameters have been measured using KEITHLEY INSTRUMENTS INC., USA. MODEL 2400, 4100306 - C33 at Cairo University, nanotechnology Center, Cairo, Egypt. The total irradiance on the solar is equal to 1000 mW/cm² and the spectrum is AM 1.5 G. The temperature was kept constant at 25°C.

Results and Discussion

FT-IR Analysis

Fig. 1 shows the FT-IR spectra for the prepared PT/Ag nanocomposite and pure polythiophene PT. The characteristic peaks for PT at 1210, 1040, 790, 710 and 620 cm⁻¹ which are assigned to C–H bending, C–H in-plane deformation, C–H out of plane deformation, C–S bending and C–S–C ring deformation [18, 35,36] respectively are shown in fig. 1. The same characteristic peaks have shown in the FT-IR spectra for the nanocomposite but with slight shift due to composite formation.

SEM - EDAX analysis

Figure 2a-d shows the SEM micrographs for pure PT, PT/Ag nanocomposite of different magnifications and energy dispersive

spectroscopy EDS for the formed nanocomposite. It is clearly shown from fig. 2a that pure PT has porous rough structure. Fig. 2b,c for the formed nanocomposite of different magnifications shows that the nanocomposite have highly dendritic structure forming tree like shape [18]. Fig. 2d shows the elemental composition of the prepared nanocomposite which confirms the presence of silver nanoparticles.

Solar cell Parameters from IV measurements:

Polythiophene (PT) is considered as one of the most broadly used donor materials for polymer solar cells (PSCs) [37-39]. Intensive research work has been done to enhance the photo absorption property of PT by incorporation of electron donating and accepting moieties into PT matrix [40-42]. The electron-donating capacity and the morphological structure are the key factors controlling the energy levels, and photovoltaic performance of PTs.

The proposed BHJSC will absorb light photons in the range matches its absorption band leading to formation of electron hole pairs called excitons. These exciton are supposed to migrate through the highly dendritic structure which confirmed by SEM measurements till reach the BHJ donor/ acceptor D/A interface and this case is known as charge transfer CT state. Actually, this migration of excitons does not essentially produce dissociation of free electrons and holes in a direct manner because they experience

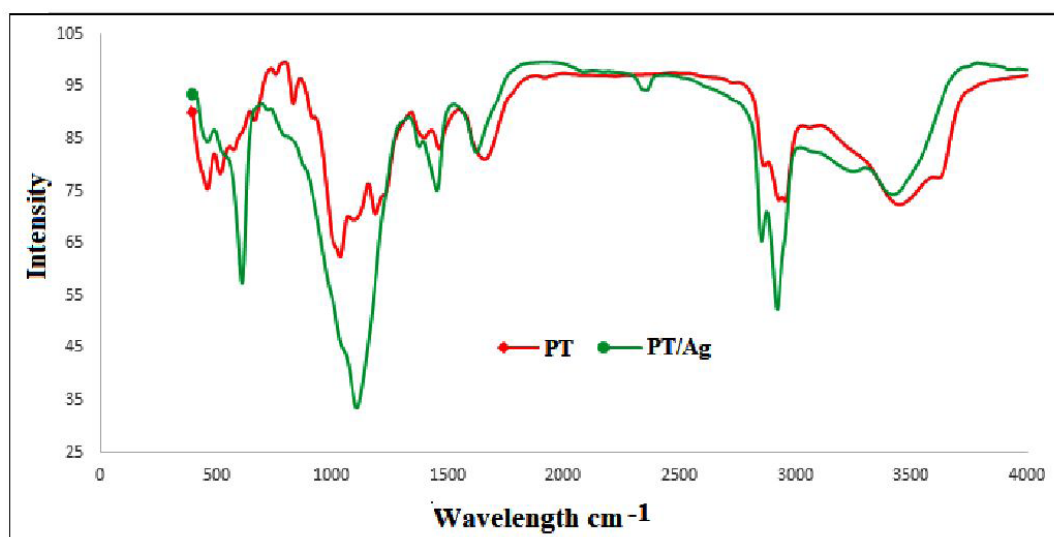


Fig. 1. FT-IR spectra for PT and PT/Ag nanocomposite.

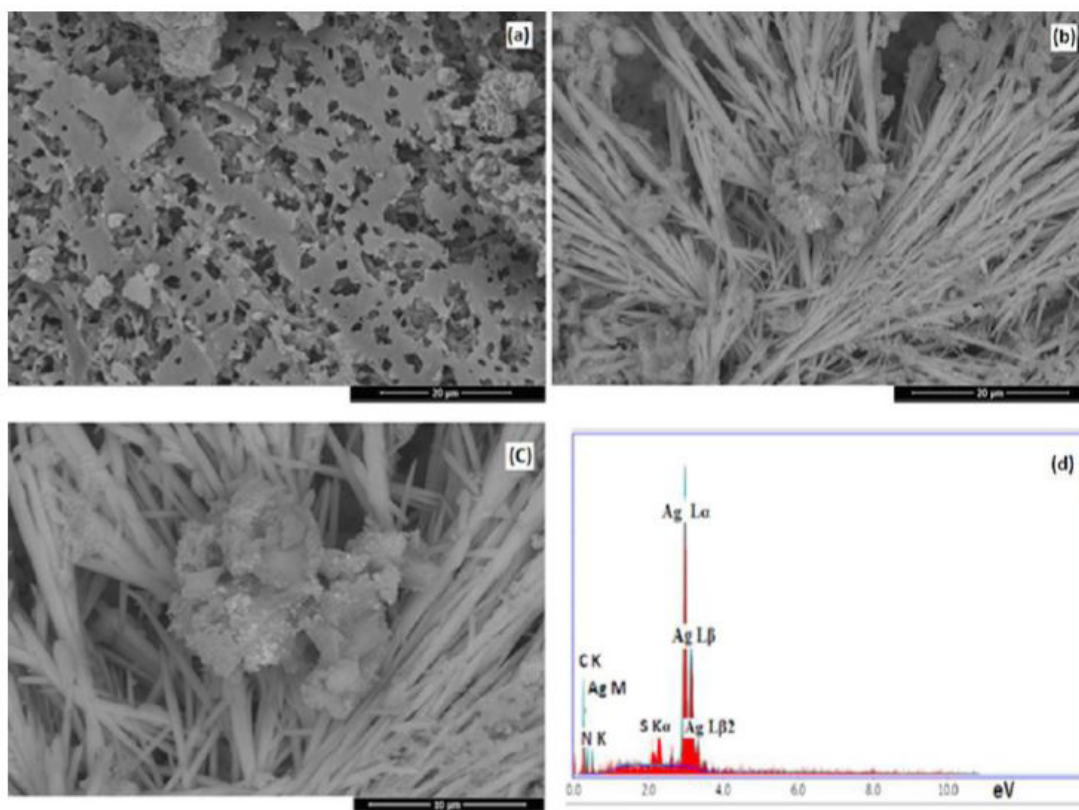


Fig. 2. SEM micrograph for a) PT, b)PT/Ag nanocomposite of magnification (6000x), c) PT/Ag nanocomposite of magnification (12000x) and c) EDS analysis of PT/Ag.

a substantial Coulomb attractive force. The superior morphological structure of the formed nanocomposite will reduce the charge transfer distances leading to fair dissociation of excitons into mobile electrons and holes.

For a consistent measurement of the current – voltage I-V characteristics, the measurements had better made under standard test conditions (STC).

The key parameters used to describe the performance of formed BHJSC are the peak power P_{max} , the short-circuit current density I_{sc} , the open circuit voltage V_{oc} , and the fill factor FF. These parameters are determined from the illuminated I-V characteristic as illustrated in Fig. 3. The power conversion efficiency PCE % can be determined from these parameters.

Figure 4 shows the I-V characteristics of BHJSC under study. The short circuit current (I_{sc}) is the current obtained when the voltage across the BHJSC is zero. The open circuit voltage (V_{oc}) is the maximum voltage obtained when the current through the BHJSC is zero. The maximum power

point (P_{max}) is the maximum power reached by the BHJSC and the produced current and voltage at this case are called I_{max} and V_{max} respectively. The fill factor FF is defined as the ratio of P_{max} divided by the product of V_{oc} and I_{sc} as illustrated in equation 1. The fill factor (FF) and the percent power conversion efficiency PCE% are used as a measure to describe the performance of the produced BHJSC. The power conversion efficiency is defined as the ratio of P_{max} to the product of the input light irradiance (I_{in}) as illustrated in equation 2.

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}} \text{ ----- Eq. 1}$$

$$PCE (\%) = \frac{P_{max}}{I_{in}} = \frac{I_{sc} \times V_{oc} \times FF}{I_{in}} \text{ ----- Eq. 2}$$

The Key parameters of the formed BHJSC under study have been determined accordingly where $I_{sc} = 15.61 \text{ mA/cm}^2$, $V_{oc} = 1.23 \text{ V}$ and $FF = 0.74$. Maximum PCE up to 14.2% was obtained

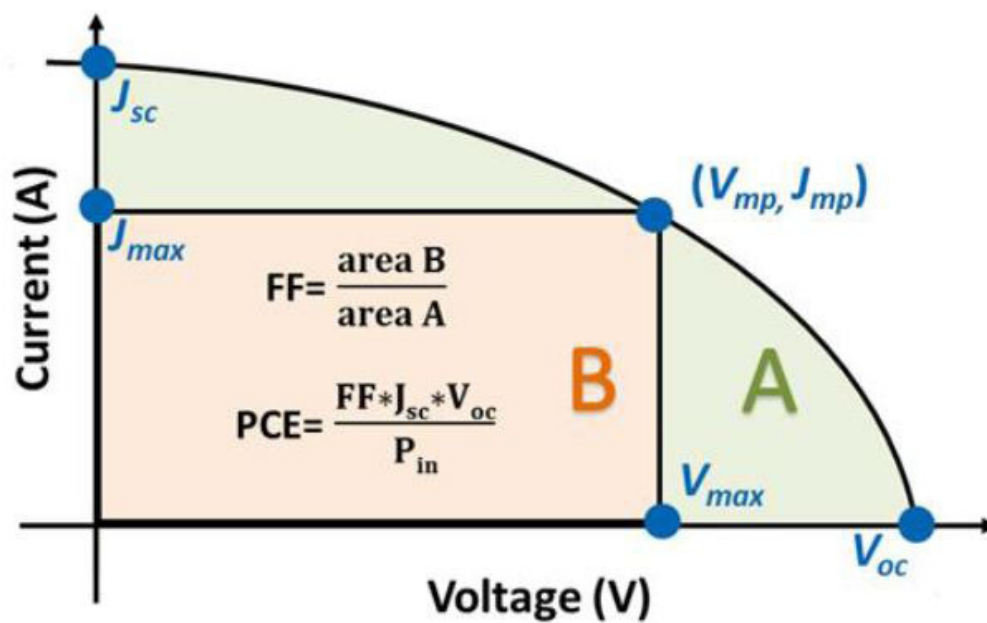


Fig. 3. Typical current density (J)-voltage (V) curve of PSCs [43].

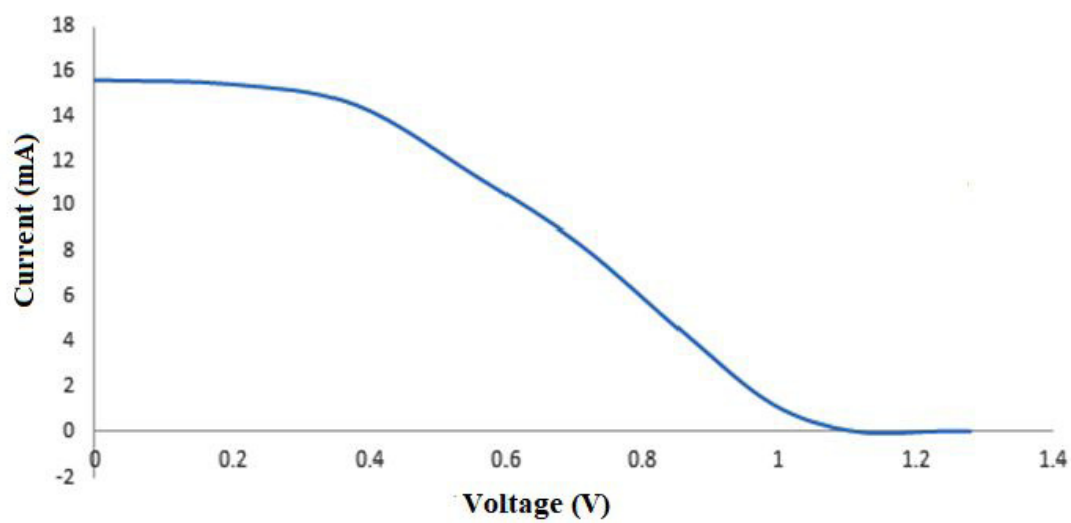


Fig. 4. (I-V) curves of PT/Ag nanocomposite based solar cell .

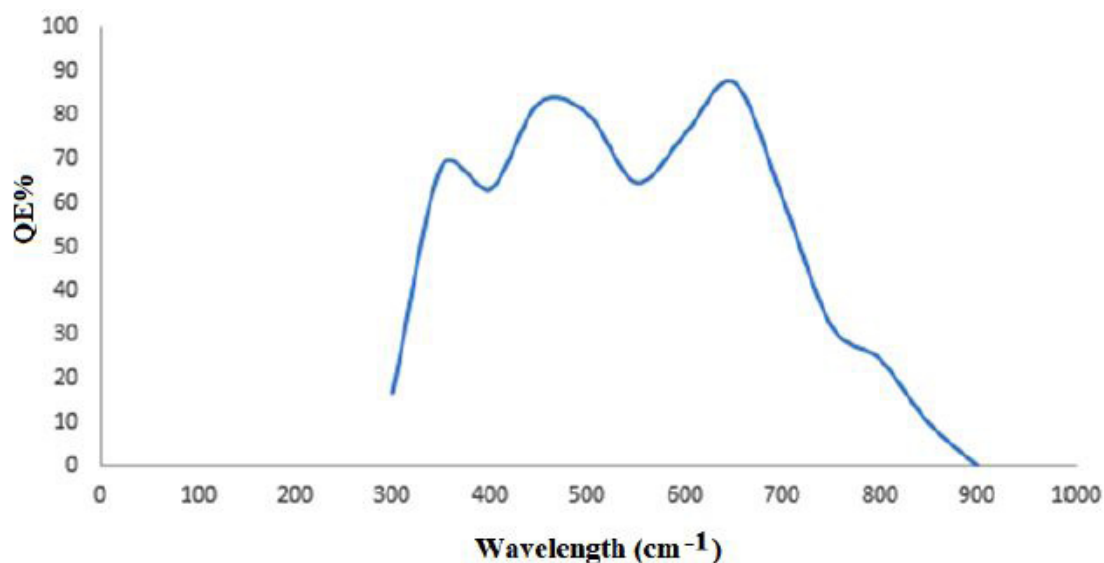


Fig. 5. The incident-photon-to-current conversion efficiency (IPCE%)

which is much more higher compared to reference PT based solar cells [44-50].

The highly enhanced PCE obtained may be ascribed to presence of Ag nanoparticles which act as photo sensitizers which absorb light energy. The present Ag nanoparticles are acting as a photosensitizers which absorb photons of light. The conduction band and valence band of nanoparticle such as silver are very close to each other where electrons are moving freely. These free electrons give rise to a surface plasmon resonance SPR absorption band, [51] due to the collective oscillation of electrons of silver nano particles in resonance with the light wave. The formed free electrons due to SPR and the large interfacial surface area of the photo active layer due to superior highly dendritic structure decrease the charge transfer distances for the produced excitons to reach fairly at the D/A interface and thus guaranteeing the exciton dissociation producing free electrons and positive holes. Furthermore, the highly dendritic structure of the photo active layer provide more CT pathways which enhances dissociation of exactions facilitating effective transfer for the free charges to the electrodes. The electrodes would collect the formed charges to produce electrical energy i.e (conversion of photo energy into electrical energy).

To explore the mechanism responsible for the enhanced performance, we analyzed the external quantum efficiency (EQE) of the formed BHJSC per incident photon under 1 sun illumination as

shown in fig 5. Quantum efficiency QE is the percentage of photons hitting the photoreactive layer of the formed BHJSC and measured in electrons per photon or amps per watt. Since the energy of a photon is inversely proportional to its wavelength, QE is often measured over a range of different

wavelengths to characterize a device's efficiency at each photon energy level. It is clearly seen from fig. 5 that the formed solar cell showed four characteristic peaks at 350, 500, 650 and a small intensity peak at 800 nm. The EQE profiles follow the absorption spectra trend, thus demonstrating that the harvested photons contribute directly to the photocurrent and confirming the lowering of the recombination side effects.

The highest quantum efficiency has been detected in the range from 500 to 650 nm wavelength region, which is the most common spectral zone of the solar radiation hitting the surface of Earth. Maximum EQE reached 87.3 % at wavelength around 650 nm, which is attributed to the absorption of conductive species polarons or bipolarons on the polythiophene backbone [52].

The superior unique structure of the nanocomposite (as elucidated from SEM) effects on other parameters so that the formed BHJSC achieve a high fill factor, dependable on the highly dendritic structure of the photo active layer.

Finally one can conclude that the prepared nanocomposite has shown superior morphological structure and has been used as photo active layer in BHJSC giving maximum PCE of 14.2%. As far as we know none of the commercial solar cells based on PT reported in open literature could achieve any of these characteristics as illustrated in table 1.

Conclusion

PT/Ag nanocomposite has been successfully synthesized and well characterized. The formed nanocomposite has been used as photo active layer for BHJSC. The Solar cell SC parameters such as I_{sc} , V_{oc} and FF have been determined via illuminated I-V characteristic. The maximum power conversion efficiency PCE% achieved is 14.2 % which is much higher than that of commercial SCs based on pure PT. This is attributed to the superior highly dendritic morphological structure of the formed nanocomposite. It was found also that maximum EQE of 87.2 % has been achieved at wave lengths in the range from 500-650 nm which is ascribed to the Π - Π^* transitions through the conjugated PT chains. As far as we know none of the commercial solar cells based on PT could achieve any of these characteristics and this will pave the way for further developments in solar cell technology.

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References

1. Badawy WA, Elmenawy SA, Hafez AN. "Improvement of the power of industrially fabricated solar cells by etching of the Si surface and the use of surface analytical techniques". *Egypt J Anal Chem.*, 22:97–113, (2013).
2. S. Günes, H. Neugebauer, and N. S. Sariciftci, "Conjugated polymer based organic
3. Solar cells," *Chem. Rev.*, 107, 1324-1338, (2007).
4. Coakley K. M., and McGehee M. D., "Conjugated polymer photovoltaic cells," *Chem. Mater.*, 16, 4533-4542, (2004).

TABLE 1: Comparison between the solar cell parameters of current study and that reported in open literature.

V_{oc} [V]	I_{sc} [mA cm^{-2}]	FF	PCE [%]	Reference
1.23	15.61	0.74	14.2	current research article
0.95	13.2	0.73	9.2	[44]
1.13	10.43	0.557	6.6	[45]
0.92	10.7	0.575	5.66	[46]
0.91	12.91	0.612	7.19	[47]
0.68	13.3	0.62	5.58	[48]
0.92	16	0.64	9.4	[49]
1.04	10	0.67	7	[50]

5. Cheng Y. J., Yang S. H., and Hsu C. S., "Synthesis of conjugated polymers for organic solar cell applications," *Chem. Rev.*, 109, vol. 11, 5868-5923, (2009).
6. Tang, C.W. Two-layer organic photovoltaic cell. *Appl. Phys. Lett.*, 48, 183-185, (1986).
7. Otori, Y.; Hoashi, T.; Yanagi, Y.; Okukawa, T.; Fujii, S.; Kataura, H.; Nishioka, Y. Organic solar cells based on ternary blend active layer of two donors PTB7, P3HT and acceptor PC61BM.
8. *J. Photopolym. Sci. Technol.*, 27, 569-575, (2014).
9. Kim, J.Y.; Kim, S.H.; Lee, H.-H.; Lee, K.; Ma, W.; Gong, X.; Heeger, A.J. New architecture for high efficiency polymer photovoltaic cells using solution-based titanium oxide as an optical spacer. *Adv. Mater.*, 18, 572-576, (2006).
10. Park, S.H.; Roy, A.; Beaupr e, S.; Cho, S.; Coates, N.; Moon, J.S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A.J. Bulk heterojunction solar cell with internal quantum efficiency approaching 100%. *Nat. Photonics*, 3, 297-302, (2009).
11. Li, G.; Zhu, R.; Yang, Y. Polymer solar cells. *Nat. Photonics*, 6, 153-161, (2012).
12. Sun, Y.; Welch, G.C.; Leong, W.L.; Takacs, C.J.; Bazan, G.C.; Heeger, A.J. Solution-processed small-molecule solar cells with 6.7% efficiency. *Nat. Mater.*, 11, 44-48, (2012).
13. Zhou, H.; Yang, L.; You, W. Rational design of high performance conjugated polymers for organic solar cells. *Macromolecules*, 45, 607-632, (2012).
14. Wang H.-J., Chen C.-P., and Jeng R.-J., "Polythiophenes comprising conjugated pendants for polymer solar cells: a review," *Materials*, vol. 7, no. 4, 2411-2439, (2014).
15. Sariciftci N. S., "Plastic photovoltaic devices," *Materials Today*, 7, vol. 9, 36-40, (2004).
16. Marks R. N., Halls J. J. M., Bradley D. D. C., Friend R. H., and Holmes A. B., "The photovoltaic response in poly(p-phenylene vinylene) thinfilm devices," *Journal of Physics: Condensed Matter*, 6, 1379, (1994).
17. Spanggaard H., and Krebs F., "A brief history of the development of organic and polymeric photovoltaics," *Sol. Energy Mater. Sol. Cells*, 83, 125-146, (2004).
18. Magdy Zahran, Maher M. Saleeb, Noha Elhalawany "Electrical and dielectrical properties of some novel polyaniline nanocomposites", *Egyptian journal of chemistry* (accepted).
19. Elhalawany N., Saleeb M. M., Zahran M. K., "New synthesis type route for preparation of some highly conductive polyaniline nanocomposites of core-shell structures" *Journal of Materials Science: Materials in Electronics*, 28:18173-18182, (2017).
20. Elhalawany N., Awad M. A., Zahran M. K., "Synthesis, characterization, optical and electrical properties of novel highly dendritic polythiophene nanocomposites with silver and/ or gold" *Journal of Materials Science: Materials in Electronics*, Volume 29, Issue 11, 8970-8977 (2018).
21. Jakle, F. Advances in the synthesis of organoborone polymers for optical, electrical and sensory applications. *Chem. Rev.*, 110, 3985-4022, (2010).
22. Cataldo S., Fabiano S., Ferrante F., Prevetti F., Patane S., and Pignataro B. Organoboron polymers for photovoltaic bulk heterojunctions. *Macromol. Rapid Commun.*, 31, 1281-1286, (2010).
23. Jakle, F. Lewis acidic organoboron Polymers. *Coord. Chem. Rev.*, 250, 1107-1121, (2006).
24. Rodriguez, M.; Maldonado, J.L.; Ramos-Ortiz, G.J.; Lamere, F.; Lacroix, P.G.; Farfan, N.; Ochoa, M.E.; Santillan, R.; Meneses-Nava, M.A.; Barbosa-Garcia, O.; et al. Synthesis and non-linear optical characterization of novel borinate derivatives of cinnamaldehyde. *New J. Chem.*, 33, 1693-1702, (2009).
25. W. Liu, M. Pink, D. Lee, J. Am. Conjugated polymer sensors built on pi-extended borasiloxane cages. *Chem. Soc.* 8703, 131 (2009).
26. D. Aradilla, F. Estrany, F. Casellas, J.I. Iribarren. All polythiophene rechargeable batteries. *Org. Electron.* 15, 40-46 (2014).
27. S. Gunes, H. Neugebauer, N.S. Sacriftci. Conjugated polymer-based organic solar cells. *Chem. Rev.* 1324, 107 (2007).
28. J.A. Mikroyannidis, M.M. Stylianakis, Q. Dong, Y. Zhou, W. Tian. New 4, 7-dithienebenzothiadiazole derivatives with cyano-vinylene bonds: Synthesis, photophysics and photovoltaics. *Synth. Met.* 1471, 159 (2009).
29. B.C. Thompson, J.M.J. Fr chet. Polymer-fullerene composite solar cells. *Angew. Chem. Int.*

- Ed. 58, 47 (2008).
30. Kim J. Y., Kim S. H., Lee H. H., Lee K., Ma W., Gong X., Heeger A. J.: New architecture for high-efficiency polymer photovoltaic cells using solution-based titanium oxide as an optical spacer. *Advanced Materials*, 18, 572–576 (2006).
 31. Kim J. Y., Lee K., Coates N. E., Moses D., Nguyen TQ., Dante M., Heeger A. J.: Efficient tandem polymer solar cells fabricated by all-solution processing. *Science*, 317, 222–225 (2007).
 32. Li D., Wang K., Huang S., Qu S., Liu X., Zhu Q., Zhang H., Wang Y. Brightly fluorescent red organic solids bearing boron-bridged p-conjugated skeletons. *J. Mater. Chem.*, 21, 15298–15304, (2011).
 33. Clarke T., Durrant J. Charge photogeneration in organic solar cells. *Chem. Rev.*, 110, 6736–6767, (2010).
 34. Cheng Y., Yang C., Hsu C. Synthesis of conjugated polymers for organic solar cells applications. *Chem. Rev.*, 109, 5868–5923, (2009).
 35. Chasteen S.V., Sholin V., Carter S.A., Rumbles G. Towards optimization of device performance in conjugated polymer photovoltaics: Charge generation, transfer and transport in poly(p-phenylene-vinylene) polymer heterojunctions. *Sol. Energy Mater. Sol. Cells*, 92, 651–659, (2008).
 36. Agina E.V., Ponomarenko S.A., Muzafrov, A.M. Macromolecular systems with the p-type conductivity. *Russ. Chem. Bull.*, 59, 1080–1098, (2010).
 37. Shanmugapriya C., Velraj G.. Investigation on structural and electrical properties of FeCl₃ doped polythiophene (PT) blended with micro and nano copper particles by mechanical mixing. *Optik* 127, 8940–8950 (2016).
 38. S. Chandra, J. Chowdhury, M. Ghosh, G.B. Talapatra. Adsorption of 3-thiophene carboxylic acid on silver nanocolloids: FTIR, Raman, and SERS study aided by density functional theory. *J. Phys. Chem. C* 115, 14309 (2011).
 39. Sariciftci, N.S.; Heeger, A.J. Conjugated Polymer-Acceptor Heterojunctions; Diodes, Photodiodes, and Photovoltaic Cells. U.S. Patent 5,454,880, (1995).
 40. He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure. *Nat. Photon.*, 6, 593–597 (2012).
 41. Dou, L.; You, J.; Yang, J.; Chen, C.C.; He, Y.; Murase, S.; Moriarty, T.; Emery, K.; Li, G.; Yang, Y. Tandem polymer solar cells featuring a spectrally matched low-bandgap polymer. *Nat. Photon.*, 6, 180–185, (2012).
 42. Sergio Romero-Servin , Manuel de Anda Villa , R. Carriles , Gabriel Ramos-Ortiz , José-Luis Maldonado , Mario Rodríguez and M. Güizado-Rodríguez” Photophysical Study of Polymer-Based Solar Cells with an Organo-Boron Molecule in the Active Layer “*Materials*, 8, 4258-4272, (2015).
 43. Zhang J. C., Zheng X., Chen M., Yang X. Y., Cao W. L. “Synthesis and application of solar cells of poly (3-decylthiophene)/N/titanium dioxide hybrid” *eXPRESS Polymer Letters* Vol.5, No.5 401–408, (2011).
 44. Filippo Pierini, Krzysztof Zembrzycki, Massimiliano Lanzi, Pawel Nakielski, Sylwia Pawlowska, Olga Urbanek and Tomasz Aleksander Kowalewski, “Single-Material Organic Solar Cells Based on Electrospun FullereneGrafted Polythiophene Nanofibers” *Macromolecules*, 50, 4972-4981, (2017).
 45. Hsing-Ju Wang , Chih-Ping Chen and Ru-Jong Jeng “Polythiophenes Comprising Conjugated Pendants for Polymer Solar Cells: A Review” *Materials*, 7, 2411-2439, (2014).
 46. Yatang Dai¹, Fanghua Zhu², Huan Zhang¹, Huan Ma¹, Wei Wang¹, Jiehong Lei^{3,*} Electrolysis and Characterization of Polythiophene and Corrosion Protection for Stainless Steel *Int. J. Electrochem. Sci.*, 11, 4084 – 4091, (2016).
 47. Qunping Fan , Wenyan Su , Xia Guo , * Bing Guo , Wanbin Li , Youdi Zhang , Kun Wang , Maojie Zhang , * and Yongfang Li ”A New Polythiophene Derivative for High Efficiency Polymer Solar Cells with PCE over 9%” *Adv. Energy Mater.*, 6, 1600430, (2016).
 48. Hao Zhang,ab Sunsun Li,ab Bowei Xu,*ab Huifeng Yao,ab Bei Yangab and Jianhui Hou *ab “Fullerene-free polymer solar cell based on a polythiophene derivative with an unprecedented energy loss of less than 0.5 eV” *J. Mater. Chem. A*, 4,18043, (2016).

49. Huo, L.; Hou, J.; Zhang, S.; Chen, H.Y.; Yang, Y. A polybenzo [1,2-b:4,5-b'] dithiophene derivative with deep HOMO level and its application in high performance polymer solar cells. *Angew. Chem. Int. Ed.*, 49, 1500–1503, (2010).
50. Zhou, H.; Yang, L.; Stuart, A.C.; Price, S.C.; Liu, S.; You, W. Development of fluorinated benzothiadiazole as a structural unit for a polymer solar cell of 7% efficiency. *Angew. Chem. Int. Ed.*, 50, 2995–2998, (2011).
51. Pierini, F., Lanzi, M., Nakielski, P., Pawłowska, S., Urbanek, O., Zembrzycki, K., & Kowalewski, T. A.. Single-Material Organic Solar Cells Based on Electrospun Fullerene-Grafted Polythiophene Nanofibers. *Macromolecules*, 50(13), 4972–4981, (2017).
52. Kundu, S., & Kelly, T.. Hydrophobic Polythiophene Hole-Transport Layers to Address the Moisture-Induced Decomposition Problem of Perovskite Solar Cells. *Canadian Journal of Chemistry*. doi:10.1139/cjc-2018-0414, (2018).
53. Rucha Desai, Venu Mankad, Sanjeev K. Gupta, and Prafulla K. Jha, “Size Distribution of Silver Nanoparticles: UV-Visible Spectroscopic Assessment”, *Nanoscience and Nanotechnology Letters* Vol. 4, 30–34, 2012.
54. Xiao'e Jia, Zhiming Chen, Chunhui Duan, * Zhenfeng Wang, Qingwu Yin, Fei Huang * and Yong Cao Polythiophene derivatives compatible with both fullerene and non-fullerene acceptors for polymer solar cells *J. Mater. Chem. C*, 7, 314, (2019).