Erciyes Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 40, Sayı 1, 2024

Erciyes University
Journal of Institue of Science and Technology
Volume 40, Issue 1, 2024

Efficiency Improvement of Organic Photovoltaic Solar Cells via Spin Radical Doping

Kevser Şahin Tıraş *

*1 Erciyes University, Faculty of Sciences, Department of Physics, KAYSERİ

(Alınış / Received: 05.03.2024, Kabul / Accepted: 19.03.2024, Online Yayınlanma / Published Online: 30.04.2024)

Keywords
Organic photovoltaics,
Magnetic field effects,
Polymers

Abstract: Upon absorption of the sunlight, an excited energy state called exciton is generated in organic photovoltaics (OPV). There exist two kinds of excitons, singlet and triplet excitons. In OPV, the power conversion efficiency (PCE) is limited by the short lifetime of singlet excitons since they recombine quickly. To overcome this problem, we have introduced the spin ½ radical galvinoxyl into the MEH-PPV: PCBM bulk heterojunction to harvest triplets efficiently. The photovoltaic device shows an enhancement in PCE compared to the device without galvinoxyl. To reveal the underlying mechanism for the increase in PCE, magneto-photoconductance (MPC) of the OPVs was measured for the films, doped with various galvinoxyl concentration rates.

Spin Radikal Katkılama Yoluyla Organik Fotovoltaik Güneş Pillerinin Verimliliğinin Artırılması

Anahtar Kelimeler
Organik fotovoltaik,
Manyetik alan etkisi,
Polimerler

Öz: Güneş ışığının absorbesi üzerine, organik fotovoltaiklerde (OPV) eksiton adı verilen uyarılmış bir enerji durumu oluşur. Singlet ve triplet eksitonlar olmak üzere iki tür eksiton vardır. OPV'de güç dönüşüm verimliliği (PCE), singlet eksitonların kısa ömürleri nedeniyle sınırlıdır, çünkü bunlar hızla rekombine olurlar. Bu sorunun üstesinden gelmek için, spin ½ radikali galvinoksili MEH-PPV: PCBM bulk heterojonksiyonuna dahil ederek tripletleri verimli bir şekilde elde ettik. Fotovoltaikler, galvinoxyl içermeyen cihaza kıyasla PCE'de artış göstermektedir. PCE'deki artışın altında yatan mekanizmayı ortaya çıkarmak için, OPV'lerin manyeto-fotokondüktansı (MPC), çeşitli galvinoksil konsantrasyon oranları ile katkılanmış filmler için ölçülmüştür.

---

*İlgili Yazar, email: kevsersahintiras@erciyes.edu.tr

1. Introduction

In order to meet the challenges of increasing energy demand, solar energy has been identified as the most important source of renewable energy. There have been many studies to improve the device efficiencies of organic photovoltaics (OPV) [1-12]. Typical bulk heterojunction structure for OPV devices consists of an active layer sandwiched between the anode and cathode. The blend of π-conjugated polymer and fullerene is simply spin-coated to create the active layer. It is well-known that the materials with delocalized π-electron systems absorb sunlight, create photogenerated charge carriers and transport these charge carriers [13,14]. The blend of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (donor-D) and 1-(3-(methoxycarbonyl)propyl)-1-1-phenyl)(6,6)C61 (PCBM) (acceptor—A) is commonly used polymer:fullerene mixture for the active layer of OPV. MEH-PPV polymer chains absorb light, and excitons are first generated in the donor nano domains; subsequent dissociation at D–A interfaces occurs due to the difference in energy levels between the donor's LUMO and the acceptor's HOMO (lowest to highest occupied molecular orbital) [15]. For the excitons to transfer to the D–A interface, they first move to the polymer domain boundary (~10 ps) where upon arrival they generate charge transfer excitons [15,16]. These excitons dissociate to create Coulombically bounded polaron pairs (PP) which have longer lifetime (a few microseconds) and are intermediate species at D-A interface [17-19]. The PP species may eventually split into "free" electron and hole polarons that can easily be gathered at the anode and cathode, respectively, and are accessible for charge transport via the A and D domains. Device efficiency (η) is low due to recombination of PP at D-A interfaces [16,20-22]. Numerous attempts related to active layer have been studied such as concentration, thickness, dopant addition etc. to optimize low η [6-12]. In the current work, we present a novel approach to decrease PP recombination at the polymer/fullerene interfaces by doping the device active layer with spin 1/2 radicals. In the context of organic solar cells and organic light-emitting diodes, the effects of additional radical dopant spins were initially investigated. It was found that for a certain doping rate both the efficiency and short circuit current of the doped devices were improved. In the present study, galvinoxyl (commercially available spin radical) (2,6-di-t-butyl-(3,5-di-t-butyl-4-oxo-2,5- cyclohexadien-1-ylidene)-p-tolyloxy) at different concentrations was doped into the blend of MEH-PPV: PCBM to observe the enhancement in device power conversion efficiency, PCE (η). We additionally measure the magneto-photocurrent (MPC) response, which is sensitive to spin-flip between singlet and triplet PP. Spin-flip mechanism enables PP separation at D-A interfaces by converting photogenerated PP from spin singlet to spin triplet via spin exchange between PP and galvinoxyl. To better understand the origin of the improved efficiency, photoluminescence (PL) of the pristine and galvinoxyl-doped MEH-PPV films was measured.

2. Materials and Methods

2.1. OPV device fabrication and characterization

Figure 1 A and B show the device structure of OPV and the chemical structures of the active layer materials, respectively. For the anode layer, 40 nm transparent indium tin oxide (ITO) coated glass substrates (Delta Technologies) were cleaned by ultrasonic treatment (in acetone, Helmanexx, deionized water and isopropanol alcohol sequentially) and followed by oxygen plasma cleaning. The conducting polymer poly (3,4-ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT: PSS), purchased from Ossila Ltd., was spin coated at 4000 rpm for 60 s at ambient conditions onto the ITO layer with 50 nm thickness to provide sufficient hole transport to the active layer. Then, they were transferred to a nitrogen-filled glovebox (O_2 < 1 ppm) for annealing at 150 °C for 30 min. The organic blend was used as the active layer was spin coated from a blend of Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4- phenylenevinylene], MEH-PPV (Sigma Aldrich) polymer as donor, [6,6]-phenyl-C_{61}-butyric acid methyl ester, PCBM (Nano-C) fullerene as acceptor and galvinoxyl (Aldrich) as spin radical (only for doped devices). The blend was prepared by dissolving MEH-PPV (8 mg/ml) and PCBM at 1:4 weight ratio in chlorobenzene. The blend was doped with different concentration rates of galvinoxyl solution between 0% to 17%. The active layer was spin-coated from the blend at 2000 rpm for 60 s and annealed at 120 °C for 1 hour. As the cathode layer, 30 nm thick Ca followed by 100 nm thick Al was thermally evaporated to provide effective electron injection to the active layer at a base pressure of 10^{-7} mbar. The device area was 1×1 mm^2. The samples were placed inside the dynamic vacuum of a cryostat located between the poles of an electromagnet to measure I-V characteristics, MPC and PL. The solar cells were tested by the solar simulator with AM1.5G filter and a xenon lamp. Keithley 2400 sourcemeter unit was used to measure I-V characteristics of the device. PL emission of the doped and undoped blend was excited by 100 mW continuous wave laser at 488 nm.

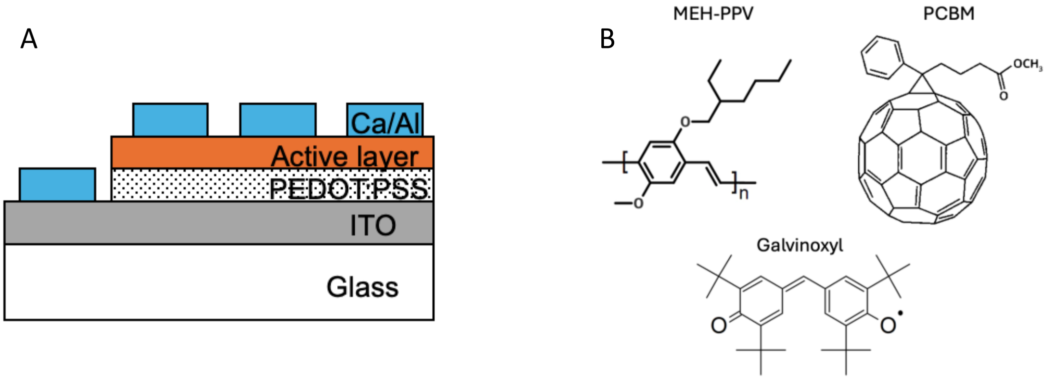

Figure1. A) Device structure of OLED, B) Chemical structures of MEH-PPV, PCBM and galvinoxyl.

2.2. Magneto-photocurrent measurements

MPC measurements were performed in a closed cycle He cryostat positioned between the poles of an electromagnet at room temperature. The magnetic field, B which the electromagnet produced was up to 300 mT. While the solar cells were illuminated with 80 mW cm^{-2} Xenon lamp, Keitley 2400 sourcemeter unit was used to measure at zero bias as the B field sweeps. The value MPC was calculated by using Equation 1,

$$MPC(B) = \left[\frac{PC(B)}{PC(0)} - 1\right] \quad (1)$$

PC(B) is photocurrent when the magnetic field is on, and PC (0) is when it is off.

3. Results

The spin 1/2 radical we chose for our experiments has a conjugated molecule with C_2 symmetry. By keeping other molecules apart, the large t-butyl groups on the molecule stabilize the radical and prevent further radical-radical contact in the solid state. Even when there is oxygen present, this molecule remains stable [23, 24]. Its chemical structure can be thought of as a resonance hybrid of two configurations with a localized unpaired spin-polarized electron on different oxygen since the unpaired electron is delocalized throughout the entire molecule.

We note that the weight ratio for the blend of MEH-PPV: PCBM was optimized at 1:4. The effect of spin ½ radical galvinoxyl doping in the active layer of MEH-PPV: PCBM on solar cell characteristics was observed. The power conversion efficiency of a solar cell is calculated by using general parameters; V_{MPP}, J_{MPP} and P_{in} as shown in Equation 2,

$$\eta = \frac{Pmax}{Pin} = \frac{V_{MPP}J_{MPP}}{Pin} \quad (2)$$

V_{MPP} is the voltage at the maximum power point, and J_{MPP} is the point current at the maximum power (P_{max}) that can be obtained by the device. P_{in} is the incident power that is provided by the solar simulator. The plot of η and J_{SC} for the solar cells depending on the doping level of the galvinoxyl spin radical is given in Figure 2 A and B, respectively. The galvinoxyl radical-induced boost in J_{SC} and η peaks at around 3% and subsequently disappears with additional increasing doping. As the doping concentration rate changed from 0% to 17%, the obtained value for η varies from ~0.7% to 0.5%. At 3% doping level η reaches the maximum value of ~0.85%. Similar change was observed for the J_{SC} which varies from ~1.8 mAcm^{-2} to ~1.6 mAcm^{-2} as the doping level changes between 0% to 17%. At 3% doping level, J_{SC} increases to 2.4 mAcm^{-2}. About half of the improvement in the device η can be attributed to a 33% rise in J_{SC}, which suggests that carrier photogeneration is either increased or carrier recombination is decreased, or both. The device performance started to suppress at higher galvinoxyl doping levels (>10%). Similar results about the enhancement of OPV and OLED devices were obtained by other groups [25-27]. The action of galvinoxyl additions is divided into two regimes by the ideal doping concentration (3%) at which η maximizes: an "enhancement" regime where η grows with doping and a "suppression" regime where η declines with doping [26].

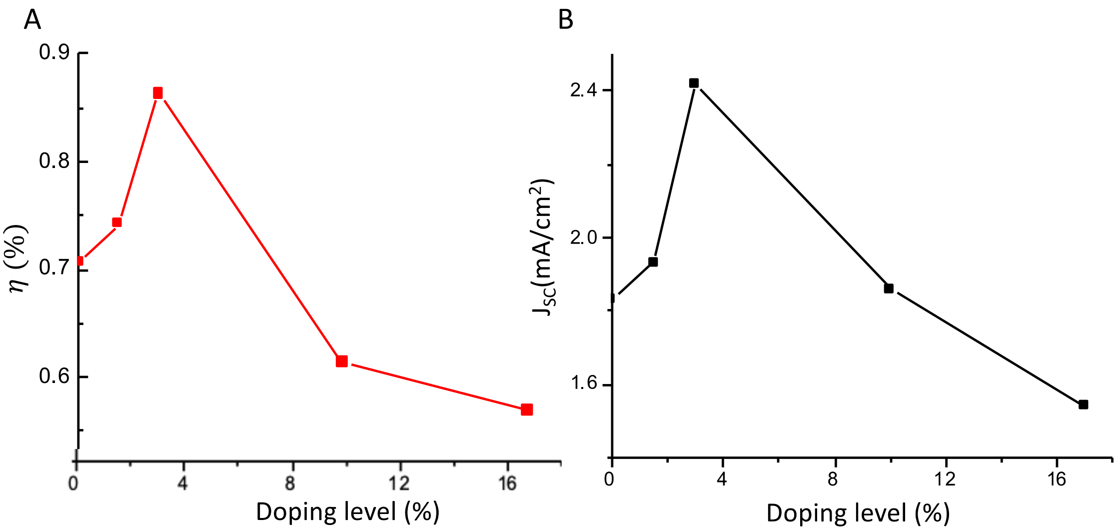

Figure2. A) η and B) Jsc versus galvinoxyl doping level plots.

The *I–V* properties of MEH-PPV: PCBM devices doped with different weight percentages of galvinoxyl radicals are displayed in Figure 3B. To see if the improvement in Jsc with the addition of galvinoxyl is also due to an improvement in device active layer optics, we compared PL spectra for the pure MEH-PPV: PCBM films and those that have been doped with galvinoxyl. Figure 3A shows the PL spectrum of pristine and galvinoxyl doped blend films. PL is due to the radiative emission of photon excited states generated by photon absorption. There are two PL emission peaks at 1.9 eV and 2.05 eV appearing in both films. As the π-electrons relax to the inter-chain states, PL emission peak at 1.9 eV appears. The other peak at 2.05 eV is the result of the relaxation of the π-electrons to the ground state [28, 29]. The quenching of the PL spectrum as the blend doped with galvinoxyl confirms that the population of the triplet excitons (longer lived excitons) increased.

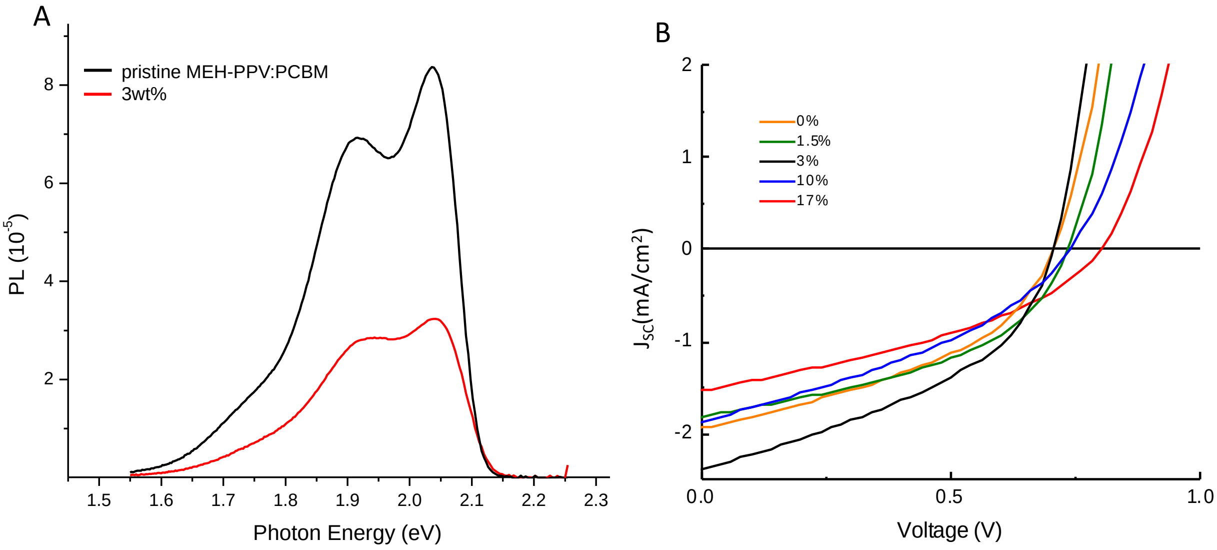

Figure3. A) PL spectrum of pristine and galvinoxyl doped (3 wt.%) MEH-PPV: PCBM blend film and OPV device and B) I–V characteristics of the OPV solar cells doped with various wt.% of galvinoxyl radical.

The ratios of singlet and triplets can be altered by an external B-field through formation and intersystem conversion, leading to MFEs in PL based on intra- and intermolecular excitation states. To understand underlying mechanism of the improved characteristics of solar cell in galvinoxyl doped devices, MPC measurements were performed. Figure 4 shows MPC response of OPV devices with various galvinoxyl doping. It is clearly seen when the galvinoxyl doping level is 3%, MPC reaches the maximum response. MPC in OPV blends is due to magnetic field manipulation of spin triplet and singlet states within the PP spin manifold [30-32]. MPC value was increased from 3% to 6% when galvinoxyl doping rate was changed from 0 wt.% to 3 wt.%. However, as the doping level increased MPC value becomes 2% which is less than the value at 0 wt.%. Consequently, the lowering of MPC with galvinoxyl weight percentage demonstrates that the spin 1/2 radicals disrupt the intersystem crossing rates between the different spin states of the PP species, emphasizing the significance of the galvinoxyl spin instead of its donor/acceptor properties. The improved carrier photogeneration following galvinoxyl doping is caused by reduced PP geminate recombination at the D–A interfaces.

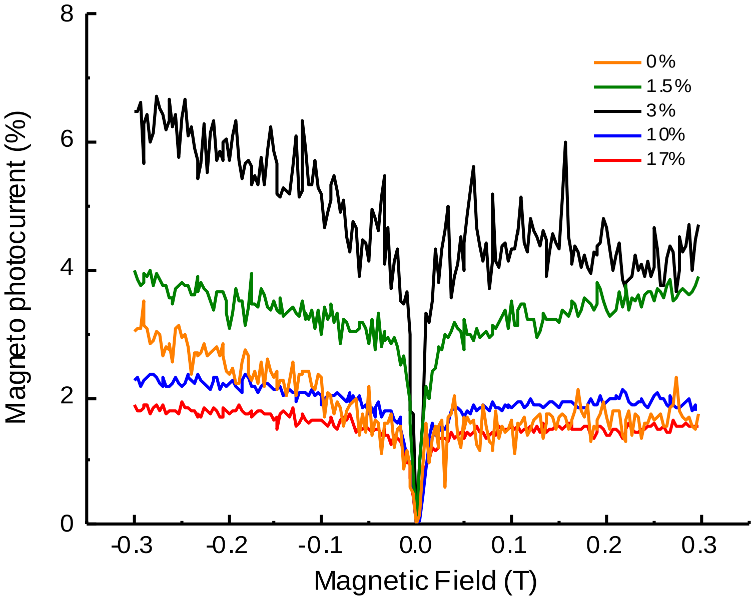

Figure4. MPC response of OPV devices doped with various wt.% of galvinoxyl radical up to field, B of 300 mT.

We notice that the pattern of the OPV enhancement with weight percentage and the MPC value with galvinoxyl weight percentage are similar. At 3 wt.%, the maximum increase in MPC is observed; at 10 wt.%, its value returns to that of undoped device. This demonstrates that there is a strong relation between the spin ½ properties of galvinoxyl additives and the enhancement of the characteristics of OPV.

4. Discussion and Conclusion

Our most recent research on spin-enhanced bulk heterojunction organic solar cells is presented in this study. We were able to improve the performance of the solar cell device by doping MEH-PPV: PCBM OPV with spin 1/2 radical galvinoxyl. We observed that this boost is directly connected to the radical's spin degree of freedom, which through spin–spin interaction lowers the rate of PP recombination at the MEH-PPV: PCBM interfaces. For the enhancement to take place, the donor/acceptor interface must exist in the active layer. Experiments show that galvinoxyl-doped OPV devices have a higher PCE value due to reduced PP recombination at the MEH-PPV: PCBM domain interfaces from spin 1/2 radical additions. Galvinoxyl, a spin 1/2 radical, is thought to improve PP separation at MEH-PPV: PCBM interfaces by changing photogenerated PP from spin singlet to spin triplet by spin exchange interaction with galvinoxyl. Since triplet PP has a longer lifetime than singlet PP, the improved intersystem crossing yields a long-lived PP species with a higher probability of dissociating into free polarons. Density functional theory (DFT) calculations related to the physical results of this model were investigated by Zhang et al. [25] At high concentrations of galvinoxyl doping, triplet-triplet annihilation of triplet PP accumulated at the D-A interface may eventually occur, resulting in radiation loss rather than dissociation into free electrons and holes.

Acknowledgment

This work was supported by Erciyes University Research Fund Grant No. FBA-2022-11983.

References

[1] Peet, J., Senatore, M.L., Heeger, A.J. and Bazan, G.C., 2009. The role of processing in the fabrication and optimization of plastic solar cells. *Advanced Materials*, *21*(14-15), pp.1521-1527.
[2] Chen, L.M., Hong, Z., Li, G. and Yang, Y., 2009. Recent progress in polymer solar cells: manipulation of polymer: fullerene morphology and the formation of efficient inverted polymer solar cells. *Advanced materials*, *21*(14-15), pp.1434-1449.

[3] Yang, K., Arif, M., Förster, M., Scherf, U. and Guha, S., 2009. Triplet excitons in a ladder-type conjugated polymer: Application in solar cells. *Synthetic metals*, *159*(21-22), pp.2338-2341.

[4] Chang, M.Y., Chen, Y.F., Tsai, Y.S. and Chi, K.M., 2008. Blending platinum nanoparticles into poly (3-hexylthiophene):[6, 6]-phenyl-C61-butyric acid methyl ester enhances the efficiency of polymer solar cells. *Journal of the Electrochemical Society*, *156*(2), p.B234.

[5] Tung, V.C., Chen, L.M., Allen, M.J., Wassei, J.K., Nelson, K., Kaner, R.B. and Yang, Y., 2009. Low-temperature solution processing of graphene– carbon nanotube hybrid materials for high-performance transparent conductors. *Nano letters*, *9*(5), pp.1949-1955.

[6] Eakins, G.L., Alford, J.S., Tiegs, B.J., Breyfogle, B.E. and Stearman, C.J., 2011. Tuning HOMO–LUMO levels: trends leading to the design of 9-fluorenone scaffolds with predictable electronic and optoelectronic properties. *Journal of Physical Organic Chemistry*, *24*(11), pp.1119-1128.

[7] Du, H., Deng, Z., Lü, Z., Yin, Y., Yu, L., Wu, H., Chen, Z., Zou, Y., Wang, Y., Liu, H. and Li, Y., 2011. The effect of graphdiyne doping on the performance of polymer solar cells. *Synthetic metals*, *161*(19-20), pp.2055-2057.

[8] Zhou, M., Wang, B., Jiang, X., Zakhidov, A.A., Ferraris, J.P., Azunskis, D. and Hanley, L., 2011. Synthesis of PbS Nanocrystal/Functionalized Conducting Polymers for Plastic Solar Cells. *International Journal of Nanoscience*, *10*(03), pp.521-532.

[9] Zhang, C., Sun, J., Li, R., Sun, S.S., Lafalce, E. and Jiang, X., 2011. Poly (3-dodecylthienylenevinylene) s: Regioregularity and Crystallinity. *Macromolecules*, *44*(16), pp.6389-6396.

[10] Gorenflot, J., Sperlich, A., Baumann, A., Rauh, D., Vasilev, A., Li, C., Baumgarten, M., Deibel, C. and Dyakonov, V., 2012. Detailed study of N, N′-(diisopropylphenyl)-terrylene-3, 4: 11, 12-bis (dicarboximide) as electron acceptor for solar cells application. *Synthetic metals*, *161*(23-24), pp.2669-2676.

[11] Zeng, W., Yong, K.S., Kam, Z.M., Chen, Z.K. and Li, Y., 2012. Effect of MoO3 as an interlayer on the performance of organic solar cells based on ZnPc and C60. *Synthetic metals*, *161*(23-24), pp.2748-2752.

[12] Zhao, Y., Guo, X., Xie, Z., Qu, Y., Geng, Y. and Wang, L., 2009. Solvent vapor-induced self assembly and its influence on optoelectronic conversion of poly (3-hexylthiophene): Methanofullerene bulk heterojunction photovoltaic cells. *Journal of applied polymer science*, *111*(4), pp.1799-1804.

[13] Yao, Y., Hou, J., Xu, Z., Li, G. and Yang, Y., 2008. Effects of solvent mixtures on the nanoscale phase separation in polymer solar cells. *Advanced Functional Materials*, *18*(12), pp.1783-1789.

[14] Perez, M.D., Borek, C., Forrest, S.R. and Thompson, M.E., 2009. Molecular and morphological influences on the open circuit voltages of organic photovoltaic devices. *Journal of the American Chemical Society*, *131*(26), pp.9281-9286.

[15] Singh, S., Pandit, B., Basel, T.P., Li, S., Laird, D. and Vardeny, Z.V., 2012. Two-step charge photogeneration dynamics in polymer/fullerene blends for photovoltaic applications. *Physical Review B*, *85*(20), p.205206.

[16] Bakulin, A.A., Rao, A., Pavelyev, V.G., van Loosdrecht, P.H., Pshenichnikov, M.S., Niedzialek, D., Cornil, J., Beljonne, D. and Friend, R.H., 2012. The role of driving energy and delocalized states for charge separation in organic semiconductors. *Science*, *335*(6074), pp.1340-1344.

[17] Benson-Smith, J.J., Goris, L., Vandewal, K., Haenen, K., Manca, J.V., Vanderzande, D., Bradley, D.D. and Nelson, J., 2007. Formation of a Ground-State Charge-Transfer Complex in Polyfluorene//[6, 6]-Phenyl-C61 Butyric Acid Methyl Ester (PCBM) Blend Films and Its Role in the Function of Polymer/PCBM Solar Cells. *Advanced Functional Materials*, *17*(3), pp.451-457.

[18] Drori, T., Holt, J. and Vardeny, Z.V., 2010. Optical studies of the charge transfer complex in polythiophene/fullerene blends for organic photovoltaic applications. *Physical Review B*, *82*(7), p.075207.

[19] Behrends, J., Sperlich, A., Schnegg, A., Biskup, T., Teutloff, C., Lips, K., Dyakonov, V. and Bittl, R., 2012. Direct detection of photoinduced charge transfer complexes in polymer fullerene blends. *Physical Review B*, *85*(12), p.125206.

[20] Ohkita, H., Cook, S., Astuti, Y., Duffy, W., Tierney, S., Zhang, W., Heeney, M., McCulloch, I., Nelson, J., Bradley, D.D. and Durrant, J.R., 2008. Charge carrier formation in polythiophene/fullerene blend films studied by transient absorption spectroscopy. *Journal of the American Chemical Society*, *130*(10), pp.3030-3042.

[21] Holt, J., Singh, S., Drori, T., Zhang, Y. and Vardeny, Z.V., 2009. Optical probes of π-conjugated polymer blends with strong acceptor molecules. *Physical Review B*, *79*(19), p.195210.

[22] Howard, I.A., Mauer, R., Meister, M. and Laquai, F., 2010. Effect of morphology on ultrafast free carrier generation in polythiophene: fullerene organic solar cells. *Journal of the American Chemical Society*, *132*(42), pp.14866-14876.

[23] Coppinger, G.M., 1957. A stable phenoxy radical inert to oxygen. *Journal of the American Chemical Society*, *79*(2), pp.501-502.

[24] Kharasch, M.S. and Joshi, B.S., 1957. Reactions of hindered phenols. I. Reactions of 4, 4'-dihydroxy-3, 5, 3', 5'-tetra-tert-butyl diphenylmethane. *The Journal of Organic Chemistry*, *22*(11), pp.1435-1438.

[25] Zhang, Y., Basel, T.P., Gautam, B.R., Yang, X., Mascaro, D.J., Liu, F. and Vardeny, Z.V., 2012. Spin-enhanced organic bulk heterojunction photovoltaic solar cells. *Nature communications*, *3*(1), p.1043.

[26] Zhang, Y., Gautam, B.R., Basel, T.P., Mascaro, D.J. and Vardeny, Z.V., 2013. Organic bulk heterojunction solar cells enhanced by spin interaction. *Synthetic metals*, *173*, pp.2-9.

[27] Wang, Y., Harmon, N.J., Sahin-Tiras, K., Wohlgenannt, M. and Flatté, M.E., 2014. Anomalous organic magnetoresistance from competing carrier-spin-dependent interactions with localized electronic and nuclear spins. *Physical Review B*, *90*(6), p.060204.

[28] Yang, S.H., Le Rendu, P., Nguyen, T.P. and Hsu, C.S., 2007. Fabrication of MEH-PPV/SIO2 and MEH-PPV/SIO2 nanocomposites with enhanced luminescent stabilities. *Reviews on Advanced Materials Science*, *15*(2), pp.144-149.

[29] Mahmoud, F.A., Elazab, I., Abo-Elenien, O.M., Abdel Fatah, A. and Ahmed, A.A., 2019. Optical characterization of Poly [2-methoxy-5-(2-ethylhexyloxy-p-phenylene vinylene](MEH-PPV): C60, MEH-PPV: C60: TiO2 and MEHPPV: C60: ZnO Thin Films. *Egyptian Journal of Chemistry*, *62*(2), pp.311-323.

[30] Zang, H., Xu, Z. and Hu, B., 2010. Magneto-optical investigations on the formation and dissociation of intermolecular charge-transfer complexes at donor− acceptor interfaces in bulk-heterojunction organic solar cells. *The Journal of Physical Chemistry B*, *114*(17), pp.5704-5709.

[31] Shakya, P., Desai, P., Kreouzis, T., Gillin, W.P., Tuladhar, S.M., Ballantyne, A.M. and Nelson, J., 2008. The effect of applied magnetic field on photocurrent generation in poly-3-hexylthiophene:[6, 6]-phenyl C61-butyric acid methyl ester photovoltaic devices. *Journal of Physics: Condensed Matter*, *20*(45), p.452203.

[32] Lei, Y., Song, Q., Zhang, Y., Chen, P., Liu, R., Zhang, Q. and Xiong, Z., 2009. Magnetoconductance of polymer–fullerene bulk heterojunction solar cells. *Organic electronics*, *10*(7), pp.1288-1292.