Composites of Betalain Dye and Wide-Energy Gap Polymers for Semitransparent Organic Solar Cells

Peshawa O. Amin , Fahmi F. Muhammadsharif * , Salah Raza Saeed , Kamal Aziz Ketuly

Posted Date: 2 April 2024

doi: 10.20944/preprints202404.0132.v1

Keywords: semitransparent solar cell; natural dye; wide bandgap polymers; BHJ structure; ternary composite

 doi:10.20944/preprints202404.0132.v1

Article

Composites of Betalain Dye and Wide-Energy Gap Polymers for Semitransparent Organic Solar Cells

Peshawa O. Amin [1], Fahmi F. Muhammadsharif [2,*], Salah Raza Saeed [3] and Kamal Aziz Ketuly [4]

[1] Chrmo Center for Research, Training and Consultancy, Charmo University, 46023 Chamchamal, Kurdistan Region, Iraq; peshawa.amin@chu.edu.iq
[2] Department of Physics, Faculty of Science and Health, Koya University, Koya KOY45, Kurdistan Region - F.R., Iraq; fahmi982@gmail.com
[3] Advanced Polymeric Materials Research Lab., Department of Physics, College of Science, University of Sulaimani, Qlyasan Street, Sulaimani 46001, Iraq; salah.raza@univsul.edu.iq
[4] Department of Medical Chemistry, College of Medicine, University of Duhok, Duhok,, Kurditan Region, Iraq; kketuly@yahoo.com
* Correspondence: fahmi982@gmail.com

Abstract: Organic solar cells are contributing extensively to the production of future large area and cost-effective sources of renewable energy with a compact environmental impact. Moreover, due to tunable optical properties of the active medium, the semi-transparent organic solar cell can be fabricated and become a promising nominee for building Integrated Photovoltaics (BIPV), vehicles, and mobile electronic devices. Therefore, three newly synthesized polymers used as were host materials for the active medium and blended with beetroot dye. Hence, based on BHJ structure two ternary systems have been constructed and utilized to fabricate semitransparent solar cells and characterized. The results show that the natural dye has a crucial impact on solar cell characteristic parameters. Consequently, large value of V_{OC} close to 1V were obtained for ternary systems and acceptor material named PINDOLE exhibits potentials for electron transport layer (ETL) and shows an improvement in both fill factor and device efficiency.

Keywords: Semitransparent solar cell; natural dye; BHJ structure; high bandgap polymers; all solution processable; ternary system

1. Introduction

Among all the sources of electricity, renewable energy-based electricity generation increased by 7.1 % in 2020 despite the economic disruption caused by Covid-19 pandemic. To achieve zero emissions, the use of renewable energy sources in power generation must grow by 12% per year from 2021 to 2030. Along this line, solar energy is accounted for 33% growth of total renewable energy sources for electricity generation in 2020 [1]. Nowadays, solar cells based on crystalline silicon are commercialized and capitalized in the global market whereas solar cells based on organic materials are in the state of progress in the field of photovoltaic research. Moreover, due to the versatile properties of organic solar cells such as solution processability, flexibility, lightweight and semi-transparency, they become promising candidates for mass production with a low cost in the near future [2].The process of converting sunlight energy into electricity involves several phases, including the generation of excitons upon absorbing the photon energy followed by excitons dissociation into free charge carriers and their collection by respected electrodes. Therefore, the device efficiency, stability and large-scale production are key parameters for future commercialization which depend on the processes of converting sunlight into electric current [2,3]. Organic semiconductors possess noteworthy characteristics such as narrow absorption window and tuneable energy gap which lead to employ them in a variety of device architecture. This is where the bulk heterojunction structure has become a standard architecture for organic solar cells [4,5]. In general, the architecture of organic solar cell consists of electrodes, active medium, and interface layers. In the bulk heterojunction

 doi:10.20944/preprints202404.0132.v1

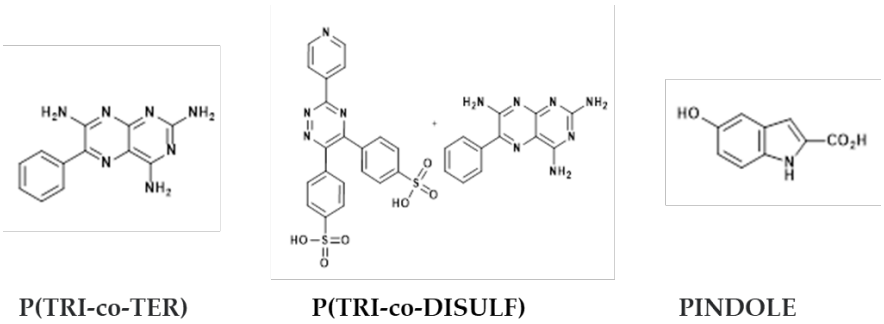
structure (BHJ), the active medium is made by blending raw materials. Moreover, due to tuneable optical properties of the active medium, the semi-transparent organic solar cell can be fabricated and become a promising candidate for building Integrated Photovoltaics (BIPV), vehicles, and mobile electronic devices [6,7]. The active medium of bulk heterojunction structure is composed of donor and acceptor blends to form single junction organic solar cells (OSCs). This binary system limits the device performance due to a narrow spectral absorption window, low mobility, and high thermal loss in organic materials. Therefore, a ternary system has become an alternative method to overcome these limitations and enhance the device performance. Ternary systems are made by inserting a third component into the binary system. Thus, a ternary system can have two donors and one acceptor (D1/D2/A) or one donor and two acceptors (D/A1/A2). Interestingly, a ternary active layer has several advantages over binary active layer such as expanding absorption window, which is directly related to the short-circuit current density (J_{SC}) and hence affecting the device efficiency. The possibility of modifying the open-circuit voltage (V_{OC}) of the cell is another advantage of the ternary active layer [8,9]. Nevertheless, inserting the third component into the binary active layer form a complex system and the role of the third component defines the type of charge transfer inside the active layer. Furthermore, the electronic energy level of the components, the weight ratio of the third component and the miscibility between the components have a vital role in the charge transfer state and collection of free carriers which in turn affects the device performance. There are four possible models for charge transfer based on miscibility, weight ratio, and electronic energy levels of the components of the ternary active layer. Thus, a careful consideration is required to form a ternary system otherwise upon inserting the third component, it would be possible to introduce a trap or disrupting the prolonged pathways of charge transfer, leading to a poor device performance [10–13]. A conjugated semiconductor polymer does not have a panchromatic absorption spectrum and this property opens a new line of application of photovoltaic devices such as semi-transparent solar cells [14]. Hence, the difference between opaque and semi-transparent organic solar cells is that in the later one the cell is transparent to the visible region of electromagnetic wave spectrum. Several approaches have been presented in literature to reach the condition of semi-transparent organic solar cell. One of these approaches is that the active layer become transparent to the visible part of the solar spectrum. Therefore, the high band gap polymers, dye molecules [15–17], and ultra-narrow band gap polymers are utilized to absorb in the UV and IR regions in solar spectrum [18–20]. To this end, this study focuses on characterizations of the three newly synthesized polymers which are two electron-rich polymers: (i) Poly (triamterene-co-terephthalate)(P(TRI-co-TER)), (ii) Poly [triamterene-co- 3-(2-pyridyl)-5, 6-diphenyl-1, 2, 4-triazine-p, p'-disulfonamide] (P(TRI-co-DISULF)) and one electron-accepting polymer: (iii) Poly (5-hydroxyindole-2-carboxylate) (PINDOLE) as host materials for the binary photoactive layers. In addition, small molecule natural dye extracted from Beetroot is utilized as a third component to form ternary photoactive layers. Hence, different solution-processed semi-transparent organic solar cells, based on ternary bulk heterojunction active layers, are fabricated and characterized.

2. Materials and Methods

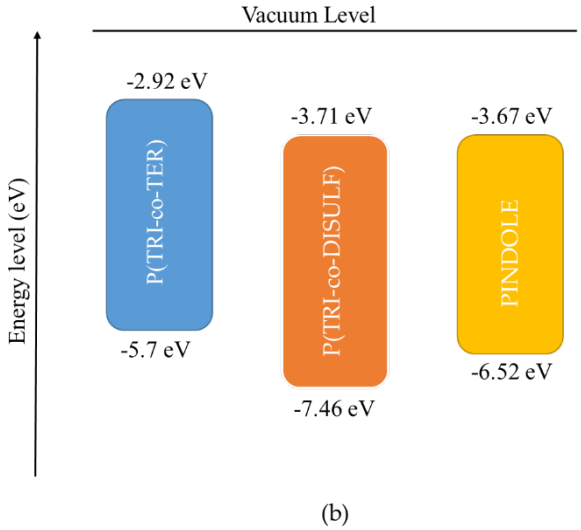
2.1. Materials

The materials and synthesis route of the host polymers and extracted dye with their characterizations are shown elsewhere [15,16]. In addition, the molecular structure and the electronic energy levels of the host polymers with their labels are presented in Figure 1.Aqueous solution of PEDOT:PSS (AI4083), PEDOT:PSS (PH1000) and ITO substrate were purchased from Ossila company, while the chemical solvents were supplied by Sigma-Aldrich.

Preprints.org (www.preprints.org) | NOT PEER-REVIEWED | Posted: 2 April 2024 doi:10.20944/preprints202404.0132.v1



(a)



(b)

Figure 1. (a) Molecular structure and (b) electronic energy levels of the host polymers.

2.2. Device Fabrication

Bulk heterojunction structure of ternary semitransparent organic solar cell was fabricated with invert architecture (ITO/Electron transport layer (ETL)/Active medium/ hole transport layer (HTL)/ PEDOT:PSS (Anode). Prior to device fabrication, the ITO substrate was cleaned with consecutive cleaning process in ultrasonic bath starting with detergent for 5 minutes and rinsed in water twice. Then, the substrate was immersed in isopropyl alcohol and sonicated for 5 minutes and rinsed twice in hot and cold water. Later on, a solution of sodium chloride with 10%wt ratio was prepared and substrates were dipped and sonicated for 5 minutes then rinsed 2 times in hot and cold water then kept in deionized water till device fabrication.

In addition, the solution of active medium was prepared by dissolving the host polymers in dimethyl sulfoxide (DMSO) with concertation of 20 mg/ml and the natural dye was used as extracted. The selection process of the optimal ratio of the active medium components was given in our previous work [21]. On the other hand, the TiO_2 solution, as an electron transport layer, was synthesized via sol-gel method and deposited via dip coating followed by thermal annealing at 600 ℃ for 2 hours.

Moreover, another electron transport layer was prepared by dissolving PINDOLE in dimethyl sulfoxide (DMSO) and dichlorobenzene (DCB) with (1:1) ratio and concertation of 40 mg/ml. Meanwhile, the top electrode PEDOT:PSS (PH1000) was modified by mixing it with the hole transport layer PEDOT:PSS (AI4083) in the volume ratio of 2:1 followed by adding 6% V/V of poly ethylene glycol. the active layers of the organic solar cells were deposited via spin coating (Spincoat G3P-15) at 4000 rpm and the final device was annealed at 120 ℃ for 10 minutes.

 doi:10.20944/preprints202404.0132.v1

2.3. Active Layers and Devices Characterization

UV–Vis spectrophotometer (UV line 9400) was utilized for optical absorption studies of the active medium at room temperature. Photoluminescence (PL) data were collected by using a Cary Eclipse Fluorescence Spectrophotometer- Serial No. MY13140005 with a PL excitation wavelength of 300 nm. Moreover, Panalytical Empyrean XRD with monochromatized CuK alfa radiation (1.5418A) was employed to carry out the structural analysis of the ternary (donor: Dye: acceptor) systems in thin film form. The Panalytical Empyrean was operated at 45 kV and 40 mA, with a Cu X-ray tube equipped with a $1 \times 1\, mm^2$ point focus and a Nickel filter on the direct beam path to absorb the $Cu\ K_\beta$ radiation. The surface morphology analysis of the active mediums was carried out by scanning electron microscopy (SEM) (TESCAN MIRA3) operating at 30 kV. The current density- voltage characteristics (J-V measurements) of the obtained devices was conducted via Keithley 4200 all-in-one machine and the fabricated devices were tested under illumination of $100\, mW.cm^{-2}$ using a pre-calibrated xenon-lamp in ambient atmosphere.

3. Results and Discussion

3.1. XRD Analysis

To examine the structural properties of the polymers and their ternary system the utmost technique of X-ray diffraction was employed, which can easily detect the structural change and vertical phase segregation during film formation. The synthesized polymers and ternary systems were deposited on quartz substrates to form thin films. However, in organic films several obstacles affect the XRD pattern for a given material and the foremost challenging one is low intensity of characteristic peaks and the shift of peak position toward the high angle zone. This is due to the low atomic number of carbons, stability, complexity and sensitivity of organic materials. Moreover, peak position, intensity and shape of the peaks in the XRD pattern reveal several characteristics of the given materials. For instance, the degree of crystallites can be measured from the intensity of the peak and crystallite size can be extracted from the shape of the peaks. The interplanar spacing and lattice constant can be measured from the peak position. As shown in Figure 2, the XRD patterns of the synthesized polymers demonstrated both types of morphology including amorphous phase and mono-crystalline phase. For instance, in the low angle zone (2θ), broad amorphous peaks were observed for all polymers, which are ascribed to the inter-chain $\pi-\pi$ stacking of pyrrole compound [22,23]. In the high angle zone (2θ), sharp peaks were observed for both P(TRI-co-DISULF) and PINDOLE, which indicate the mono-crystalline phase except for the P(TRI-co-TER) which showed only one small peak. Thus, polymer chains are packed together in an ordered manner for both P(TRI-co-DISULF) and PINDOLE with small lattice distance (d-spacing) [24].

 doi:10.20944/preprints202404.0132.v1

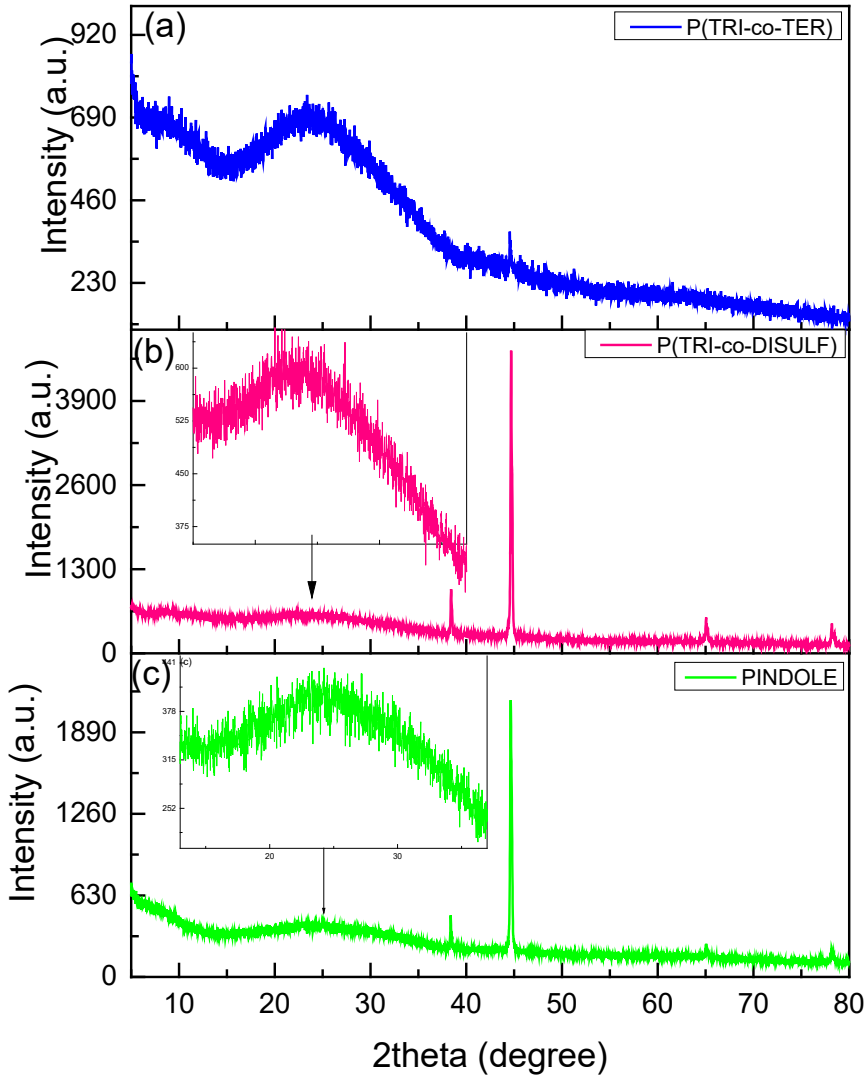


Figure 2. XRD spectra of synthesized polymers:(a) P(TRI-co-TER), (b) P(TRI-co-DISULF), and (c) PINDOLE.

Consequently, the dye molecules greatly affect the structural properties in the ternary systems, thereby disappearing the characteristic peaks. In addition, changing the intensity of the XRD peaks in the ternary systems indicates that the interaction between the third components and host polymers occurs. Thus, the dye molecules contribute in the host polymer chains to increase the crystallite domain or disrupt the polymer chains, and hence the amorphous domain becomes dominant [25,26]. As shown in Figure 3, the amorphous domain has increased when the beetroot dye was inserted into the binary system (P(TRI-co-TER):PINDOLE) and the characteristic XRD peaks were totally diminished. This might be due the presence of impurities in the extracted Beetroot dyes, which in turn acts to disrupt the polymer chains of the host polymers.

 doi:10.20944/preprints202404.0132.v1

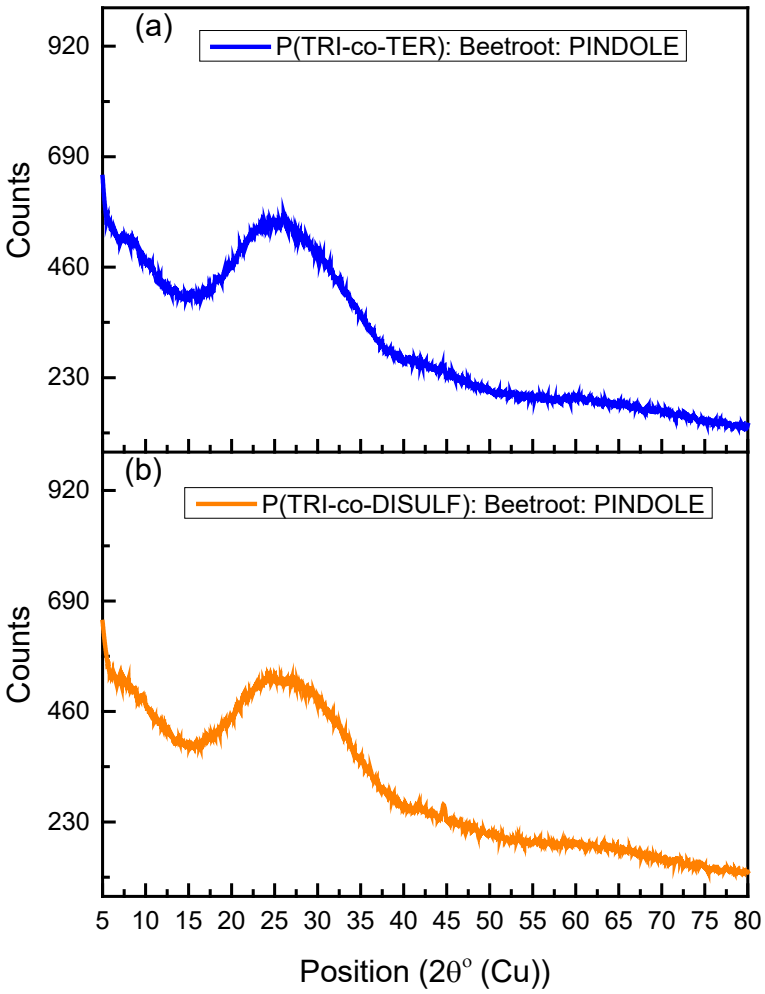


Figure 3. XRD spectra of the ternary systems; (a) P(TRI-co-TER):Beetroot Dye: PINDOLE and (b) P(TRI-co-DISULF): Beetroot Dye: PINDOLE.

3.2. Optical Study

Figure 4 shows the normalized absorbance spectra for both systems composed of P(TRI-co-TER):Beetroot dye:PINDOLE (Figure 4a) and P(TRI-co-DISULF):Beetroot dye:PINDOLE (Figure 4b). In addition, based on the investigated light-matter interaction, one can determine the applicability of the active mediums for potential applications in photovoltaic devices. For instance, in the application of semitransparent solar cells, the active medium should be semitransparent to the visible light. As for the opaque solar cells, it is imperative to have an expanded absorption window covering from the UV towards the IR region [7].

Meanwhile, the absorption bands in the UV and visible regions can be ascribed to the $\pi - \pi^*$ and $n - \pi^*$ transitions of delocalized excitons in the polymer chain as well as intramolecular charge transfer (ICT) between the electron-rich moiety and electron-deficient moiety of the main chain, respectively [27–31]. Figure 4 illustrates the effect of blending the dye molecules with the binary systems. It can be concluded that the extracted dye has acted upon prolonging the absorption spectra of the binary system from the UV region towards the visible region. Hence, the intramolecular charge transfer (ICT) between the electron-rich moiety and electron-deficient moiety of the main chain becomes predominant with the addition of beetroot dye. Also, the absorption of the ternary system

 doi:10.20944/preprints202404.0132.v1

in the visible region was decreased compared to that of the binary system, which is of benefit for the application of semitransparent organic solar cells.

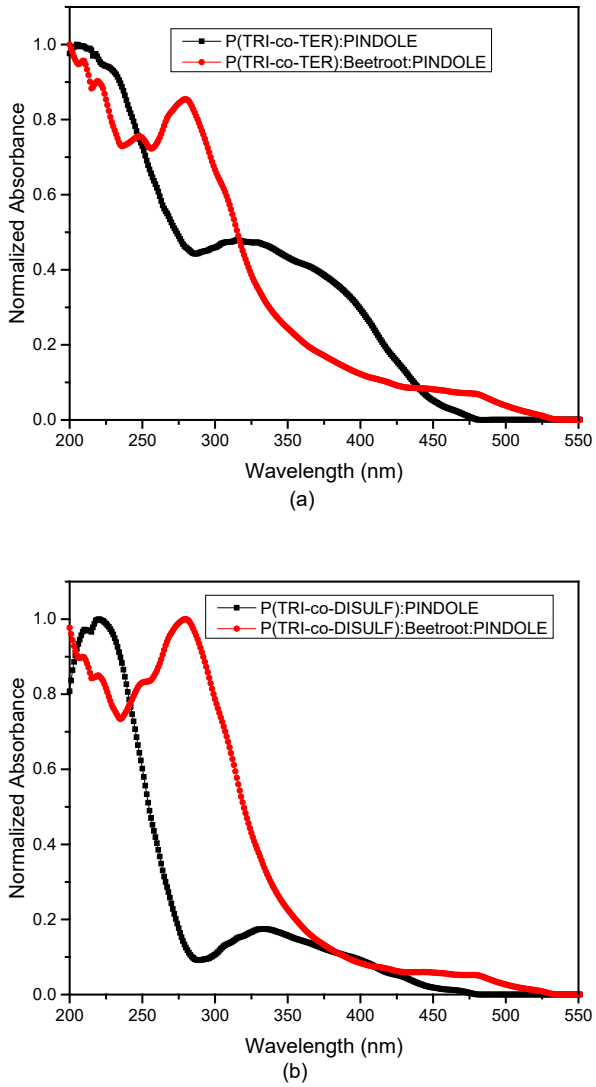


Figure 4. Plot of absorbance spectra for ternary systems (a) P(TRI-co-TER): Beetroot Dye: PINDOLE and (b) P(TRI-co-DISULF): Beetroot Dye: PINDOLE..

In the photovoltaic devices, upon harvesting a photon by conjugated polymers, the excitons are formed inside the active medium, but an additional energy is required to dissociate the excitons into free carriers so that to be collected by their respective electrodes. Therefore, photoluminescence (PL) spectroscopy is a useful technique that can provide additional information about the excitons dissociation and charge dynamics in the ternary systems of the BHJ structure. In addition, investigating the PL emission peaks for a given system provide essential confirmations of charge or energy transfer inside the active materials [32,33]. For instance, if the emission peak from one of the host polymers overlaps the absorption peak of the second host polymer that means the energy transfer has taken place between the two polymers. Alternatively, increasing the peak intensity in the blend films confirm the energy transfer, whereas the quenching of the PL peak intensity in blend phase designates the excitons dissociation and charge transfer occurrence in the active medium [34].

As shown in Figure 5, in the binary systems the PL emission peaks of the donor materials, named P(TRI-co-TER) and P(TRI-co-DISULF), excited at 300 nm, were greatly quenched by about 85% when they were blended with the acceptor material (PINDOLE). This indicates excitons dissociation and

 doi:10.20944/preprints202404.0132.v1

charge transfer has occurred in the binary active medium. Nonetheless, by adding the third component (natural dyes), the peak emission of the PL spectra of the ternary systems was increased compared to that of the binary system, especially for the P(TRI-co-DISULF):Beetroot Dye:PINDOLE ternary system, leading to a less efficient charge transfer. Therefore, in the binary thin films, the quenching of peak emission is due to the aggregation of chromophores of the conjugated polymers, while in the ternary system the morphology of the active medium was reformed and due to addition of the third component the interspacing between the host polymer domains become larger than the diffusion length of the excitons, thus the probability of geminate recombination increases [35]. Nevertheless, the ternary system of P(TRI-co-TER): Beetroot Dye: PINDOLE shows a more efficient charge transfer compared to that of the ternary system of P(TRI-co-DISULF): Beetroot Dye: PINDOLE.

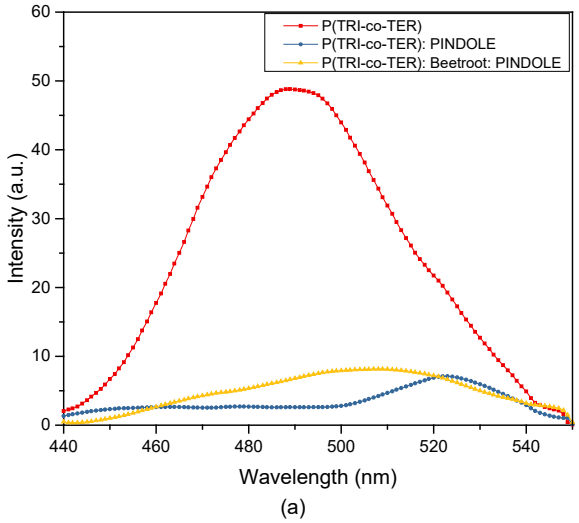


Figure 5. Photoluminescence (PL) emission spectra of (a) P(TRI-co-TER): Beetroot Dye: PINDOLE (b) , and P(TRI-co-DISULF): Beetroot Dye: PINDOLE.

3.3. Morphology Investigation

The surface morphology studies of the active medium in thin film form have been investigated by scanning electron microscopy (SEM). Figures 6 (a-b) show the surface images for the active mediums consisting of P(TRI-co-TER):Beetroot Dye: PINDOLE and P(TRI-co-DISULF): Beetroot Dye:

 doi:10.20944/preprints202404.0132.v1

PINDOLE, respectively. Beside the surface defects, the dye molecules homogenously dispersed in the binary matrix [36]. Moreover, upon inserting the dye molecules into P(TRI-co-TER): PINDOLE and P(TRI-co-DISULF): PINDOLE, respectively , a rough surface with a newly domain were formed for the dye molecules [35,37].

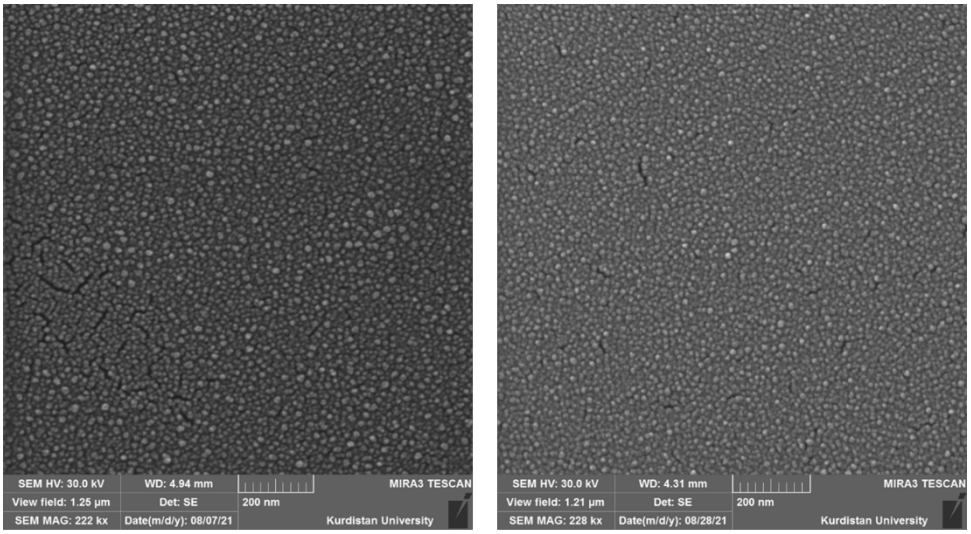


Figure 6. SEM images of the surface of the ternary active mediums (a) P(TRI-co-TER):Beetroot Dye: PINDOLE, and (b) P(TRI-co-DISULF): Beetroot Dye: PINDOLE..

3.4. Device Performance

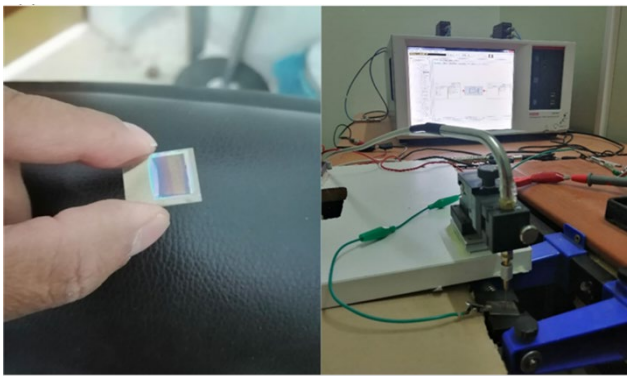
The conventional architecture for a bulk heterojunction based organic solar cell is in the form of anode/hole transport layer/Active medium/electron transport layer/cathode from bottom to top. This design is commonly utilized for most of the efficient organic solar cells, although it has a drawback of low stability. Therefore, an alternative architecture known as invert structure has shown to be more stable in solution processable solar cells [38]. Thus, in this work, the organic solar cells were fabricated following the inverted structure (cathode/electron transport layer/active medium/hole transport layer/anode).

In addition, to explore the performance of the fabricated devices, the *J-V* characteristic curves were used to extract the solar cell parameters, namely the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE). Moreover, the short circuit current depends on the spectral absorption of the active medium and the open circuit voltage is correlated to the differences of electronic energy levels (HOMO and LUMO) for donor and acceptor materials.

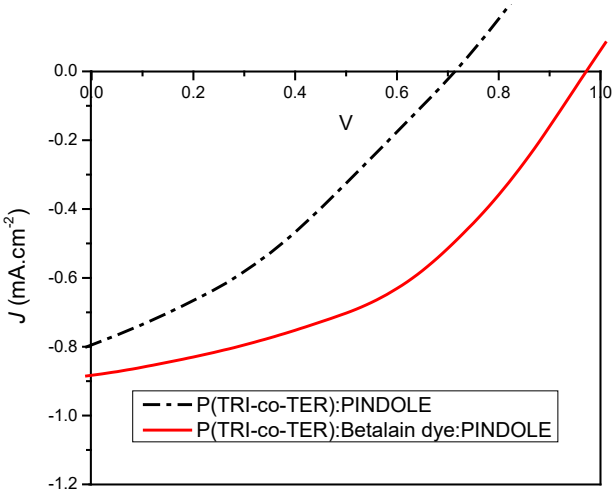
Therefore, the introduction of the third component (the dye) into the binary systems plays a vital role in enhancing J_{sc}. This can be due to widening the absorption window and tuning V_{oc}, which is a function of the photoactive layer composition [39,40]. For instance, Khlyabich and co-workers showed that with a proper selection of materials both I_{sc} and V_{oc} can be improved in the ternary system [39].

In our work, two different active layers were utilized to fabricate the semitransparent organic solar cells, namely P(TRI-co-TER): Beetroot: PINDOLE and P(TRI-co-DISULF): Beetroot:PINDOLE. The architecture of all-solution processed semitransparent organic solar is as follows; Indium-tin oxide (ITO) (bottom electrode)/TiO2 (ETL)/Active layer/PEDOT:PSS (AI4083) (HTL)/PEDOT: PSS (PH1000) (top electrode). The *J-V* characteristic curves for both systems are shown in Figure 7 and the solar cell parameters are tabulated in Table 1.

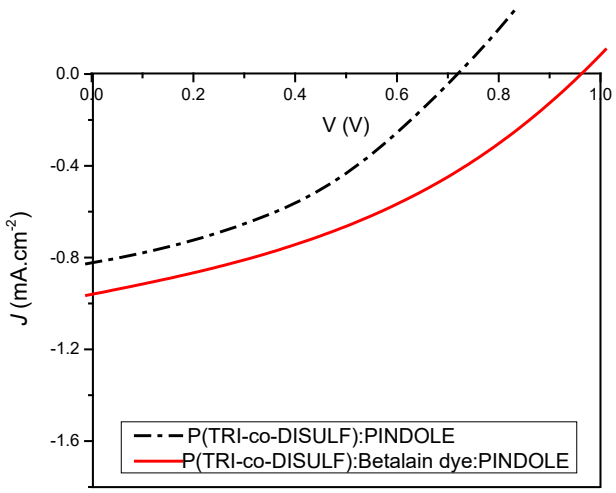
Preprints.org (www.preprints.org) | NOT PEER-REVIEWED | Posted: 2 April 2024 doi:10.20944/preprints202404.0132.v1



(a)



(b)



(c)

Figure 7. (a) photograph of the fabricated solar cells, (b) J-V curves for the devices with binary and ternary of P(TRI-co-TER):Beetroot: PINDOLE, and (c) J-V curves for the devices with binary and ternary of P(TRI-co-DISULF): Beetroot: PINDOLE.

 doi:10.20944/preprints202404.0132.v1

Table 1. The measured parameters of the semitransparent organic solar cells based on the binary and ternary systems.

Active Layer	V_{oc} (V)	J_{sc} ($mA.cm^{-}$	FF (%)	PCE (%)
P(TRI-co-TER): PINDOLE	0.71	0.79	12.83	0.072
P(TRI-co-TER): Beetroot: PINDOLE	0.97	0.88	27.6	0.23
P(TRI-co-DISULF): PINDOLE.	0.72	0.82	17.14	0.1
P(TRI-co-DISULF): Beetroot: PINDOLE.	0.96	0.96	21.39	0.19

As can be seen from the photovoltaic parameters, the beetroot dye has led to improve both of the short current density and open circuit voltage. This indicates that the dye molecules have been well dispersed into the binary systems. However, the devices experienced a poor performance which is linked to the process of recombination and extraction of free carriers. Furthermore, low value of the fill factor (FF) indicates the overall free carriers upon photon absorption is not well extracted and transported toward the respective electrodes. One of the key factors that affect the charge extraction and reduce the bimolecular recombination is the interface layers between the active layer and electrodes. Hence, the interface layers should be able to influence the electronic energy level and form the quasi fermi level as well as ohmic contacts with the electrodes [41].

In addition, metal oxides such as ZnO and TiO_2 were broadly used as an electron transport layer in the invert structure. However, all solutions processed solar cells show some limitations. For instance, Schmidt et al. showed that the fill factor is a function of ambient conditions of the interface layers and it has a vital role in charge extraction. Therefore, the interaction between titania and oxygen increased the surface negativity resulting a charge movement impedance and consequently the reduction of fill factor dominant value [42].

Alternatively, organic materials can become inevitable and promising candidate for cathode interface layers, especially hydrophilic conjugated polymers because of their low temperature operation, controllable chemical composition and morphology. In addition, the invert structure forming vertical phase separation produces a concentration gradient for donor and acceptor moieties. Hence, increasing acceptors concentration develops prolonged pathway of the electron movement.

Subsequently, extraction of electrons via bottom electrode enhances both fill factor and device efficiency of the respected device [43,44]. Herein, PINDOLE was used as an acceptor polymer in the ternary system and then utilized as its host polymer on one hand and as an electron transport layer on the other hand. Therefore, the obtained devices showed an improvement in both fill factor and device efficiency compared to those with TiO_2 as an ETL. The photovoltaic parameters and *J-V* curves for the fabricated devices are depicted in Table 2 and Figure 8.

Preprints.org (www.preprints.org) | NOT PEER-REVIEWED | Posted: 2 April 2024 doi:10.20944/preprints202404.0132.v1

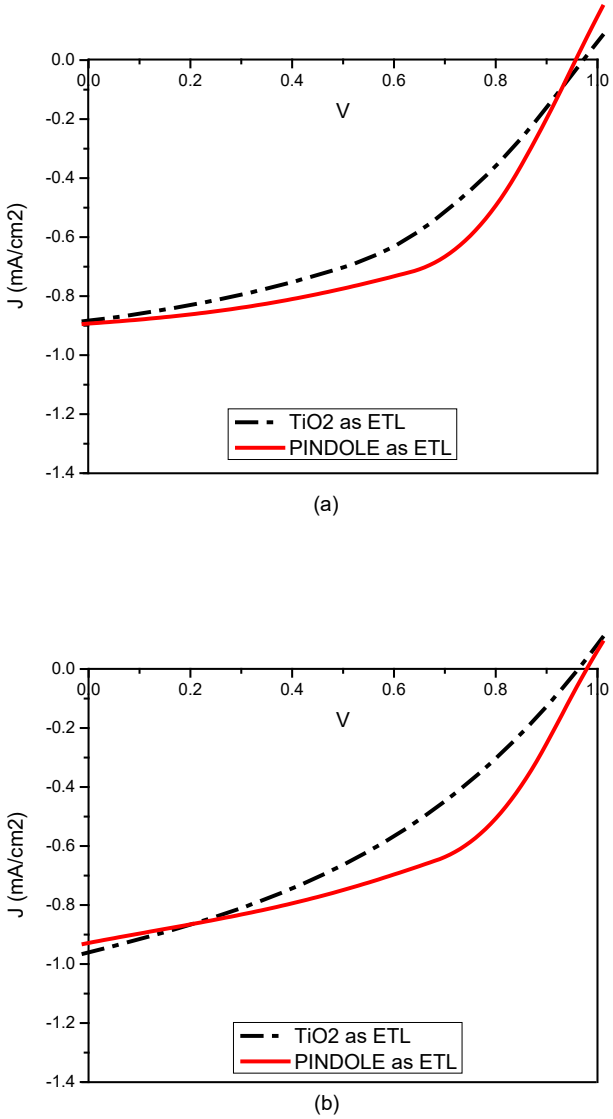


Figure 8. (a) J-V curves for ternary system of P(TRI-co-TER): Beetroot: PINDOLE, and (b) J-V curves for ternary system of P(TRI-co-DISULF): Beetroot: PINDOLE.

Table 2. solar cell parameters of the different ternary systems of different electron transport layers (ETLs).

Active Layer		ETL	V_{oc} (V)	J_{sc} $(mA.cm^{-2})$	FF (%)	PCE (%)
P(TRI-co-TER):	**Beetroot:**	TiO_2	0.97	0.88	27.6	0.23
P(TRI-co-TER):	**Beetroot:**	PINDOLE	0.96	0.89	37.14	0.31
P(TRI-co-DISULF):	**Beetroot:**	TiO_2	0.96	0.96	21.39	0.19
P(TRI-co-DISULF):	**Beetroot:**	PINDOLE	0.98	0.92	35.13	0.31

According to Table 2, *FF* values were improved due to the utilization of PINDOLE as an ETL. Thus, the designation for the acceptor PINDOLE reveals its potential application as the cathode interface layer, although the device performance still requires more improvement. Hence, the top electrode affects drastically the free carrier extraction for semitransparent solar cells, beside the active

Preprints.org (www.preprints.org) | NOT PEER-REVIEWED | Posted: 2 April 2024 doi:10.20944/preprints202404.0132.v1

medium, this should be transparent in the visible range. Several approaches were proposed to address this issue and the conductive polymer, poly(3,4-ethylenedioxythiophene):Poly(4-styrenesulfonate) (PEDOT:PSS) shows a promising potential for the top electrode of semitransparent solar cells. This is due to its high transparency in the visible region, its thermal stability, and solution processability.

Nevertheless, the pristine PEDOTE:PSS shows a low conductivity, henceforth the top electrode is not strong enough to collect the charge carriers and to extract them to the external load. Therefore, several emergent techniques were used to improve the conductivity of the pristine PEDOT:PSS [45,46]. Lee et al. enhanced the conductivity of PEDOT:PSS by adding 12% of ethylene glycol (EG), which was also mixed with the hole transport layer in the ratio of 2:1 [38]. In this work, to enhance the top electrode conductivity the methods of Lee and his co-workers are adapted and the obtained results are depicted in Figure 9 and Table 3.

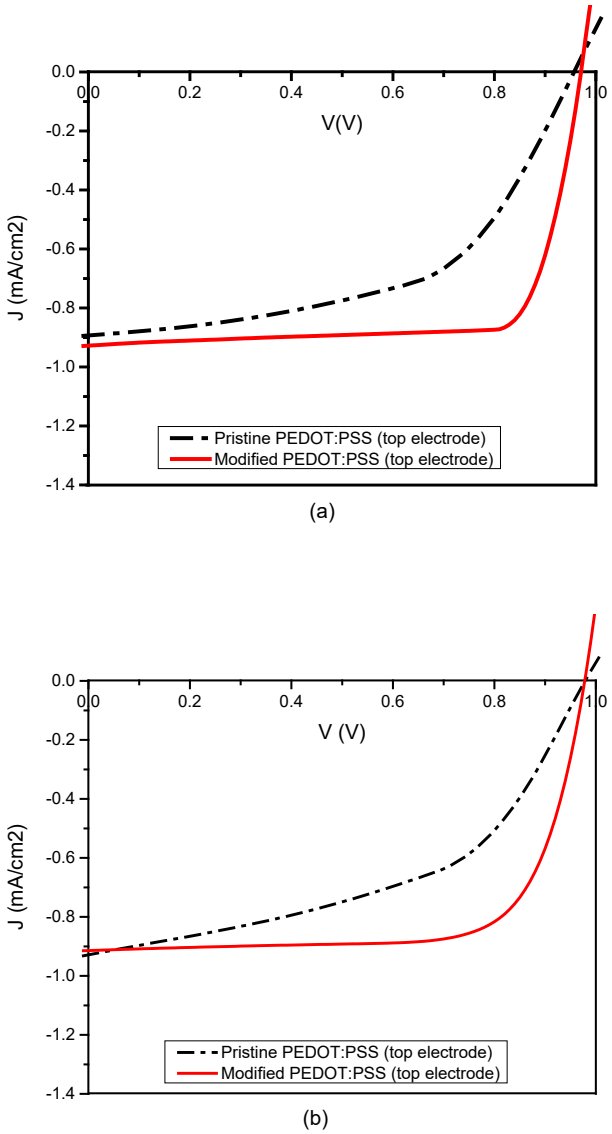


Figure 9. (a) J-V curves for ternary system of P(TRI-co-TER): Beetroot: PINDOLE, and (b) J-V curves for ternary system of P(TRI-co-DISULF): Beetroot: PINDOLE..

Interestingly, the fill factor is drastically increased by more than 90% compared to that of the pristine PEDOT:PSS top electrode. Also, the device efficiency was enhanced by 70%. In addition, due

 doi:10.20944/preprints202404.0132.v1

to the modified top electrode, the series resistance of the devices was drastically decreased, whereas the shunt resistance was increased for both systems. These changes in both series and shunt resistance indicate that more photogenerated charge carriers are extracted to the external circuit and charge recombination at the junction was reduced. It worth noticing that the attained values of V_{oc} for all obtained ternary devices in this work is close to $1V$. Therefore, compared to other studies in literature, it can be concluded that the voltage loss for these cells is reduced due to the relatively high band gap of the active layers.

Table 3. solar cell parameters of the different ternary systems with pristine and modified PEDOT:PSS top electrode.

Active Layer	**ETL**	**Top Electrode**	V_{oc} (V	J_{sc} ($mA.cm^{-}$	**FF** (%	**PCE** (%	R_s (kΩ	R_{sh} (MΩ	**Year [Ref.]**
P(TRI-co-TER): Beetroot: PINDOLE	PINDOLE	Pristine PEDOTE: PSS	0.96	0.89	37.14	0.31	100.8	2.8	This work
P(TRI-co-TER): Beetroot: PINDOLE	PINDOLE	Modified PEDOTE: PSS	0.97	0.92	65.23	0.58	28.9	3.3	This work
P(TRI-co-DISULF): Beetroot: PINDOLE.	PINDOLE	Pristine PEDOTE: PSS	0.98	0.92	35.13	0.31	118.9	1.07	This work
P(TRI-co-DISULF): Beetroot:	PINDOLE	Modified PEDOTE: PSS	0.98	0.91	58	0.52	34.2	6.1	This work

 doi:10.20944/preprints202404.0132.v1

PINDOLE.									
P3HT:PCBM	ZnO	Modified PEDOTE:PSS	0.57	6.9	51.2	2	-	-	2019[38]
PBDTTT-C : Cy7-T : PC70BM	TiO_2	Transparent laminated electrode	0.71	10.4	68	5.5	-	-	2017[47]
PBDB-TF:Y6:BDC-4F-C8	PDINN	15 nm Ag	0.82	20.32	66	11.5	-	-	2021[48]
PTB7-Th :IEICO-4F :T2-OEHRH	ZnO NPs	SAS	0.72	15.01	63	6.73	-	-	2021[49]
J71: Y6: PC71BM	ZnO	Au 0.8nm:Ag 15nm	0.802	14.68	60.15	7.08	-	-	2021[50]

4. Conclusions

In conclusion, two new electrons rich and one electron deficient polymers have been employed as a host material for all solution processable ternary semitransparent organic solar cell. In addition, natural dye from beetroot successfully extracted and used as a third component in the photoactive layer. Moreover, two ternary systems prepared and characterized and the results show that the red shift of absorbance spectra were evident due to cooperation of dye molecules. As well as from the PL spectra the binary systems of the host polymers exhibit efficient charge transfer however after inserting the dye molecules less efficient charge transfer apparent. Consequently, the results from XRD and SEM support that because of impurity in the extracted dye the amorphous phase increased and roughness of the obtained ternary system observed alternatively led to less efficient charge

 doi:10.20944/preprints202404.0132.v1

transfer. Last but not least, the invert architecture was utilized to fabricate bulk heterojunction structure solar cell and the *J-V* characteristic curve were employed to evaluate the performance of the obtained cells. Furthermore, the cells shows an improvements when the dye molecules inserted as well as the interphase layer with the top electrode were modified. Alternatively, for all ternary systems in this study the value of V_{OC} almost constant and around 1V attained for different cells.

Author Contributions: POA: Writing - original draft preparation; FFM, SRS, KAK: Writing-review and editing.

Funding: "Funding is not available for this work"

Institutional Review Board Statement: "Not applicable" for studies not involving humans or animals.

Data Availability Statement: The data and material are available within the manuscript.

Acknowledgments: The authors gratefully acknowledge the Ministry of Higher Education and Scientific Research-Kurdistan Regional Government-Charmo University—College of Science —Department of Physics for the financial support. KAK thanks the Erasmus+ scheme for facilitating collaboration between the University of Duhok and the University of Glasgow. The University of Glasgow authors thank the EPSRC for funding (EP/R020914/1) and MDS thanks the Royal Society for a University Research Fellowship (UF150104)

Conflicts of Interest: The authors declare that there is no conflict of interest regarding the publication of this paper.

References

1. IEA (2021), Renewable Power, IEA, Paris https://www.iea.org/reports/renewable-power.
2. Tan, C. A.-W.; Wong, B. T., Unraveling the Mystery of Ternary Organic Solar Cells: A Review on the Influence of Third Component on Structure–Morphology–Performance Relationships. *Solar RRL* **2021,** 5, (11), 2100503.
3. Xu, Z.-X.; Roy, V. A. L.; Low, K.-H.; Che, C.-M., Bulk heterojunction photovoltaic cells based on tetra-methyl substituted copper(ii) phthalocyanine : P3HT : PCBM composite. *Chemical Communications* **2011,** 47, (34), 9654-9656.
4. Gasparini, N.; Jiao, X.; Heumueller, T.; Baran, D.; Matt, G. J.; Fladischer, S.; Spiecker, E.; Ade, H.; Brabec, C. J.; Ameri, T., Designing ternary blend bulk heterojunction solar cells with reduced carrier recombination and a fill factor of 77%. *Nature Energy* **2016,** 1, (9), 16118.
5. Chang, S.-Y.; Cheng, P.; Li, G.; Yang, Y., Transparent polymer photovoltaics for solar energy harvesting and beyond. *Joule* **2018,** 2, (6), 1039-1054.
6. Anctil, A.; Lee, E.; Lunt, R. R., Net energy and cost benefit of transparent organic solar cells in building-integrated applications. *Applied Energy* **2020,** 261, 114429.
7. Brus, V. V.; Lee, J.; Luginbuhl, B. R.; Ko, S. J.; Bazan, G. C.; Nguyen, T. Q., Solution-Processed Semitransparent Organic Photovoltaics: From Molecular Design to Device Performance. *Advanced Materials* **2019,** 31, (30), 1900904.
8. Kouijzer, S.; Li, W.; Wienk, M.; Janssen, R., Charge transfer state energy in ternary bulk-heterojunction polymer–fullerene solar cells. *Journal of Photonics for Energy* **2014,** 5, 057203-057203.
9. Torimtubun, A. A. A.; Follana-Berná, J.; Sánchez, J. G.; Pallarès, J.; Sastre-Santos, Á.; Marsal, L. F., Fluorinated Zinc and Copper Phthalocyanines as Efficient Third Components in Ternary Bulk Heterojunction Solar Cells. *ACS Applied Energy Materials* **2021,** 4, (5), 5201-5211.
10. Savoie, B. M.; Dunaisky, S.; Marks, T. J.; Ratner, M. A., The Scope and Limitations of Ternary Blend Organic Photovoltaics. *Advanced Energy Materials* **2015,** 5, (3), 1400891.
11. Khlyabich, P. P.; Rudenko, A. E.; Street, R. A.; Thompson, B. C., Influence of Polymer Compatibility on the Open-Circuit Voltage in Ternary Blend Bulk Heterojunction Solar Cells. *ACS Applied Materials & Interfaces* **2014,** 6, (13), 9913-9919.
12. Goh, T.; Huang, J.-S.; Bartolome, B.; Sfeir, M. Y.; Vaisman, M.; Lee, M. L.; Taylor, A. D., Panchromatic polymer–polymer ternary solar cells enhanced by Förster resonance energy transfer and solvent vapor annealing. *Journal of Materials Chemistry A* **2015,** 3, (36), 18611-18621.
13. Yang, L.; Zhou, H.; Price, S. C.; You, W., Parallel-like bulk heterojunction polymer solar cells. *Journal of the American Chemical Society* **2012,** 134, (12), 5432-5435.
14. Amin, P. O.; Muhammadsharif, F. F.; Saeed, S. R.; Ketuly, K. A., A Review of the Improvements in the Performance and Stability of Ternary Semi-Transparent Organic Solar Cells: Material and Architectural Approaches. *Sustainability* **2023,** 15, (16), 12442.
15. Amin, P. O.; Ketuly, K. A.; Saeed, S. R.; Muhammadsharif, F. F.; Symes, M. D.; Paul, A.; Sulaiman, K., Synthesis, spectroscopic, electrochemical and photophysical properties of high band gap polymers for potential applications in semi-transparent solar cells. *BMC Chemistry* **2021,** 15, (1), 25.

 doi:10.20944/preprints202404.0132.v1

16. Amin, P. O.; Muhammadsharif, F. F.; Saeed, S. R.; Ketuly, K. A.; Sulaiman, K., The effect of donor-π-acceptor unit on the optoelectronic parameters of poly(triamterene-co-terephthalate):betalain dye composite system. *AIP Conference Proceedings* **2022,** 2398, (1), 020068.
17. Amin, P. O.; Muhammadsharif, F. F.; Saeed, S. R.; Sulaiman, K., A Study On the Optoelectronic Parameters of Natural Dyes Extracted from Beetroot, Cabbage, Walnut, and Henna for Potential Applications in Organic Electronics. *Journal of Fluorescence* **2022,** 32, (1), 203-213.
18. Kazemifard, S.; Naji, L.; Afshar Taromi, F., Enhancing the photovoltaic performance of bulk heterojunction polymer solar cells by adding Rhodamine B laser dye as co-sensitizer. *Journal of Colloid and Interface Science* **2018,** 515, 139-151.
19. Bliznyuk, V. N.; Gasiorowski, J.; Ishchenko, A. A.; Bulavko, G. V.; Rahaman, M.; Hingerl, K.; Zahn, D. R. T.; Sariciftci, N. S., Photovoltaic cells based on ternary P3HT:PCBM:polymethine dye active layer transparent in the visible range of light. *Applied Surface Science* **2016,** 389, 419-427.
20. Hwang, H.; Sin, D. H.; Park, C.; Cho, K., Ternary Organic Solar Cells Based on a Wide-Bandgap Polymer with Enhanced Power Conversion Efficiencies. *Scientific Reports* **2019,** 9, (1), 12081.
21. Amin, P. O.; Muhammadsharif, F. F.; Saeed, S. R.; Ketuly, K. A., A new approach to optimize the active layers of photovoltaic devices using area under the curve of absorption profile. *Optical and Quantum Electronics* **2022,** 54, (8), 510.
22. Wang, Q.; Zhang, S.; Ye, L.; Cui, Y.; Fan, H.; Hou, J., Investigations of the Conjugated Polymers Based on Dithienogermole (DTG) Units for Photovoltaic Applications. *Macromolecules* **2014,** 47, (16), 5558-5565.
23. Mir, F. A., Structural, morphological and ac conductivity study of PrFe0.5Ni0.5O3 thin film. *Microelectronic Engineering* **2014,** 122, 59-63.
24. Ahmed, B.; Raghuvanshi, S.; Srivastava, A.; Krishna, J.; Wahab, M., Optical and structural study of aromatic polymers irradiated by gamma radiation. **2012**.
25. Wan, J.; Chen, Z.; Zeng, L.; Liao, X.; He, Q.; Liu, S.; Zhu, P.; Zhu, H.; Chen, Y., Realizing high-performance organic solar cells through precise control of HOMO driving force based on ternary alloy strategy. *Journal of Energy Chemistry* **2022,** 65, 133-140.
26. Gao, L.; Zhang, Z.-G.; Bin, H.; Xue, L.; Yang, Y.; Wang, C.; Liu, F.; Russell, T. P.; Li, Y., High-Efficiency Nonfullerene Polymer Solar Cells with Medium Bandgap Polymer Donor and Narrow Bandgap Organic Semiconductor Acceptor. *Advanced Materials* **2016,** 28, (37), 8288-8295.
27. Yuanshuai Huang, F. W., Min Zhang, Suli Mei, Ping Shen, Songting Tan, Synthesis and photovoltaic properties of conjugated polymers with an asymmetric 4-(2-ethylhexyloxy)-8-(2-ethylhexylthio)benzo [1,2-b:4,5-b] dithiophene unit. *Dyes and Pigments* **2015,** 115, 58-66.
28. Jeong I, C. S., Yi A, Kim J, Cho JH, Kim HJ, Suh H, Syntheses and photovoltaic properties of 6-(2-thienyl)-4H-thieno [3,2-b]indole based conjugated polymers containing fluorinated benzothiadiazole. *Polymer* **2017**.
29. Wang J, Y. P., Wu Y, Liu G, Cui C, Shen P, Synthesis and optoelectronic property manipulation of conjugated polymer photovoltaic materials based on benzo[d]-dithieno [3,2-b;2′,3′-f]azepine. *Polymer* **2018**.
30. Joo Young Shim, T. K., Juae Kim, , Jinwoo Kim, Il Kim, , Jin Young Kim, Hongsuk Suh, Trifluoromethyl benzimidazole-based conjugated polymers with deep HOMO levels for organic photovoltaics. *Synthetic Metals* **2015,** 205, 112-120.
31. Juae Kima, Sangmin Chae, Ahra Yi, Seungyeon Hong, Hyo Jung Kim, Hongsuk Suh, Characterization of push-pull type of conjugated polymers containing 8H-thieno [2,3-b]indole for organic photovoltaics. *Synthetic Metals* **2018,** 245, 267-275.
32. An, Q.; Zhang, F.; Zhang, J.; Tang, W.; Deng, Z.; Hu, B., Versatile ternary organic solar cells: A critical review. *Energy Environ. Sci.* **2015,** 9.
33. Ameri, T.; Khoram, P.; Min, J.; Brabec, C. J., Organic ternary solar cells: a review. *Advanced Materials* **2013,** 25, (31), 4245-4266.
34. Zhong, L.; Gao, L.; Bin, H.; Hu, Q.; Zhang, Z.-G.; Liu, F.; Russell, T. P.; Zhang, Z.; Li, Y., High Efficiency Ternary Nonfullerene Polymer Solar Cells with Two Polymer Donors and an Organic Semiconductor Acceptor. *Advanced Energy Materials* **2017,** 7, (14), 1602215.
35. Akel, S.; Sharif, M. A.; Al-Esseili, R.; Al-Wahish, M. A.; Hodali, H. A.; Müller-Buschbaum, P.; Schmidt-Mende, L.; Al-Hussein, M., Photovoltaic cells based on ternary P3HT:PCBM: Ruthenium(II) complex bearing 8-(diphenylphosphino)quinoline active layer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2021,** 622, 126685.
36. Çaldıran, Z.; Erkem, Ü.; Baltakesmez, A.; Biber, M., Effects of the PENTACENE as doping material on the power conversion efficiency of P3HT:PCBM based ternary organic solar cells. *Physica B: Condensed Matter* **2021,** 607, 412859.
37. Lewińska, G.; Jeleń, P.; Kanak, J.; Walczak, Ł.; Socha, R.; Sitarz, M.; Sanetra, J.; Marszałek, K. W., Investigation of Dye Dopant Influence on Electrooptical and Morphology Properties of Polymeric Acceptor Matrix Dedicated for Ternary Organic Solar Cells. *Polymers* **2021,** 13, (23), 4099.

 doi:10.20944/preprints202404.0132.v1

38. Lee, D. J.; Heo, D. K.; Yun, C.; Kim, Y. H.; Kang, M. H., Solution-Processed Semitransparent Inverted Organic Solar Cells from a Transparent Conductive Polymer Electrode. *ECS Journal of Solid State Science and Technology* **2019,** 8, (2), Q32-Q37.
39. Khlyabich, P. P.; Rudenko, A. E.; Thompson, B. C.; Loo, Y.-L., Structural Origins for Tunable Open-Circuit Voltage in Ternary-Blend Organic Solar Cells. *Advanced Functional Materials* **2015,** 25, (34), 5557-5563.
40. Gasparini, N.; Salvador, M.; Fladischer, S.; Katsouras, A.; Avgeropoulos, A.; Spiecker, E.; Chochos, C. L.; Brabec, C. J.; Ameri, T., An Alternative Strategy to Adjust the Recombination Mechanism of Organic Photovoltaics by Implementing Ternary Compounds. *Advanced Energy Materials* **2015,** 5, (24), 1501527.
41. Xiao, B.; Wu, H.; Cao, Y., Solution-processed cathode interfacial layer materials for high-efficiency polymer solar cells. *Materials Today* **2015,** 18, (7), 385-394.
42. Schmidt, H.; Zilberberg, K.; Schmale, S.; Flügge, H.; Riedl, T.; Kowalsky, W., Transient characteristics of inverted polymer solar cells using titaniumoxide interlayers. *Applied Physics Letters* **2010,** 96, 243305-24908.
43. Sun, F.-Z.; Shi, A.-L.; Xu, Z.-Q.; Wei, H.-X.; Li, Y.-Q.; Lee, S.-T.; Tang, J.-X., Efficient inverted polymer solar cells with thermal-evaporated and solution-processed small molecular electron extraction layer. *Applied Physics Letters* **2013,** 102, (13), 133303.
44. Zhu, Y.; Xu, X.; Zhang, L.; Chen, J.; Cao, Y., High efficiency inverted polymeric bulk-heterojunction solar cells with hydrophilic conjugated polymers as cathode interlayer on ITO. *Solar Energy Materials and Solar Cells* **2012,** 97, 83-88.
45. Chou, T.-R.; Chen, S.-H.; Chiang, Y.-T.; Chang, T.-T.; Lin, C.-W.; Chao, C.-Y., Highly conductive PEDOT:PSS film by incorporating secondary doping and post-treatment for ITO-free polymer dispersed liquid crystal display. *Molecular Crystals and Liquid Crystals* **2017,** 647, (1), 28-36.
46. Yu, Z.; Xia, Y.; Du, D.; Ouyang, J., PEDOT:PSS Films with Metallic Conductivity through a Treatment with Common Organic Solutions of Organic Salts and Their Application as a Transparent Electrode of Polymer Solar Cells. *ACS Applied Materials & Interfaces* **2016,** 8, (18), 11629-11638.
47. Makha, M.; Testa, P.; Anantharaman, S. B.; Heier, J.; Jenatsch, S.; Leclaire, N.; Tisserant, J.-N.; Véron, A. C.; Wang, L.; Nüesch, F.; Hany, R., Ternary semitransparent organic solar cells with a laminated top electrode. *Science and Technology of Advanced Materials* **2017,** 18, (1), 68-75.
48. Zhang, Y.; Luo, D.; Shan, C.; Liu, Q.; Gu, X.; Li, W.; Choy, W.; Kyaw, A., High-Performance Semitransparent Organic Solar Cells Enabled by Improved Charge Transport and Optical Engineering of Ternary Blend Active Layer. *Solar RRL* **2021,** 6.
49. An, N. G.; Lee, T.; Heo, J.; Kim, J. W.; Song, S.; Lee, W.; Walker, B.; Lim, E.; Kim, J. Y., Exploiting Ternary Blends to Accurately Control the Coloration of Semitransparent, Non-Fullerene, Organic Solar Cells. *Solar RRL* **2021,** 5, (3), 2000742.
50. Zhang, Y.; He, X.; Babu, D.; Li, W.; Gu, X.; Shan, C.; Kyaw, A.; Choy, W., Efficient Semi-Transparent Organic Solar Cells with High Color Rendering Index Enabled by Self-Assembled and Knitted AgNPs/MWCNTs Transparent Top Electrode via Solution Process. *Advanced Optical Materials* **2021,** 9, 2002108.