https://doi.org/10.3311/PPch.43773

Periodica Polytechnica Chemical Engineering

Enhancing the Efficiency and Operational Stability of P3OT:PCBM Organic Solar Cells *via* Additive Engineering

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Received: 22 February 2026, Accepted: 28 May 2026, Published online: 14 July 2026

Abstract

This paper addresses the fundamental challenges of efficiency and temporal stability in poly(3-octylthiophene) (P3OT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)-based organic solar cells, which often suffer from instability in the active-layer micromorphology under operating conditions. A comparative study of three additive classes with different physical states was conducted: a high-boiling solvent (1,8-diiodooctane, DIO), a solid organometallic additive (ferrocene, Fc), and a polymeric additive (polyethylene glycol, PEG). Optical (UV–Vis), structural (XRD, Raman), and morphological (atomic force microscopy) characterizations reveal that each additive regulates film formation through a distinct mechanism. DIO slows solvent evaporation and promotes refined nanophase separation and enhanced ordering; Fc induces nucleation-driven ordering; and PEG smooths the surface and suppresses defects. These effects translate into improved photovoltaic performance, particularly in short-circuit current density and fill factor. The DIO-treated device achieved the highest power conversion efficiency (3.33%) compared to 1.93% for the reference device. Aging studies further demonstrate that solid and polymeric additives provide superior resistance to thermal and photo-induced degradation compared to solvent-treated devices. These findings highlight that selecting an appropriate additive class is an effective strategy to simultaneously enhance efficiency and long-term stability in P3OT:PCBM organic solar cells.

Keywords

organic solar cells, additive engineering, charge transport, device stability, P3OT:PCBM

1 Introduction

The rapidly increasing global energy demand, coupled with growing environmental concerns, has intensified the search for low-cost and sustainable renewable energy technologies [1–3]. Organic solar cells (OSCs) are one of the probable alternatives because of their lightweight, mechanical flexibility, and ability to be used in areas of large size, low temperature production methods including roll to roll printing. These benefits make OSCs particularly appealing in the next generation of portable and flexible energy harvesting systems [4–7].

Bulk-heterojunction (BHJ) structures made of conjugated polymer donors (D) and fullerene acceptors (A) have been widely studied in the context of OSCs. Specifically, polymer-fullerene systems including poly(3-alkylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) have been long used as model systems in the study of charge generation, transport and recombination in organic photovoltaic systems [8–11]. Poly(3-octylthiophene) (P3OT):PCBM blends are cost-effective and easy to prepare, and hence can be considered better candidates in terms of scalable device preparation. P3OT:PCBM has various applications in comparison to other polymer-fullerene systems: the material is cheap, easy to work with, and forms a film [12–14]. It contains a simple structure and is highly sensitive to the processing conditions, which make it an effective model system in the study of morphology performance relationships [8].

Nevertheless, P3OT devices are still limited with poor power conversion efficiency (PCE) and lack long term operational stability [15, 16]. All these shortcomings are mainly linked to the inherent instability of the BHJ microstructure [17]. Uncontrolled aggregation of PCBM molecules and the random orientation of polymer chains usually result in adverse nanoscale phase separation, ineffective

Cite this article as: Salim, R. D., Aziz, B. S., Hussein, A. A. "Enhancing the Efficiency and Operational Stability of P3OT:PCBM Organic Solar Cells *via* Additive Engineering", Periodica Polytechnica Chemical Engineering, 2026. https://doi.org/10.3311/PPch.43773

pathways of charge transport, and trap-assisted recombination [18–21]. These problems are further enhanced with time as morphology evolution due to thermal and optical driving causes considerable charge losses and a quick breakage of the device. Thus, the active layer morphology with a simple fabrication process control is one of the primary concerns of P3OT-based OSCs development [22, 23].

More recently, additive engineering is a promising technology that can be successfully employed to control the dynamics of forming thin-films and to control the BHJ microstructure without causing complications in the manufacturing process [24]. Additives may have a significant effect on phase separation behavior, crystallinity, and charge transport properties by selectively tuning solvent evaporation rates, molecular packing or interfacial interactions [25]. Thus far, the majority of reported literature has involved investigating one category of additives that tend to be high boiling point solvents that exhibit short term efficiency gain effects but does not provide much information about long term stability improvement mechanisms [26, 27]. This leaves a distinct knowledge gap to be addressed on systematic comparisons of additive classes of chemicals and physical differences of additions and their corresponding positions in controlling efficiency stability trade-offs in OSCs. Specifically, the varying effect of both liquid processing additives, solid molecular additives, and polymeric modifiers on the evolution of morphology and the longevity of devices is under-studied [28, 29].

A thorough and comparative additive-engineering approach is proposed in this work in order to solve the efficiency stability trade-off that has long been experienced in P3OT:PCBM organic solar cells. Three chemically and physically different additives are studied systematically, a high boiling processing solvent (1,8-diiodooctane, DIO), a solid organometallic material (ferrocene, Fc), and a polymeric modifier (polyethylene glycol, PEG). This study correlates clearly additive physical state, molecular interactions, and volatility with bulk-heterojunction morphology evolution, charge-transport properties and degradation pathways unlike the previous studies that mainly focus on the short-term improvement of efficiency by the use of a single additive class. Combining sophisticated morphological characterization with thorough electrical and stability studies, the current publication provides a clear picture of what is attained in short-term performance and what is attained in long-term operation stability when implementing additive classes in order to attain high efficiency and long-term operation stability of P3OT-based organic solar cells.

2 Materials and experimental methodology

2.1 Materials

The [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) fullerene acceptor and regioregular Poly(3-octylthiophene-2,5-diyl) donor polymer were purchased from Sigma-Aldrich and used as received. In the case of the additives used as the subject of this study, 1,8-Diiodooctane was taken as a high-boiling solvent additive and ferrocene and polyethylene glycol (molecular mass 2000 Da) as solid/polymer additives. Dichlorobenzene (DCB) was taken as the main solvent in the preparation of the active layer solutions with the hole-transport layer (HTL) poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios™ P VP AI 4083, Heraeus, Hanau, Germany). The rest of the solvents and chemicals were of an analytical purity.

2.2 Device fabrication

The usual layered organic solar cells were built with the structure indium tin oxide (ITO)/PEDOT:PSS/P3OT:PCBM/LiF/Al addressing well-known procedures that have been previously reported in the literature, to guarantee reproducibility [30–32]. ITO-patterned glass substrates with a sheet resistance of around 15 Ωsq^{-1} were pre-treated in the ultrasonic cleaner using detergent solution, deionized water followed by acetone and isopropanol (15 min each) to clean them. The substrates were dried in a nitrogen stream after which the UV-ozone treatment was applied on the substrates after 20 min to eliminate the organic contaminants present in the substrates and enhance the wettability of the surfaces. A spin coated layer of PEDOT:PSS (Clevios™ P VP AI 4083) of about 40 nm was deposited on a substrate followed by thermal annealing at an operating temperature of 120 °C and a time period of 15 min in the air to dry off all moisture. The solutions of active layers were made in a nitrogen-filled glovebox by dissolving P3OT and PCBM in the DCB at a mass ratio of 1:1 and the overall concentration of the solution was 20 $mg\,mL^{-1}$. Overnight stirring at 50 °C was done to allow total dissolution and homogeneity of solutions [30, 31].

In order to adopt the additive-engineering strategy, the master solution was broken down into four batches that were examples of a reference solution, which had no additives, DIO at 3 vol% as a high-boiling-point solvent additive, and two other solutions containing ferrocene and PEG at 1 wt.% relative to the polymer content [32]. Photovoltaic performance was used to determine the optimality of the selected concentrations within this range and the optimal

concentration of each additive was subsequently used to further characterize the films (1 wt.%). The films were spin-coated on top of the PEDOT:PSS layer at 800 rpm for 40 s to a final film thickness of approximately 100 nm. Thermal treatment of all devices at 140 °C for 10 min. was then done to ensure the polymer crystallinity formation and maximization of the bulk-heterojunction morphology, which is paramount in P3OT-based systems [31]. Lastly, the cathode electrode (LiF (1 nm)/Al (100 nm)) was thermally evaporated in high vacuum (~10^{-6} Torr (1.33×10^{-4} Pa)) under a shadow mask with an active device area of 0.1 cm^2.

The schematic representation of the device architecture, material component, and principle of functioning of the fabricated P3OT:PCBM organic solar cells, is presented in Fig. 1. The devices have the traditional layered design of Glass/ITO/PEDOT:PSS/P3OT:PCBM/LiF/Al, with PEDOT:PSS being the hole-transfer layer and LiF/Al being the cathode, as illustrated in Fig. 1(a). The chemical structures of the active materials and additives used in this paper such as P3OT, PCBM, DIO, ferrocene and polyethylene glycol are shown in Fig. 1(b). The related energy-level alignment and charge generation cycle under light is shown in Fig. 1(c), which shows the charge generation in the P3OT donor, charge dissociation at the donor-acceptor interface, and electron and hole transfer at the cathode and anode, respectively.

2.3 Characterization and measurement

The optical properties were initially assessed by the UV-Vis spectroscopy (Shimadzu UV-2600 spectrophotometer, Shimadzu Corp., Kyoto, Japan) to determine light absorption and estimate the optical bandgap of the active layers. X-ray diffraction (XRD) (Bruker AXS, Karlsruhe, Germany) was also used to do structural characterization to determine how the three additives (DIO, Fc, and PEG) affect the polymer crystallinity and molecular packing. Atomic force microscopy (AFM) in tapping-mode (Dimension Icon AFM, Bruker Nano Surfaces, Santa Barbara, CA, USA) was further used to obtain the surface morphology and phase separation of the thin films.

The photovoltaic activity of the prepared devices was determined by determining current density–voltage (J–V) properties in the dark and with light illumination with a Keithley 2400 SourceMeter (Tektronix, Beaverton, OR, USA) with a solar simulator (Newport Oriel Sol3A Class AAA, Newport Corp., Irvine, CA, USA) at an AM 1.5G spectrum at a normal light intensity of 100 mW cm^{-2}. The intensity of the illumination was regulated by a certified silicon reference cell. The stability was measured in the long-term through the normalized PCE in controlled aging conditions in the presence of 500 h. In the same set up as in the initial characterization devices were periodically measured at an AM 1.5G (100 mW cm^{-2}) illumination.

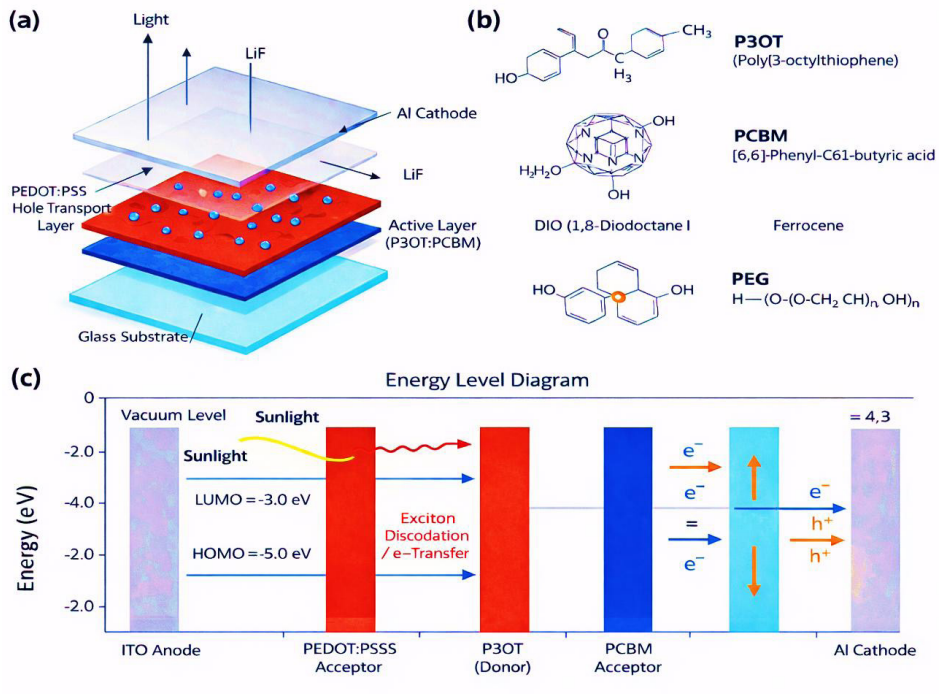

Fig. 1 Schematic illustration of the fabricated P3OT:PCBM organic solar cell showing (a) the device architecture, (b) the chemical structures of the active materials and additives, and (c) the energy-level diagram and charge transport mechanism

3 Results and discussion

Fig. 2 shows the UV - Vis absorption of the P3OT:PCBM blend and the modified films with various additives (DIO, Fc, and PEG). The pure P3OT:PCBM sample has a broad absorption band in the visible region (around 450-600 nm) principally due to the electronic transitions of the conjugated P3OT polymer that are $\pi - \pi^*$ based, and the shorter wavelength absorption is due to PCBM. When introducing DIO, the absorption intensity is greatly increased demonstrating an improvement in molecular ordering and $\pi - \pi^*$ stacking in the active layer. PEG and Fc additions also lead to moderate increments in the absorption relative to the reference film, which indicates that the electronic structure and morphology of the blend are altered partially. All in all, the increased absorption especially at the visible wavelength suggests an increased ability to absorb light that can lead to improved photovoltaic performance [10, 11].

Fig. 3 demonstrates that the XRD patterns of the P3OT:PCBM films indicate that structural ordering is highly dependent on the additives (Fc, PEG and DIO) introduced. The crystalline mixture shows a typical diffraction peak at $2\theta \approx 5.4$ and a more diffuse one at $2\theta \approx 23°$, which is the (100) lamellar stacking of P3OT and the (010). These considerations demonstrate that the semicrystalline form of P3OT appears in the donor acceptor matrix as it has been reported before in the structure analysis of P3OT:PCBM systems [8]. With the addition of additives, the peak intensity is evidently increased especially in the DIO-treated film, suggesting that the crystallinity is enhanced and the molecular packing is better. This action could be attributed to the use of high-boiling-point additives like DIO to decrease the rate of solvent evaporation, hence encouraging the self-organization and lamellar organization of chains of polymer. The growth in the diffraction intensity implies the presence of larger coherent crystalline domains, in line with the Scherrer relation, and enhanced $\pi - \pi^*$ stacking, which supports the movement of charge carriers. Fc and PEG also cause intermediate structural improvement, which is probably due to partial restructuring of the donor acceptor morphology and, decreased structural disorder. In general, the trend (DIO > PEG ≈ Fc > pristine) observed indicates that additive engineering can be successfully used to enhance the microstructural organization of the active layer in line with previous reports on the morphology optimization of polymer-fullerene solar cells.

Raman spectroscopy was used to improve the microscopic knowledge of the structure changes caused by the additives in the prepared films (Fig. 4). A strong Raman band at 1450 cm^{-1} was observed in all of the samples, and is ascribed to the symmetric C=C stretching vibration of the thiophene backbone in polythiophene-based polymers

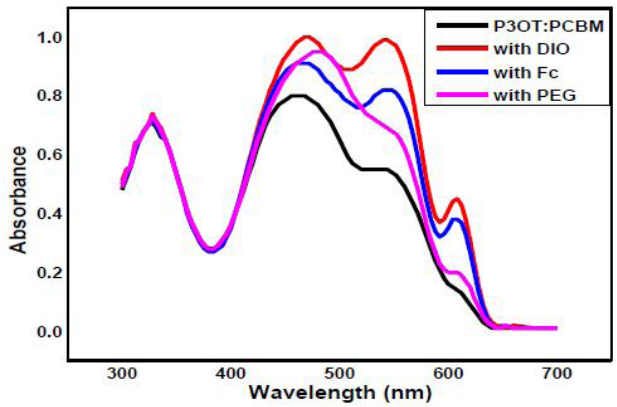

Fig. 2 UV–vis absorption spectra of P3OT:PCBM films, Fc, PEG and, DIO with PCBM:P3OT

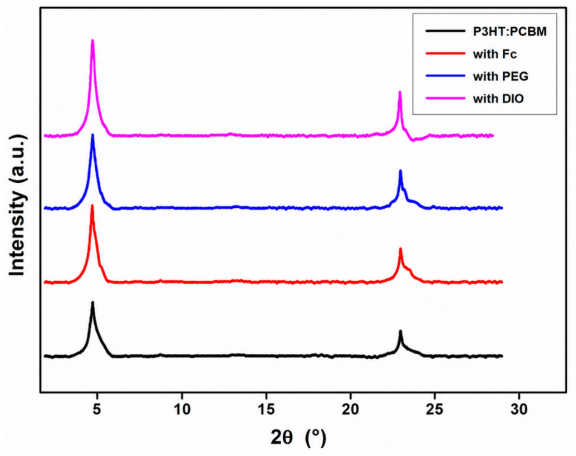

Fig. 3 XRD curves of P3OT:PCBM films with Fc, PEG, and DIO additives

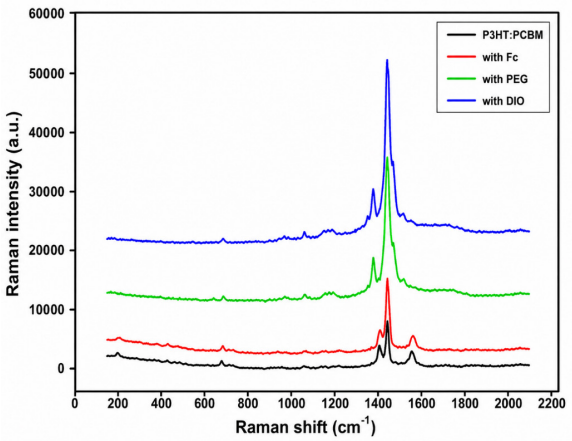

Fig. 4 Raman spectra of P3OT:PCBM films with Fc, PEG, and DIO additives

including P3OT [33, 34]. A sharp redshift of this band was evidenced when additive incorporated, which came to be 1452 cm^{-1} in the reference film, about 1448 cm^{-1} and 1447 cm^{-1} in the DIO- and Fc-treated films respectively. This type of change to lower wavenumbers has been widely accepted as unambiguous molecular evidence of longer effective conjugation lengths and greater planarization of the backbone, both due to a decreased disordered conformation and elimination of torsional defects along the polymer chains. This heightened molecular order facilitates the stronger intermolecular 1,4–π–π stacking interactions, necessary in the effective charge transport in conjugated polymer systems [33, 34]. The analysis of Raman spectroscopy is entirely in line with the previous analysis (XRD) that showed increased crystallinity and a better lamellar arrangement of the additive-treated films. All these results combined indicate that molecular reorganization induced by additives is highly critical in optimizing the electronic structure of the P3OT:PCBM active layer, which enhances the efficiency of charge flow as well as to the enhanced photovoltaic performance of the treated devices [10].

Fig. 5 shows height images taken in two dimensions in a scan size of 5 × 5 μm^2 and it is abundantly clear that additive type has a strong impact on the formation of thin-films and phase distribution in the P3OT:PCBM active layer. Fig. 5(a) is a reference film that has a very heterogeneous morphology with large spherical PCBM aggregates and areas of high surface roughness. This is due to the high solvent evaporation kinetics which lead to freezing of the polymer chains in disordered structures and coarse phase separation. These dimensions are larger than a common diffusion length (~10 nm), and hence the chance of charge recombination before dissociation is raised, which is the direct reason behind low short-circuit current density (Jsc) and fill factor (FF) of the reference device [35].

Table 1 presents the quantitative data of root mean quare (RMS) surface roughness. The maximum value of roughness (7.32 nm) was observed in the reference sample, which indicated the presence of large PCBM agglomerates which prevent interfacial contact. Conversely, PEG use led to a steep drop in roughness to (1.51 nm), which proves the ability of PEG to act as a leveling agent to enhance contact with the electrode, which becomes the reason behind the low series resistance (Rs) in the present sample. The Fc-treated sample exhibited a moderate RMS roughness of 3.28 nm, consistent with the formation of a nanofibrillar network.

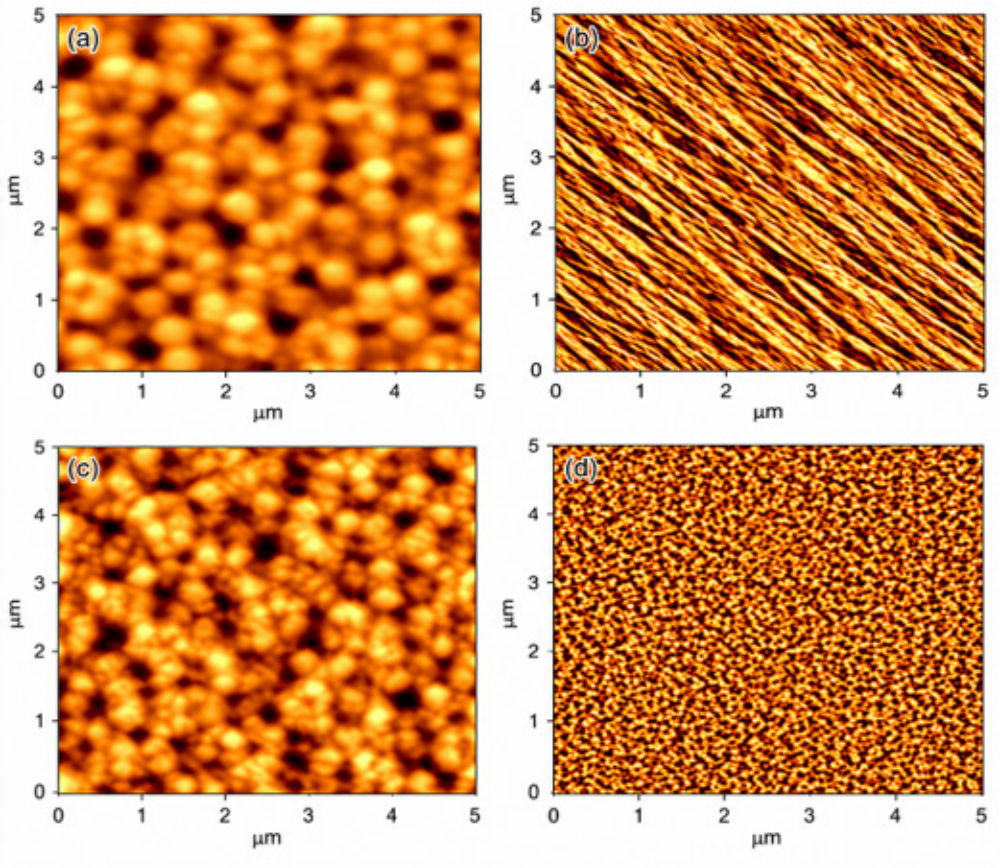

Fig. 5 AFM images of P3OT:PCBM films with Fc, PEG, and DIO additives

Table 1 The RMS roughness and corresponding morphological descriptions of P3OT:PCBM thin films without additives and with Fc, PEG, and DIO

Sample	RMS (nm)	Morphological description
P3OT:PCBM	7.32	Coarse aggregates with high surface roughness
With Fc	3.28	Nanofibrillar network induced by nucleation; moderate roughness due to crystallinity
With PEG	1.51	Ultra-smooth and homogeneous surface; significant reduction in defects
With DIO	2.52	Fine nanophase separation with a bicontinuous network structure

This texture increases the interfacial area for exciton dissociation while being more regular than the large, random agglomerates in the reference film. Lastly, the roughness of DIO sample was relatively low (2.52 nm), and it is an indication of good mixing and fine separation of the phases.

In an attempt to derive a clear physical explanation of the effects of the various types of additives on the morphology development of the active layer, the critical observations made in the AFM and XRD, Raman, and UV studies are summed up in a comparative schematic (Fig. 6). Fig. 6 is a simplified graphical picture of the correlation between the film-forming processes or additives and the consequence donor-acceptor architecture, and how they affect the phase separation, crystallinity of the polymer and the formation of interfaces. The figure simplifies the structure patterns into one scheme to enable direct correlation of the microstructure and photovoltaic performance and long-term stability of the devices. This schematic model gives a single pattern of explaining how morphology evolution is governed by additive physical state, which further influences charge generation, transport, and long-term device stability that is addressed in the succeeding schemes.

In order to confirm the values of the short-circuit current density as well as to obtain a more profound understanding of the wavelength-dependent charge generation, the external quantum efficiency (EQE) spectra of the devices created were recorded, as indicated in Fig. 7. The devices have a wide photoresponse with a range of 350 to 650 nm, which is in line with the absorption property of P3OT polymer.

Additive-treated samples exhibit a general increase in EQE throughout the spectrum, which is an improvement in light harvesting and reducing of recombination losses because of improved morphology of bulk-heterojunction. Notably, the DIO-treated device achieved the highest EQE across the entire spectral range, with a pronounced enhancement in the long-wavelength region (~600 nm). This improvement is typically associated with better polymer ordering and more efficient exciton dissociation. On the contrary, despite the high vibronic features observed in the EQE spectrum of the Fc-treated device, which is indicative of a better molecular ordering, the size of the EQE improvement is small when considering the DIO-treated

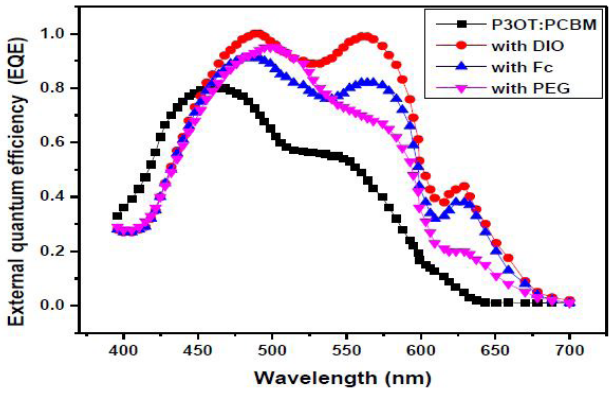

Fig. 7 External quantum efficiency spectra of P3OT:PCBM films with Fc, PEG, and DIO additives

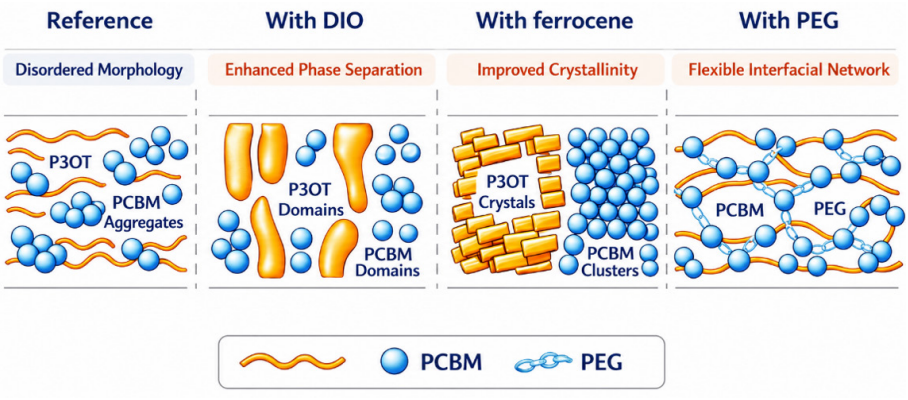

Fig. 6 Schematic illustration of the morphological evolution of P3OT:PCBM active layers under the influence of different additives

device. This result indicates that Fc-induced improvements in optical absorption and ordering are not entirely converted into an efficient charge extraction process, presumably because of an inefficient use of available charge-transport mechanisms and higher internal resistances. In the meantime, PEG-treated device shows a spectrum-wise balanced EQE enhancement, which is in line with the electrical measurements showing improved interfacial quality and lower series resistance. On the whole, the obtained EQE data support the J–V properties, showing that solvent-assisted optimization of morphology (DIO) is most useful to increase the generation of photocurrent but solid and polymeric additives are useful to provide structural ordering and interfacial stabilization and not necessarily enhancing the maximum current.

The current density–voltage analysis (Fig. 8) indicates that morphology engineering by additive incorporation is an extremely efficient technology that can be used to improve photovoltaic characteristics of the P3OT:PCBM system. The DIO-treated sample had the best power conversion efficiency (PCE) of 3.33% that is closely associated with a concomitant increase in short-circuit current density (Jsc = 7.36 mA cm^2) and fill factor (FF = 0.67). The key factors contributing to this high performance are the fact that there is a sharp decrease in series resistance (Rs) to 6.9 Ω·cm^2, which enables the efficient collection of charge and reduces ohmic losses, and shunt resistance (Rsh) is increased to 2100 Ω·cm^2, which, in turn, effectively inhibits leakage currents and non-radiative mechanisms of recombination [20, 23].

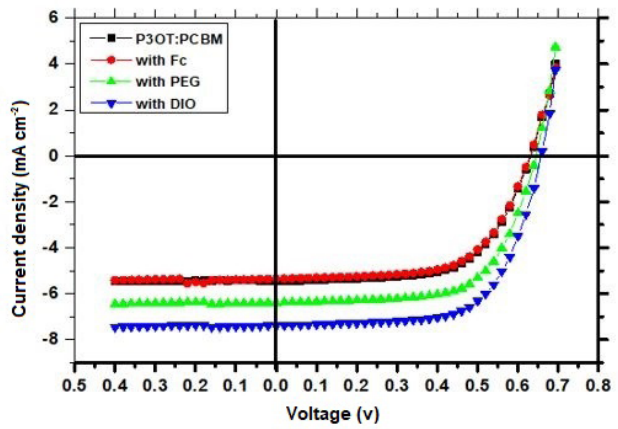

Fig. 8 J–V Characteristic of P3OT:PCBM films with Fc, PEG, and DIO additives

Comparatively, PEG-contained devices showed a more moderate performance improvement, which is in line with an enhanced interfacial transfer of charge and decreased contact resistance. Although Fc treated devices demonstrated signs of better molecular order, they still had poorer electrical performance due to increased internal resistance compared to the DIO treated devices suggesting less optimized pathways to transport charge. All in all, trends in Fig. 8 demonstrate that DIO is the best additive to use in gaining an advantageous balance between resistive losses and charge collection efficiency, in line with solvent additive assisted optimization of morphology in polymer solar cells [24].

The values of fill factor that were obtained in this work (0.67) were compared to the values that are reported previously, this is greater than reported FF ranges of comparable polymer-fullerene systems by Parmer et al. [10] (0.50–0.62) and Li et al. [30] (0.55–0.65) and is substantially greater than the value of P3OT:PCBM solar cells (0.38) [36]. The given enhancement underscores the positive contribution of additive-assisted optimization of the morphology to the improvement of the functioning of the given devices.

In order to quantitatively determine the trends in the J–V characteristics (Fig. 8), the most important photovoltaic parameters obtained in the collaborative analysis of the current density–voltage characteristics such as the short-circuit current density (Jsc), open-circuit voltage (Voc), fill factor (FF), power conversion efficiency (PCE), series resistance (Rs), and shunt resistance (Rsh) of the P3OT:PCBM devices are summarized in Table 2 in the reference and additive-treated samples.

The initial photovoltaic performance and long term stability profile comparison shows that there is a definite trade off in the functional behavior of the additives under study as depicted in Fig. 9. Whilst the DIO-treated devices provide the best initial power conversion efficiency by properly optimising the initial stage bulk heterojunction morphology, they show a comparatively quick

Table 2 Photovoltaic coefficients of P3OT:PCBM organic solar cells under the influence of different additives (DIO, PEG,and Fc)

Device	Jsc (mA cm^{-2})	Voc (V)	FF	PCE (%)	Rs (Ω cm^2)	Rsh (Ω cm^2)
P3OT:PCBM	5.38	0.61	0.58	1.93	18.6	980
With Fc	5.27	0.61	0.56	1.82	19.7	910
With PEG	6.35	0.64	0.62	2.52	12.5	1450
With DIO	7.36	0.66	0.67	3.33	6.9	1630

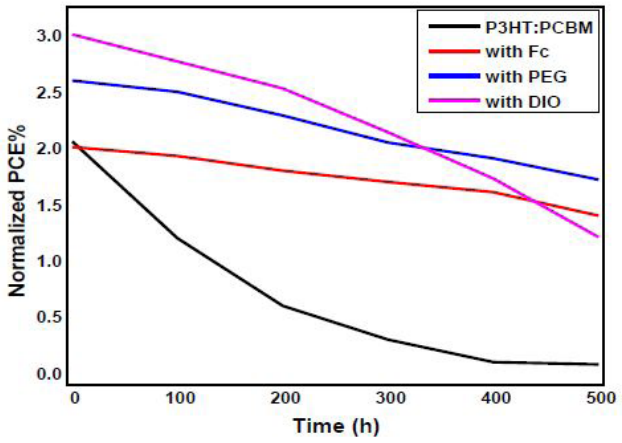

Fig. 9 Stability study normalized PCE vs. Time of P3OT:PCBM films with Fc, PEG, and DIO additives

performance decline with time. This degradation action is typically linked to further evolution of morphology and aggregation of molecular with residual high boiling point solvent which becomes more destabilized as the optimized nanostructure evolves [23, 24].

In addition, the optimized DIO-treated device had a higher PCE of 3.33%, which is higher than or comparable to values obtained using similar P3OT:PCBM systems (usually less than 2%) [12] and early polymer fullerene solar cells (2-3%). This establishes the fact that the additive engineering is an effective way to enhance the work of the P3OT:PCBM system.

PEG on the other hand is an excellent stabilizing additive with almost no changes in device efficiency after the 500 h aging period. This stability can be explained by the better interfacial binding and large-scale phase separation suppression even in the case of long-term thermal and photo-stress, and this leads to the highest operational stability of those systems that were investigated [20]. Having no morphological stabilization mechanism, the reference device experiences an extreme degradation of electrical characteristics because of unregulated morphology evolution and contact with the environment. Meanwhile, the devices with Fc have a lower and more linear behavior of degradation, which is also explained by the stabilizing effect of solid additives, but with poorer charge collection efficiency than the solvent-assisted DIO system [28, 29].

4 Conclusions

In the present work, additive-engineering approach was thoroughly used to examine the impact of additive physical state on the performance and stability of P3OT:PCBM organic solar cells. There were three different additives of which a high-boiling solvent (DIO), a solid organometallic additive (Fc), and a polymeric additive (PEG) were systematically compared. The findings have shown that every additive controls the bulk-heterojunction morphology in a distinct mechanism. DIO is a good promoter of polymer ordering and nanoscale phase separation resulting in the optimum photovoltaic performance with a maximum power conversion efficiency (PCE) of 3.33% and a better fill factor of 0.67. Fc, on the contrary, favors the molecular arrangement and does not completely convert to the efficient charge extraction by raising the internal resistance. PEG, however, has a remarkably high impact on the interfacial homogeneity and minimization of defects, which leads to the equal charge transport and improved stability of operation. Notably, there was an evident trade-off between efficiency and stability over the long-run. DIO-treated devices showed a high level of performance at the beginning but PEG-based devices showed a high level of stability at long aging conditions. These results emphasize the fact that physical characteristics of the additive are a very important factor in determining charge transport mechanisms as well as the degradation mechanisms. On the whole, the work can give a more profound insight into the connection of the additive type, morphology development, and device functioning. The findings provide feasible principles of developing effective and consistent organic solar cells by rational choice of classes of additives, the way to the enhanced performance of solution-processed photovoltaic systems.

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