## Research highlight

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# Efficient bulk heterojunction photovoltaic devices based on modified PCBM

**Abstract:** Organic bulk heterojunction solar cells are a promising candidate for low-cost next-generation photovoltaic systems. In bulk heterojunction polymer solar cells, conjugated polymers and fullerene derivatives [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) function as the electron-donating and electron-accepting materials, respectively. In this paper, we report the photovoltaic response of the solution-processed bulk heterojunction (BHJ) solar cell based on poly (2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)  (MEH-PPV): modified PCBM (MPCBM) blend. The BHJ showed power conversion efficiency (PCE) up to 1.78%. The PCE has been further improved up to 1.95% after thermal annealing of the active layer. The increase in the PCE with the thermally annealed blend is mainly attributed to the improvement in incident photon to current efficiency (IPCE) and short circuit photocurrent ($J_{sc}$).

**Keywords:** active layer; annealing; MEH-PPV; modified PCBM; organic bulk heterojunction.

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## 1 Introduction

Polymer-based organic solar cells have attracted attention as a renewable energy source due to their low cost, ease of manufacture, and compatibility with flexible substrates [1, 2]. Materials such as small organic molecules [3, 4], star-shaped oligomers [5, 6], and conjugated low-band gap polymers [7, 8] due to their inexpensive, easily processable and tailored functionality by molecular design and chemical synthesis are under extensive research worldwide. One of the important alternative followed to improve the photovoltaic efficiencies is donor-acceptor (D-A) proximity in the devices by using blends of donor-like and acceptor-like molecules or the polymers, which are called D-A bulk heterojunction solar cells [9–11]. Thus, in bulk heterojunction polymer solar cells, conjugated polymers and fullerene derivatives [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) function as the electron-donating and electron-accepting materials, respectively [12, 13]. This composite layer can be prepared as a large area in a single step by using techniques such as spin coating, inkjet printing, spray coating, gravure coating, roller casting, etc. [14]. By a simple spin coating from a solution of these homogeneous blends of conjugated polymer and fullerene derivatives, largely increased interfacial area (where charge separation occurs and recombination is reduced) can be achieved.

The main difference between the conventional or inorganic solar cells and the BHJ solar cells are the charge transport mechanism as well as their photovoltaic behavior, as in BHJ solar cell excitons are generated in the

photovoltaic layers, and at the donor-acceptor interfaces, these excitons dissociates into electrons and holes.

Electroluminescent semiconducting polymers (ELSCPs) have good optoelectronic characteristics because their polymer main chains are composed of alternately conjugated double bonds and because the delocalized $\pi$ electrons can move along each main chain or hop between the adjacent main chains [15]. There is a wide application of poly para-phenylenevinylene (PPV) and its derivatives in organic solar cells due to their semiconducting and luminescence properties. Thus, poly (2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), which is a class of PPVs and a well-known luminescent polymer material having low driving voltage and high luminescent efficiency [16, 17], has been widely utilized in fluorescent sensors, electrochromic devices [18–20], polymer light-emitting diode [21], and as a donor material in the BHJ photovoltaic cells [22]. This hairy rod polymer MEH-PPV is highly soluble in common organic solvents, such as tetrahydrofuran (THF), chlorobenzene, chloroform, xylene, and toluene because its backbone is bonded with the short flexible ethereal side chains [23]. The photoactive layer of organic solar cells based on poly (2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) and [6,6]-phenyl $C_{61}$ butyric acid methyl ester (MEH-PPV:PCBM), have been studied over the past years [24, 25], and many attempts for making efficient photovoltaic (PV) cells using these composite films have been published, with limited efficiency [26, 27]. In 2013, Yang et al. have synthesized a MEH-PPV:PCBM (1:4 weight ratio) BHJ device and added ditertbutyl peroxide (DTBP) as an additive and found the increase in the efficiency for the device containing 0.5 wt% DTBP was highest [28]. Jung et al. also prepared solutions of conjugated polymer MEH-PPV and PCBM in xylene (XY), O-dichlorobenzene (O-DCB), chloroform (CF), chlorobenzene (CB), toluene, and THF in the optimized 1:4 weight ratio [29].

To increase the power conversion efficiency (PCE) value, the $V_{oc}$, $J_{sc}$, and FF of the device were needed to be enhanced. The $V_{oc}$ can be augmented by raising the lowest unoccupied molecular orbital (LUMO) level of the fullerene relative to the highest occupied molecular orbital (HOMO) level of the donor [30, 31]. The $V_{oc}$ of a BHJ solar cell may also be increased using electron irradiation method [32]. Ideally, the polymers should have a broad absorption area in the solar spectrum; thus, efficient light harvesting can be ensured and a high charge carriers mobility for charge transport with a suitable energy levels of polymers is required that matches those of the fullerides. The discovery of photoinduced electron transfer from a conjugated polymer as a donor to buckminsterfullerene $C_{60}$ as an acceptor [9] provided a molecular approach to enhanced photovoltaic conversion.

In 2004, cell (MEH-PPV:PCBM) with 2.9% efficiency was demonstrated under 100 mWcm$^{-2}$ illumination intensity [24]. Yang et al. reported a lower conversion efficiency for similar cells based on MEH-PPV and polymers with substituents containing $C_{60}$ moieties [33]. Thus, to enhance the performance and/or efficiency of a BHJ photovoltaic cell, we need to make much more effort to modify the substituent of PCBM by introducing substituents on its phenyl ring [34, 35] or by replacing the phenyl ring with other groups [36, 37]. PCBM bisadduct [38] and PCBM multiadduct [39] as well as endohedral fullerenes [40] were reported as PV acceptor material in the last few years. The LUMO energy levels for these fullerene derivatives are higher, which results in higher $V_{oc}$ as well as higher PCE [38, 40] for P3HT-based solar cells.

Synthesis of a modified PCBM, which is soluble in THF, was reported by Mikroyannidis et al. [41]. Owing to the presence of the cyanovinylene 4-nitrophenyl segment, the modified PCBM showed stronger absorption in the visible region of solar spectrum than the PCBM. In 2013, Matsuo et al. reported that the addition of a dihydromethano group to the fullerenes improves the performance of BHJ organic solar cells [42]. Recently, the highest efficiency of 3% has been demonstrated for a MEH-PPV:MAPbI$_3$-based BHJ like solar cell by Rizzo et al. [43]. The efficiencies obtained for different BHJ photovoltaic devices are summarized in Table 1.

In this paper, we have reported the photovoltaic response of the solution-processed bulk heterojunction (BHJ) solar cell based on the MEH-PPV:modified PCBM blend. The electrical and optical properties of the blend have been investigated. We have also observed the effect of thermal annealing on the photovoltaic performance of the MEH-PPV:modified PCBM or MEH-PPV:MPCBM-based devices.

# 2 Materials and methods

## 2.1 Materials and characterization methods

The polymer solar cells based on an interpenetrated network of conjugated polymer poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), fullerene derivative [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) and its modified form (MPCBM) were fabricated. MEH-PPV, PCBM, and PEDOT:PSS were purchased from Aldrich Chemicals and used as such. The modified PCBM

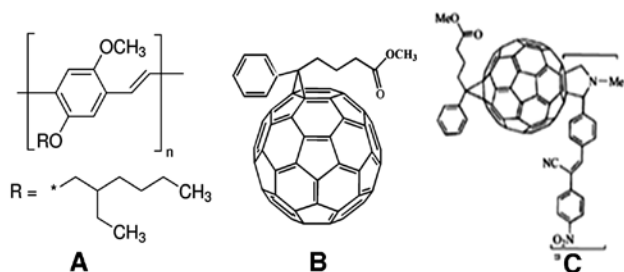**Table 1:** The efficiencies obtained for different BHJ photovoltaic devices.

| S. no. | Device | $V_{oc}$ (V) | $J_{sc}$ (mAcm$^{-2}$) | FF | PCE ($\eta$%) | References |
|---|---|---|---|---|---|---|
| 1 | P3HT/bisPC60BM | 0.724 | 9.14 | 0.68 | 4.5 | [38] |
| 2 | P3HT/PC60BM | 0.61 | 8.94 | 0.60 | 2.4 | [39] |
| 3 | BDT-based low band gap polymer PBDTTT-E | 0.62 | 13.2 | 0.63 | 5.15 | [44] |
| 4 | BDT-based low band gap polymer PBDTTT-C | 0.70 | 14.7 | 0.64 | 6.58 | [45] |
| 5 | BDT-based low band gap polymer PBDTTT-CF | 0.76 | 15.2 | 0.66 | 7.73 | [46] |
| 6 | P3HT/PC60BM | 0.62 | 10.9 | 0.62 | 4.18 | [37] |
| 7 | D1:PCBM | 0.84 | 6.12 | 0.51 | 2.62 | [47] |
| 8 | PB:PCBM (annealed) | 0.80 | 7.9 | 0.56 | 3.54 | [7] |
| 9 | BDT-based low band gap polymer PBDTTT-S | 0.76 | 14.1 | 0.58 | 6.22 | [48] |
| 10 | MEH-PPV:PCBM:BCP | 0.75 | 2.95 | 0.44 | 0.98 | [49] |
| 11 | MEH-PPV:PCBM:Bphen | 0.74 | 3.98 | 0.44 | 1.30 | [49] |
| 12 | M2:PCBM | 0.68 | 3.94 | 0.46 | 1.23 | [50] |
| 13 | M2:F | 0.84 | 6.75 | 0.48 | 2.72 | [50] |
| 14 | PDTG-TPD polymer-based device | 0.86 | 14.0 | 0.67 | 8.1 | [51] |
| 15 | DCV5T-Bu$_4$:PCBM [CB:CN (0.375%) as solvent] | 1.11 | 6.5 | 0.41 | 3.0 | [52] |
| 16 | DCV5T-Bu$_4$:PCBM (ODCB as solvent) | 1.08 | 5.7 | 0.40 | 2.5 | [52] |
| 17 | BBTSBS/PCBM(annealed 120°C) | 0.62 | 0.56 | 0.29 | 0.10 | [53] |
| 18 | MEH-PPV:PCBM:GNP | 0.56 | 0.80 | 0.59 | 0.26 | [54] |
| 19 | P3HT:PCBM | 0.60 | 9.58 | 0.69 | 4.10 | [55] |
| 20 | P3HT/PC70BM with 2% n-dodecylthiol | 0.641 | 8.59 | 0.58 | 0.032 | [56] |
| 21 | Tempered P3HT:PCBM | 0.58 | -8.61 | 0.59 | 2.99 | [57] |
| 22 | PEDOT:PSS/PPABT:TiO$_2$ nanoparticles | 0.26 | 1.29 | 0.37 | 0.125 | [58] |
| 23 | AnE-PVstat:PCBM | 0.825 | 5.13 | 0.58 | 2.46 | [59] |
| 24 | AnE-PVstat:PCBM with 0.01% of Ag NPs | 0.76 | 8.46 | 0.48 | 3.10 | [59] |
| 25 | PEDOT:PSS (P3HT/PCBM/PEDOT:PSS) | 0.60 | 11.92 | 0.62 | 4.43 | [60] |
| 26 | P3HT/PCBM/MoOx (annealed 250°C as a HEL) | 0.65 | 12.4 | 0.53 | 4.63 | [60] |
| 27 | AgInSe2.PCBM.P3HT | 0.50 | 3.71 | 0.40 | 0.75 | [61] |
| 28 | MEH-PPV:MAPbI$_3$ | 0.81 | 9.11 | 0.36 | 3.0 | [43] |

(MPCBM) was supplied by Prof. Mikroyannidis, University of Patra, Greece and its synthesis was given elsewhere [41]. The chemical structure of the donor (MEH-PPV) and the acceptor (PCBM and Modified PCBM) is shown in Figure 1. All other materials and solvents were commercially purchased and were used as supplied. UV-vis spectra were recorded on a Hitachi-330 spectrometer with THF as solvent. The morphological images of the films were obtained from scanning electron microscope (Zeiss, 20 KV). The crystallinity of the blends was studied using the X-ray diffraction (XRD) technique (Panalytical make USA) having CuKα, as the radiation source of wavelength λ=1.5405 Å with the composite films coated on the quartz substrate. The current-voltage (J-V) measurement of the devices was carried out on a computer-controlled Keithley-238 source meter.

## 2.2 Device fabrication and characterization

The bulk heterojunction devices were fabricated according to the following procedure. First, the indium-doped tin oxide (ITO)-coated glass substrate was cleaned with detergent, then ultrasonicated in deionized water, acetone, and isopropyl alcohol and finally dried overnight in an oven at 80°C. To supplement this bottom electrode, a hole transport layer of PEDOT:PSS (BAYTRON, conductive grade) of thickness 80 nm was spin coated from aqueous solution on the ITO-coated glass substrate and was subsequently dried at 80°C for 20 min. However, Xu et al. has found efficiencies for the different ratios of MEH-PPV:PCBM blends



**Figure 1:** Chemical structures of (A) MEH-PPV, (B) PCBM, and (C) modified PCBM (MPCBM).

(1:3, 1:4, and 1:5) and reported the highest efficiency for 1:4 ratio as 1.42% after annealing [62]. Thus, the blend solutions of MEH-PPV:PCBM (1:4) and MEH-PPV:MPCBM (1:4) were prepared using THF as a solvent in a concentration of 10 mg/ml and stirred for 2 h. The photoactive layer of the prepared blend solutions was deposited by spin coating on the top of the PEDOT:PSS layer. Finally, an aluminum (Al) electrode (thickness about 100 nm) was deposited by thermal evaporation under high vacuum ($1 \times 10^{-5}$ mbar). The effective area of the devices is 20 mm². For thermal annealing, the blend films were placed on a hot plate and annealed at a temperature of 100°C for 10 min, before the deposition of Al electrode. The device structure is shown in Figure 2.

We have designated the devices based on different blends as follows:
ITO/PEDOT:PSS/MEH-PPV:PCBM/Al (Device D1).
ITO/PEDOT:PSS/MEH-PPV:MPCBM/Al (Device D2).
ITO/PEDOT:PSS/(MEH-PPV:MPCBM) thermally annealed/Al (Device D3).

The current-voltage (J-V) measurement of these devices was carried out on a computer-controlled Keithley-238 source meter in the dark as well as under illumination. A halogen light source was used to give an irradiance of 100 mW/cm² (equivalent of one sun at AM 1.5) at the surface of the device.

# 3 Results and discussion

## 3.1 Electrical properties of MEH-PPV and MPCBM

The energy level diagram of MEH-PPV, PCBM, and MPCBM are shown in Figure 3. The LUMO levels of PCBM and MPCBM are -3.95 eV and -3.80 eV, respectively. The LUMO level of MPCBM is raised by 0.15 eV in comparison with
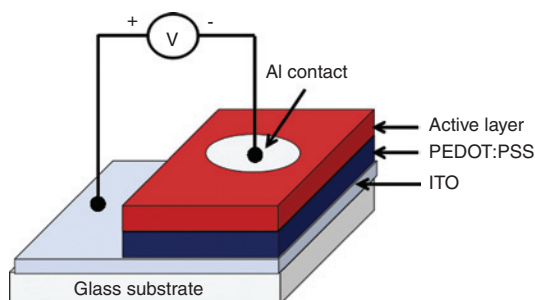


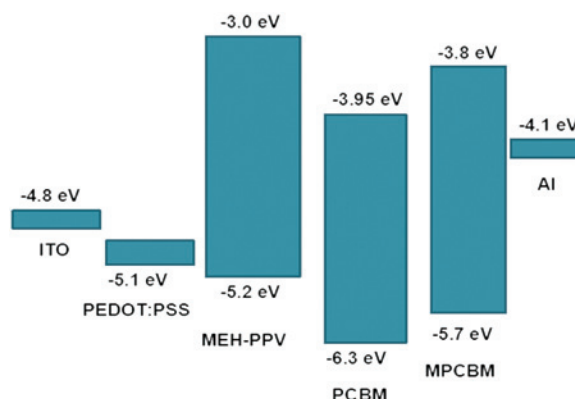**Figure 2:** Schematic diagram of bulk heterojunction devices.



**Figure 3:** Energy level diagram of MEH-PPV, PCBM, and MPCBM.

that of PCBM. The LUMO and HOMO levels of used materials were determined by using cyclic voltammetry (CV) measurements. To calculate the same, the following equations were used [63, 64]:

$$E_{HOMO} = -q \left( E_{ox}^{onset} + 4.7 \right) \text{ eV}$$

$$E_{LUMO} = -q \left( E_{red}^{onset} + 4.7 \right) \text{ eV}$$

where, $E_{red}^{onset}$ is the onset reduction potential measured in volts (V) versus Ag+/Ag.

$E_{ox}^{onset}$ is the onset oxidation potential measured in volts (V) versus Ag+/Ag.

This shift is attributed to the presence of the cyanovinylene 4-nitrophenyl segment in the molecule of MPCBM, which increase its electron affinity or acceptor strength. The higher LUMO energy level of MPCBM is desirable for its application as acceptor in polymer bulk heterojunction photovoltaic devices to get a higher $V_{oc}$. As the LUMO (-3.80 eV) of MPCBM is very close to the work function of the Al (-4.1 eV) electrode, the interface between MPCBM and Al forms a nearly ohmic contact (barrier of about 0.30 eV) for electron injection from the LUMO level of MPCBM to Al. Similarly, the HOMO (-5.2 eV) of MEH-PPV is very close to the work function of PEDOT:PSS (-5.1 eV) electrode, the interface between MEH-PPV and ITO electrode form a nearly ohmic contact for hole injection from the HOMO level of MEH-PPV to ITO electrode. This indicates that MEH-PPV and MPCBM behave as p-type (electron donor) and n-type (electron acceptor) organic semiconductor, respectively.

It can be seen from the energy level diagram that the band gap of MEH-PPV is 2.20 eV, and the difference between the LUMO levels of MEH-PPV and MPCBM is about 0.80 eV. This difference is greater than the exciton binding energy, which is a prerequisite for efficient photoinduced charge separation in the BHJ active layer.

## 3.2 Optical properties of blends

The absorption spectra of MEH-PPV, PCBM, modified PCBM (MPCBM) and its blend are shown in Figure 4. It can be seen that the absorption spectra of the blend show the combination of the individual components. In particular, the absorption peak around 510 nm corresponds to MEH-PPV, which is associated with the interchain π-π⋆ transition [65], whereas the peak around 630 nm corresponds mainly to MPCBM. The addition of PCBM to MEH-PPV shows an increment in the optical absorption which means that PCBM helps in light harvesting in the visible region. The absorption peaks of MPCBM appears in the UV region (<400 nm). Interestingly, MPCBM showed a much stronger absorption than PCBM for the region of 400–800 nm.

The modified PCBM (MPCBM) showed a stronger absorption in the visible region of solar spectrum than PCBM due to the presence of the cyanovinylene 4-nitro-phenyl segment [66, 67]. It has been well established that the incorporation of this segment to various polymers [3, 8] or small molecules [3, 4, 66, 67] broadened their absorption spectra and extended them into the near-infrared (NIR) region. The MEH-PPV:MPCBM blend also shows a broad absorption from 350 to 640 nm, which closely matches with the solar spectrum. Therefore, we expect more photons to be absorbed by the MEH-PPV:MPCBM blend compared to MEH-PPV:PCBM.

The blend with MPCBM shows not only a broader band absorption but also an enhanced intensity of the absorption, which is further increased when the blend is thermally annealed at 100°C for 10 min. This type of increase in the optical absorption after thermal annealing has been observed for conjugated polymers [68] and small molecules [69]. This feature is attributed to the aggregation/interchain interactions and the increase in the crystallinity of the material, which enhances the intensity of π-π⋆ electronic transitions. Therefore, the carrier mobilities in the thermally annealed BHJ organic solar cells (OSCs) are more balanced and may be one of the factors increasing the PCE of the devices on the basis of the thermally annealed active layer. The thin film absorption of MEH-PPV:MPCBM blend also red shifts and displays more distinct vibronic structures, when blend is annealed at 100°C temperature for 10 min. The red shift in absorption of blend indicates an increased intermolecular ordering and planarity in the polymer backbone.

## 3.3 Photovoltaic properties of devices based on BHJ

The current-voltage (J-V) characteristics of the devices under illumination intensity of 100 mW/cm² are shown in Figure 5. The photovoltaic parameters, i.e. short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and PCE of the devices are listed in Table 2. It can be seen from this table that the $V_{oc}$ is increased from 0.75 V for PCBM-based device to 0.89 V for the MPCBM-based device. The higher value of $V_{oc}$ for the PSC device based on MEH-PPV:MPCBM is attributed to the higher LUMO energy level of MPCBM because it is well known that the $V_{oc}$ of PSCs is proportional to the difference between the HOMO of the donor and the LUMO of the acceptor [70]. The increase in the $J_{sc}$ for the device based on the MEH-PPV:MPCBM in
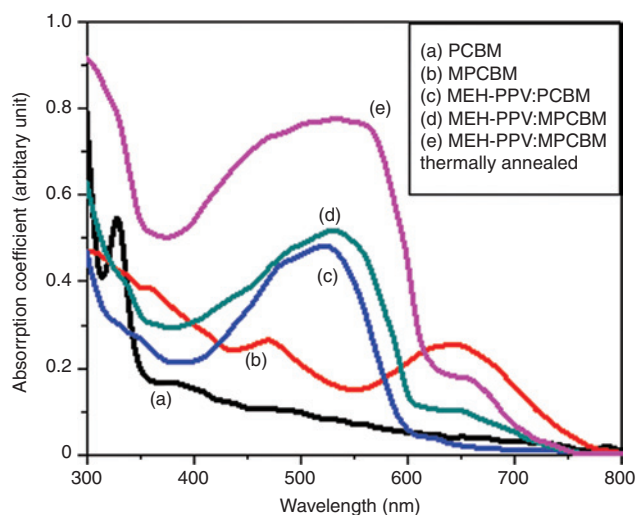


**Figure 4:** UV-vis absorption spectra of PCBM, MPCBM, MEH-PPV:PCBM, MEH-PPV:MPCBM and MEH-PPV:MPCBM thermally annealed.
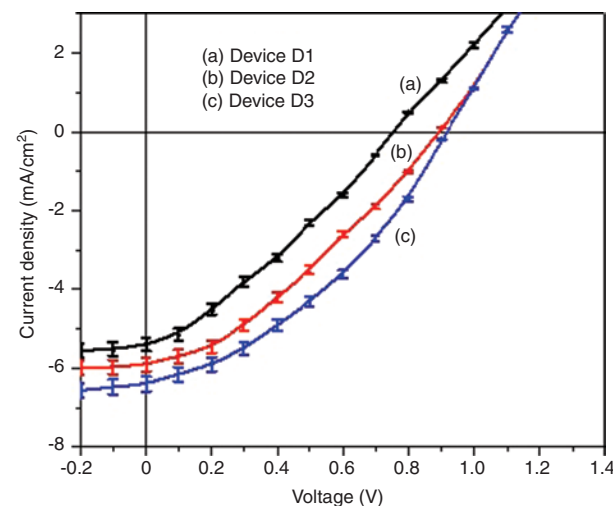


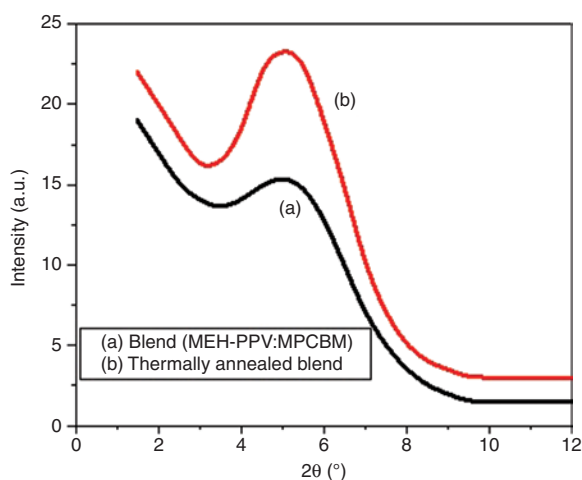**Figure 5:** J-V characteristics curve of different designated devices.

**Table 2:** Photovoltaic parameters of devices D1, D2, and D3.

| Devices | Short circuit current ($J_{sc}$) (mA/cm²) | Open circuit voltage ($V_{oc}$) (V) | Fill factor (FF) | Power conversion efficiency ($\eta\%$) |
|---|---|---|---|---|
| (D1) | 5.60 | 0.75 | 0.31 | 1.30 |
| (D2) | 5.90 | 0.89 | 0.34 | 1.78 |
| (D3) | 6.20 | 0.90 | 0.35 | 1.95 |

comparison to MEH-PPV:PCBM is attributed to the broader absorption of the MEH-PPV:MPCBM blend, which causes an enhancement in the photogenerated excitons in the blend, resulting in a slightly higher photocurrent.
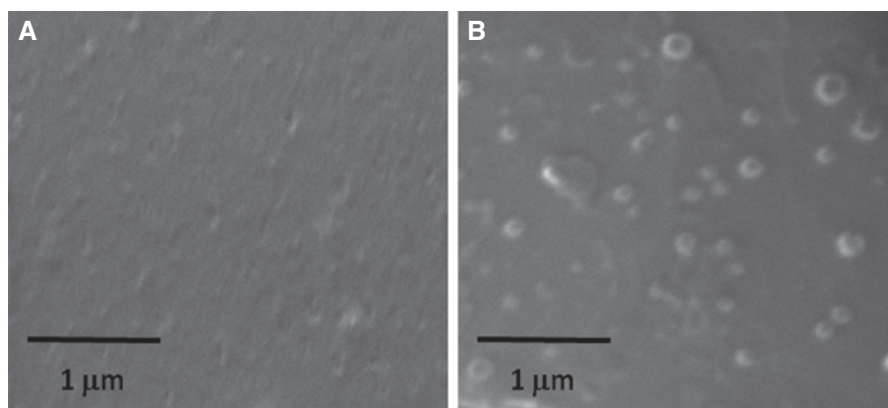
## 3.4 X-ray diffraction

Thin film XRD was used to determine the differences in crystallinity of the blended films before and after thermal



**Figure 6:** XRD patterns of MEH-PPV:MPCBM blend and thermally annealed blend.

annealing. Figure 6 gives the diffraction patterns of the as-cast and annealed blends. The as-cast blend film exhibits a peak centered at $2\theta = 5.0°$ as shown in Figure 6. The diffraction intensity of the thermally annealed blend increases, which indicates a higher degree of crystallinity. These changes in the film crystallinity after thermal annealing agree with what is observed in the absorption spectra. Because most of the fullerene acceptors, such as PCBM, do not show any diffraction patterns in the range of $2\theta$ values used [71], the changes in crystallinity of the blended film after thermal annealing are mainly attributed to an increase in crystallite size of the donor material (MEH-PPV). The increase in the crystallinity of MEH-PPV upon thermal annealing leads to an improvement in the hole mobility that increases the overall PCE.

## 3.5 Surface morphology

The morphology of the spin-coated polymer thin films is an important factor to fabricate polymer solar cells [72, 73]. The surface morphological changes of MEH-PPV:modified fullerene (1:4) films and its thermally annealed films were monitored using SEM as shown in Figure 7A and B, respectively. It can be clearly seen from the SEM images that surface morphology of the thermally annealed MEH-PPV:MPCBM layers shows higher surface peaks and an obvious increase in surface roughness as shown in Figure 7B. This can be the result of an increased nanoscaled phase separation between the crystalline MEH-PPV and the modified PCBM (MPCBM) acceptor. Increase in surface roughness allows more space for MEH-PPV crystallites to form, thus, increases crystallinity (as per proved by XRD pattern) as well as interfacial contact area between the PEDOT:PSS and MEH-PPV:MPCBM layer. This allows more



**Figure 7:** SEM images of (A) MEH-PPV:MPCBM film and (B) MEH-PPV:MPCBM thermally annealed blend films.

efficient hole collection at the anode, which improves $J_{sc}$ and FF and also increases absorption of the active layer.

## 4 Conclusions

We have fabricated polymer solar cells with the MEH-PPV:MPCBM blend, sandwiched between ITO/PEDOT:PSS and Al electrodes. The $V_{oc}$ and $J_{sc}$ values of the BHJ device based on MEH-PPV:MPCBM blend cast from THF solvent reached 0.90 V and 5.90 mA/cm², respectively, leading to an overall PCE of ~1.78%, which is significantly improved compared to a BHJ device based on MEH-PPV:PCBM (1.30%). The increase in $J_{sc}$ has been attributed to the stronger absorption of MPCBM in the visible region, which is missing for PCBM. However, the increase in the $V_{oc}$ has been ascribed to the higher LUMO. Moreover, this has been further increased to 1.95%, when the MEH-PPV:MPCBM blend was thermally annealed before the deposition of the Al electrode. We have observed that the improvement in the PCE has been mainly attributed to the increase in the $J_{sc}$.

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