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Enhanced lifetime of organic photovoltaic diodes utilizing a ternary blend including an insulating polymer

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Abstract

We report on the lifetime of unencapsulated organic photovoltaic diodes (OPVs) based on a ternary blend of poly(3-hexylthiophene) (P3HT), phenyl-C_{61}-butyric acid methyl ester (PCBM) and a soft insulating polymer, poly(methyl methacrylate) (PMMA) as compared to reference binary P3HT:PCBM OPVs. The performance of ternary devices was shown to decay more slowly than that of their binary counterparts to an extent that depends on the relative humidity (RH). The power conversion efficiency of ternary OPVs when stored in a low humidity environment (1% RH) decayed to 80% of their initial value after 200 hours, almost double that of the reference binary OPVs. AFM measurements suggest that the PMMA forms pillars within the P3HT:PCBM matrix. It is proposed that the PMMA absorbs water in the active layer, and in doing so, slows the rate of deep trap formation that would otherwise lead to enhanced Shockley-Read-Hall recombination.

Keywords: Lifetime, degradation, bulk heterojunction, organic photovoltaic.

1. Introduction

Organic photovoltaic diodes (OPVs) are a promising technology that has attracted considerable interest because of the possibility of fabricating large area, flexible, low-cost and lightweight devices [1–3]. However, the lifetime of OPVs is a key factor hindering commercialization [4,5]. Although the lifetime of poly(3-hexylthiophene) (P3HT) : phenyl-C61-butyric acid methyl ester (PCBM) devices can be up to 1000 hours [6], this still represents significantly worse performance than, for example, inorganic silicon photovoltaics, which have a lifetime approaching 25 years [7]. The degradation mechanisms in OPVs are not fully understood [8] and a considerable effort is needed to improve their lifetime. OPVs degrade due to both chemical and physical processes. Chemical degradation may result from light [9], temperature [10], oxygen and water [11,12], with water and oxygen being considered the principal factors [4,12]. These molecular species can cause oxidation of the OPV materials [13] and electrodes [14], in turn leading to electronic traps [15] and low performance. The rate of degradation due to water increases with relative humidity (RH)[16]. Deterioration in performance can also result from changes in the bulk heterojunction (BHJ) morphology [5]. For example, several studies have showed that BHJ materials aggregate over time, thereby reducing exciton dissociation and hence short circuit current [2,17].

The use of insulating polymers as a third component in OPV blends has been suggested as a strategy to improve their lifetime [4]. This approach, whereby the ‘active’ organic semiconductor is blended with an inert insulating polymer, has been used in organic field effect transistors (OFETs), where it has been shown to increase lifetime with minimal effect on electronic properties [18,19]. For example, blending high-density polyethylene (HDPE) with P3HT in an OFET results in a lifetime of around four months in air, as compared to a reference P3HT OFET which lasted only a few hours [20]. Arias *et al*. [21] added poly(methyl methacrylate) (PMMA) to poly[5,50-bis(3-dodecyl-2-thienyl)-2,20-bithiophene] (PQT-12) OFETs and stored these devices in air. The thin film structures with PMMA had an improved lifetime of 48 hours as compared to PQT-12 OFETs, which had a lifetime of only 20 hours. Notwithstanding this initial success in the use of insulating polymers to improve the lifetime of OFETs, there are relatively few studies on the application of this technique in OPVs. Ferenczi *et al.* [18] showed that adding up to 50 weight percent of HDPE or isotactic polystyrene (i-PS) to P3HT:PCBM OPVs had minimal detrimental effect on intial device performance. Indeed, Wu *et al.* [22] have demonstrated that adding PMMA to a P3HT:PCBM blend can actually improve the initial fill factor and open circuit voltage of the resulting OPV. This was suggested to be due to a reduced number of vacancies and leakage pathways.

In this paper, we investigate the use of PMMA as a ternary component in P3HT:PCBM OPVs as a means to reduce degradation and increase lifetime. The PMMA has been selected because it is readily available and compatible with the solvents used for P3HT:PCBM OPVs (dichlorobenzene in this study). The performance of ternary P3HT:PCBM:PMMA OPVs are measured over time in a variety of ambient conditions and compared to reference P3HT:PCBM OPVs. It is found that adding PMMA to the OPV blend improves lifetime to an extent that depends on RH, with larger RH leading to smaller improvements in lifetime. Atomic force microscopy (AFM) and conductive AFM measurements suggest that the PMMA forms columnar features dotted within an otherwise largely P3HT:PCBM matrix. It is proposed that the PMMA absorbs ambient water vapor, and in doing so, reduces the rate of trap formation in the active OPV materials.

2. Experimental

Indium tin oxide (ITO) coated glass substrates were patterned into stripes by etching the substrates using zinc powder and hydrochloric acid. The patterened substrates were sonicated in Decon 90 solution (2% aqueous), deionized water, acetone and then with propanol-2-ol for 15 minutes each followed by drying with N_2 gas. The cleaned substrates were exposed to oxygen plasma (Yield Engineering Systems Inc., YES-R3) for 5 minutes with a radio frequency (RF) power of 100 W. The conductive polymer poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) PEDOT: PSS (CLEVIOS P VP AI 4083) was filtered using a 0.2 µm poly(tetrafluoroethylene) (PTFE) syringe filter and spun-cast onto the clean ITO surface at 2500 rpm for 45 s prior to annealing at $140^{o}C$ for 10 min in ambient atmosphere.

Solutions of regioregular P3HT (Rieke Metals, $M_w = 50–70\ kg\ mol^{-1}$) and PCBM (Lumtec, $M_w = 0.91\ kg\ mol^{-1}$) were prepared by dissolving each material in anhydrous 1,2-dichlorobenzene (DCB) separately, and mixing in a weight ratio of (1:1). In order to make a ternary blend solution, a PMMA ($M_w =97\ kg\ mol^{-1}$) solution was first prepared by dissolving in DCB and stirring for two days in a N_2 glovebox to achieve a clear solution. The P3HT: PCBM (1:1) solution was stirred for 3 hours before 14 wt% of PMMA was added to achieve a solution with a concentration of 35 mg ml^{-1}. Both binary and ternary OPV blends were stirred for 24 hours before spin-coating onto PEDOT: PSS films at 1000 rpm for 1 min. The active layers were kept under high vacuum for around 24 hours prior to the deposition of 150 nm of Al through a shadow mask to result in 4 separate OPVs per substrate. Devices were annealed at 120^{o}C for 10 min in the glovebox prior to lifetime tests.

The performance of the OPVs was determined by using a Keithley 2400 source meter, both in the dark and under AM 1.5 illumination from a solar simulator (Oriel Sol1A 94021A). All solar simulator measurements used a mask to restrict illumination to an active area of 0.79 mm^2. Each set of experiments involved measurements on 20 nominally identical OPVs to ensure reliable statistics. Only the results from representative average devices are shown here. The devices were stored in a dark environment with ambient air at different humidities. An environmental chamber was used to provide high humidity (85%, 65% RH), while low humidity (1% RH) was achieved by storing devices in a desiccator containing silica gel. These are compared to a standard ambient (50 % RH). In all cases, the RH was measured over the course of the aging process with a humidity sensor.

Conductive atomic force microscopy (C-AFM) was used to measure the distribution of conductivity in the active layer. The measurement was performed in a clean room environment using a Dimension 3100 microscope and Nanoscope IVa controller (Bruker). Gold–coated (with a Cr adhesion layer) contact –mode AFM probes (Budget Sensors ContGB-G, nominal spring constant = 0.2 N m^{-1}) were used for all measurements under a forward bias of 1 V. The height and current images were taken simultaneously.

3. Results and Discussion

Figure 1 illustrates the effect of humidity on the power conversion efficiency (PCE) of the binary P3HT: PCBM and ternary P3HT: PCBM: PMMA OPVs, hereafter referred to as binary and ternary OPVs, respectively. It is clear that the rate of degradation increases with humidity. The PCE of both sets of devices is negligible or nil after 300 hours of being stored at 50% RH, while at 1% RH, both sets of devices still show measurable performance after 800 hours. Table 1 lists the lifetime of the cells at different humidity levels. Here, we quantify lifetime of the devices by T_{80} and T_{20}, which represent the time the device takes to degrade to 80% and 20% of its initial efficiency, respectively. Given that both sets of devices were stored in an environment with ambient oxygen, these data agree with previous findings that the principal degradation mechanism in P3HT: PCBM OPVs under normal operating conditions (i.e. ~40-50% RH) involves interaction with water [16,23] . However, we note that the quantitative relationship between RH and lifetime (i.e. T_{80}) shown in Table 1 is non-linear for both binary and ternary OPVs. This may indicate that the lifetime of OPVs is determined by a variety of mechanisms, only some of which involve water. We speculate that the lifetime of OPVs at 1% RH is only partly limited by water-based degradation, and that we may be probing a regime in which oxygen-based degradation is more prominent. Devices stored in dry N_2 show no measurable drop in PCE after more than 1400 hours of aging, as illustrated in Figure SI 1 (see Supplementary Information).

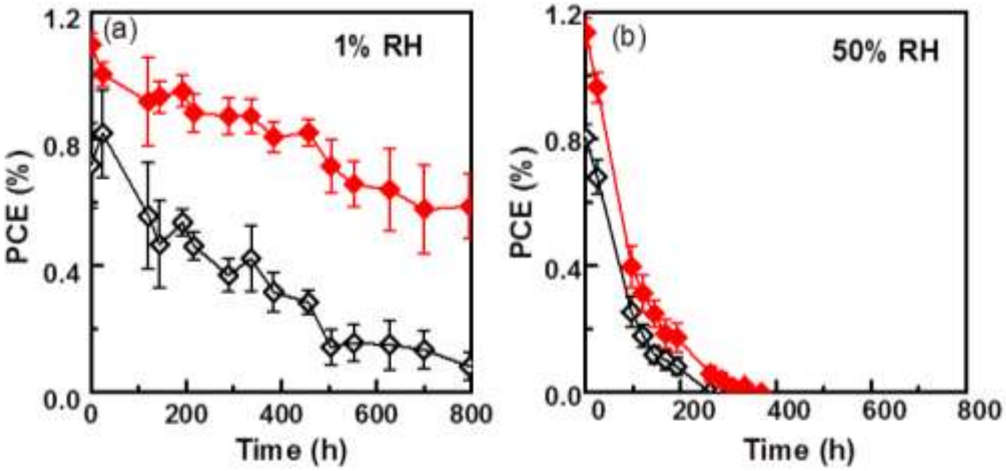

Figure 1. Power conversion efficiency (PCE) as a function of time for P3HT: PCBM (1:1) blend, (open diamonds), and ternary (1: 1: 0.3) P3HT: PCBM: PMMA blend, (closed diamonds), stored at relative humidity levels of (a) 1% and (b) 50%.

Table 1. Lifetime of devices based on binary and ternary blends at different humidity levels

Humidity level	**Binary devices**		**Ternary devices**	
	T_{80}(h)	**T_{20}(h)**	**T_{80}(h)**	**T_{20}(h)**
65%	3	21	3	21
50%	24	120	24	168
1%	120	504	216	>1000

It is also found that ternary OPVs have better initial performance than their binary counterparts. The performance of the devices improved as the amount of PMMA was increased until an optimum efficiency was reached at 14 wt%. The improved performance with addition of PMMA is in agreement with other Wu *et al* [22] and Li

[24]. Wu *et al.* [22] argued that PMMA reduces the formation of vacancies and leakage pathways that may act as traps, while Li [24] proposed that PMMA may reduce the distance travelled by carriers to the electrodes.

The improvement in lifetime for a ternary OPV when compared to a binary OPV counterpart is shown to depend on RH. When devices were stored at RH of 85%, both the binary and ternary OPVs had $T_{20} < 4$ hours (see Supplementary Information Figure SI 2). As the RH decreased to 50%, T_{20} was shown to be marginally better in the ternary OPV, but if RH was reduced still further to 1%, both T_{20} and T_{80} were markedly better for the ternary OPV. Under these latter conditions, T_{20} exceeded 1000 hours.

Figure 2 shows typical current density (J) vs voltage (V) curves under illumination (a and b) and in the dark (c and d) for binary and ternary OPVs stored in 1% RH (a and c) and 50% RH (b and d). The differences in the initial performance of OPVs for 1% and 50% RH are ascribed to small variations in the thickness of the active layer. However, we note that the film thickness of binary and ternary devices were similar (see Table SI 1 in Supplementary Information) which means that the ~0.4% improvement in PCE with addition of PMMA is unlikely to be due to film thickness variations. Instead we argue that the initial performance of the binary and ternary blends is different due to the same reasons noted by Wu *et al* [22] and Li [24].

From Figure 2, it is evident that the open circuit voltage (V_{OC}) remains relatively constant for the aged devices at both humidity levels. Aging the devices in 50% RH is shown to affect the short circuit current density (J_{SC}) and fill factor (FF), while aging devices in 1% RH, is shown to only affect J_{SC}. Table SI 1 (Supplementary Information) shows the performance parameters of both sets of devices in 1% and 50% RH for devices as deposited and after 144 hours. Figure 2 (c and d) shows the J-V curves in the dark for both sets of devices. The dark current is seen to reduce with aging for both binary and ternary OPVs, but the reduction for binary devices is greater. This may indicate that aging P3HT:PCBM OPVs under 1% and 50% RH over the 1000 hour timescale involves degradation of charge transport in either the P3HT or PCBM, perhaps indicating the formation of traps. This is supported by the apparent series resistance (R_S), which is here defined as the inverse slope of the J-V curve in the dark at voltages larger than 0.8V where the J-V characteristic is linear [22]. The ternary devices do not show a significant change in R_S while a noticeable increase was observed in binary devices at both humidity levels, as shown in Table SI2 (c and d). However, the increase in apparent series resistance may also be due to an increase in the contact resistance between the electrodes and the active materials [25] due to the diffusion of oxygen and electrode materials into the active layer [3]

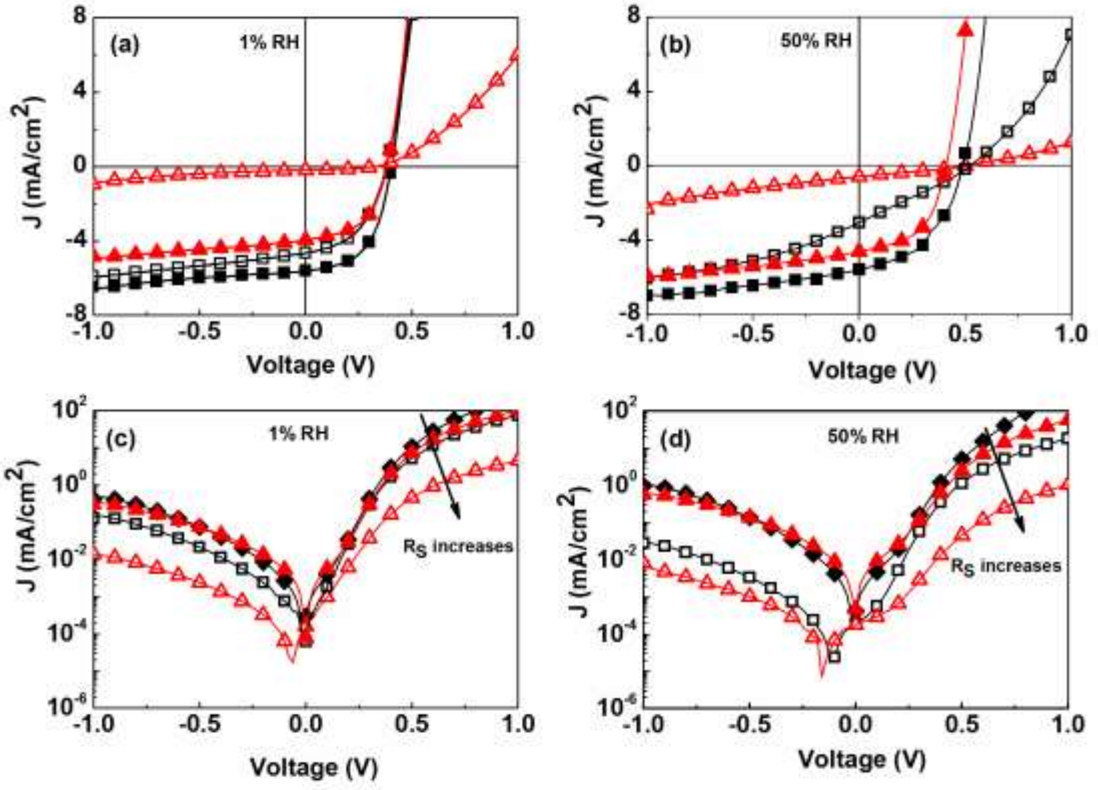

Figure 2. J-V curves under AM 1.5 (a & b) and in the dark (c & d) for typical binary P3HT: PCBM (1:1) (red triangles) and ternary P3HT: PCBM: PMMA (1: 1: 0.3) (black squares) OPVs. (a & c) devices stored in 1 % RH at different degradation time, filled symbols for initial measurement, open symbols for aged devices (after 800 h). (b &d) devices stored in 50 % RH, the aged devices (after 260 h).

Ultraviolet-visible absorption spectra of ternary and binary thin films before and after aging were measured and are shown in Figure SI 3 (Supplementary Information). The absorbance of the ternary blend films was similar to the binary film, suggesting that crystallization of P3HT is unaffected by the addition of PMMA. Moreover, no significant change in the absorption occurred after T_{20} and $T_{80,}$ indicating that crystallization of P3HT is unaffected by the aging process. The similar absorption characteristics of binary and ternary blends before and after aging also rule out photo-bleaching as a possible mechanism for the loss in PCE shown in Figure 1. Fourier transform infrared spectroscopy (FTIR) measurements were also performed (see Supplementary Information Figure SI 4). The results revealed no observable chemical change in the P3HT or PCBM after being stored in 1% and 50% RH for more than 800 hours [10]. Hence, the formation of oxidized species in the active layer is slow here; we attribute this to devices being stored in the dark between tests, which in turn will mitigate photo-oxidation [10,26]. However, the sensitivity of the FTIR measurement may have been insufficient to have detected minor chemical changes.

These data suggest that the degradation observed in the present devices is primarily electronic in origin, and strongly linked with the presence of water. Notwithstanding the absence of chemical changes observed in FTIR measurements, we propose that the main route of degradation of the present devices is the formation of trap states through reaction with water [27] which has the effect of reducing J_{sc} and FF. We note that water can diffuse into the active layer through the PEDOT: PSS [28] or the Al contact [14]. However, Kawano *et al.* [29] showed that hygroscopic PEDOT: PSS is susceptible to degradation by water, hence we cannot rule out the observed aging data being due to a change in the PEDOT:PSS layer. In either case, ternary devices are shown to have superior performance during aging tests. For example, after 144 hours in 50% RH, the ternary OPVs out-performed their binary counterparts in terms of R_S ($4.9\ \Omega\ cm^2$ vs $83\ \Omega\ cm^2$), FF (40% vs 32%) and J_{SC} ($1.5\ mA\ cm^{-2}$ vs $0.95\ mA\ cm^{-2}$), as shown in Table SI1 and SI2.

AFM and C-AFM were used to explore how PMMA influences the morphology and conductivity. A comparison between fresh binary and ternary blend films is shown in Figure 3.

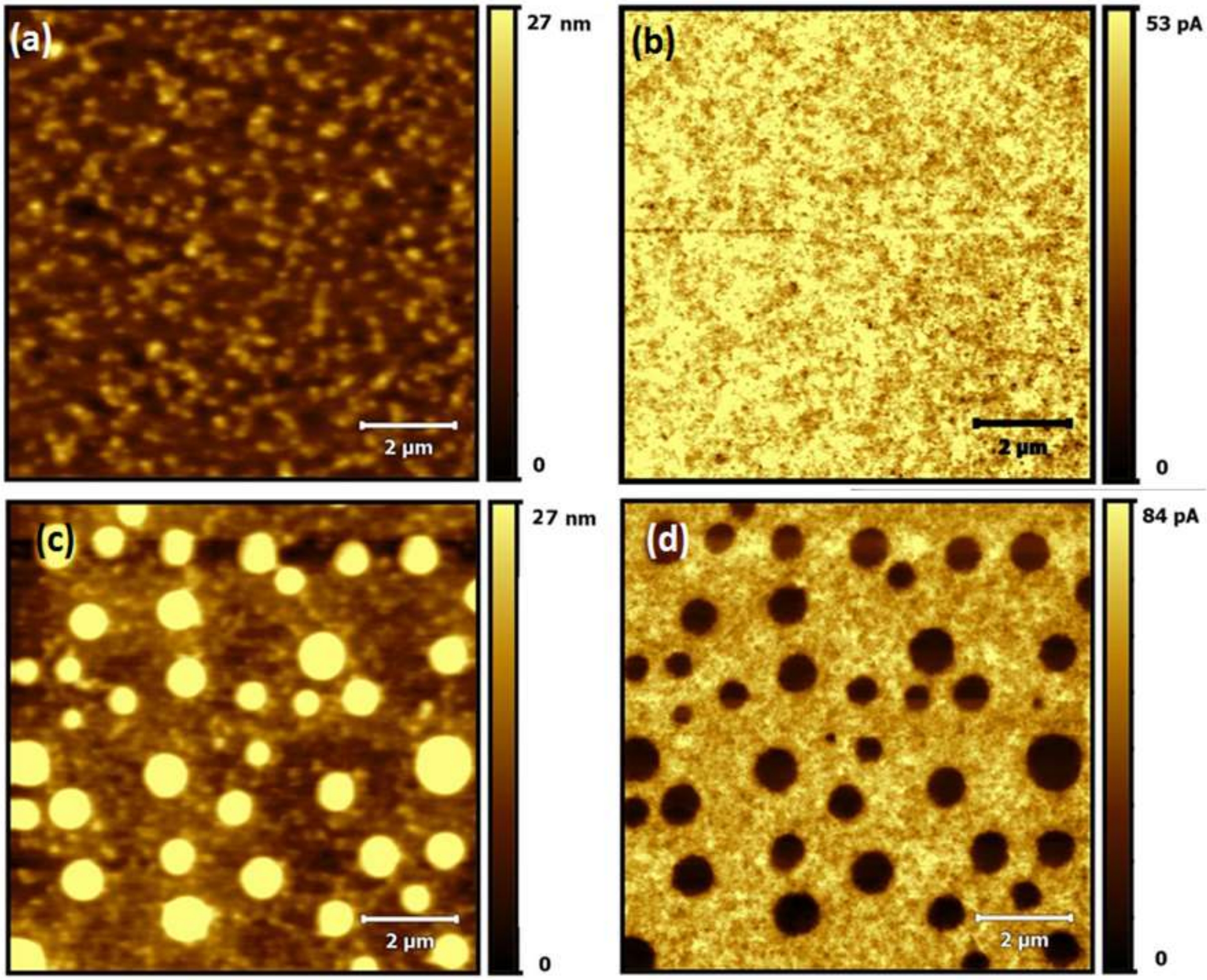

Figure 3. AFM topography images (a & c) of as-deposited P3HT: PCBM (1:1) film and (1: 1: 0.3) P3HT: PCBM: PMMA film respectively. (b & d) current maps of topography, for the same areas, at 1 V bias.

The addition of PMMA results in islands of approximately 1 µm in diameter (Figure 3c) not present in the binary film (Figure 3a). The current map in Figure 3d reveals that the islands have poor conductivity, indicating that they are PMMA- rich, and in turn, that P3HT and PCBM are concentrated primarily in the region between the PMMA-rich islands. Further AFM measurements on the underside of the active layer films following float-off (shown in Figure SI5) suggest that the PMMA-rich regions penetrate the active layer, forming pillars. It is perhaps surprising that PMMA has a beneficial effect on OPV lifetime considering the morphology, since it can be seen that PMMA does not form a protective wetting layer. This suggests that PMMA may be acting as a ‘gettering’ agent for water in the film. Table 1 reveals that PMMA has a beneficial impact on lifetime for low RH, but that for higher RH (50% and above) the improvement in lifetime is substantially reduced or absent. This is consistent with the suggestion that PMMA is acting as a gettering agent, since the capability of PMMA to absorb water that would otherwise react with the active layer will necessarily be limited. Returning to the C-AFM images of Figure 3, it is evident that the P3HT:PCBM rich regions in both the ternary and binary films show variations in current that would be expected due to local variations in conductivity [28], although we do not observe P3HT fibrils. Figure 4 shows similar C-AFM images for the binary and ternary blend films following storage at RH 50% and 1% for 500 h.

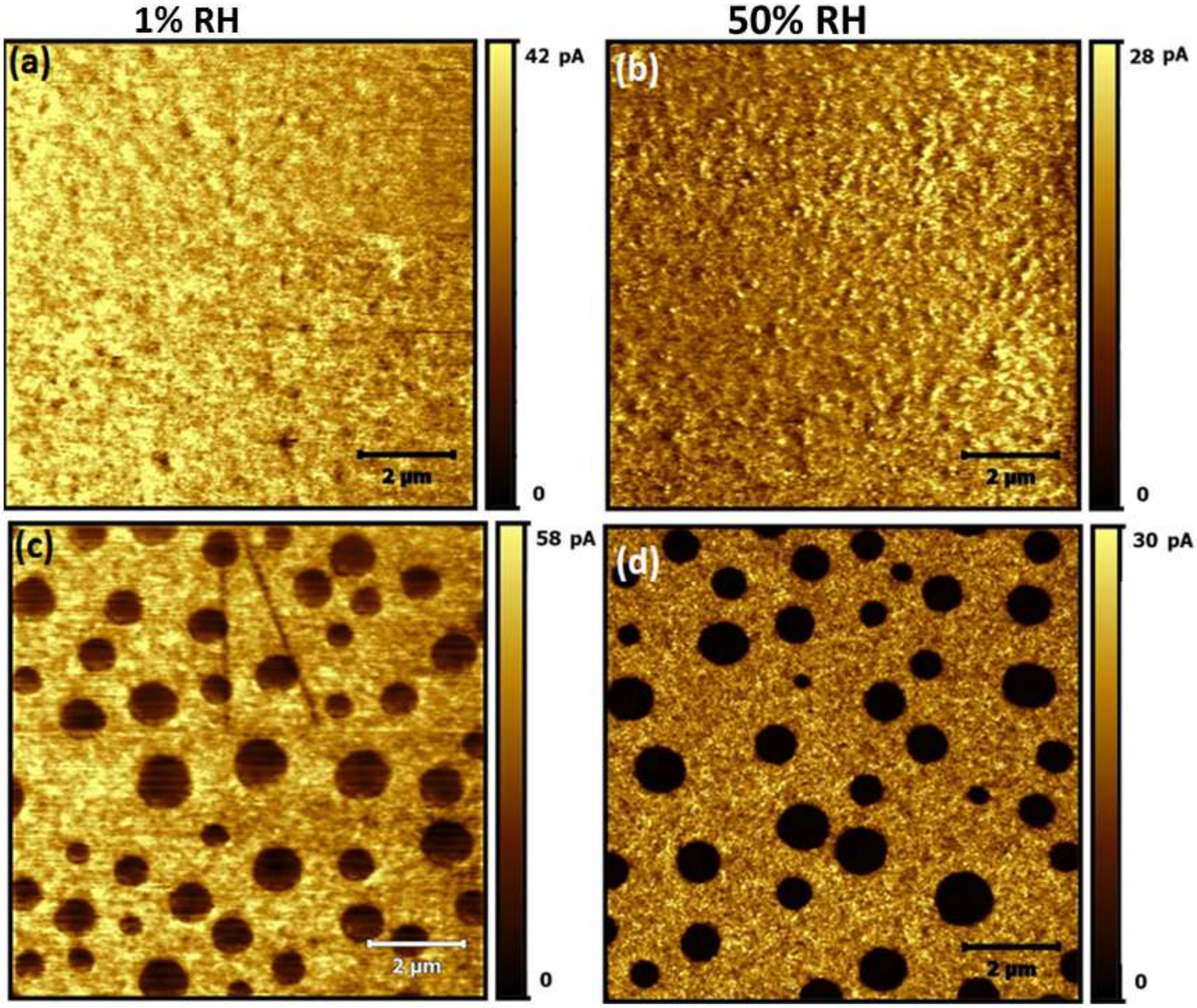

Figure 4 Current images of aged P3HT: PCBM (a and b) and P3HT: PCBM: PMMA (c and d) films stored in 1% RH (a and c) and 50% RH (b and d). All images were taken at 1 V bias after 500 h.

The conductivity of the binary films was shown to be lower than the equivalent ternary film stored at the same RH, although the difference in conductivity is larger at 1% RH than in 50% RH. This again is consistent with the suggestion that PMMA is acting as a gettering agent for water, since aging at higher RH appears to saturate the PMMA, leading to similar conductivity of ternary and binary films following aging. Although the data appear to be consistent with PMMA acting as a gettering agent, for the morphologies examined, the distance of a particular P3HT: PCBM-rich region from a PMMA-rich region appears to have little effect on the rate of degradation. This indicates that water may diffuse several microns through the film prior to reacting with the P3HT or PCBM. Although finite conductivity is measured in all cases, binary and ternary OPVs aged for 500 h in 50% RH have vanishingly small PCE (Figure 1). This suggests that recombination mechanisms are additionally affected by the formation of traps.

To obtain further insight, C-AFM images were analyzed statistically. The average current and the standard deviation were measured in seven different regions with an approximate area of (1.7 µm × 0.6 µm) for each film as shown in Table SI3 (see supplementary information). In ternary blend films, the data were extracted from areas between PMMA pillars, which are anticipated to be P3HT: PCBM rich. Figure 5 illustrates the histograms of the current for typical areas chosen from both binary and ternary devices as deposited and after 500 h in low and high humidity. As might be expected from Figure 4, each histogram shows that the conductivity has a roughly normal distribution, indicating the absence of aging-induced ‘hot spots’ or ‘dead spots.’ The initial current in the ternary devices is higher than the binary equivalent, as might be anticipated due to the superior initial performance of the ternary OPVs (Figure 1). After aging for 500 h at 1% RH the average current fell by ≈ 30% for both devices. This contrasts with the OPV performance (Figure 1) which shows ternary devices aging less rapidly under 1% RH than the binary device. Again, this suggests that the electronic properties of the OPV are degraded by aging, but that the loss in PCE is not solely due to changes in mobility caused by trap formation [15]. Traps may be due to structural reasons, such as defects associated with the polymer backbone [30], incomplete bonding forming vacancies [28], or chemical reaction with oxygen or other contaminants [15,16,27]. It has been suggested that structural defects in P3HT largely cause shallow traps [31], while chemical reactions between the active layer materials and water or oxygen leads to deeper traps [15]. It appears that the degradation in the conductivity shown in the C-AFM images of Figure 5 is only partly related to the degradation in PCE shown in Figure 1. We speculate that the degradation in PCE is largely due to the formation of deep traps, which is partially arrested by the addition of PMMA. We propose that the deep traps lead to enhanced Shockley-Read-Hall (SRH) recombination [32] which in turn reduces PCE. This is consistent with the observed loss in performance being primarily *via* J_{SC} and FF. In other work, SRH recombination has been used to model accurately non-geminate recombination in a range of organic light emitting devices [33]. We propose that the degradation in conductivity observed in Figure 5 is instead principally due to the formation of shallow traps in the active layer, which are primarily of physical origin [22], and consequently the addition of PMMA does not arrest the degradation of conductivity in ternary films.

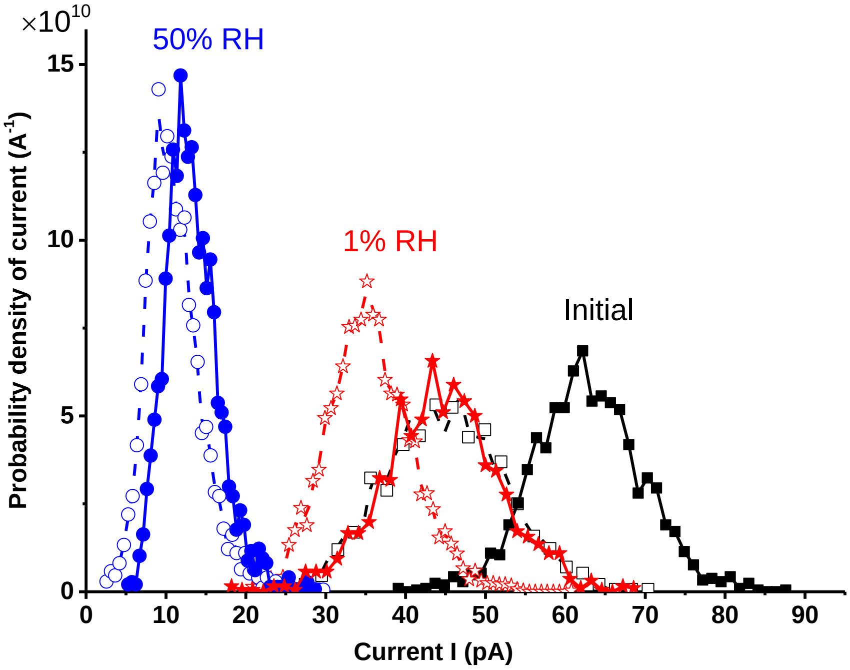

Figure 5. Histogram curves of current probability distribution of P3HT: PCBM films (open symbols) and P3HT: PCBM: PMMA films (closed symbols) measured initially as- deposited and after 500 h, stored in 1% RH and 50% RH. The measurements were performed on typical small areas (1.7µm x 0.6 µm) of each device.

4. **Conclusion**

This work has shown that the addition of PMMA to P3HT: PCBM OPVs improves both the initial performance and lifetime of devices. Measurements at a variety of relative humidities suggest that the PMMA acts as a water gettering agent. It is also shown that the lifetime improvement with PMMA reduces with increasing relative humidity, suggesting that the polymer can become saturated. AFM and C-AFM studies reveal that the addition of PMMA results in a morphology containing PMMA-rich pillars separated by P3HT: PCBM rich regions not dissimilar to that seen in a binary P3HT: PCBM film. Surprisingly, it is shown that the electrical conductivity does not degrade at different rates across the ternary blend film, suggesting that water diffuses microns through the film prior to reacting with the active material. The rate at which conductivity degrades, as measured by C-AFM in the dark, is similar in both binary and ternary devices. This suggests that multiple degradation mechanisms are at work, and that PMMA only assists in extending the lifetime associated with some degradation pathways. We propose that the PCE of P3HT: PCBM devices are largely limited by reaction with water, and that PMMA can slow down the process of degradation by absorption of water. Our work demonstrates that an electrically inert, partially hygroscopic material can be blended with an OPV active layer to improve device lifetime. Further experiments to reveal the water absorption mechanism of PMMA will elucidate the potential of this approach. We note that saturation of the PMMA is indicated, suggesting that different materials may extend lifetime still further.

Acknowledgements

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