
Elisa Escasán,† Elena López-Elvira,‡ Arturo M. Baró,‡ Jaime. Colchero,† and Elisa Palacios-Lidón†,*

† Dep. Física, Edificio ClOyN (Campus Espinardo), Universidad de Murcia, E-30100, Spain
‡ Dep. Surfaces and Coatings, Instituto de Ciencia de Materiales de Madrid—CSIC (Campus Cantoblanco), E-28049 Madrid, Spain

ABSTRACT: The wavelength dependence of the nanoscale light induced processes taking place in MEH-PPV/TCBM blended thin film samples has been studied by means of Kelvin probe microscopy implemented with controlled external sample illumination. First, both materials have been characterized individually and then these results have been used to explain the behavior of the blended sample. It has been found that green light mainly induces reversible photophysical processes with an effective photocharge generation and charge redistribution. On the contrary, under blue illumination, samples suffer a strong degradation that dominated the overall photoreponse.

The use of organic materials in optoelectronic devices offers a cheap and versatile alternative to traditional semiconductor technology.† The wide variety of organic molecules that can be selected according to the desired physical properties and the simplicity of the deposition techniques allow the fabrication of tunable large area devices.‡ In recent years, huge progress has been achieved in this field to overcome the drawbacks of the organic devices, such as low efficiency and degradation. Recently, organic solar cells with an efficiency of 8.62% have been obtained, demonstrating the capabilities of the “plastic optoelectronic” approach.‡ In these kinds of devices, the building blocks are long polymeric chains or complex molecules. When they are close-packed to form a solid-state device, the intermolecular and intramolecular interactions that govern the overall device behavior are complicated and their charge transport properties cannot be explained with classical semiconductor theories.¶–‡ In addition, the working principle of many plastic optoelectronic devices lies on the “bulk heterojunction” concept in which a p- (usually a semiconducting polymer) and an n-type (usually a fullerene derivate) material are blended to form a disperse p-n junction increasing the active area.¶–‡ Therefore, to optimize the device performance, a complete understanding of the interactions taking place within individual materials as well as between different materials is needed.

Since these interactions occur at the nanoscale, to study the processes that are taking place appropriate characterization tools with a lateral resolution of a few nanometers are desired, complementing the information obtained with macroscopic techniques. The use of scanning force microscopy (SFM) related techniques and in particular Kelvin probe microscopy (KPM) allows one to simultaneously measure the topography and electronic information, such as the contact potential (CP) with a lateral resolution of a few tens of nanometers.¶–‡ In addition, if KPM is combined with external illumination, information about the light induced electro-optical processes can be extracted.¶–‡ This technique has been successfully applied to organic polymer blends and complex molecules giving valuable information.¶–‡ Most of these works study the correlation of the nanoscale morphology of the donor–acceptor blend with the charge generation, charge separation and charge transport within the blend, which is of vital importance since these parameters limit the efficiency of the macroscopic organic devices. To do that, typically consecutive KPM images are acquired in darkness and under illumination in the same sample region are compared to obtain the local light-induced CP variations which are related with a surface photovoltage (SPV) effect. However, the interpretation of the CP images is not straightforward in terms of photophysical processes such as charge generation, redistribution, and recombination, since photochemical reactions that degrade the polymer can also take place. An excellent review of the basic principles of the SPV effect, the different contributions to the SPV signal, as well as its applications is found in ref 24.

In the present work, we will focus our attention mainly on the dependence of the electro-optical properties with the illumination wavelength instead of in the relation between the electro-optical properties and the nanomorphology of the donor–acceptor heterojunction. To do that, KPM combined with external illumination has been used to characterize blended samples of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and [6,6]-thienyl C61 butyric acid methyl ester (TCBM) (1:4% in weight from chloroform...
solution). In these samples, the phase separation takes place at lengths of about 100 nm. This phase separation is larger than the typical exciton diffusion length in semiconducting polymers (~10–20 nm) and it is probably not the best morphology to optimize a photovoltaic polymer device. However, it is larger than the KPM lateral resolution and therefore the behavior of the individual phases can be unambiguously studied. The SPV evolution as a function of the illumination time has been studied by applying the recently proposed “two traces method.” In contrast to the acquisition of consecutive “off”/“on” whole images, this method has the advantage that each “off”/“on” line can be directly compared, and artifacts due to drift or tip changes are minimized. With this methodology, reversible photophysical phenomena and permanent photochemical degradation can be distinguished. Green (λ = 535 nm) and blue (λ = 480 nm) wavelengths have been chosen for the sample illumination because they are within the materials absorption band and ensure interband transitions. To fully understand the underlying processes that take place when the two materials are blended to form the bulk heterojunction, first the p-type MEH-PPV semiconducting polymer and the n-type fullerene like TCBM are separately studied. We found that in both materials, the light-induced processes strongly depend on the wavelength of the light. These results are used to explain the electro-optical response of the MEH-PPV:TCBM blended sample. It has been found that, as in the individual materials, the electro-optical response depends on the illumination wavelength. Under green illumination, the sample behavior can be well explained as a disperse p-n junction with well defined p-type MEH-PPV semiconducting polymer and the n-type fullerene like TCBM. However, under blue illumination, the p-n disperse junction is not clear and the sample response is mainly dominated by a degradation process that photobleaches the sample.

## MATERIALS AND METHODS

Poly[2-methoxy-S-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (average M, 150 000–250 000) and the fullerene derivative [6,6]-Thienyl C61 butyric acid methyl ester (TCBM) (Molecular weight 916.91) were purchased from Sigma-Aldrich and were used without further purification. Thin film samples of pure MEH-PPV and TCBM as well as blended MEH-PPV:TCBM (1:4) samples were prepared by spin-coating (3000 rpm) from chloroform solution on top of indium tin oxide coated PET (ITO:PET) (Sigma Aldrich) substrates previously cleaned with isopropanol. This substrate is frequently used in plastic optoelectronic devices as a transparent electrode because it is flexible, cheap, and flat. The resulting film thickness is about 200 nm.

This work has been carried out at room temperature and ambient conditions using a homemade SFM controlled with a Nanotec electronic. The SFM was operated in an amplitude modulation mode (AM-DSFM) using Platinum coated silicon tips (Budget Sensors, k = 3 N/m and f = 75 kHz). KPM images were acquired in frequency-modulated mode (FM-KPM) with an AC voltage of 500 mV at 7 kHz. More details of FM-KPM set up are described elsewhere. Free WSxM software has been used for the images acquisition and processing.

To combine SFM capabilities with controlled external illumination, the SFM was implemented in an inverted optical microscope (Nikon Eclipse TE2000-E) equipped with 10× (NA = 0.3, W.D. = 16 mm) and 40× (NA = 0.6, W.D. = 3.6–2.8 mm) Nikon objectives (Plan Fluor type). The first is used to select a clean and dust-free sample region and the second is used to illuminate during the KPM measurements. For the sample illumination, an LEDs source (Prizmatix) with different wavelengths and tunable intensity is attached to the optical microscope. In this work, all of the measurements were performed with green (λ = 535 nm) and blue (λ = 480 nm) light using bottom illumination, that is, through the transparent electrode (ITO: PET), as in a solar cell. An illumination intensity of 9 × 10^{17} photons s^{-1} cm^{-2} was used. This illumination is referred to the number of photons that reach the ITO:MEH-PPV interface and it was estimated by measuring with a silicon photodiode the intensity passing through an ITO:PET clean substrate placed at the same sample position and dividing the total intensity by the illumination area (~300 μm^2). Therefore, the reflectance at the back ITO:PET surface that it is around the 20% of the total incoming light has been already taken into account.

The absorption coefficient of the materials has been obtained for each of the wavelengths by measuring the transmittance of the samples. Applying the Beer–Lambert law:

\[
\alpha_0 = -\frac{1}{d} \ln \left( \frac{I}{I_0} \right)
\]

(1)

where I is the intensity transmitted intensity though the sample, \(I_0\) is the reference intensity taken as the transmitted intensity though an ITO bare substrate, and d is the sample thickness measured with the SFM by scratching the sample. The estimated values are \(\alpha_{\text{MEH-PPV}}(535 \text{ nm}) = 12.7 \times 10^4 \text{ cm}^{-1}\), \(\alpha_{\text{TCBM}}(535 \text{ nm}) = 1.75 \times 10^4 \text{ cm}^{-1}\), \(\alpha_{\text{MEH-PPV:TCBM}}(535 \text{ nm}) = 3.2 \times 10^4 \text{ cm}^{-1}\) for green light and \(\alpha_{\text{MEH-PPV}}(480 \text{ nm}) = 16.8 \times 10^4 \text{ cm}^{-1}\), \(\alpha_{\text{TCBM}}(480 \text{ nm}) = 3.1 \times 10^4 \text{ cm}^{-1}\), \(\alpha_{\text{MEH-PPV:TCBM}}(480 \text{ nm}) = 5.8 \times 10^4 \text{ cm}^{-1}\) for blue light. These values are in agreement with typical values found in the literature for the same materials.

It should be noticed that, in our experimental setup, the red laser (660 nm) of the beam deflection SFM detection system is always present during the “off” and “on” CP measurements. It is expected that the red wavelength does not strongly affect the CP measurements since it is not within the absorption band of MEH-PPV (between 600 and 450 nm). However, to minimize possible red light induced CP changes due to sub band transitions and to improve the SFM resolution, the optical detection system was designed to focalize the laser beam within the cantilever thickness (laser spot less than 20 μm), reducing the scattering below the cantilever and sample heating. In addition, the laser spot was not focalized at the end of the cantilever but it was moved slightly back. Even if this reduces the sensitivity of the detection system, it also avoids the exposure of the measured region to the red laser light. In the present experiments, it has been found that the red light does not induce temperal changes of the CP and, therefore, we will assume that measured CP changes are due only to the external illumination. From now, we will define the in darkness situation (“off”) if only the red laser is turned on, and we will consider the under illumination situation (“on”) when external illumination is applied to the sample.

Photoinduced processes have been studied with the line by line two traces method described in detail elsewhere. Briefly, the fundamental idea of this method is that the tip scans each horizontal line twice. During the first trace, the scan line is performed in darkness while during the second pass the light is switched on, being the only difference between them the
external illumination. This process is repeated for all horizontal lines. In this way, two simultaneous images are recorded for all measured channels (“off” image in darkness and “on” image under external illumination). Therefore each “off”/“on” line can be directly compared and the surface photovoltage, defined as $SPV = -\Delta CP = -(CP_{on} - CP_{off})$, is obtained. The measurements have been performed in three steps. First, a suitable area was selected and the topography and CP images were recorded in darkness to characterize the initial state that will be used as reference to evaluate photoinduced changes. Second, the electro-optical properties of the sample are studied by means of the two traces method. Finally, topography and CP images are again recorded in darkness to check any light induced permanent change and/or to study possible long time charging/discharging processes.

To obtain the sample evolution as a function of the illumination time in the individual materials, each horizontal line of the “off” CP and “on” CP (and $\Delta CP$) image acquired during the two traces method is averaged. We note that this averaging process on the one hand reduces noise, but it also results in spatial averaging of all features along a line. By plotting this average for all the image lines, a CP vs time graph is obtained. Note that with the two traces method two “off”/“on” curves are obtained from the “off” and the “on” images, respectively. Since the illuminated region is much larger than the SFM scanning area, consecutive “off” CP lines are taken in a region that has been already illuminated. Therefore, the evolution of this signal has the information of the permanent and/or long time processes and can be used as “in darkness” CP reference for the following “on” line.31

To analyze the CP and $\Delta CP$ images of the MEH-PPV/TCBM blended samples, the previous spatially averaged analysis is not valid, but also lateral information is needed since different phases coexist within the sample. To establish a possible correlation between topography and CP images, a two complementary mask method has been used. As will be shown below, the MEH-PPV/TCBM blended sample surface consists of a homogeneous distribution of grains. Hence, with an appropriated analysis of the topography image, it is possible to generate two complementary masks; one selecting the high regions (top of the grains) and the other one the low regions (intergrains grains network). In this work, the analysis cutoff has been chosen to be about the half height of the grain high. These masks can be applied to the CP images to “mask” the regions which correspond to the lower and higher regions in the topography, respectively.32

### RESULTS AND DISCUSSION

The work is organized as follows: first the MEH-PPV, the TCBM, and the MEH-PPV/TCBM blended samples are characterized in darkness. Then the wavelength dependent light-induced phenomena are studied for individual MEH-PPV and TCBM thin film samples and finally similar experiments are performed for MEH-PPV/TCBM blended samples. In all samples, the same methodology has been used: Once a representative sample region is selected, the photo response to green light (535 nm) is characterized by means of two traces method. Then the sample is kept in darkness for a period of time until a stable CP value is recovered. Finally, in the same region, the two traces method is again applied to study the photo response to blue light (480 nm).

It is not the aim of this work to review the basic concepts of the SPV principle.24 However, some remarks should be made. First, it is important to notice that the formation of an SPV only occurs if there is net charge redistribution. This means that after the neutral exciton photogeneration, the corresponding electron and hole pair should be separated. This happens in the surface charge regions of the polymer interfaces and in the quasi neutral bulk region in the presence of Dember potentials where the internal build-up electrical fields needed to split the exciton are present. Second, as explained in ref 24, the SPV is not strictly a surface property but it is also sensitive to the quasi-neutral bulk (via the Dember effect) and to buried surfaces with the only limitation being the absorption length of the photons. In the present experiments due to the moderate illumination intensity, the quasi-neutral bulk region effects are expected to be negligible and only possible effects taking place at the ITO:polymer, polymer:air or MEH-PPV/TCBM interface will contribute to the SPV. In the present experiments, sample thickness (∼200 nm) is larger or of the order of the absorption length ($l_s$) of the photons in the different materials ($l_{355 \text{ nm}} = 80 \text{ nm}$ and $l_{480 \text{ nm}} = 60 \text{ nm}$ for MEH-PPV, $l_{355 \text{ nm}} = 571 \text{ nm}$ and $l_{480 \text{ nm}} = 320 \text{ nm}$ for TCBM). $l_{355 \text{ nm}} = 300 \text{ nm}$ and $l_{480 \text{ nm}} = 170 \text{ nm}$ for the MEH-PPV/TCBM blend) and a great number of photons will be absorbed before they cross the whole sample. Since in our experimental setup the sample illumination is performed although the buried ITO:polymer interface, it is important to quantify the amount of photons that reach the free sample surface to determine the sample regions that can potentially contribute to the SPV signal. Using eq 1, the intensity at the free sample surface is found to be about $10^{16}-10^{17} \text{ photons s}^{-1} \text{ cm}^{-2}$. This intensity is large enough to induce also SPV effects in the polymer:air interface. Hence, we can conclude that in our experiments, effects in both interfaces can contribute to the SPV measurements. In the following sections, we will come back to this point when needed.

#### Characterization of the Materials in Darkness

The present work is focused on the study of the light-induced electro-optical properties at the nanoscale and their dependence with the wavelength of the light. To do so, first, a detailed characterization of the initial state is needed. Figure 1 shows the typical topography and CP images of thin film samples of MEH-PPV, TCBM, and MEH-PPV:TCBM acquired in darkness on pristine samples never illuminated before. It can be seen that both the MEH-PPV and the TCBM thin films have a mostly flat surface (Figure 1a,c). On the MEH-PPV sample, due to its low solubility, some “bumps” of nondissolved polymer aggregates may be found on the surface of the thin film.33 The morphology of the MEH-PPV:TCBM blended sample does not resemble the morphologies of the constituent materials; instead it shows a granular structure with a grain size of about 100 ± 30 nm.

In the corresponding KPM images (Figure 1b,d,f) it can be appreciated that the MEH-PPV sample has small CP domains (∼80 nm size) with a CP difference of about 60 mV. Further discussion of this CP domain structure can be found in refs 25, 34–36. The TCBM sample surface presents large CP regions of several hundreds of nanometers with a CP difference of about 50 mV. The MEH-PPV/TCBM KPM image (Figure 1f) shows a well-defined CP structure with dark regions surrounded by a brighter network and a CP difference of about 150 mV. Neither for the pure MEH-PPV nor for the TCBM films is the CP domain distribution correlated with topography features. On the contrary in the blended sample a direct correlation can be established between the topography and the KPM image; dark CP regions in the KPM image correspond to the top of the
grains in topography while the brighter CP network corresponds to the intergrains regions. Previous results performed in MDMO-PPV/PCBM blended reported very similar topography and CP as the ones showed in the present work. In those works, the topography grains (dark KPM regions) were identified as PCBM-rich clusters embedded in a MDMO-PPV matrix (bright KPM regions).

**Electro-optical Properties of the MEH-PPV.** Results obtained in the MEH-PPV thin film sample for green and blue illumination are summarized in Figure 2, showing the “on”, the “off” CP as well as the ΔCP curve as a function of time. In a typical “two trace experiment” the “on” and “off” periods are a few seconds. Thus charges photo generated during the “on” trace that are trapped in long living states do not have enough time to relax during the “off” trace. This means that the following “on” trace excites the polymer from an already excited (or not completely relaxed) state. Therefore, the corresponding ΔCP tendency implies that the ΔCP value depends on the original polymer state. This should be taken into account if a MEH-PPV illumination protocol is designed or if it is used in a pulsed device.

When the MEH-PPV sample is illuminated with blue light, a very different behavior is found. Although the ΔCP is also positive, the initial value is much larger and tends to decrease monotonically as the illumination time increases until it vanishes after approximately 800 s. The corresponding CP_{off} and CP_{on} curves tend to increase with illumination time until they overlap. If at this point the light is switched off, then the CP does not recover its initial value; instead, it stays at a higher value indicating that polymer degradation has taken place. This is also confirmed by an optical inspection of the sample which clearly shows that the illuminated region has been photo-bleached. The photodegradation of PPV-based polymers have been extensively studied. Even if there is still some controversy about the possible degradation mechanism, it is well accepted that in ambient air ether and double bonds are

Figure 2. MEH-PPV: (a) CP_{off} (black dots) and CP_{on} (green and blue dots) versus time graph obtained from the line average of the CP_{off} and CP_{on} images acquired using the two traces method for green and blue illumination following the procedure explained in the main text. (b) ΔCP = CP_{on} − CP_{off} vs time obtained from the “on” and “off” curves of (a). The vertical dashed lines indicate the moment when the light is switched on and off during the two traces method. The gray points in (b) correspond to the interval between green and blue light experiments where a traditional one trace image is acquired in darkness. Hence is not possible to calculate the ΔCP.
more sensitive to photo oxidation.\textsuperscript{38} This leads to a reduction of the conjugation length and the absorbance maximum decreases while it is shifted to higher energies explaining the polymer photobleaching.\textsuperscript{39} From the present results, we conclude that the MEH-PPV degradation is strongly wavelength sensitive: while green light mainly induces photo physical reversible processes and a negligible degradation, the irradiation with blue light dramatically degrades the polymer losing the photoactivity.

\textbf{Electro-optical Properties of the TCBM.} A similar experiment as the one discussed in the previous section was carried out for a TCBM thin film. The corresponding results are presented in Figure 3. The first obvious difference between the individual materials is that for TCBM, the CP\textsubscript{on} shifts to lower values when the light is switched on independently of the light wavelength used (green or blue). Therefore, a negative \(\Delta CP\) typical of an n-type material is found. Under green illumination, CP\textsubscript{on} and CP\textsubscript{off} as well as \(\Delta CP\) do not show any tendency for increasing illumination times. A constant \(\Delta CP\) of about \(-75\) mV is measured. Moreover, the CP\textsubscript{off} is always similar to the initial one. This indicates that as in MEH-PPV, the green light does not produce degradation on the time scale of the present experiments. However, contrary to MEH-PPV, for the case of TCBM no slow relaxation photophysical processes are found since the initial state is instantly recovered once the light is turned off. This can be explained taking into account the higher electron mobility of the TCBM \((\mu\approx10^{-3}\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1})\) compared to the low hole mobility of the MEH-PPV \((\mu\approx10^{-6}\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1})\).\textsuperscript{40,41}

The behavior of TCBM is different when blue instead of green light is used to illuminate the sample. Initially, a \(\Delta CP\) of about \(-80\) mV is measured, similar to the value measured with green light. However, under blue illumination both CP\textsubscript{on} and CP\textsubscript{off} curves present an increasing tendency until they reach a saturation value after about 300s. In addition, although the \(\Delta CP\) decreases for increasing illumination times, it does not go to zero as for MEH-PPV, but it tends to a constant value of about 30 mV. When blue light is finally switched off, the initial CP is not recovered. Instead, a higher CP is measured indicating that blue light also induces the degradation of the TCBM. As before, this assumption is confirmed by optical inspection of the illuminated region which has become more transparent than the non irradiated one. Although in the literature many degradation studies of fullerene derivates blended with semiconducting polymers can be found, only a few papers are focused on the degradation of the fullerene derivates themselves.\textsuperscript{38} In them, it was reported that under UV–vis light irradiation, the C\textsubscript{60} moiety degrades much faster than the substituent. This could be an explanation of the present results since the initial fast decay of the \(\Delta CP\) signal can be attributed to the degradation of the C\textsubscript{60} moiety, while the remaining \(\Delta CP\) signal can be due to the much slower degradation of the substituent.

\textbf{Electro-optical Properties of the MEH-PPV:TCBM Blend.} It has been already shown above that when MEH-PPV and TCBM are blended to form the bulk heterojunction, the samples present two kinds of regions with higher and lower CP that are usually associated with MEH-PPV and TCBM rich regions, respectively.\textsuperscript{17} These two different regions are expected to have a different behavior under light exposure. In the individual materials, the overall CP and \(\Delta CP\) evolution for increasing illumination time was analyzed by averaging each line of the “on”/“off” CP images, which implies spatial averaging. However, to study light-induced processes in blended samples, it is not sufficient to have temporal information, also a high spatial resolution is needed. This lateral information should be directly extracted from the CP\textsubscript{on} and CP\textsubscript{off} images as well as from the \(\Delta CP = CP_{\text{on}} - CP_{\text{off}}\) images calculated from the corresponding images. The results obtained for a MEH-PPV:TCBM thin film sample using the two traces method with green illumination are shown in Figure 4. The two CP regions are well distinguished both in the CP\textsubscript{off} and CP\textsubscript{on} images (Figure 4b,c). In addition, it can be seen (Figure 4d) that when the light is switched on some regions present a p-type behavior with \(\Delta CP > 0\) (\(\sim30\) mV) (MEH-PPV like behavior) while other regions show a \(\Delta CP < 0\) (\(\sim50\) mV), as in an n-type material (TCBM-like behavior).

It was mentioned above that dark and bright CP regions are correlated with the grains and intergrains regions of the topography image, respectively. In order to further illustrate this point, as explained in the Experimental Section, we applied two complementary masks obtained from the topography image to the CP images; one blocking the top of the grains and the other one the intergrains region (Figure 4a, left and right bottom panels, respectively). In order to avoid confusion, we note that each of the lower panels of Figures 4b–d correspond to the same region marked with a rectangle on the corresponding upper image observed through the two different complementary masks. When these masks are applied to the CP\textsubscript{off} and CP\textsubscript{on} images (Figure 4b, bottom panels) the strong correlation between bright and dark CP regions with intergrains and grains regions, respectively, is confirmed: in both cases, the left half of the image has a higher average CP (the color of the nonmasked part of the image is brighter) than the right half of the image (the mask that leaves the top of the grains region unblocked), where the CP that is seen through the mask is clearly lower. To study the light-induced behavior of the

Figure 3. TCBM: (a) CP\textsubscript{eff} (black dots) and CP\textsubscript{on} (green and blue dots) versus time graph obtained from the line average of the CP\textsubscript{off} and CP\textsubscript{on} images for green and blue illumination. (b) \(\Delta CP\) vs time obtained from the “on” and “off” curves of (a). The vertical dashed lines indicate when the light is switched on and off. The gray points in (b) correspond to the interval between green and blue light experiments where a traditional one trace image is acquired in darkness.

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different CP regions individually, the same masks are applied to the ΔCP image (Figure 4d bottom panel). It is seen that bright CP regions have a ΔCP > 0 (more yellow color is observed through the mask) that resembles the MEH-PPV behavior, while the dark CP regions present mostly a negative ΔCP (more blue color is observed through the mask) corresponding to a TCBM-like behavior. We find that the light-induced positive and negative ΔCP shift in each of the regions (about +30 mV and −50 mV) is lower than the one found in the individual materials (+120 mV and −75 mV for MEH-PPV and TCBM, respectively). Since the lateral resolution of the KPM technique is larger than the typical p and n regions size, 12 in the present case, the sample seems to be composed of TCBM rich regions that form granular clusters embedded in a rich MEH-PPV matrix and not pure MEH-PPV and TCBM regions. Moreover, the correlation between topography and ΔCP image is not always well-defined; a few grains in topography present ΔCP > 0. There are some large granular regions that present a higher CP than the rest of the sample having ΔCP essentially null. This can be attributed to sample heterogeneities with a different TCBM:MEH-PPV ratio or clusters covered by a thin MEH-PPV film. 17 Finally, under green illumination, the average
ΔCP is only shifted about −10 mV with respect to the zero. From these results, we can conclude that the photogenerated charge is effectively redistributed in the p-type MEH-PPV and n-type TCBM-rich regions shifting their CP to positive and negative values, respectively. The CP_{on} and CP_{off} values are constant with the illumination time in both regions, and the initial CP value is instantaneously recovered when the light is switched off. Hence, the presence of TCBM in the blend inhibits the long living charge trapping in the MEH-PPV. This fact contrasts with previous KPM measurements under illumination reported by Maturowá et al.23 performed in thin film (100 nm) MDMO-PPV:PCBM blends spin-cast from toluene solution. In those experiments, the CP was dominated by the charge trapping in long living states rather than by an electron and hole redistribution, as is found in our experiments. This was attributed to electron trapping mainly in the PCBM phase and it was modeled with a 2D charge diffusion model in which both materials are in contact with the underlying electrode. On the contrary, in the present experiments no sign of electron trapping in the TCBM is found, neither in the pristine nor in the blended sample. In fact, the electron trapping is found to take place only in the pristine MEH-PPV and it is reduced when TCBM is added. As has been mentioned above, the nanomorphology of the blend plays a crucial role in the electro-optical properties. Those samples present a phase separation of the order of several hundreds of nanometers, much larger than the phase separation in our (also thicker) samples that is about 100 nm. In addition, it was shown that the underlying contact material strongly affects the CP_{on}. In the present samples, the active layer is directly deposited on the ITO while in Maturowá’s samples a PEDOT:PSS layer is included. This layer blocks the diffusion of the electrons to the contact. Finally, those experiments were performed with a tungsten white lamp with a broad spectral distribution. Even if yellow-red wavelengths are above the materials absorption band, they can produce sub band transition from (or to) localize states to the conduction band (or from the valence band) that can affect the SPV.24 As was discussed above, in our experiments this contribution is negligible.

A very different behavior is observed when the sample is illuminated with blue light. The results are shown in Figure 5. In the CP_{on} and CP_{off} images (Figure 5b,c), it can be appreciated that the bright and dark CP regions that are well distinguished at the first illumination stages become blurred for larger illumination times. In addition, the mean CP_{on} and CP_{off} values increase with the illumination time and do not recover their initial value once the light is switched off indicating that photodegradation has taken place. This behavior is similar to the one found in the pure materials. In the ΔCP image (Figure 5d), it is seen that at short illumination times, the sample presents a p-type positive ΔCP, and no regions with n-type negative ΔCP are observed. However, ΔCP is not homogeneous but different regions with ΔCP ≈ ±100 mV and ΔCP = 0 mV can be distinguished. As the illumination time increases, the situation is reversed and the most of the sample surface has a ΔCP < 0, although some regions remain with a small positive ΔCP.

A similar mask-based analysis as the one used with green illumination is performed to check if there is any correlation between the initial bright and dark CP regions and regions with different ΔCP as well as to study its evolution as a function of the illumination time (Figure 5 bottom panels). Surprisingly, no correlation is found: regions with different ΔCP cannot be assigned to any topography feature neither with the bright and dark regions in the CP images. This means that under blue illumination, the rich MEH-PPV and the rich TCBM regions associated to bright and dark regions, respectively, in the in darkness CP image do not behave as p- or n-type. On the contrary, initially the light induces changes in the whole MEH-PPV/TCBM blended sample that seem to be dominated by the MEH-PPV, being the ΔCP positive while at longer exposures times, the sample behaves mostly as TCBM being the ΔCP negative. This can be explained taking into account that MEH-PPV and TCBM have not completely segregated, instead we have MEH-PPV- and TCBM-rich regions. In addition, the degradation induced by blue light is different in both materials. For the same illumination intensity, while the MEH-PPV completely loses its photoactivity after a certain period of time (after 800s in our case), the TCBM is degraded quickly at the beginning (after 300s in our case), but it keeps a remaining negative ΔCP even for very long exposures. Since at the wavelength used in this study, the absorption coefficient of the MEH-PPV is about 1 order of magnitude larger than the TCBM one, the faster degradation of the MEH-PPV phase is probably related to the larger number of photons absorbed in it. Therefore, initially the MEH-PPV dominates the sample CP behavior until it becomes highly degraded, then the sample can be considered as TCBM clusters that are degraded but still photoactively distributed in a non-photoactive matrix. It should be noticed that if the degradation time of the MEH-PPV is taken as the moment when the average ΔCP goes from positive to negative values, a significant difference between the time needed to degrade the MEH-PPV in a pure sample and in a blended one is found. This is in good agreement with previous results confirming that the addition of fullerene derivates to the MEH-PPV retards its degradation.38 None of the previous KPM studies performed under illumination in similar systems take into account the possible contribution in the CP due to photodegradation. This is because they are usually performed under UHV or N₂ atmosphere.16,23 Under oxygen-free conditions, the degradation is reduced. However, it should be highlighted that depending on the illumination conditions, the contribution of the degradations to the CP measurements cannot be negligible. In fact, even under UHV or N₂ conditions, the degradation is not completely suppressed since the polymer suffers photolysis.42

**CONCLUSIONS**

In summary, we have characterized the nanoscale electro-optical properties of MEH-PPV and TCBM thin film samples as well as the p-n “bulk heterojunction” in MEH-PPV/TCBM blended samples by using KPM combined with external illumination. In the pure samples, it has been found that green light only induced photophysical reversible processes. On the contrary, the samples irradiated with blue light suffered a strong material degradation leading to photobleaching. However, blue light degradation effects are different in both materials: while in MEH-PPV, the photoactivity is quickly lost, in TCBM there is a small photoactivity remaining that survives even for long exposures.

In the MEH-PPV/TCBM blended sample, even when the sample is kept in darkness, two well differentiated types of CP regions are found. These regions that are strongly correlated with the topography grains and intergrains regions can be ascribed to TCBM and MEH-PPV rich regions respectively. Under green illumination, while the MEH-PPV rich regions...
present a p-type behavior, the TCBM-rich regions show an n-type one as expected for a p-n disperse junction. This means that the photogenerated exciton is effectively split and the electron and hole are redistributed in the corresponding materials. In addition, no sign of sample photodegradation due to green light exposure has been found. On the contrary, when the sample is illuminated with blue light, the p- and n-type regions are not well-defined, and no correlation with the initial CP regions can be established. Instead, the sample response is dominated by the degradation of the individual materials: at low illumination times, the sample behaves mainly as MEH-PPV, whereas for longer illumination it shows a TCBM-like behavior.

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: elisaple@um.es*

**Notes**

The authors declare no competing financial interest.

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(32) Topography image flooding as well as the mask application to the CP images has been done with the WSxM free available software.


