Photochemical Transformations in Fullerene and Molybdenum Oxide Affect the Stability of Bilayer Organic Solar Cells

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Thin films of fullerene C₆₀ and molybdenum oxide (MoO₃) are ubiquitously used as electron acceptor material and hole extraction interfacial layer for the fabrication of organic photovoltaic (OPV) cells. It is well known that light exposure induces color changes in MoO₃ (photochromism) and the formation of intermolecular bonds between C₆₀ molecules (photopolymerization). The influence of these photoinduced reactions on the long-term stability of OPV cells, however, has not previously been studied in detail. We present a study and discuss the early (< 5 days) aging mechanisms occurring in illuminated ITO/MoO₃/organic cyanine dye/C₆₀/Alq₃/Ag bilayer solar cells under nitrogen atmosphere. We identify a degradation process at the organic heterojunction and the formation of Mo⁵⁺ species during illumination that adversely affect cell behavior. For these widely used materials, our results suggest that light processing is a first necessary step before OPV characteristics can be meaningfully rated.

1. Introduction

Rapid progress is made in the field of organic photovoltaics and power conversion efficiencies of 8-10% have repeatedly been reported.^[1-3] As exciting as these advances are, an important requirement for their commercialization is the demonstration of OPV cells that maintain the initial performance over an operating time of several years. However, increasing the lifetime of OPV cells remains a major challenge, with extrinsic (water, oxygen or light) and intrinsic (e.g. morphology changes) stress factors inducing cell degradation in a complex and often interrelated way.^[4-8]

Buckminsterfullerene C₆₀ and molybdenum trioxide MoO₃ are very widely used materials in OPV cells. C₆₀ has been a key molecule in the development of the entire OPV field and is still frequently used as electron acceptor material.^[9-12] More recently, MoO₃ has been recognized as a promising anode interfacial layer in OPV cells. The low charge

injection/extraction barrier at MoO₃/organic interfaces is believed to be due to the favorable energy level alignment between the high work function value of MoO₃ and the highest occupied molecular orbital of an organic molecule.^[13] However, due to the complex chemistry of that material and the strong impact of sample preparation history on the electronic properties, a coherent understanding of the hole extraction process across MoO₃ in OPV cells is still lacking.^[14-21] Thin MoO₃ films have been deposited by thermal evaporation^[22] or via coating-processes using precursor solutions or nanoparticle dispersions.^[14,20,23-25]

It is well known that both C₆₀ and MoO₃ are photosensitive materials, but possible implications on the stability of OPV cells are largely unidentified. Visible and UV light exposure of oxygen-free solid C₆₀ can transform monomers into dimers, oligomers and polymers via the formation of intermolecular bonds in a 2+2 cyclo-addition process.^[26,27] The thermal decomposition reaction back to the monomers must be taken into account for temperatures above 100 °C.^[28] The distance between neighboring C₆₀ molecules decreases by ~10% when a weak van der Waals bond is replaced by two covalent bonds. Therefore, the polymerization reaction is associated with a decrease of the bulk volume.^[29,30] A similar photochemical reaction occurs for [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) films. Exposing PCBM monomers to light leads to the formation of dimers, although higher oligomers are not produced, probably for steric reasons. The importance of this process has been realized for high-resolution electronic active patterning purposes of fullerene thin films.^[31,32] In the OPV field, the PCBM dimerization has recently been found to be responsible either for a device performance loss, due to a reduced electron mobility, or an enhanced morphological stability of the active blend film, resulting in an increase of the overall cell lifetime under modest thermal stress conditions.^[33,34]

Thin films of MoO₃ can be permanently coloured blue by excitation using UV light.^[35] The photochromic mechanisms are still not fully resolved and controversially discussed. The occurrence of optical absorption in the visible and near-infrared wavelength region is

associated with oxygen vacancies and the presence of lower valence Mo^{5+} states in MoO_{3-x} ^[36-38] since pure MoO_3 shows little photochromism.^[35,39] In one model, it is proposed that colour centres are formed when photo-excited electrons are trapped in oxygen vacancies.^[38] These trapped electrons can be excited into the conduction band by red light resulting in a blue film colour. In the presence of hydrogen donors, an additional mechanism must be considered. When excited with UV light, electrons and holes are formed in MoO_3 , followed by reaction of the holes with surface-absorbed molecules, causing the film to be negatively charged. The positive ions on the surface then diffuse into the film driven by Coulomb force, forming the hydrogen molybdenum bronze $\text{H}_x\text{Mo}_x^{5+}\text{Mo}_{1-x}^{6+}\text{O}_3$.^[19,40] The film colour develops due to charge transfer between Mo^{5+} and neighbouring Mo^{6+} . A similar charge transfer can occur after self-trapping of excited electrons in low-energy sites leading to Mo^{5+} .^[35] Irrespective of the processes leading to film colour, the presence of Mo^{5+} seems to be a necessity. Notably, the Mo^{5+} content has been reported to increase during illumination, concomitant with the increase of the visible absorption.^[35,38,39]

Interestingly, it seems that despite these extensive research activities on the phototransformations occurring in C_{60} and MoO_3 thin films, their importance in conjunction with the stability of OPV cells containing these materials has not been identified and addressed to date.^[8,41-50] Here, we present a detailed study on the early aging mechanisms in such solar cells during illumination and link degradation to the occurrence of photopolymerization in C_{60} and photochromism in MoO_3 directly. To avoid morphological stability issues known from blended organic donor-acceptor films, we have chosen a simple bilayer film design composed of an organic cyanine dye (Cy3-P) donor / C_{60} acceptor heterojunction.^[51] OPV cells were fabricated in the so-called regular geometry by sandwiching the organic film between an ITO/ MoO_3 anode and an Ag cathode. In this architecture, impinging light travels first through MoO_3 followed by the organic bilayer.

Thereby, both photosensitive materials are simultaneously exposed to sunlight and can be studied at the same time.

2. Results and Discussion

2.1. Kinetics of Phototransformations

Figure 1 shows the temporal evolution of UV-vis spectra for thin films of Cy3-P, C₆₀ and MoO₃ that were irradiated for 24 h under OPV device relevant conditions at 1 sun intensity. No changes are observed for the dye film indicating that Cy3-P is photostable when illuminated in the absence of oxygen and water (Figure 1a).^[51] For C₆₀, the energy of the lowest, optically forbidden, singlet excitation is at about 1.9 eV, the spectral intensity in the region 2.4-2.8 eV is due to charge-transfer-type excitations between molecules in the film, and the first allowed electronic transitions is at about 3.6 eV.^[27,52,53] Upon irradiation, the C₆₀ absorption band at 349 nm broadens and the maximum blueshifts slightly to 342 nm after 24 h (Figure 1b). Note the characteristic increase in absorption at 321 nm during illumination. No further changes in absorption were observed for irradiation times longer than 24 h. For MoO₃, illumination continuously increases the absorption in the near-infrared region (Figure 1c). Changes in the UV-vis absorption spectra are best visualized for pure C₆₀ and MoO₃ films, but very similar trends were observed for Cy3-P/C₆₀ and MoO₃/Cy3-P bilayer films and for the full ITO/MoO₃/Cy3-P/C₆₀ solar cell layer stack as well (Figure S1).

For C₆₀, changes in the UV-vis spectrum are due to the light-induced dimerization, oligomerization and finally three-dimensional polymerization between fullerene molecules.^[26] This reaction can be followed by Raman spectroscopy (Figure S2).^[28] We used the decrease of the 1468 cm⁻¹ band representing the pristine C₆₀ molecules as a direct measure for the kinetics of the dimerization reaction (Figure 1d). The reaction proceeds rapidly during the

first ~6 h with a dimerization yield of ~70% and then levels off, both for pure C₆₀ and Cy3-P/C₆₀ films.

We found a good correlation between Raman data and the relative increase of the UV-vis absorption at 321 nm (Figure 1e). Therefore, UV-vis spectroscopy can be used as a convenient tool to follow the light-induced C₆₀ transformation. Even after 24 h light irradiation, however, the polymerization is not complete and C₆₀ monomers, oligomers and polymer chains coexist in the film, as inferred from Raman spectra. Despite this incomplete transformation, C₆₀ films became insoluble in the solvent toluene during light processing (Figure S3), confirming the intermolecular bond formation process.^[26,28,29]

The kinetics of the MoO₃ phototransformation was evaluated from the increase in the absorption spectra at 700 nm (Figure 1f). Similar to C₆₀, changes are most pronounced during the first few hours of illumination, but pure MoO₃ films transform more effectively than MoO₃/Cy3-P bilayers. Optical modeling showed that the integrated absorbance is ~ 6% higher for a pure MoO₃ sample compared to the one with an additional Cy3-P layer (Figure S4 and Figure S5). This is much less than the observed difference in Figure 1f. Therefore, it is likely that the reaction routes leading to film coloration are different when comparing pure MoO₃ with a metal oxide that is covered with an organic layer.

2.2. Device Performance During Light Processing

Figure 2 shows the J-V characteristics for a cell during 24 h illumination. At time = 0, V_{oc} = 0.86 V, J_{sc} = 4.4 mA cm⁻² and FF = 68% were measured, resulting in a power conversion efficiency of $\eta = 2.6\%$. For longer times, both V_{oc} and J_{sc} decayed in a two-step process, and a fast initial decrease during the first ~ 6 h leveled off for longer irradiation times. This trend very much resembles the kinetics of phototransformations observed in C₆₀ and MoO₃. Fill factors (FF) of our solar cells were high and changes in FF were small. During the first hour,

FF increased to 73% and then slightly decreased to a final value of 65%. Similar small relative FF changes of less than 10% were found throughout this study (Figure S6).

We have measured the stability of cells using three different approaches in order to identify the critical materials inducing degradation and to rate their relative importance. In a first set of experiments, individual layer stacks were pre-irradiated for 24 h at room temperature before completing the cells. J-V characteristics of these devices were then measured for another 24 h under continuous irradiation. Because each additional layer also creates an interface with the subjacent material, J-V trends cannot be related clearly to bulk material or interface processes without further experiments. Starting values of V_{oc} and J_{sc} are indicated in Figure 2c and 2d (▼ 1 – 4), the temporal development over the following 24 h is shown in Figure 2e and 2f. It should be noted that we can only extract trends from this analysis rather than quantitative data. First, the scattering in currents from different samples was relatively large ($\pm (0.2\text{--}0.4) \text{ mA cm}^{-2}$, Table S1). In addition, the amount of light absorbed by individual materials changes when present in different layer stacks. When a full device is illuminated, the top Ag electrode acts as a mirror and light that is not absorbed is reflected back through the active layers.

Pre-irradiation of a glass/ITO substrate (▼ 1) had no influence on the initial cell performance and the subsequent degradation followed the typical two-stage behavior. On the other hand, pre-irradiation of MoO_3 -containing layers resulted in decreased, but stable for the long-term, V_{oc} values after cell fabrication, with values almost matching those of an untreated cell after 24 h illumination (Figure 2c and 2e). This result strongly suggests that mainly MoO_3 is responsible for the observed voltage decay, since pre-irradiation of this layer alone is sufficient to induce the observed changes.

The results in Figure 2d further show that pre-irradiation of a C_{60} -containing layer (▼ 4) induced the largest drop in starting current, indicating the adverse influence of the

photopolymerization reaction. During further illumination, however, the current remained stable. Additionally, pre-treated MoO₃ and MoO₃/C₆₀-P cells started at reduced current values, but these devices showed the known current decay trend, due to the proceeding C₆₀ phototransformation. An interesting question is whether the overall long-term stability can be improved by a pre-irradiation step of individual layers before the cell is completed. This is not the case, since un-treated and pre-irradiated cells all ended up a $\eta = 1.3\%$ (Table S1) after 24 h of illumination. This corresponds to a performance loss of 50%.

In a further approach, we were able to separate the phototransformation kinetics of C₆₀ and MoO₃ to some extent by lowering the temperature during illumination. It is well known that C₆₀ molecules rotate above $\sim -15\text{ }^{\circ}\text{C}$ almost freely about their lattice positions. Below that temperature the rotation becomes restricted and finally freezes below $\sim -190\text{ }^{\circ}\text{C}$.^[54] It has further been shown that the photopolymerization efficiency is correlated with the C₆₀ rotation rate. For low temperatures, the reaction is effectively absent, and at the threshold temperature the polymerization starts.^[28]

Cell stability was measured at $-30\text{ }^{\circ}\text{C}$. At this temperature, the C₆₀ photopolymerization is considerably slowed down and reached 20% after 24 h of illumination. This corresponds to a degree of transformation that is attained after $\sim \frac{1}{2}$ h at $43\text{ }^{\circ}\text{C}$. On the other hand, no temperature dependence was found for the photoreaction of MoO₃ (Figure S7). Voltage trends at low and high temperatures were identical (Figure 2e, labels 0 and 5). This supports our above findings that mainly the phototransformation in MoO₃ is responsible for the drop in V_{oc} . We can further approximate that at $43\text{ }^{\circ}\text{C}$ phototransformations in C₆₀ and MoO₃ almost equally contribute to the observed current decay (Figure 2f).

Finally, irradiation in selective wavelength regions was used to address the influence of phototransformations in C₆₀ and MoO₃ on cell stability individually. We used a cutoff filter that blocks light at wavelengths below 550 nm to separately excite C₆₀ from MoO₃.^[13,18] Illuminating MoO₃ with filtered light did not induce any changes in the UV-vis absorption

spectrum, but the polymerization of C_{60} still took place (**Figure 3a**). After 24 h, the C_{60} photo transformation reached a degree of about 50%, lower than the 80-90% transformation observed when white light was used.

J-V characteristics were measured over a period of 120 h and for the first 96 h of illumination filtered light was used. During the first 24 h V_{oc} decayed by $\sim 6\%$ only (Figure 3b), much less than the $\sim 32\%$ when using white light. In addition, part of the V_{oc} drop is due to heating the cell during illumination.^[55] Open circles in Figure 3b indicate V_{oc} values measured after storage in the dark allowing the cell to cool down to room temperature. During 24 - 96 h of illumination, V_{oc} remained essentially constant. This clearly confirms that the major part of V_{oc} degradation is not induced by the C_{60} photopolymerization. After 96 h the filter was removed and white light was used for illumination. The drop in V_{oc} during the time period 96 - 120 h must be due to photoinduced transformations in MoO_3 and/or at the metal oxide/Cy3-P interface, since the C_{60} polymerization has already taken place using filtered light. The J_{sc} trend over a period of 120 h illumination supports our findings that both phototransformations in C_{60} and MoO_3 contribute approximately equally to the current decrease (Figure 3c). J_{sc} drops by $\sim 13\%$ during the first 96 h of filtered light illumination due to the polymerization of C_{60} , and another $\sim 12\%$ due to MoO_3 when using white light during 96-120 h.

2.3. Degradation Mechanisms

It is clear that temporal trends in UV-Vis spectra and J-V characteristics cannot be linked to specific failure mechanisms directly.^[5] The unchanging dye absorption spectrum during illumination and the similar J-V characteristics of cells using pre-irradiated MoO_3 and MoO_3 /Cy3-P layers indicate that the bulk of the dye film is stable and that the influence of Cy3-P on degradation must be small. This is also supported by the relative stability of cells during 96 h illumination using wavelengths above 550 nm where a Cy3-P film has actually

the absorption maximum ($\lambda_{\text{max}} = 578 \text{ nm}$). To detect small amounts of Cy3-P degradation products at the metal oxide/dye interface, we carried out ESI-HRMS experiments (Supporting Information S8). Also these measurements confirmed the photostability of Cy3-P and no transformation products could be clearly assigned to photoinduced reactions during white light illumination under nitrogen. The experimental observation (Figure 1f) that the increase in visible absorbance is relatively suppressed for MoO_3 when coated with Cy3-P remains unexplained at this time, but probably cannot be linked to the chemical instability of Cy3-P. A similar result on the complex metal oxide/organic interface has been reported recently, and it was found that the evolution of Mo^{5+} states upon thermal annealing was larger for pure MoO_3 when compared to a MoO_3 /organic layer.^[20]

We now consider the impact of light-induced C_{60} polymerization on cell performance. Firstly, it has been reported that the C_{60} electron mobility μ_e drops by 10% upon full polymerization.^[29] In our case the transformation is not complete, and a partial polymerization is expected to induce the formation of traps due to spatial and/or energetic heterogeneity, effectively lowering μ_e further. By opto-electrical simulations (Supporting Information S9), however, we could show that a lowering of μ_e over 2 orders of magnitude (from $8 \cdot 10^{-2}$ to $8 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) does not explain the observed drop in J_{sc} and V_{oc} (Figure 3). This is supported by the very high fill factors of our devices.

Next, we examine the impact of the volume decrease of a C_{60} film upon polymerization. We suggested previously that this could result in the formation of voids effectively decreasing the contact area between C_{60} and the adjacent layers.^[51] AFM images of pristine and illuminated Cy3-P/ C_{60} bilayer films are shown in **Figure 4**. Before illumination, the film is pinhole-free with a root-mean square (rms) roughness of 1.6 nm. During phototransformation, cracks are formed and the topography smoothens (rms roughness 0.3 nm). At the C_{60} /top metal interface, a decrease of the physical contact area would diminish the active electrode area leading to a reduction in charge extraction. This phenomenon has

been experimentally found for solar cells using a calcium/aluminium electrode and resulted in a rapid decay of J_{sc} , while FF and V_{oc} remained relatively stable.^[56] We found the same J_{sc} values for full cells that were illuminated for 24 h and for devices where the Ag electrode was evaporated only after pre-irradiation of the ITO/MoO₃/Cy3-P/C₆₀/Alq₃ layer stack (Figure 2d). This indicates that in our case a reduction of the contact area between C₆₀ and Ag is probably not occurring.

To examine a possible formation of voids at the hidden dye/C₆₀ heterojunction, we used fluorescence spectroscopy as a probe that is sensitive to a changing charge generation yield. By comparing bilayer film spectra before and after illumination, we indeed observed a substantial increase of the dye emission (Figure 4c, Figure S10). Additionally, the C₆₀ emission increased after light treatment with a concomitant redshift due to the fullerene polymerization, in agreement with literature.^[26,34] This supports the proposal that, due to a reduction of the interface contact area when the polymerizing C₆₀ film contracts, a fraction of excitons in Cy3-P and C₆₀ cannot be separated anymore and must decay partly by fluorescence. This scenario is further consistent with the spectrally resolved external quantum efficiency data displayed in Figure 4d. During illumination, IPCE values uniformly decreased across the entire spectral range where C₆₀ and Cy3-P absorb. This excludes degradation processes which affect the exciton diffusion lengths in Cy3-P or C₆₀ individually, since then the IPCE change would exhibit a wavelength dependency.

We cannot clearly relate the small relative (8%) V_{oc} drop during 96 h of filtered light illumination to the C₆₀ photopolymerization. Again, initial V_{oc} values of cells fabricated by evaporating the top metal electrode after a pre-illumination period were lowered, excluding an adverse effect occurring at the C₆₀/Ag interface during photopolymerization. In addition, the reduced charge generation yield at the heterojunction does not induce a V_{oc} drop (Supporting Information S9). In principle, an increase of the energy of the C₆₀ lowest unoccupied molecular orbital could explain the observed V_{oc} decay.^[57,58] It appears, however, that while

polymerization of C₆₀ induces a small decrease of the optical bandgap (as inferred from photoluminescence), this change is primarily associated with an energy shift of the highest occupied molecular orbital, as measured by UPS (Figure S11).^[59,60]

Our results show that illumination of a MoO₃ thin film with UV light induces a substantial drop in cell performance over time. We can connect this trend with the photochromic phenomenon in MoO₃, and thereby to the presence of Mo⁵⁺ species directly. XPS was used to detect the presence of reduced Mo species (Figure S12). Experiments were carried out for as-deposited MoO₃ films and after 24 h illumination. While for untreated films Mo⁵⁺ was not detected, Mo⁵⁺/Mo⁶⁺ was ~ 0.03 after 24 h. This clearly confirms that during illumination Mo⁵⁺ is formed and that these species are closely linked to the occurrence of photochromism.

Slightly sub-stoichiometric MoO_{x<3} is n-doped,^[13,14,19,37] with the presence of Mo⁵⁺ resulting in the formation of isolated, occupied gap states during illumination close to the conduction band.^[13,15] These states cause the Fermi level (E_F) to be shifted upwards, thus reducing the work function. UPS spectra were measured on as-prepared and illuminated MoO₃ films (Figure S13). The work function for untreated MoO₃ was measured at ~5.6 eV, and was reduced to ~5.3 eV after illumination, consistent with the expected trend. At the same time, a substantial amount of gap states arose between 1 eV and 2 eV below E_F.

Cy3-P has a deep-lying HOMO energy of ~5.7 eV, as measured by cyclic voltammetry.^[61] This suggests a balanced energetic situation at the MoO₃/dye interface for short illumination times, allowing for efficient hole extraction via electrons that travel towards the organic interface and recombine with photogenerated holes. During illumination, the reduction of the work function results in an unfavorable change in the energy alignment between MoO₃ and Cy3-P, reducing cell performance.

In general, the presence of Mo⁵⁺ and their subtle influence on solar cell performance is not fully elucidated so far and results seem to be contradictory in some cases. Using the

poly(3-hexylthiophene), P3HT, /PCBM material system and ITO/MoO₃ as anode, it was reported that an increased density of Mo⁵⁺ is detrimental to the device performance.^[20] These findings are contrary to the results of experiments that showed that Mo⁵⁺ can play a dominating role in improving cell performance.^[21] For P3HT/PCBM OPV cells, it was found that V_{oc} and J_{sc} were reduced when using a MoO₃ hole collection layer as compared to poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate).^[17] At the same time, FF was enhanced due to the reduced series resistance in MoO_x. This was explained by charge recombination at Mo⁵⁺ gap states.

One issue relates to the varying reported values of electronic states in MoO₃ that so sensitively depend on the processing history before characterizing the device. For example, the electron affinity, work function and ionization energy of vacuum-deposited MoO₃ are at 6.7, 6.9 and 9.5 eV, respectively.^[16] A short air exposure reduces the values by about 1 eV.^[17] A quick shift to lower values was even found for MoO₃ samples that were stored under nitrogen for several hours, due to residual water in the glovebox.^[18]

For organic molecules in contact with metal oxides, it was observed that energy level alignment between the materials donor and acceptor states occurs when the organic's ionization energy equals the substrate's Fermi energy.^[13] Ground state electron transfer was also observed from organic semiconductors to freshly evaporated MoO₃.^[18] De-doping over time was explained by changes in the MoO₃ energy levels, resulting in a suppression of charge transfer when the MoO₃ electron affinity becomes smaller than the ionization energy of the organic material.

These results imply that the influence of the MoO₃ photochromism on OPV cell stability might depend sensitively on the ionization energy of the used organic donor material and must be studied from case to case. We note that the photochromism is not limited to the pure metal oxide and the MoO₃/Cy3-P material system we studied here in detail. In preliminary work, we found similar absorbance changes in illuminated MoO₃ when coated

with P3HT or PTB7 (Figure S14), notably polymers that are among the most widely used and best-performing OPV materials. Possible implications on the long-term stability of these OPV cells are the subject of ongoing work.

3. Conclusions

Our results suggest that for regular OPV cell architectures comprising MoO₃ and C₆₀, performances should be measured and reported only after a preceding light processing step. The polymerization of C₆₀ appears to be an inevitable consequence when exposed to light, and when using sunlight the relevant photochemistry influencing device behavior develops over a timescale of a few hours. The same timescale was found here for the film coloration to occur in MoO₃, but in the general case, this might be sensitive to the chemical and electronic nature of the overlying organic donor layer. There are two apparent routes to prevent the photochromic effect in MoO₃. In the regular device geometry, a filter that blocks light at wavelengths below ~ 400 nm can be used, corresponding to the optical bandgap of MoO₃. This prevents film coloring but such OPV cell will display a lowered performance, because a considerably fraction of current is generated in the UV wavelength region, typically due to light absorption by the fullerene component. The second possibility is to use MoO₃ in the so-called inverted device structure. In this geometry, the metal oxide is situated next to the top electrode and protected by the underlying organic materials that will absorb most of the impinging light.

4. Experimental Section

Solar cells with active areas of 3.1 and 7.1 mm² in the configuration glass/140 nm ITO/30 nm MoO₃/20 nm Cy3-P/40 nm C₆₀/2 nm Alq₃/80 nm Ag were fabricated as reported.^[51] Materials were ITO (Geomatec, resistivity 20 Ohms square⁻¹), 1-ethyl-2-[3-(1-ethyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-propenyl]-3,3-dimethyl-3H-indolium hexafluorophosphate (Cy3-P,

FEW Chemicals), MoO₃ (Sigma Aldrich, 99.99%), C₆₀ (SES Research, 99.5% or 99.9%), tris-(8-hydroxyquinoline) aluminium (Alq₃, Sigma-Aldrich, 99.995%) and Ag (Cerac, 99.99%). All evaporations were carried out in the same vacuum chamber ($\sim 4 \cdot 10^{-6}$ mbar) with deposition rates of 0.2 Å s⁻¹ for C₆₀, Alq₃ and MoO₃, and of 0.5 Å s⁻¹ for Ag.

Film thicknesses were determined by profilometry (Ambios XP1). AFM measurements were performed on a Nanosurf Mobile S in tapping mode at a resonance frequency of 170 kHz using silicon cantilevers. Current-voltage (J-V) characteristics were measured using 100 mW cm⁻² simulated AM 1.5G solar irradiation on a calibrated solar simulator from Spectra-Nova. IPCE spectra were measured using a monochromator and the light from a 300 W Xe lamp together with an AM1.5G filter set. The monochromatic light intensity was determined using a calibrated Si-diode. Raman measurements were performed in ambient conditions with a Horiba Labram Evolution 800 spectrometer. Absorption spectra were measured on a Varian Cary 50 UV-vis spectrophotometer. Fluorescence spectra were measured on Horiba Jobin Yvon Fluorolog. Electrospray-high resolution mass (ESI-HRMS) measurements were performed on an Agilent 6530 QTOF mass spectrometer. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed in an OMICRON photoelectron spectrometer under UHV (5×10^{-11} mbar range) conditions. A discharge lamp (He I: $h\nu$: 21.2 eV) and VSW EAC 300HR energy analyzer were used. MoO₃ samples were biased at -9.6 V relative to the spectrometer and measured at room temperature. The Fermi level of the spectrometer was determined by measuring the Fermi edge of a Cu crystal. A 300 W Xe lamp was used as a light source for illumination of C₆₀ films between consecutive UPS spectra. In situ X-ray photoelectron spectroscopy (XPS) surface analysis was performed in a modified VG EscaLab spectrometer with a base pressure below 10^{-9} mbar. XPS spectra were collected with a SPECS PHOIBOS 100 analyzer using a non-monochromatic x-ray source (Mg K alpha: 1253.6 eV). The binding energy was re-calibrated using the O1s peak set to

530.0 eV. Further experimental details on Raman, ESI-HRMS, UPS and XPS measurements are given in the Supporting Information.

Samples were never exposed to ambient atmosphere during fabrication and light processing. Devices were fabricated in a glove box under nitrogen ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 10$ ppm) and were then mounted into a homemade air-tight transfer box. J-V characteristics were measured and light processing was carried out outside the glovebox using the solar simulator. The actual temperature in the transfer box during illumination at ambient was 43 °C. For the pre-irradiation of individual layer stacks, samples were transferred under N_2 into a separate glove box ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 1$ ppm). Light from a Xe lamp was directed from outside into the glove box and the intensity was adjusted to ~ 1 sun with a radiant power meter from LOT Oriel using a calibrated thermopile. Similarly, experiments at -30 °C were carried out in a climate chamber equipped with a glass front door. Cells were placed in the transfer box and the Xe lamp with an intensity of 60-70 mW cm^{-2} was directed from outside into the chamber. The J-V characteristics during light processing were measured in-situ at -30 °C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Absorption spectra and kinetics of phototransformations. UV-vis absorption spectra of films on glass upon illumination by a xenon lamp at 1 sun intensity under nitrogen of (a) 20 nm cyanine dye Cy3-P, (b) 40 nm C₆₀, (c) 30 nm MoO₃. (d) Kinetics of light-induced C₆₀ transformation from Raman spectra. (e) Correlation between changes in UV-vis ($\Delta_{Abs,321nm} = \frac{Abs_{t,321nm} - Abs_{t=0,321nm}}{Abs_{t=0,321nm}}$) and Raman spectra. (f) Kinetics of light-induced MoO₃ transformation from UV-vis spectra ($\Delta_{Abs,700nm} = \frac{Abs_{t,700nm} - Abs_{t=0,700nm}}{Abs_{t=0,321nm}}$).

Figure 2. Cell performance during white light illumination. **(a)** Schematic representation of the cyanine dye/C₆₀ solar cell and the molecular structure of Cy3-P. **(b)** Current-voltage characteristics of glass/ITO/MoO₃/Cy3-P/C₆₀/Alq₃/Ag solar cells upon illumination at 1 sun intensity under nitrogen at 43 °C. Temporal development of **(c)** the open-circuit voltage (V_{oc}) and **(d)** the short-circuit current (J_{sc}), shown are average values from 5 cells. ▼ denote starting values using individual layer stacks that were pre-irradiated for 24 h before completing the device, ▼1 = ITO, ▼2 = ITO/MoO₃, ▼3 = ITO/MoO₃/Cy3-P, ▼4 = ITO/MoO₃/Cy3-P/C₆₀/Alq₃. Temporal development of normalized **(e)** V_{oc} and **(f)** J_{sc} upon illumination. Labels 0 and 5 indicate complete cells that were irradiated at 43 °C and at -30 °C, respectively.

Figure 3. Cell performance using selective irradiation wavelengths. (a) UV-vis absorption spectra of C₆₀ and MoO₃ films upon illumination with a xenon lamp at room temperature and using a cutoff filter that blocks light at wavelengths below 550 nm. Temporal development of (b) V_{oc} and (c) J_{sc} upon illumination. During the first 96 h, a cutoff filter was used. Open circles indicate measurements after cooling the cell to room temperature.

Figure 4. Effects of C₆₀ photopolymerization. AFM phase images of a Cy3-P/C₆₀ film (a) before and (b) after illumination. (c) Fluorescence spectra on glass/MoO₃ substrates of a bilayer film with simultaneous excitation of the dye and C₆₀. Emission signals are shown for as-prepared films, and after 96 h irradiation with filtered ($\lambda > 550$ nm) light. For Cy3-P, the emission peak is at $\lambda = 589$ nm. The emission peak of pristine C₆₀ is at $\lambda = 725$ nm with a shoulder at 693 nm, after illumination the emission shifts to $\lambda = 734$ nm. (d) Incident photon-to-current conversion efficiency (IPCE) spectra during illumination at 1 sun intensity.