Uncovering solvent-engineering mechanisms in Y6:PM6 solar cells

Cite as: APL Mater. 11, 051116 (2023); doi: 10.1063/5.0143878
Submitted: 27 January 2023 • Accepted: 1 May 2023 • Published Online: 19 May 2023

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Note: This paper is part of the Special Topic on Advances in Organic Solar Cells.

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ABSTRACT
Additives, like 1-chloronaphtalene (CN), are commonly used in Y6:PM6 solar cells as they lead to an increased power conversion efficiency. In this work, we investigate the influence of CN during spin coating of Y6:PM6 dissolved in chloroform via an in situ transmission setup. We show that, in the presence of CN, the film formation of Y6:PM6 can be divided into two parts: one related to the evaporation of chloroform and one related to the evaporation of CN. This is mostly related to Y6 being dissolved in CN. We find that even for low CN concentration, the film formation is not completed for several minutes after the spin coating process. Furthermore, the removal of CN is needed to achieve a smooth film surface. We demonstrate that this fast removal can be achieved by spin coating the electron transport layer PDINN from methanol. The methanol is acting as an anti-solvent for the CN, leading to its removal from the film. Using this approach, solar cells fabricated with a high CN concentration of 5% feature a comparable performance to ones with more common concentrations between 0.5% and 1%.

I. INTRODUCTION
Organic photovoltaics have made tremendous progress in the recent years with the synthesis of Y6 (2,2′-((2Z,2′Z)-(12,13-bis (2-ethylhexyl) - 3,9-diundecyl - 12,13-dihydro - [1,2,5]thiadiazolo [3,4-e]thieno [2′,3′:4,5]pyrrolo [3,2-g]thieno [2′,3′:4,5]thieno [3,2-b]indole - 2,10-diyl) bis (5,6-difluoro - 3-oxo - 2,3-dihydro - 1H-indene - 2,1-diylidene)) dimalononitrile) as non-fullerene acceptor in combination with PM6 (Poly (3,4-ethylenedioxythiophene)) as donor.

II. METHODS
Solar cells are produced in a p-i-n structure using ITO/PEDOT:PSS/Y6:PM6/PDINN/Ag (indium tin oxide/poly (3,4-ethylenedioxythiophene) polystyrene sulfonate/Y6:PM6/N, N′-Bis[3-((Dimethylamino)propylamino)propyl]perylene-3,4,9,10-tetracarboxylic diimide/silver). The ITO glass (purchased from Präzisions Glas & Optik GmbH) is cleaned in deionized water, acetone, and isopropanol for 8 min each and then treated with oxygen plasma for 7 min. PEDOT:PSS (AI 4083 from Ossila) is filtered through a 0.45 μm filter and then spin coated dynamically at 2000 rpm for 30 s and then baked at 120 °C for 10 min. The active layer is spin coated from a Y6:PM6 solution in chloroform at 1500 rpm for 30 s. The electron transport layer PDINN is spin coated from a solution in methanol at 2000 rpm for 30 s. The spin coating process is monitored via an in situ transmission setup.
solution application while the sample is spinning at end speed) at 4000 rpm for 30 s. Afterward, the samples are annealed at 150 °C for 20 min. To cool down to room temperature again, the samples are placed in a nitrogen chamber, where they are kept until the deposition of the active layer. Y6 and PM6 (purchased from Solarmer Materials Inc.) are dissolved separately in chloroform (CF) with varying ratios of CN at 18 mg mL$^{-1}$ overnight. The CN concentration represents the volumetric ratio of the CF-CN solvent. For spin coating, the blend is mixed at least three hours before spin coating in a ratio of 1.2:1 (Y6:PM6 solution). 15 μl of the solution is spin coated dynamically at 4000 rpm on the PEDOT:PSS layer. The PDINN (purchased from Solarmer Materials Inc.) is dissolved in methanol at 1 mg mL$^{-1}$ and dynamically spin coated (15 μl) on the active layer at 3000 rpm. The transmittance of the active layer and the PDINN layer is measured during spin coating via a self-built setup, featuring a time resolution of 380 μs. The spin coater is flushed with nitrogen during the measurements. The maximum laser intensity at the measurement position is 1.09 mW/cm$^2$. The start of the application is determined via the transmittance signal and is defined as the time, the first solution droplet reaches the substrate. Afterward, a 100 nm silver layer is evaporated on top of the samples. Each sample features three pixels with a photovoltaic area of 13.3 mm$^2$. Solar cell performance is measured using an in-house built setup at 100 mW/cm$^2$ from −0.1 to 1.0 V. Atomic force microscope measurements are done with the AFM Park NX10 from Park Systems in the non-contact mode. UV–vis absorption measurements are performed using a Cary 5000 from Agilent Technologies Inc.

III. RESULTS AND DISCUSSION

A. Influence of CN on Film Formation

Comparing the absorption of Y6 in solution and thin film, a remarkable shift of the position of the main absorption feature from ≈740 nm to ≈800 nm, respectively, is found (see the supplementary material, Fig. S1). Similar findings have been reported previously with the position of the Y6 feature in a film related to the aggregation size of the molecules. Investigation of the spin coating process reveals that this shift is, in fact, a continuous shift during an aggregation phase. This phase starts ≈0.4 s after blend application and lasts for ≈0.15 s, as shown in Fig. 1 (top row, left column). After this phase, a fairly constant signal is found for the samples without CN (top row, right column).

When adding CN to the solution, differences in film formation can be found. Calculations of the Hansen solubility parameters propose that CN should mainly influence Y6, which can be confirmed via solubility measurements, as shown in Fig. S2. For a desired concentration of 10 mg mL$^{-1}$, nearly all Y6 materials are dissolved, while
PM6 is not fully dissolved, even in a prepared solution of 3 mg mL\(^{-1}\). Measuring the absorption of Y6 and PM6 solutions dissolved in pure chloroform and pure CN shows only minor differences in their respective spectra. Therefore, one cannot distinguish if the materials are dissolved in CF or CN, which has to be considered for absorption measurements.

Adding CN prolongs the film formation (see Fig. 1). For higher CN concentrations, a smaller initial spectral shift can be found (left column), while afterward (right column), continuous changes in the transmittance spectrum are visible. By tracking the minimum position of the Y6 transmittance over spin coating time, as shown in Fig. 2, one finds that the shift can be divided into two parts. The first shift starts at around the same time after the solution application (\(\approx 0.4\) s), independent of the CN concentration. The duration of this shift is also similar for all concentrations (\(\approx 0.15\) s), while it is bigger for samples prepared from the solution containing less CN. After the initial fast shift, a further slow shift can be detected for samples prepared from the solution containing CN. Samples with 0.5% undergo a 10 nm (777–787 nm) shift on average, and samples with 1% CN undergo a 15 nm (765–780 nm) shift. For samples prepared with 5% CN, the shift is only 2 nm (739–741 nm).

The initial shift can be related to the evaporation of CF as the start is nearly independent of the CN concentration. When no CN is present, the film formation is finished and no further spectral changes can be detected. In the presence of CN, some Y6 is still dissolved in the CN itself. The higher the initial CN concentration, the larger the dissolved amount due to the increased volume of CN available. This results in less aggregated Y6 molecules for higher concentrations of CN, which leads to the more blueshifted feature position.

After the evaporation of the CF, the CN evaporates slowly due to its considerably higher boiling point of 263 °C. During this CN evaporation, the Y6 molecules are aggregating. For a concentration of 5%, the evaporation is very slow. Therefore, most of the Y6 is still non-aggregated in solution after typical spin coating durations between 30 s and 1 min. This explains why there is just a slight further redshift present, which still continues for longer waiting times.

Long-term measurements show that the spectral changes continue for multiple minutes, presumably until all CN is fully evaporated (see Fig. 3). For a concentration of 5%, the distinct Y6 transmission feature vanishes. AFM measurements show a clear difference between the samples: we find a smooth surface for low concentrations [see Figs. 4(a) and 4(b)], while for high concentrations, large crystals are found (c), which can easily be resolved via an optical microscope (d). These crystals cover the entire substrate, the biggest ones featuring a diameter over 200 \(\mu\)m, and peak heights around 500 nm.

Spin coating neat Y6 with a CN concentration of 5% shows similar results as the blend when spin coating the solution onto a PM6 layer; see Figs. S3 and S4 (which is not observed when just spin coating the Y6 on the glass substrate or a PEDOT layer). This means that some interaction with the PM6 is necessary to form these
crystals. The findings indicate that, in fact, a vertical separation of PM6 and Y6 occurs in the film as proposed. The low solubility of PM6 in CN leads to fast aggregation of PM6 as soon as the chloroform evaporates. As Y6 is still dissolved, it can rise to the top of the substrate with the CN. In case of higher CN concentrations, much of the Y6 is still dissolved, and as the evaporation only occurs slowly, the large crystals can form on top of PM6. However, already at a small CN concentration, multiple minutes after spin coating, still spectral changes can be detected. This indicates that the CN is remaining in the film for minutes, meaning the film formation of the active layer is not finished at the end of the standard spin coating process. The time between the end of the spin coating process and the next processing step, like applying an ETL, can, therefore, influence the solar cell performance significantly. Thus, it is critical to remove the CN completely before the next processing step. One possibility is to apply solvent-engineering by using the anti-solvent method commonly used in perovskite solar cells. For PM6:Y6, methanol could be used as an anti-solvent.

B. Spin Coating the ETL as Anti-solvent

Spin coating the commonly used electron transport material PDINN dissolved in methanol ≈30 s after the Y6:PM6 blend application acts as well as an anti-solvent for the CN. However, for samples without CN, the spectra before and after application are nearly identical (see Fig. 5), and a fast redshift of the Y6 feature is found in the presence of CN. After ≈1 s, no further changes in transmission can be detected. When applying only methanol (without PDINN), the samples show identical behavior as samples treated with the PDINN solution, indicating that, in fact, methanol is the relevant driving force for this shift (see the supplementary material, Fig. S5) by removing the CN from the film. Unfortunately, no Y6 peak position tracking is possible during these measurements, as the transmittance is not measurable during solution application due to lensing effects. As soon as a spectrum is measurable again, the spectral shift of Y6 is already finished, implying a very fast removal (< 0.1 s) of the remaining CN from the substrate. This shows that methanol is acting as an efficient anti-solvent for the CN–Y6 mixture, as CN is soluble in methanol.

Applying this anti-solvent method using the PDINN solution 30 s after spin coating the blend, a similar topology is found for samples with low and high CN concentrations (see Fig. 6). This is in contrast to the delayed processing shown above, where large crystals are formed for 5% CN concentration.

Measuring the solar cell performance shows an improvement in the power conversion efficiency (PCE) for all samples where CN is present in the solution. This is not only true for the champion devices (for JV graphs see Fig. S6 in the supplementary material, but also on average, as given in Table I. This is especially noteworthy as a high amount of 5% CN concentration is giving similar performance (if anti-solvent treatment is applied in time), which has—to our knowledge—not been demonstrated before. These cells, while showing a lower median PCE compared to the other concentrations, show a slightly higher $V_{OC}$ compared to the others. The reason for this increase in $V_{OC}$ is not clear yet and needs further investigation. A possible explanation could be that the Y6 is more mobile in the film as it is still dissolved. It could be, therefore, that the vertical segregation is leading to a thin layer of almost pure Y6 close to the top electrode, improving charge extraction and hindering recombination at this interface. We also want to emphasize that, with the anti-solvent treatment, no $V_{OC}$ loss is found for all CN concentrations. In contrast, such a loss is commonly reported when thermal annealing on the active layer is used.
TABLE I. Solar cell parameters for different CN concentrations. The numbers show the parameters of the champion devices of each concentration. The numbers in brackets are the median for each category as shown in Fig. S7. For the PCE distribution, see Fig. S8.

<table>
<thead>
<tr>
<th>Concentration CN (%)</th>
<th>$J_{SC}$ in mA/cm$^2$</th>
<th>$V_{OC}$ in V</th>
<th>FF in %</th>
<th>PCE in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25.4 (24.2)</td>
<td>0.866 (0.861)</td>
<td>66.5 (65.3)</td>
<td>14.6 (14.0)</td>
</tr>
<tr>
<td>0.5</td>
<td>26.4 (25.4)</td>
<td>0.885 (0.864)</td>
<td>72.7 (67.6)</td>
<td>17.0 (14.4)</td>
</tr>
<tr>
<td>1</td>
<td>25.3 (25.2)</td>
<td>0.877 (0.861)</td>
<td>76.4 (71.1)</td>
<td>17.0 (15.0)</td>
</tr>
<tr>
<td>5</td>
<td>25.4 (24.8)</td>
<td>0.893 (0.880)</td>
<td>71.9 (64.8)</td>
<td>16.3 (14.1)</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

We demonstrated that CN has a strong effect on the film formation of Y6:PM6 blend layers. This is mostly related to the interaction of Y6 and CN. Due to its low evaporation rate, the CN is not removed from the film during spin coating. There it has a long lasting influence on the film formation. The Y6, which is dissolved in CN, can rise to the top of the film, leading to the already reported vertical segregation. This has to be considered when fabricating solar cells featuring an inverted layout. To achieve reproducible results, one needs a way to remove the CN in a fast and controlled manner from the film, as otherwise the sample storing time before the next layer can have a significant influence on the final film morphology. One possible approach is the solvent-engineering method using methanol as an anti-solvent. If the anti-solvent is applied shortly after the active layer, one can achieve similar solar cell performance for a wide range of CN concentrations. The observed increase in $V_{OC}$ may also show a new way of optimizing organic solar cells in the future. No film annealing, reducing the open circuit voltage, is necessary when using CN as an additive. While, in this study, only the influence of CN on Y6:PM6 films has been demonstrated, we expect similar effects for other additives featuring a quite different evaporation rate to its host solvent. It is, therefore, important to think about the removal of the additive. Using an in situ transmittance setup as demonstrated here can assist with two tasks: first, helping to identify the influence of additives and the crucial steps in film formation, and second, enabling a more systematic approach to alter the film formation. Both allow for a more systematic approach to improve film formation and reproducibility.

SUPPLEMENTARY MATERIAL

Additional measurements and information is given in the supplementary material. It contains additional data, such as absorption and transmission spectra, AFM images of the films, and solar cell results.

ACKNOWLEDGMENTS

This work has been financially supported by DFG Project Nos. 419282603, KR 5044/3-1 and SPP2196 (Project No. 424156582).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Timo Raab: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). Tobias Seewald: Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). Stefan Kranner: Investigation (equal); Writing – review & editing (equal). Lukas Schmidt-Mende: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES