

# Influence of molybdenum oxide interface solvent sensitivity on charge trapping in bilayer cyanine solar cells

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## Absorbance spectra of glass/MoO<sub>3</sub>/Cy3-P samples

Absorbance spectra of thin Cy3-P layers coated from TFP and CB are presented in Figure S1. The layers were deposited on glass/MoO<sub>3</sub> to realize a better substrate wetting than on glass.

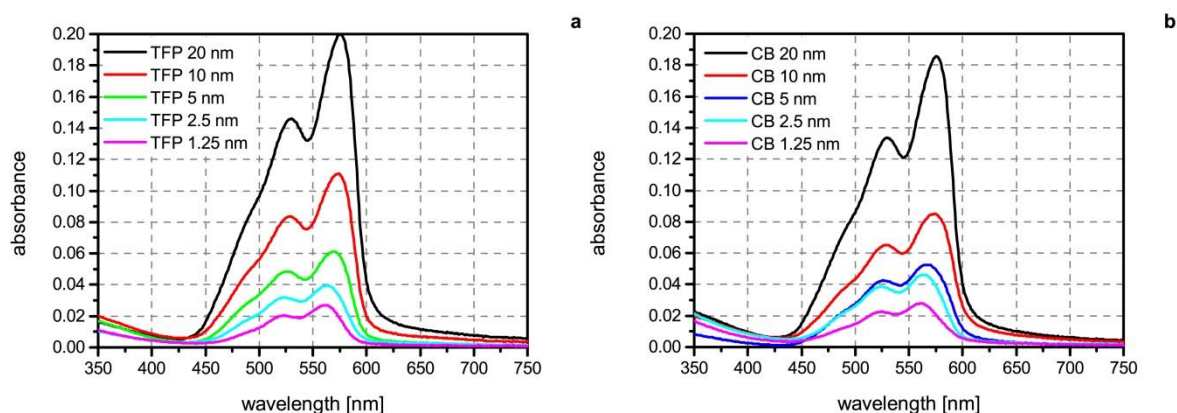


Figure S1. Absorbance spectra of different Cy3-P films coated on glass/MoO<sub>3</sub> from TFP (a) and CB (b), respectively. A constant glass/MoO<sub>3</sub> background was subtracted here.

For each solvent a solution was prepared that resulted in a film thickness of approximately 20 nm. This solution was diluted with pure solvent in a 1:1 ratio to achieve the solution for 10 nm. This procedure was repeated down to a theoretical film thickness of 1.25 nm. The absorbance of the TFP layers scales nicely with the intended thickness. The peak exhibits a slight trend to higher absorbance values compared to the expectation from the solution concentration. For CB films the concentration-absorption relation is worse. Especially the decrease from 5 to 2.5 nm is much less than expected. This bad scaling performance is attributed to the dewetting effect which leads to inhomogeneous Cy3-P films directly observable in the SPM images (Figure S6). The absorbance spectra are also less reproducible when measured on different spots on the same sample, as expected for dewetted films.

### Dielectric constant

The dielectric constant for Cy3-P was determined on a 70 nm thick film sandwiched between an ITO and an Ag electrode using impedance spectroscopy. Figure S2 shows the measured capacitance as a function of frequency of one cell. The constant value at intermediate frequencies ( $10^4 - 10^5$  Hz) was used as the geometric capacitance to calculate the dielectric constant of Cy3-P. Using the plate capacitor model a value of  $\epsilon_{\text{Cy3-P}} = 4.5$  was determined.

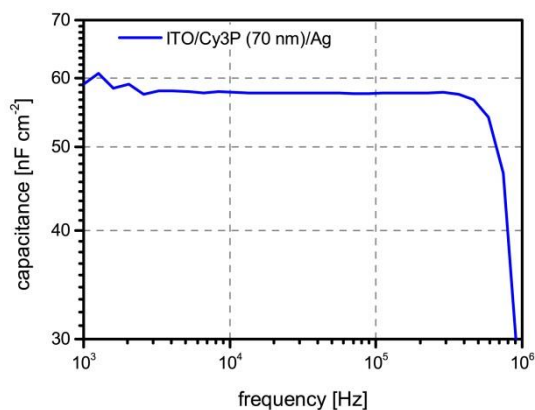


Figure S2. Capacitance as a function of the frequency measured by impedance spectroscopy on an ITO/Cy3-P (70 nm)/Ag device.

### Recombination in thick films

The photo-CELIV transients with varied delay times of 38 nm thick films coated from both solvents and the extracted charge carrier densities are presented in Figure S3.

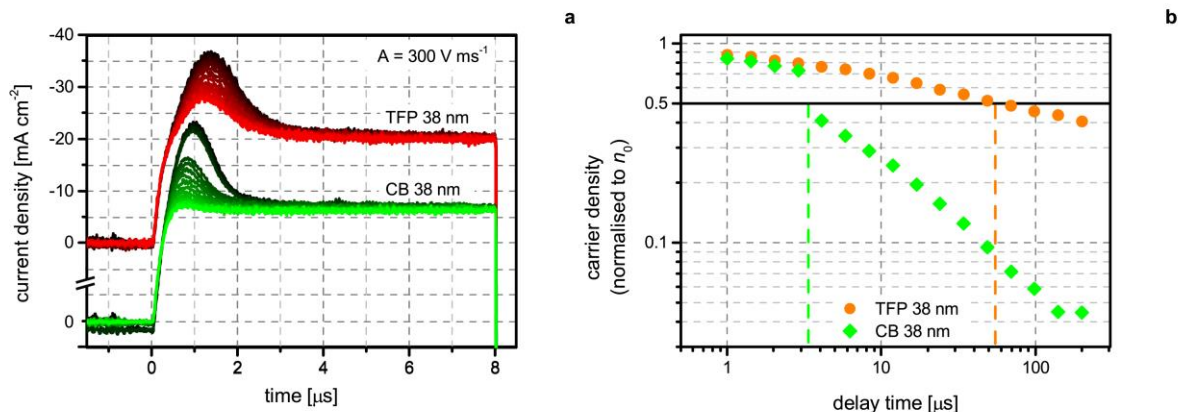


Figure S3. (a) Photo-CELIV transients with varied delay times between 0 and 200 μs of TFP and CB cells with 38 nm thick Cy3-P films. (b) Normalised charge carrier density calculated from the transients shown in (a). Carrier half lifetime is indicated by a dashed vertical line.

After a delay time of 200 μs we still extract about 40% of the initial charge carriers from the 38 nm thick TFP device. This is considerably less than what was measured for 20 nm thin films which indicates a change in recombination kinetics and demonstrates that an important fraction of photogenerated charge carriers now follows fast recombination kinetics. Clearly, the proportion of the rapidly recombining charge carriers is significantly smaller as compared to devices with the same thickness using CB as coating solvent, where more than 90% of the holes have recombined after 200 μs. This indicates that both, trapped and freely diffusing charge carriers are present in TFP coated films of 38 nm. Additionally, the number of photo-generated holes trapped at the MoO<sub>3</sub>-cyanine interface is reduced in 38 nm thick films with respect to 20 nm thick films, because of the larger distance between the anode interface and the donor-acceptor junction, close to which positive charge carrier distribution is confined at open circuit voltage. Thus the effect of anode interface traps is lowered but is still influencing the recombination dynamics.

### Photo-CELIV of inverted cells

An inverted bilayer solar cell using C<sub>60</sub> as an acceptor and Cy3-P coated from TFP as a donor was fabricated as described in detail elsewhere (G. Wicht *et al.*, Solar Energy Materials and Solar Cells 117, 2013, 585-591). The photo- and dark-CELIV transients are presented in Figure S4. No clear overshoot in the photo-CELIV curve is observed. Therefore the difference between photo- and dark-CELIV is also depicted in Figure S4 which shows a clear peak around 1 μs. The calculated device mobility using this peak is  $\mu = 2.4 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  which is close to the value obtained from the regular cells coated from CB discussed in the paper.

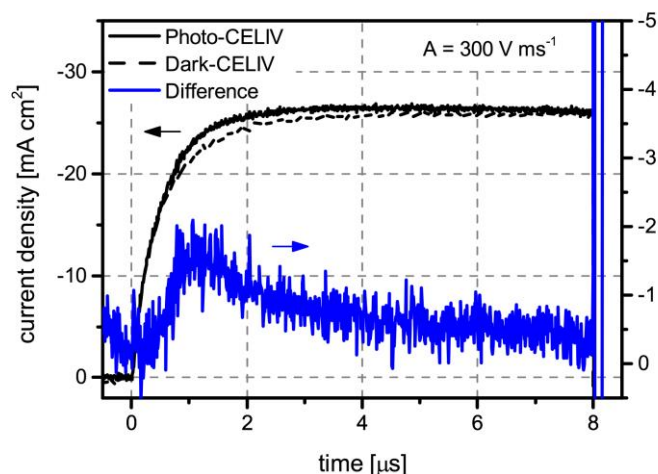


Figure S4. Photo- (solid black) and dark-CELIV (black dashed) transients on the left ordinate and difference (blue, right ordinate) of those showing a peak around 1  $\mu\text{s}$ .

### SPM images of Cy3-P films

To investigate the presence of residual TFP solvent in cyanine films, 20 nm thick Cy3-P films were spin coated on a 10 nm thick  $\text{MoO}_3$  substrate. The samples were either dried at room temperature in the glove box over night or in the vacuum chamber for 2.5 h. The morphology was analysed by scanning probe microscopy (SPM) and revealed an rms roughness of 0.63 nm for the films dried in the glove box (Figure S5a). Films dried in the vacuum chamber exhibit humps with a height of about 10 nm.

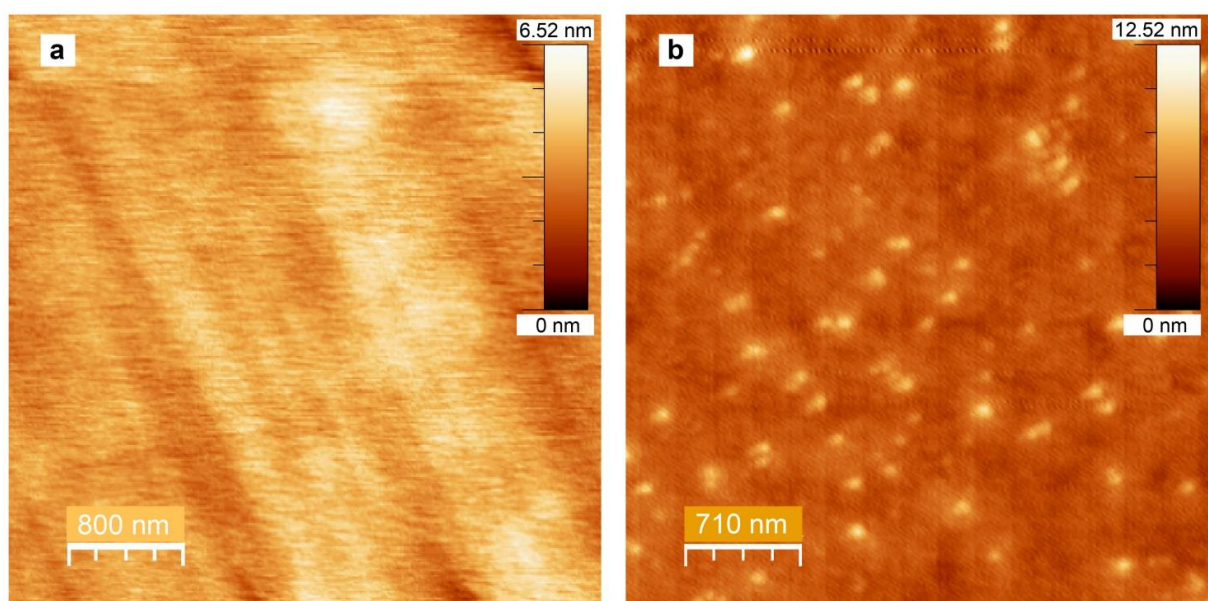


Figure S5. SPM images of glass/ $\text{MoO}_3$ /Cy3-P samples coated from TFP. The film was either dried in the glove box (a) or for 2.5 h in the vacuum chamber (b).

A clear difference between the different drying conditions was observed. While the one kept in the glove box is smooth, the vacuum dried one is homogeneously covered with volcano-like peaks. It is likely that the morphological change is caused by effusion of TFP accumulated at the  $\text{MoO}_3$  interface which is leading to cyanine humps on the surface.

In Figure S6 an SPM image of a Cy3-P film coated from CB that was kept in the glove box for several days is presented. The solution was prepared to achieve a nominal thickness of 5 nm on glass/ITO/ $\text{MoO}_3$ . However the image reveals a dewetting problem using such diluted CB solutions.

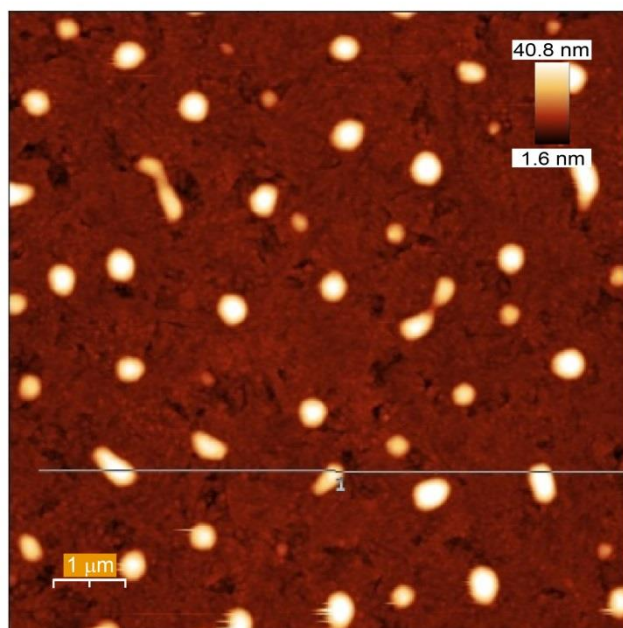


Figure S6. SPM images of glass/ $\text{MoO}_3$ /Cy3-P samples coated from CB. The nominal thickness of the cyanine film was 5 nm but the image shows clear dewetting problems.

### **XPS analysis of thin Cy3-P films**

X-ray photoelectron spectroscopy (XPS) was measured on glass/ITO/ $\text{MoO}_3$ /Cy3-P samples that were freshly prepared at most 2 h before the measurement. Cy3-P was spin coated from TFP solutions with different concentrations to achieve film thicknesses of 2.5 nm, 10 nm and 40 nm, respectively. XPS results of the three samples are displayed in Figure S7.



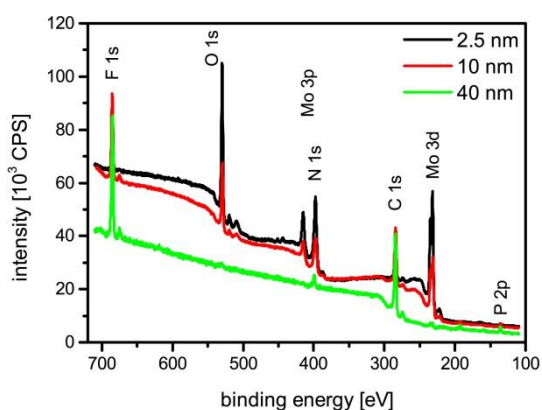


Figure S7. XPS spectra of glass/ITO/MoO<sub>3</sub>/Cy3-P films with different Cy3-P thicknesses coated from TFP. Film thicknesses are indicated in the legend and the atomic orbitals with corresponding binding energy are indicated in the graph.

For the 40 nm thick Cy3-P layer the spectrum shows peaks for F, N, C and P which can all be attributed to the dye film itself. Small intensity peaks are observable around 240 eV and 530 eV which correspond to Mo and O, respectively and originate from the underlying layer. The thinner the Cy3-P film the larger the signal providing from the MoO<sub>3</sub> substrate. At the same time the signal for F, C and P decreases as the Cy3-P layer gets thinner. Unfortunately the N 1s signal is overlapping with the one from Mo 3p which makes the calculation of the atomic fraction of nitrogen more complicated. In Table S1 we summarize the calculated composition of the Cy3-P films with different thicknesses. As an approximation the cross sections of the individual atoms were used.

	2.5 nm	10 nm	40 nm
F [at%]	3.4	11.3	19.1
P [at%]	0.38	1.6	3.6
C [at%]	22.9	45.3	70.5
N [at%]	---*	---*	5.4
F : P	<b>8.9</b>	<b>6.9</b>	<b>5.3</b>
F : C	0.15	0.25	0.27
N : C	---*	---*	0.076

Table S1. Atomic percent of F, P, C and N atoms in the three samples obtained from the XPS spectra shown in Figure S7. \*Values for nitrogen were difficult to extract due to the overlapping Mo 3p signal.

For the thickest film the atomic concentration ratio N:C of about 0.076 agrees well with the value of 0.074 for the pure dye suggesting that no additional solvent is measured. The F:C ratio of 0.22 is somewhat larger than the predicted value of 0.27 and suggests that Cy3-P has a higher affinity to locate at the air vacuum interface than the counterion  $\text{PF}_6^-$ . Finally, the F:P ratio of 5.3 corresponds within experimental error to expected value of 6, corroborating above assumption that no solvent is detected by XPS for the 40 nm thick film. For the thinner films the atomic F:C ratios are in qualitative agreement with an increased solvent accumulation close to the  $\text{MoO}_3$  surface. As the film thickness decreases the F:C ratio decreases in agreement with the fact that the solvent concentration increases. It has to be noted that the chemical shift of 6 eV for  $\text{CF}_2$  with respect to  $\text{CH}_2$  (see e.g. NIST X-ray Photoelectron Spectroscopy Database, <http://srdata.nist.gov/xps/Default.aspx>) could not be observed due to the interfering plasmon resonance at 309 eV. The uncertainty in the N:C ratio is quite large since the dominant and overlapping Mo 3p signal introduces a large error in the correction of the nitrogen signal for the thin Cy3-P layers. Only the F:P ratio is clear-cut since it has no overlapping peaks. Any deviation of the expected ratio of 6 proper to the  $\text{PF}_6^-$  anion can then be attributed to solvent contribution, since only TFP solvent contributes with additional fluorine atoms. Strikingly the F:P ratio increases from 5.3 to 6.9 and 8.9 for Cy3-P thicknesses of 40 nm, 10 nm and 2.5 nm, respectively. This strongly supports our hypothesis that TFP solvent is adsorbed close to the  $\text{MoO}_3$  interface and provides a rough estimation of the solvent concentration in the thinnest film of 75 mol% of solvent.