

# Understanding the low voltage losses in high-performance non-fullerene acceptor-based organic solar cells

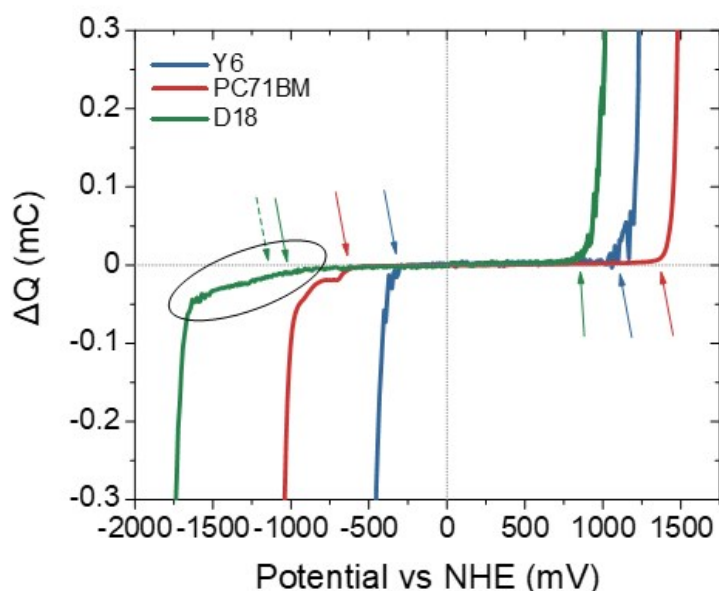
Jakob Hofinger<sup>1\*</sup>, Christoph Putz<sup>1,2</sup>, Felix Mayr<sup>1</sup>, Katarina Gugujonovic<sup>1</sup>, Dominik Wielend<sup>1</sup>, Markus C. Scharber<sup>1\*</sup>

<sup>1</sup>Linz Institute of Organic Solar Cells (LIOS), Institute of Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, 4040 Linz Austria

<sup>2</sup>Division of Soft Matter Physics, Institute of Experimental Physics, Johannes Kepler University Linz, Altenbergerstrasse 69, Linz 4040, Austria

## Supporting Information

### Electrochemistry



**Figure S1: Electrochemical characterization.** EVS measurements of the used OPV Materials D18, Y6 and PC71BM. The arrows indicate the respective onset of reduction or oxidation. The dashed arrow indicates an estimation of the LUMO level of D18 calculating  $\text{HOMO}_{\text{D18}} + \text{optical gap}$ .

EVS is a good tool to estimate the HOMO and LUMO levels of OPV materials. The measurement is performed close to equilibrium conditions (see methods) and allows to determine the onset of oxidation or reduction more precisely than in cyclic voltammetry measurements. Typical CV measurements are analyzed by fitting tangents to the baseline and the oxidation or reduction peak. This type of analysis is prone to substantial evaluation errors and can be avoided using EVS. Here the onset of the reaction is defined as the first deviation from the baseline. As shown in Figure S1 the oxidation onset can be evaluated precisely for all 4 investigated materials. The reduction onset of the acceptors can be identified clearly. It should be emphasized that the indirect nature of the fullerene molecule can also be identified in the EVS spectrum. It seems like a limited reaction starts already at -600mV vs. NHE, while a strong reduction is observed at approximately -900mV vs. NHE. The reduction onset for the D18 polymer is hard to define as indicated by the black ellipse. Thus, the presented LUMO levels of the polymers could exhibit significant errors. Fortunately, the investigated systems consist of large bandgap polymers and low bandgap acceptors with moderate or low  $\Delta_{\text{HOMO}}$  offsets. In any case, the LUMO level of the polymer is expected to be significantly higher than the LUMO of the acceptor. Thus, a precise measurement of the LUMO level of the polymer is not required.

### Device geometry

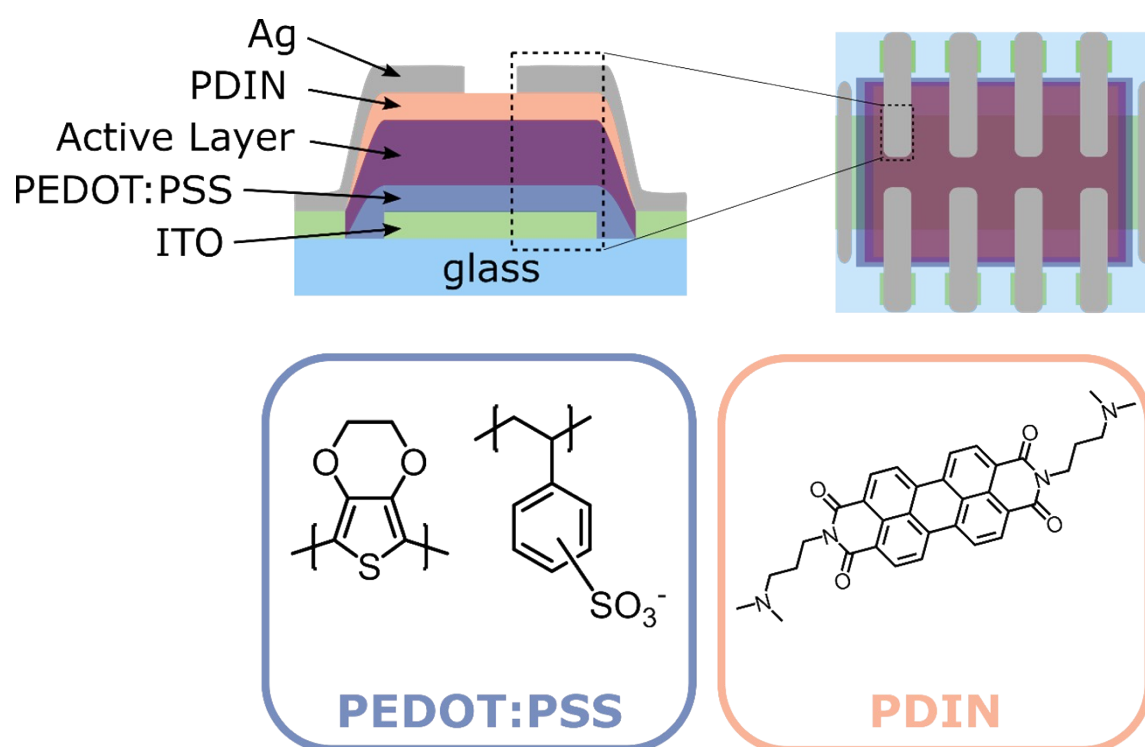
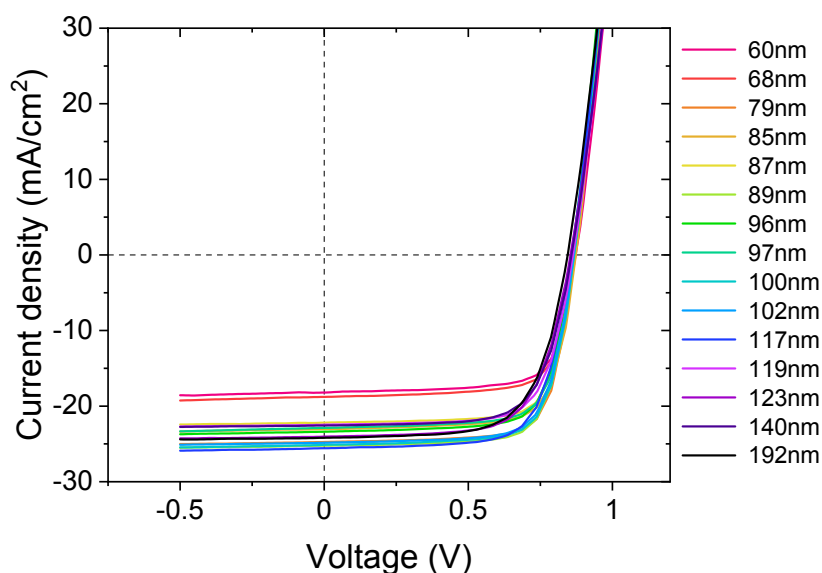


Figure S2: Device geometry and chemical structures of PEDOT:PSS and PDIN.

## Thickness variation of D18:Y6 solar cells

| Thickness<br>(nm) | VOC<br>(V) | JSC<br>(mA cm <sup>-2</sup> ) | FF<br>(%) | PCE<br>(%) |
|-------------------|------------|-------------------------------|-----------|------------|
| 60                | 0.87       | -18.20                        | 73.8      | 11.7       |
| 68                | 0.87       | -18.78                        | 74.3      | 12.1       |
| 79                | 0.87       | -24.75                        | 74.5      | 16.0       |
| 85                | 0.87       | -23.05                        | 73.9      | 14.8       |
| 87                | 0.87       | -22.19                        | 74.7      | 14.4       |
| 89                | 0.86       | -25.24                        | 73.6      | 16.0       |
| 96                | 0.86       | -23.39                        | 73        | 14.7       |
| 97                | 0.87       | -22.88                        | 73        | 14.5       |
| 100               | 0.87       | -25.12                        | 72.8      | 15.9       |
| 102               | 0.86       | -24.85                        | 72.8      | 15.6       |
| 117               | 0.86       | -25.57                        | 70.8      | 15.6       |
| 119               | 0.86       | -22.46                        | 71.4      | 13.8       |
| 123               | 0.85       | -24.04                        | 67.5      | 13.8       |
| 140               | 0.86       | -22.56                        | 69.4      | 13.5       |
| 192               | 0.84       | -24.19                        | 66.8      | 13.6       |

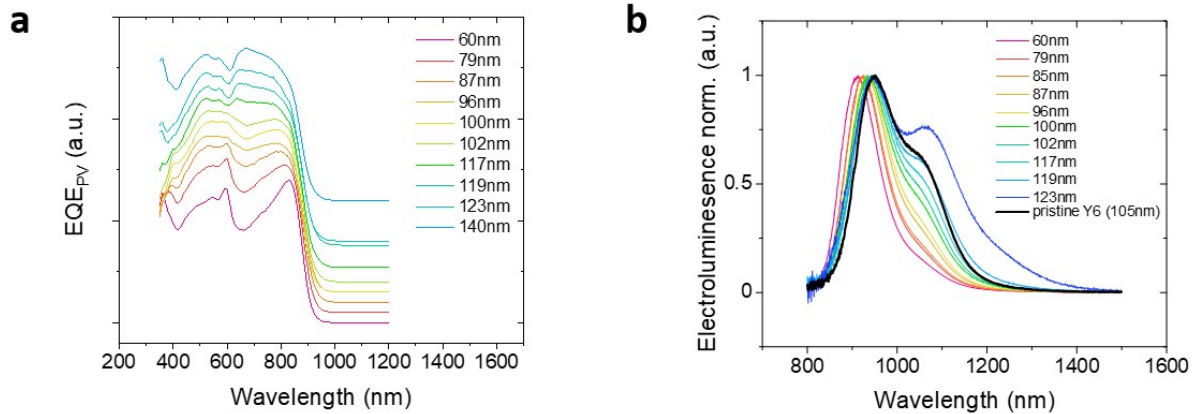
**Table S1: Photovoltaic parameters of D18:Y6 (1:1.6) solar cells with different thicknesses of the active layer.** The presented values are averages over at least 8 cells.



**Figure S3: JV-curves of D18:Y6 (1:1.6) solar cells with different thicknesses.** The presented curves are averages over at least 8 cells. The respective photovoltaic parameters are summarized in Table S1.

The various active layer thicknesses of D18:Y6 (1:1.6) solar cells were achieved by different concentrations of the active layer solution (7 mg/ml, 9 mg/ml, 11mg/ml in chloroform) and spin speeds ranging from 1000-5000rpm. It should be mentioned that solar cells with almost 200nm thick active layers showed a high PCE of 13.6%. Furthermore, the highest FF values were found for the

thinnest devices. Figure S2 clearly shows that the JSC of devices with 60nm and 68nm is slightly reduced. For the thin devices, the active layer was not thick enough to absorb all the incoming photons and leads to a reduced JSC. The result suggests that an active layer thickness of at least 80nm is required to reach high JSC values.

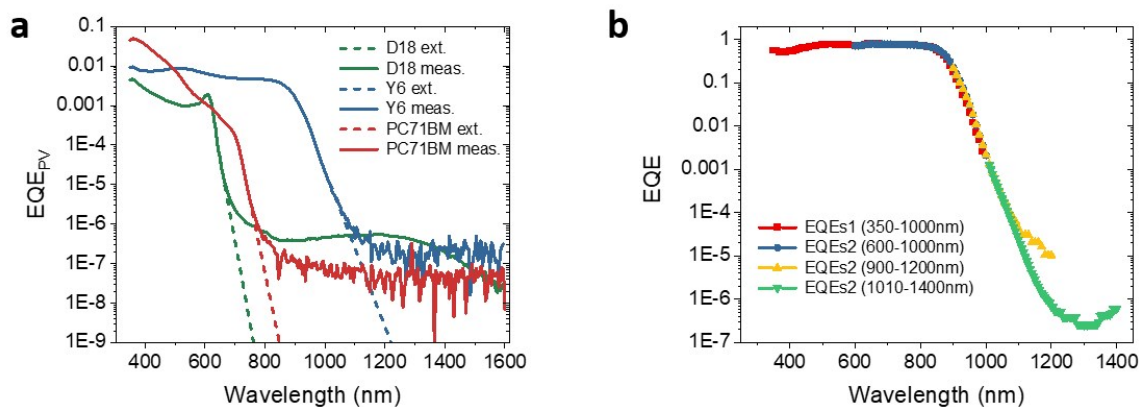


**Figure S4: EQE<sub>PV</sub> and EL spectra of D18:Y6 solar cells with various active layer thicknesses.**

For better visibility, the EQE<sub>PV</sub> spectra are presented in arbitrary units. Increasing the thickness strongly affects the shape of the EQE<sub>PV</sub>. Thin devices exhibit two pronounced peaks which can be identified as the pristine absorption peaks of D18 and Y6. Upon increasing the thickness, the gap between the peaks is reduced until a plateau of an almost constant EQE<sub>PV</sub> is formed. The observed behavior is assumed to be caused by interference effects resulting from the different layer thicknesses of the solar cells.

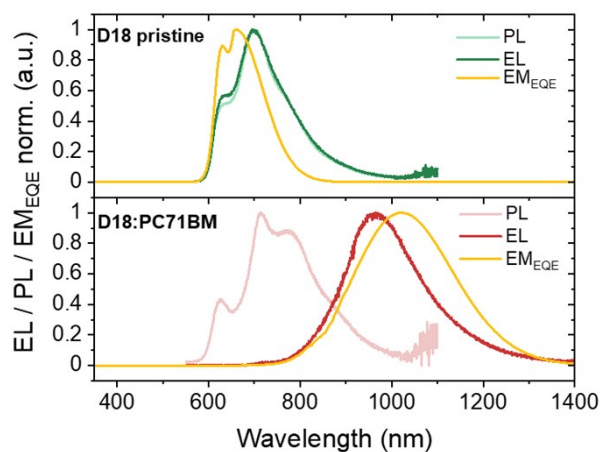
EL measurements show a similarly strong influence on the active layer thickness. Increasing the active layer thickness gradually increases the shoulder around 1100nm. Furthermore, the maximum of the EL peaks shifts towards lower wavelengths for thinner devices. Again, this behavior is assumed to be caused by interference effects.

#### Additional EQE<sub>PV</sub> measurements



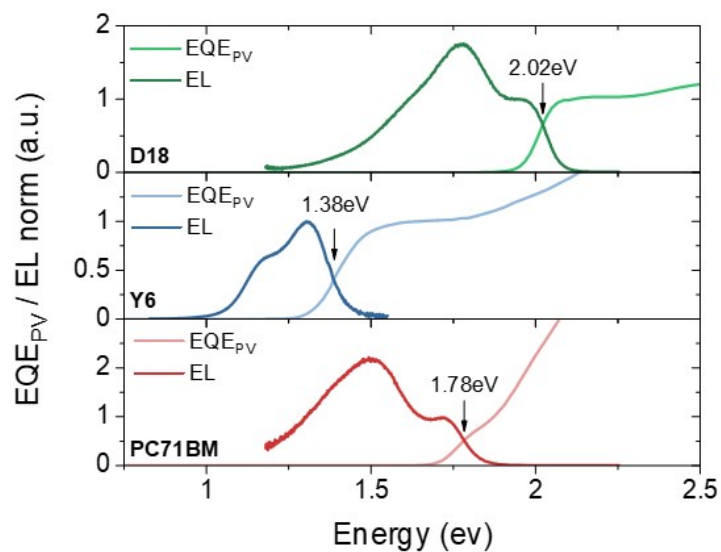
**Figure S5: EQE<sub>PV</sub> measurements. a**, Measured EQE<sub>PV</sub> spectra of pristine devices (solid curves) and their respective linearly extended EQE<sub>PV</sub> spectra (dashed curves). **b**, Individual EQE<sub>PV</sub> measurements of a typical D18:Y6 solar cell. The spectra were measured with different setups, spectral regions and amplification. An excellent overlap of the EQE<sub>PV</sub> spectra from the individual measurements can be observed.

## EL / PL / $EM_{EQE}$ measurements



**Figure S6: Photo- and electroluminescence characterizations.** Comparison of PL / EL /  $EM_{EQE}$  spectra of pristine D18 and D18:PC71BM devices.

## Evaluation of the Optical Gap



**Figure S7: EQE<sub>PV</sub> and EL spectra of D18, Y6 and PC71BM.** The high-energy EL and low-energy EQE<sub>PV</sub> peaks were normalized to 1. The crossing point between EQE<sub>PV</sub> and EL spectra of the pristine materials was used to determine their optical gaps.

|                   |               | $V_{oc}$<br>(V) | $J_{sc}$<br>(mA cm <sup>-2</sup> ) | FF<br>(%) | PCE<br>(%) |
|-------------------|---------------|-----------------|------------------------------------|-----------|------------|
| <b>D18:Y6</b>     | measured      | 0.87            | 24.46                              | 70.5      | 15.2       |
|                   | SQ-limit      | 1.09            | 33.98                              | 89.0      | 33.2       |
|                   | % of SQ-limit | 79.8%           | 72.0%                              | 79.2%     | 45.6%      |
| <b>D18:PC71BM</b> | measured      | 0.98            | 11.26                              | 71.4      | 8.0        |
|                   | SQ-limit      | 1.48            | 20.07                              | 91.3      | 27.1       |
|                   | % of SQ-limit | 66.1%           | 56.1%                              | 78.2%     | 29.3%      |

**Table S2: Measured photovoltaic parameters of D18:Y6 and D18:PC71BM solar cells in comparison with their respective parameters in the SQ-limit.**