Supporting Information

Effect of Solvent Additives on the Morphology and Device Performance of Printed Non-fullerene Acceptor Based Organic Solar Cells

Kerstin S. Wienhold‡, Volker Körstgens‡, Sebastian Grott‡, Xinyu Jiang‡,
Matthias Schwartzkopf†, Stephan V. RothΣ-Π, and Peter Müller-Buschbaum‡,∫,*

‡Technische Universität München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany.

Σ Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg.

ΠKTH, Department of Fibre and Polymer Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden.

∫Heinz Maier-Leibnitz-Zentrum, Lichtenbergstr. 1, 85748 Garching, Germany.

*muellerb@ph.tum.de
Experimental details

a) Scattering experiments

Grazing incidence small angle X-ray scattering (GISAXS) and grazing incidence wide angle X-ray scattering (GIWAXS) experiments were carried out at the MiNaXS beamline P03 at the PETRA III synchrotron source at DESY, Hamburg. Measurements were performed with a focused X-ray beam (10 x 27 µm²) with a wavelength of 0.09763 nm and an incidence angle of 0.35°. A beamstop was applied at the specular beam position to avoid oversaturation of the detector. GISAXS measurements were carried out at a sample-detector-distance of 3176 mm. A Pilatus 1M detector (Dectris Ltd.) with a pixel size of 172 µm was used for detecting the scattering signal. An open source Python program named DPDAK (Directly Programmable Data Analysis Kit) provided from the DESY was used for calibration (sample-detector distance, beam center) and data analysis. Horizontal line cuts are performed at the strongest scattering contribution, the critical angle of PBDB-T-SF which was calculated in advance to be 0.11° for the used X-ray energy of 12.7 keV.

GIWAXS measurements on PBDB-T-SF:IT-4F thin films were performed at a sample-detector-distance of 179 mm using a Pilatus 300k (Dectris Ltd) detector with a pixel size of 172 µm. Tube cuts were performed in the q-range from 2.2 – 2.6 nm⁻¹ for the (100) PBDB-T-SF and 2.65 – 2.9 nm⁻¹ for the (100) IT-4F Bragg peak. In addition, the central cake cut is done covering a qz range of 0 – 20 nm⁻¹.

GIWAXS measurements on the pure IT-4F and PBDB-T-SF printed with 0.25 vol% DIO were performed with a Ganesha SAXSLAB instrument with a sample-detector distance of 95.67 mm, a wavelength of 0.154 nm with a beam size of 100 µm in vertical and 200 µm in horizontal direction. The incidence angle was aligned to 0.35°. The scattering data were collected using a Pilatus 300 K (Dectris Ltd.) with a pixel size of 172 µm. The central cake cut is done covering a qz range of
0 – 20 nm\(^{-1}\) and tube cuts were performed in the q-range from 2.2 – 2.6 nm\(^{-1}\) for the (100) PBDB-T-SF and 2.65 – 3.2 nm\(^{-1}\) for the (100) IT-4F Bragg peak.

Before data analysis, the background originating from the glass substrate was subtracted. All GIWAXS data were corrected using GIXSGUI, a MATLAB toolbox (visualization, reshaping, cuts).

b) Surface morphology

The morphology of slot-die coated active layers was probed with a Zeiss NVision 40 scanning electron microscope (5 kV acceleration voltage, 4 mm working distance). The SEM images were contrast adjusted with ImageJ.

Atomic force microscopy was performed with an Asylum Research MFP-3D instrument in tapping-mode (scan area 1 µm x 1µm, 75 kHz resonance frequency). Gywddion was used for data visualization and analysis.

**Thin film deposition**

![Image of slot die coater](image)

**Figure S1.** Photograph of the meniscus guided-slot die coater.
A meniscus guided slot-die coater is used for printing of active layers of PBDB-T-SF:IT-4F out of chlorobenzene. A syringe pump is applied to provide a constant flow rate during printing. The solution is guided through a solution guide mask and a shim mask, which are attached inside the printer head. The flow rate, printing velocity, height (distance between printer head and substrate) and concentration of the solution are adjustable parameters. In this work, a flow rate of 10 µl/s, a printing velocity of 10 mm/s, a height of 1 mm and a concentration of 7 mg/ml are optimized to get a film thickness of (100 ± 15) nm. Photographs of a representative printed thin film and a printed organic solar cell are shown in Figure S2.

**Figure S2.** (a) Photograph of a printed thin film on a 7.5 cm x 2.5 cm glass substrate with printing direction from left (start) to right (end). The glass substrate is cut to a size of 2.5 x 2.5 cm after printing. (b) Photograph of a printed organic solar cell (2.5 cm x 2.5 cm, 0.12 cm² pixel size). A part of the active layer is removed for contacting the ITO electrode.
GISAXS measurements

Figure S3. 2D GISAXS data of printed PBDB-T-SF:IT-4F films with different DIO concentrations: (a) 0.00 vol% DIO, (b) 0.25 vol% DIO, (c) 0.50 vol% DIO and (d) 1.0 vol% DIO.
GIWAXS measurements

**Figure S4.** 2D GIWAXS data of printed PBDB-T-SF:IT-4F films with different DIO concentrations: (a) 0.00 vol% DIO, (b) 0.25 vol% DIO, (c) 0.50 vol% DIO and (d) 1.0 vol% DIO.
Figure S5. 2D GIWAXS data of the pure (a) IT-4F and (b) PBDB-T-SF films printed out of chlorobenzene with 0.25 vol% DIO.
Figure S6. Selected integrals of 2D GIWAXS data of pure IT-4F (red dots) and pure PBDB-T-SF (blue dots) films printed with 0.25 vol% DIO. The azimuthal q integral is shown for (a) IT-4F and (b) PBDB-T-SF. The solid line is a guide to the eye. Tube cuts of (c) the IT-4F (100) Bragg peak (2.65 < q < 3.2 nm<sup>-1</sup>) and (d) the (100) PBDB-T-SF Bragg peak (2.2 < q < 2.6 nm<sup>-1</sup>). The peaks are analysed by fitting of Gaussian functions (solid lines). The FWHM is determined to be (10.3 ±1.5) ° for IT-4F and (25.1 ±1.7) ° for PBDB-T-SF. The grey bar masks the non-accessible q-range.
**Tauc Plot**

In the UV/vis range, the band structure for a direct transition can be described with the following relationship (1):

\[
\alpha = A \cdot (h\theta - E_g)^{1/2} \quad (\text{Equation S1})
\]

A Tauc plot is created for active layers printed with varying 1,8-diiodooctane concentrations (0.00, 0.25, 0.50 and 1.0 vol%). The absorption coefficient \(\alpha\) is calculated from the UV/vis absorbance spectra (\(A\): absorbance). The optical bandgap \(E_g\) of the printed active layers is independent of the amount of solvent additive within the measured concentration range and is determined to be 1.55 ± 0.04 eV.

![Tauc plot](image)

**Figure S7.** Tauc plot of a printed active layer based on PBDB-T-SF:IT-4F processed without solvent additive. The plot is extracted from the UV/vis absorbance spectra. The optical band gap is determined to be (1.55 ± 0.04) eV (red line).