In Situ Printing: Insights into the Morphology Formation and Optical Property Evolution of Slot-Die-Coated Active Layers Containing Low Bandgap Polymer Donor and Nonfullerene Small Molecule Acceptor

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organic solar cells (OSC)

advantages:

- ✓ mechanically flexible
- ✓ light weight
- ✓ low-cost production
- ✓ non-toxic materials

challenges:

- low efficiencies compared to conventional silicon solar cells
- ➢ investigation of high-efficiency materials/ solvent additives
- scale-up to industrial scale
- ➢ printing of active layers

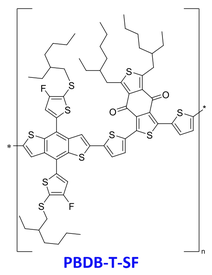
applications:

- architecture
- clothes
- art

[1-6]

active materials

donor (polymer)

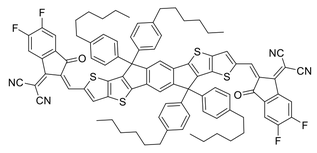


PBDB-T-SF

Poly[(2,6-(4,8-bis(5-(2-ethylhexylthio)-4-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]

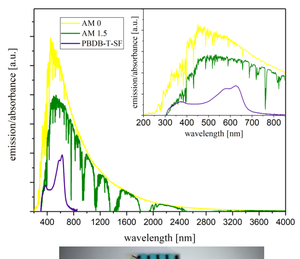
+

acceptor (small molecule)



IT-4F

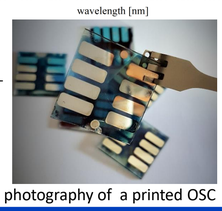
3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene



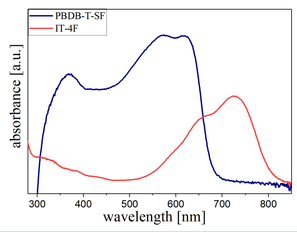
absorbance and photoluminescence

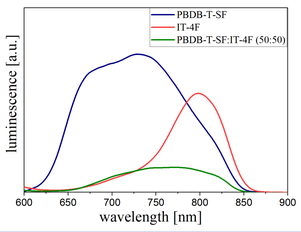
- efficient absorption of sun light by the polymer
- red shifted absorption spectra of acceptor compared to the polymer
- luminescence quenched in presence of acceptor
  → efficient energy transfer from donor to the acceptor

→ **PBDB-T-SF:IT-4F based OSC achieve an power conversion efficiency (PCE) of 13% [7]**

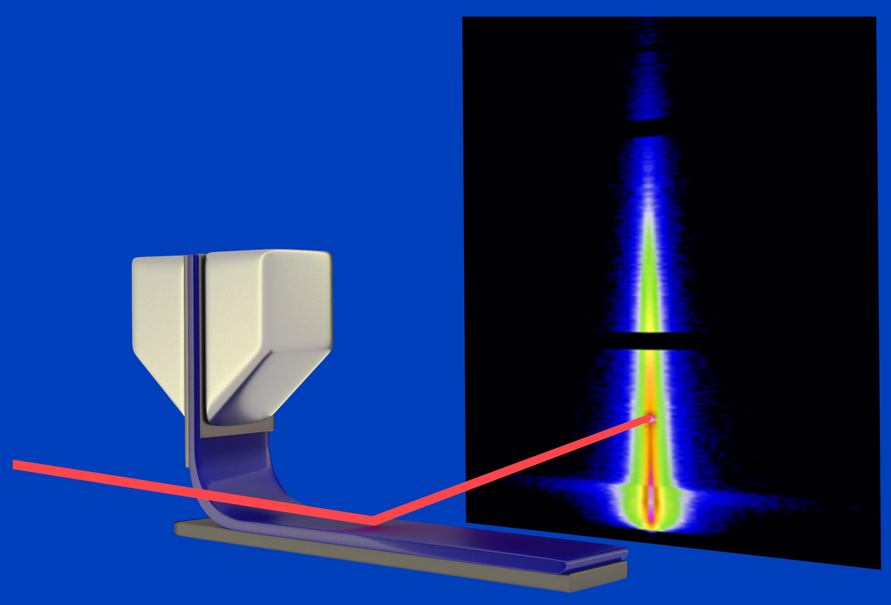


photography of a printed OSC

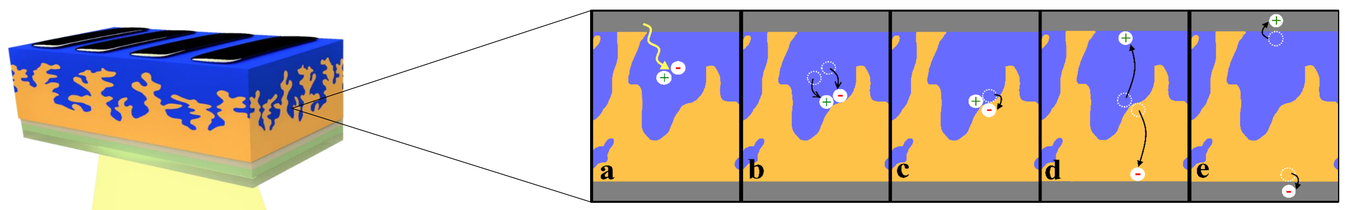




in situ grazing incidence small angle X-ray scattering (GISAXS)



energy conversion

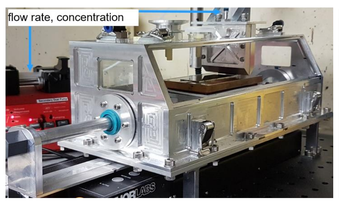


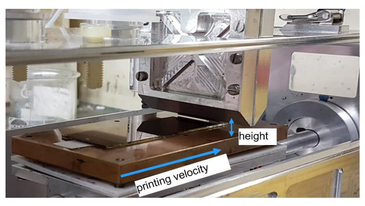
a. absorption of sun light and generation of excitons
b. exciton diffusion to the polymer/small molecule interface
c. exciton dissociation into free charge carriers
d. charge transport to the electrodes
e. charge exctraction at the electrodes

meniscus guided slot-die coating

advantages of printing OSC:

- ✓ up-scalable
- ✓ low-cost production
- ✓ low concentration of solution





main components of the printer:

- syringe pump
- printer head
- motor for moving sample holder
- windows for closed atmosphere

adjustable parameters:

- concentration
- flow rate
- printing velocity
- height

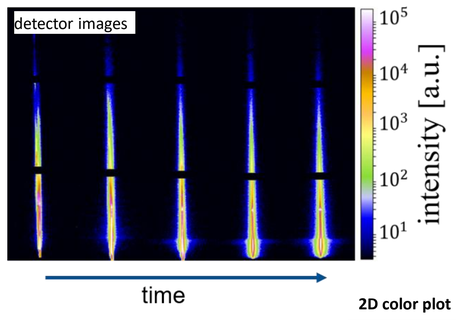
in situ printing

grazing incidence small angle X-ray scattering (GISAXS):

- ✓ larger sample area
- ✓ inner morphology is probed
- ✓ high statistical significance
- ✓ suitable for amorphous materials

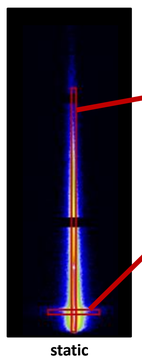
➡ structure formation from the start of the printing to the final dry film can be followed in Situ

➡ **significant structure growth already visible at the detector images**



in situ printing with GISAXS:

- measured at the beamline P03 at the DESY, Hamburg
- high brillance
- small measurement times (0.1 s per image)
- sample-detector distance of 3176 mm
- energy: 12.7 keV
- small incidence angle of 0.35°



static

vertical and horizontal cut:

vertical cut:

- reflected specular beam
- Yoneda region (critical angle of PBDB-T-SF at 0.11° for 12.7 keV) → horizontal cut

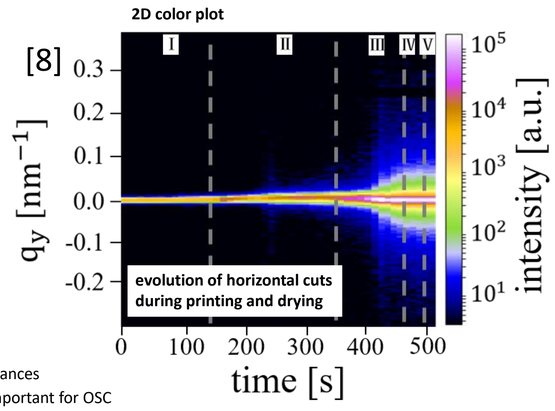
horizontal cut:

→ modeling structure sizes and distances:

- effective interface approximation of the distorted wave Born approximation (DWBA) and local monodisperse approximation (LMA)
- polymers as cylindrical domains

In Situ

2D color plot

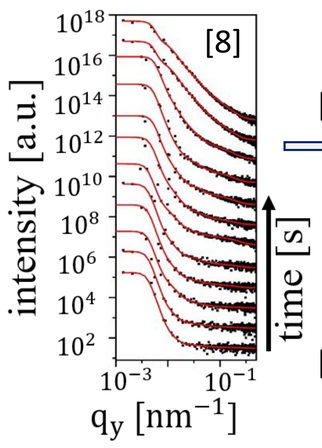


in Situ GISAXS data and model

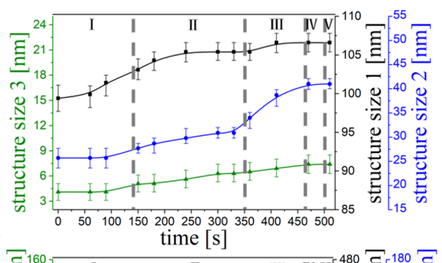
data modeling:

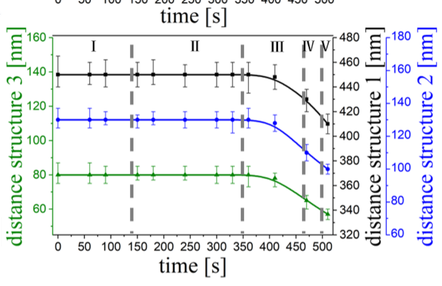
- 3 structures and 3 corresponding distances
- 40 nm structure size (blue) is most important for OSC

- GISAXS data
- model



evolution of horizontal cut (black dots) during printing and drying and corresponding model (red)



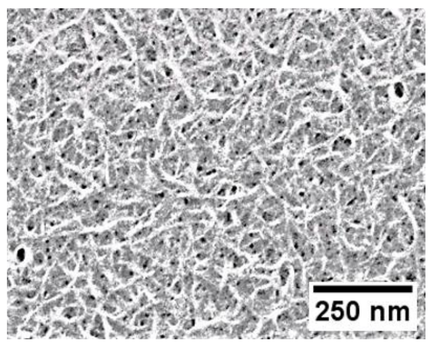


➢ structures grow during the printing and drying
➢ distances are reduced at the end of drying

5 phases of drying [8]:

1. wet film, no significant growth of structures
2. first structure formation, slow structure growth
3. fast growth of strucutres
4. reduction of distances
5. final dry film, no change of structure sizes and distances

morphology of the active layer (dry film)



scanning electron microscopy

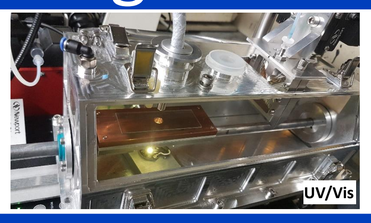
in situ optical microscopy and UV/Vis

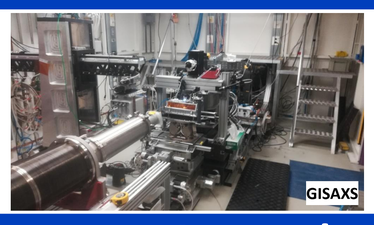
In situ printing:

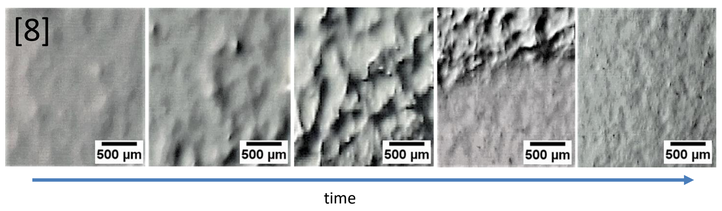
→structure formation during printing important for the PCE of OSC

→ printing and drying needs to be understood

[8]



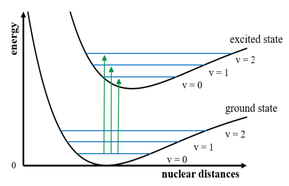




drying of a thin film of PBDB-T-SF:IT-4F printed at room temperature out of chlorobenzene:

1. wet film, flat surface
2. slightly wavy surface
3. distinct wavy surface
4. withdrawl of wet film, drying from edges of substrate to the middle
5. final dry film

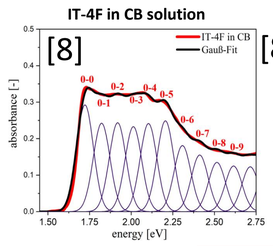
Frank Condon principle energy diagramm



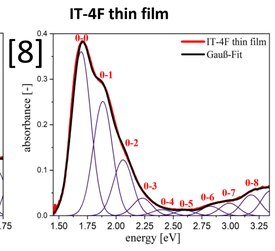
UV/Vis spectroscopy:

- electronic transitions from the electronic ground state to the excited state
- vibrational levels determined with Gaussian fit (of equal width)
  - **amplitude:** probability
  - **width:** order/disorder of the system

IT-4F in CB solution



IT-4F thin film



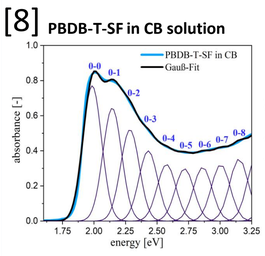
PBDB-T-SF: Gaussian functions

- width changes (0.25 eV to 0.27 eV)
- probability of transition changes
- shift of center position of Gaussian functions: shift of energy levels
- no band gap shift during drying

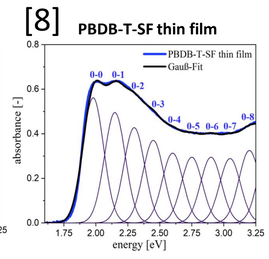
IT-4F: Gaussian functions

- width changes (0.19 eV to 0.27 eV)
- probability of transition changes
- shift of center position of Gauss function: shift of energy levels
- band gap shift towards lower energy

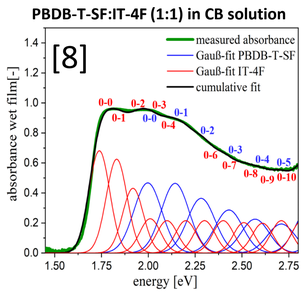
PBDB-T-SF in CB solution



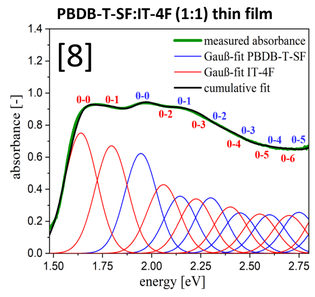
PBDB-T-SF thin film



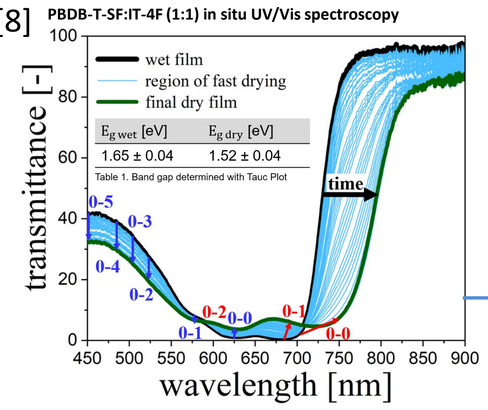
PBDB-T-SF:IT-4F (1:1) in CB solution



PBDB-T-SF:IT-4F (1:1) thin film



PBDB-T-SF:IT-4F (1:1) in situ UV/Vis spectroscopy



$E_{g\,wet}$ [eV]	$E_{g\,dry}$ [eV]
1.65 ± 0.04	1.52 ± 0.04

Table 1. Band gap determined with Tauc Plot

shift of energy levels

	IT-4F	IT-4F	IT-4F	IT-4F	PBDB-T-SF	PBDB-T-SF	PBDB-T-SF	PBDB-T-SF
transition	0-0	0-1	0-2	0-3	0-0	0-1	0-2	0-3
in wet film [eV]	1.73	1.83	1.92	2.01	2.00	2.14	2.28	2.43
in dry film [eV]	1.64	1.80	2.06	2.23	1.95	2.15	2.30	2.44

Table 1. electronic transitions of PBDB-T-SF and IT-4F during printing and drying, error = ± 0.01 eV

references

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