Gracing incidence scattering as a method to understand the influence of non-halogenated solvents on the morphology of organic solar cells

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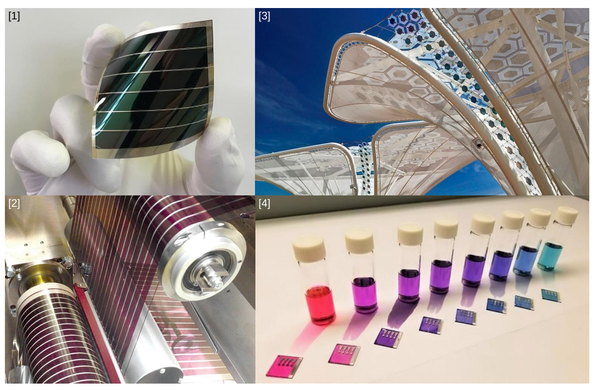
Organic solar cells

Advantages:

- low material consumption
- mechanically flexible
- highly tuneable properties
- easily scalable production

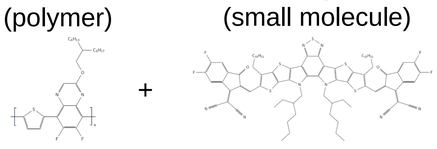
Challenges:

- very complex molecules / polymers
- harmful by-products during fabrication e.g. halogenated solvents
- limited stability of active layers



Bulk-heterojunction (BHJ) materials

Donor (polymer) + Acceptor (small molecule)



PTQ-2F
Poly [(thiophene)-alt-(6,7-difluoro-2-(2-hexyldecyl-oxy)quinoxaline)]

BTP-4F
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'] thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene)) bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile

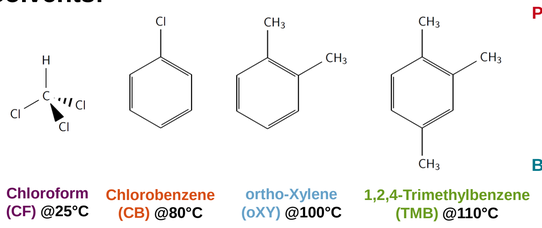
Working principle

1. photon absorption and exciton generation inside the BHJ
2. exciton diffusion to the interface
3. exciton dissociation at the interface and formation of free charge carriers
4. charge carrier transport to the respective electrodes

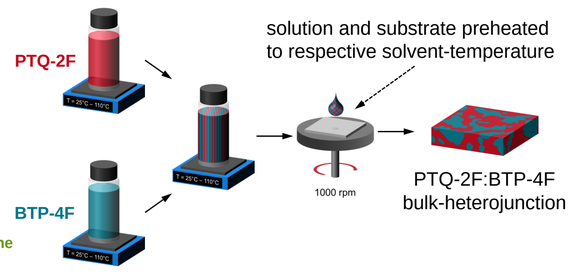
Goal:
Investigation of ›green‹ solvent alternatives to traditional organochlorides

Thin film and device fabrication

Solvents:

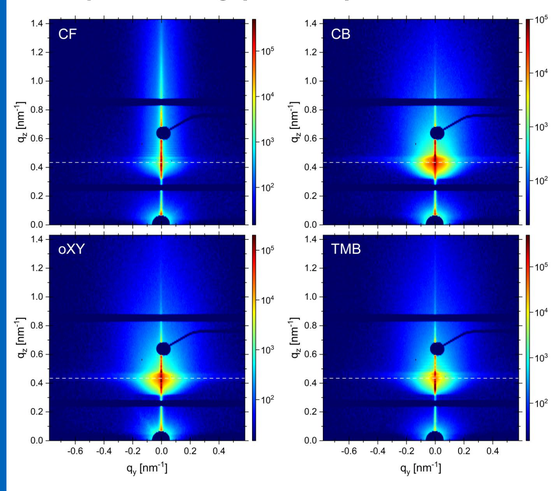


Chloroform (CF) @25°C | Chlorobenzene (CB) @80°C | ortho-Xylene (oXY) @100°C | 1,2,4-Trimethylbenzene (TMB) @110°C



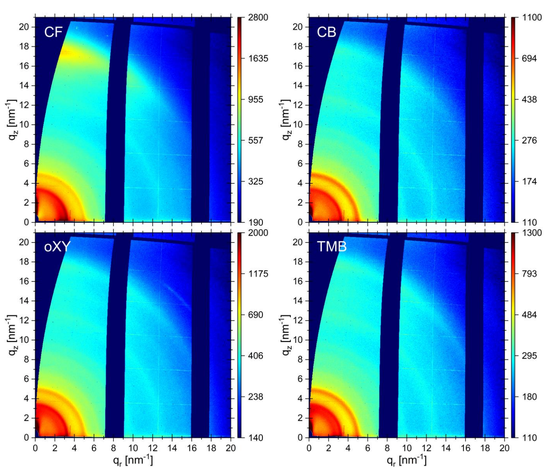
Solvent dependent changes in film morphology

Grazing-incidence small-angle x-ray scattering (GISAXS)



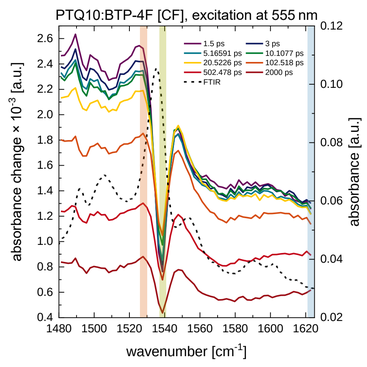
- reduced scattering width in CF-processed BHJ films
  → indicates lower uncorrelated roughness of internal interfaces
  → larger feature size

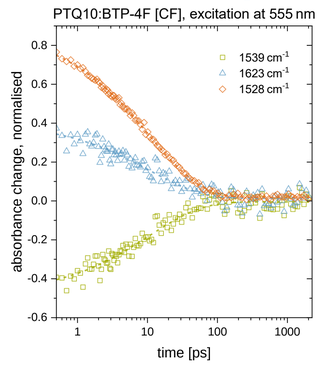
Grazing-incidence wide-angle x-ray scattering (GIWAXS)



- strong π-π stacking diffraction along q_z in CF-processed BHJs
  → higher degree of order and strong preference of face-on molecular packing orientation
- increased isotropy in non-CF-processed BHJs

Time-resolved transient absorption spectroscopy





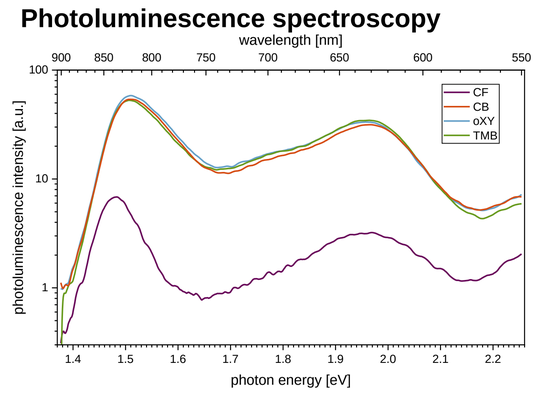
Fano-resonances fitted with stretched exponential function

- excitation @ 555 nm:
  CF: t = 10,6 ps, β = 0,58
  oXY: t = 21,3 ps, β = 0,68
  TMB: t = 16,9 ps, β = 0,68
- excitation @ 800 nm:
  CF: t = 2,1 ps, β = 0,42
  oXY: t = 4,8 ps, β = 0,40
  TMB: t = 2,1 ps, β = 0,36

- Fano-resonances in BHJ films show power-density-dependency for short time scales (~ 10 ps) → indicates bi-molecular process
- intensities of Fano-resonances converge at ~ 100 ps → mono-molecular process
- power-density-dependency disappears in pure BTP-4F

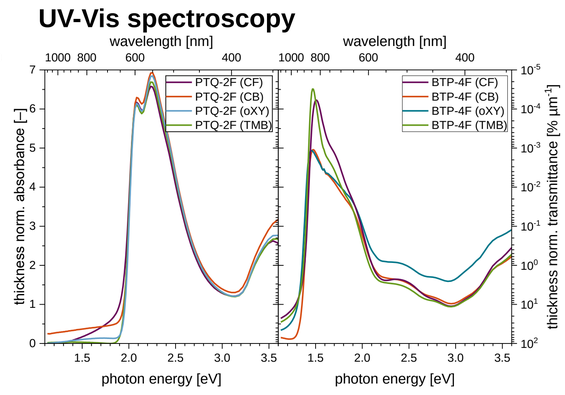
Influence on optical properties of BHJ films

Photoluminescence spectroscopy



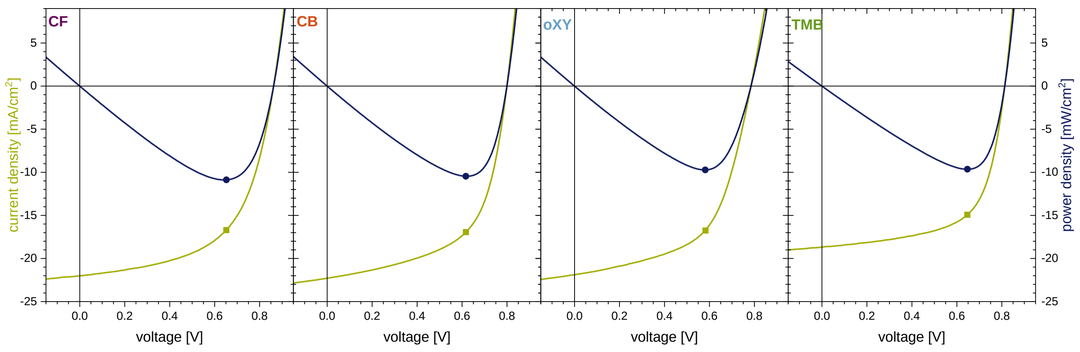
- improved photoluminescence (PL) quenching in CF-processed BHJ films
  → higher effectivity in charge separation between donor and acceptor
- red shift of BTP-4F emission in CF

UV-Vis spectroscopy

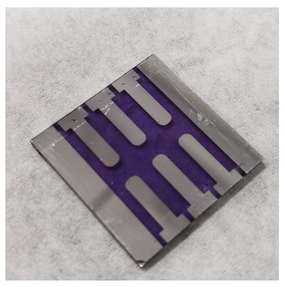


- spectrum of PTQ-2F not significantly affected by solvent
- absorption spectrum of BTP-4F shifted
  - Change in aggregation behaviour
  - Blue-shift for CF → H-aggregate
  - CF leads to more interchain π-π-stacking

Solvent influence on solar cell performance

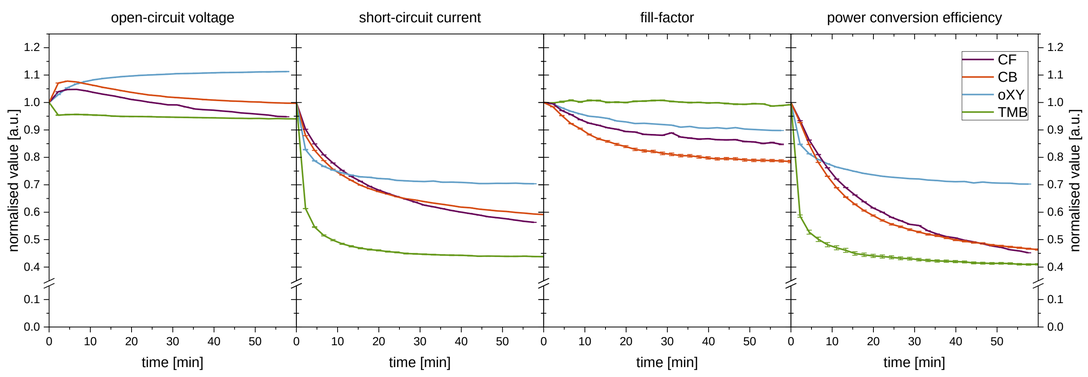


	CF	CB	oXY	TMB	
V_{OC}	0.868	0.799	0.785	0.813	V
I_{SC}	23.3	22.3	21.9	18.7	mA cm^{-2}
MPP	11.6	10.5	9.7	9.6	mW cm^{-2}
FF	57.3	58.7	56.7	63.5	%
PCE	**11.4**	**10.7**	**9.9**	**9.8**	**%**

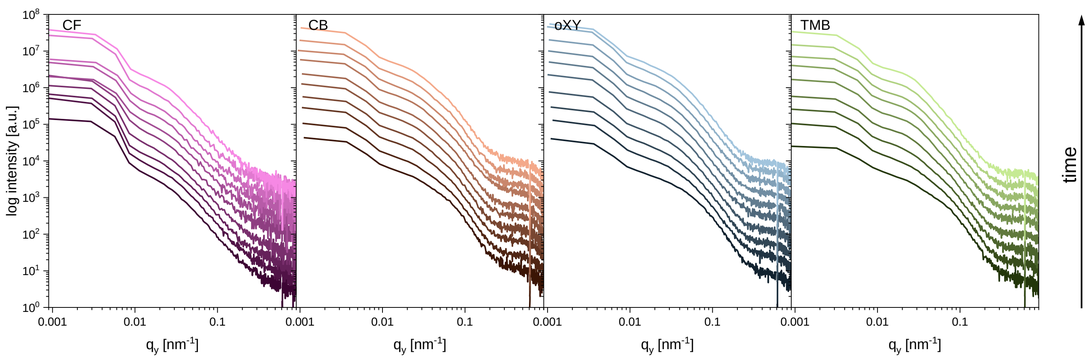


- non-halogenated solvents reduce solubility behaviour of BTP-4F acceptor and decrease solar cell performance
- slight reduction in open circuit voltage (V_{OC}) by > 50 mV corresponding to BTP-4F absorption red-shift
- TMB exhibits highest fill-factor (FF), power conversion efficiency (PCE) highest in CF

In-operando degradation studies of solar cells at 1.5 AM with synchronous GISAXS



- similar behaviour by CF & CB; V_{OC} shortly increases; decrease in I_{SC} dominates loss in PCE
- oXY retains highest PCE (70% after 1 h); V_{OC} permanently raised; I_{SC} stagnates at 70%
- TMB exhibits strongest performance loss; strong initial loss in ISC; FF permanently increased slightly; no increase in V_{OC}



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References
[1]www.pv-magazine.com
[2] smart.electronicsforu.com
[3] horizon-magazine.eu
[4] scitechdaily.com