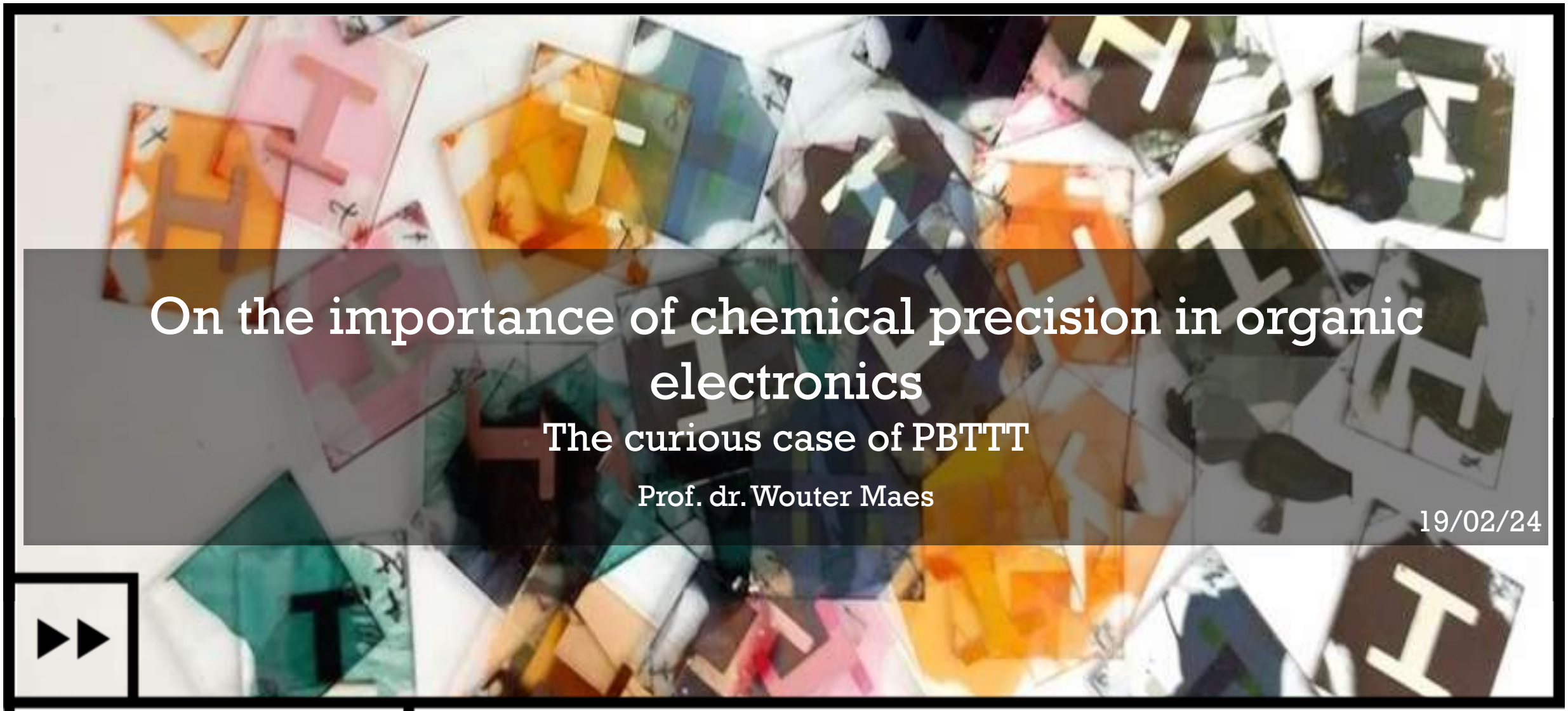

On the importance of chemical precision in organic electronics

The curious case of PBTTT

Prof. dr. Wouter Maes

19/02/24

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KNOWLEDGE IN ACTION

IMO-IMOMEC UHASSELT imec

DSOS DESIGN AND SYNTHESIS OF ORGANIC SEMICONDUCTORS

Energy Ville

fwo

38th Australasian Polymer Symposium - Auckland

Introduction to the DSOS group

conjugated polymers and small molecules

organic electronics and advanced healthcare

3 postdocs & 10 Ph.D. students

DSOS
DESIGN AND SYNTHESIS OF ORGANIC SEMICONDUCTORS

design, synthesis, purification and characterization

Prof. Koen Vandewal

Institute for Materials Research (IMO-IMOMEC)

new Science Tower facilities @UHasselt (Belgium)

https://www.uhasselt.be/DSOS @woutermaes_dsos

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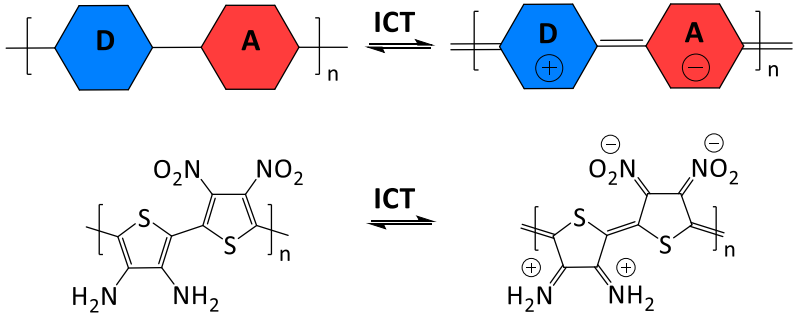
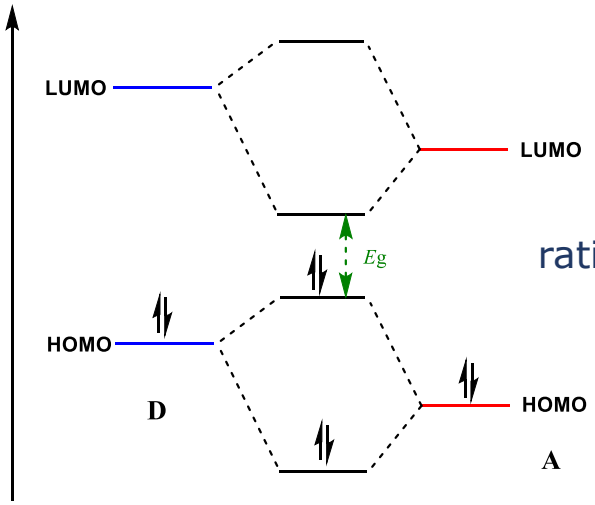
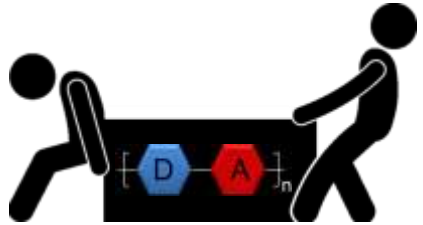
Intro - push-pull type conjugated polymers

Donor-acceptor (D-A) approach

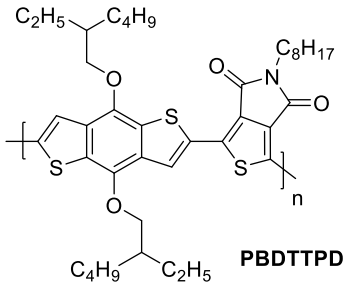




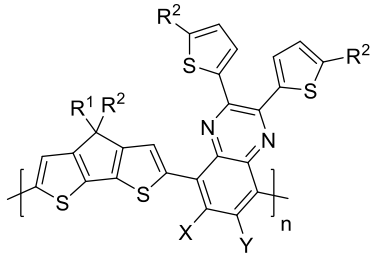
rational (tailored) bandgap control



Examples

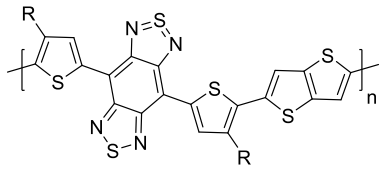


PBDTTPD



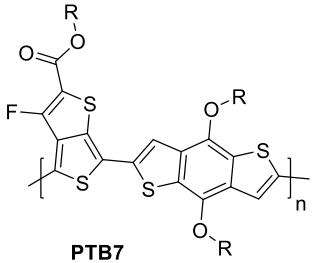
PCPDTQx(F)

R = alkyl



PTBBTT-TT

R = alkyl



PTB7

R = 2-ethylhexyl

alternating copolymers
mostly heteroaromatic monomers
very large structural diversity

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Application fields

organic photovoltaics (OPVs)

organic photodetectors (OPDs)

organic light-emitting diodes (OLEDs)

organic electrochemical transistors (OECTs)

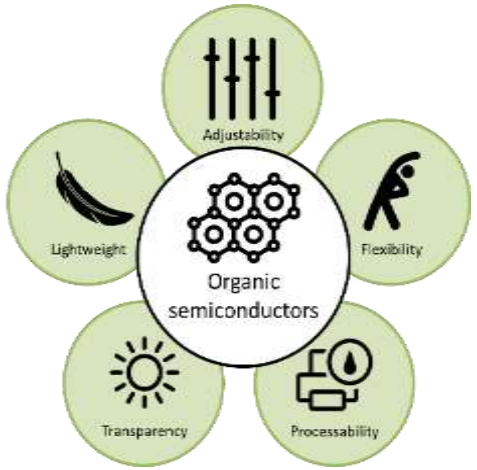
organic thermoelectrics

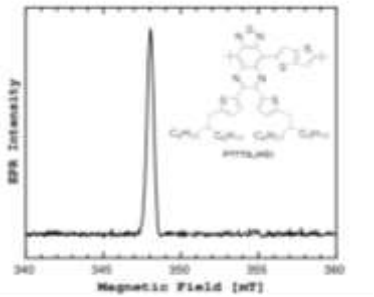
organic spintronics

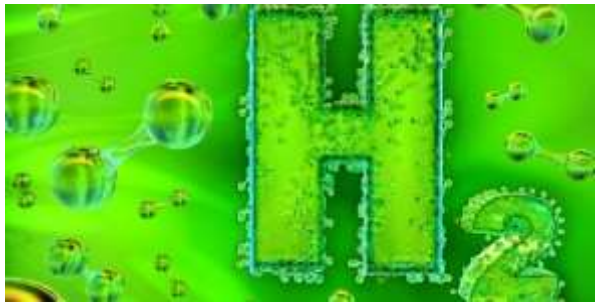
intrinsically stretchable and healable/wearable bioelectronics

photocatalytic hydrogen evolution

…







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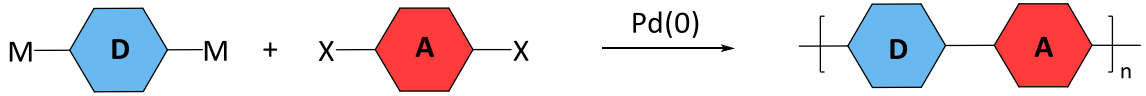
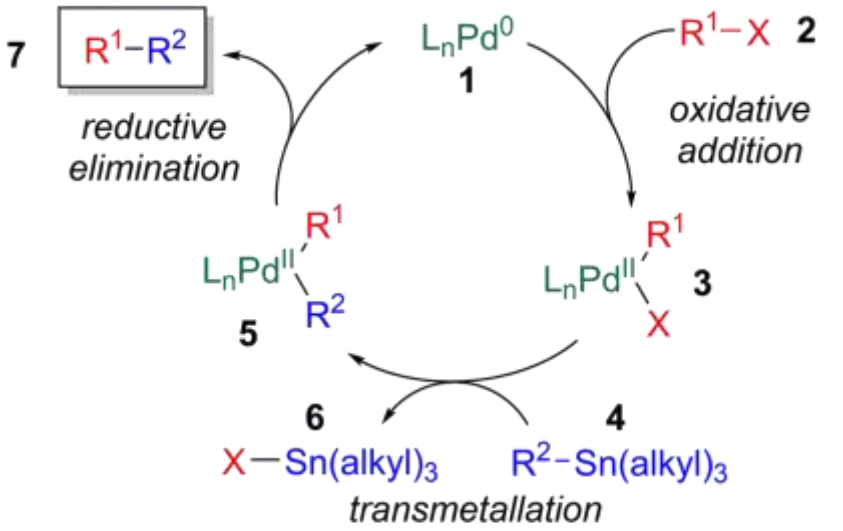
Synthetic strategies

Pd-catalyzed Stille/Suzuki cross-coupling (or DArP) → perfectly alternating materials (implicitly assumed)



Catalytic cycle of the Stille reaction (simplified version)



R¹, R² = allyl, alkenyl, aryl; X = Cl, Br, I, OTf, etc.
L = phosphine; alkyl = Me, Bu

Traditional approach
- combine monomers and catalyst
- heat overnight
- scavenge catalyst
- soxhlet extractions
- precipitation and filtration
- ready for device analysis

Crshugrue - Own work, modified from Kurti, L.; Czako, B. Strategic Applications of Named Reactions in Organic Synthesis; Elsevier: Burlington, 2005

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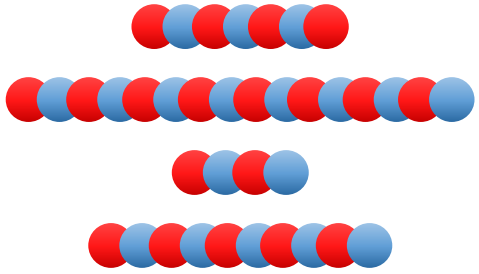
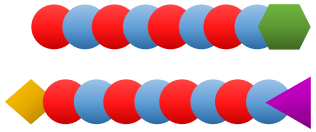
Problem – reproducibility issues / batch-to-batch variations

Origin

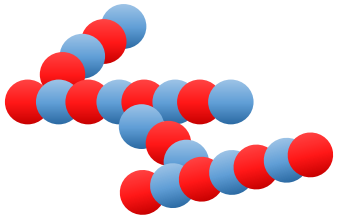


molar mass (dispersity)

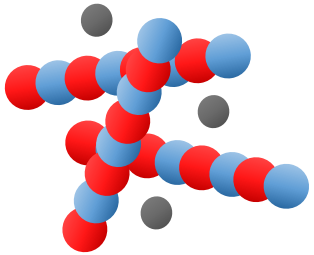


end-capping

homocoupling



branching (cross-linking)

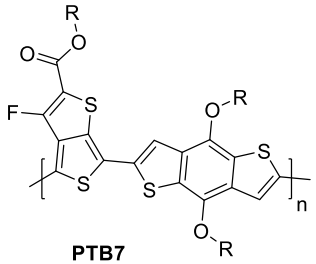


metal impurities

Not only in academia; commercial suppliers struggle with reproducibility as well and this is still not solved!

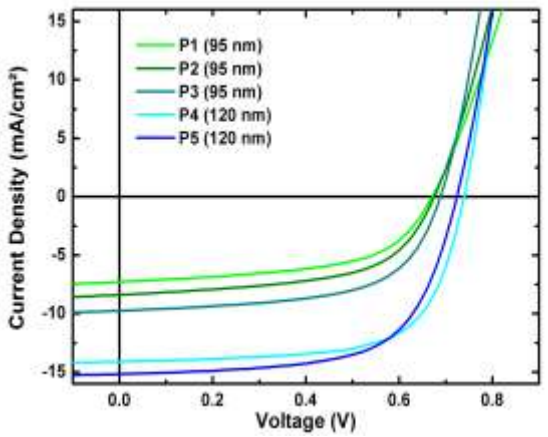
Example

OPV polymer



PTB7
R = 2-ethylhexyl

➔ 5 commercial batches from 2 companies



Batch	V_{oc} [mV]	$J_{sc\ JV}$ [mA cm^{-2}]	FF [%]	PCE [%]
P1	670	7.3	56	2.7
P2	675	8.4	57	3.3
P3	690	9.7	61	4.0
P4	740	14.1	67	7.0
P5	720	15.2	64	7.0

G. Pirotte *et al.*, *Adv. Electron. Mater.* **2018**, 1700481 – DOI:10.1002/aelm.201700481
T. Vangerven *et al.*, *Chem. Mater.* **2015**, *27*, 3726 – DOI:10.1021/acs.chemmater.5b00939

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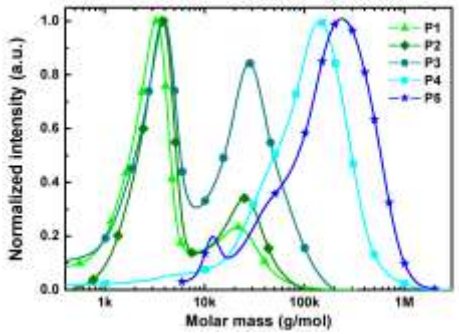
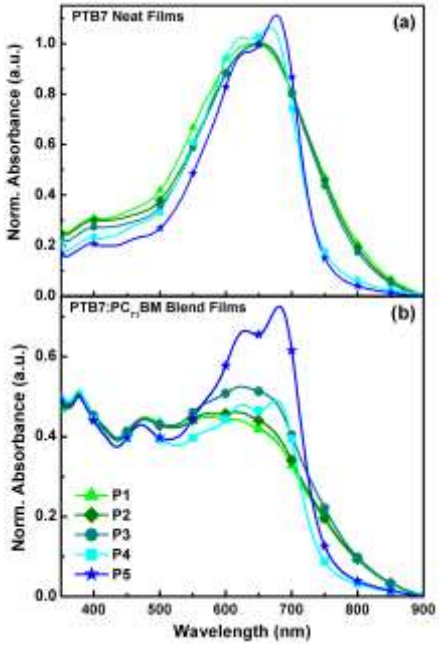
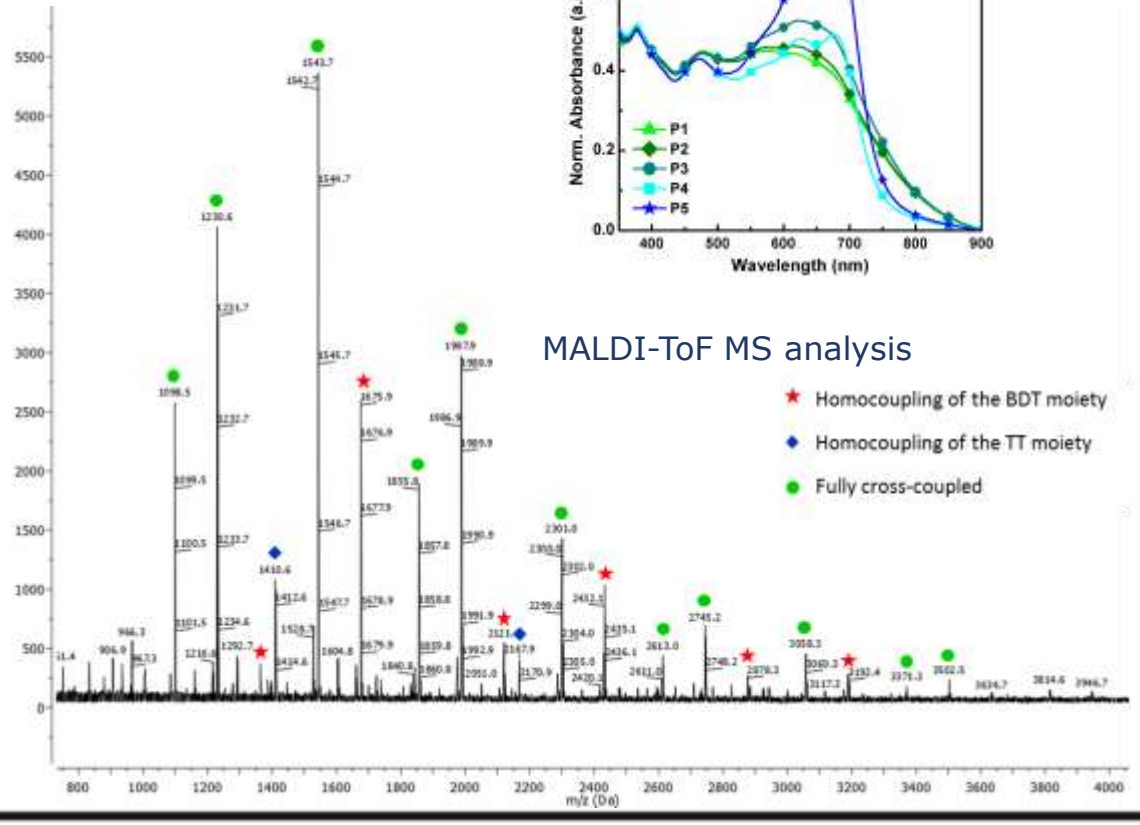
GPC analysis



UV-Vis analysis

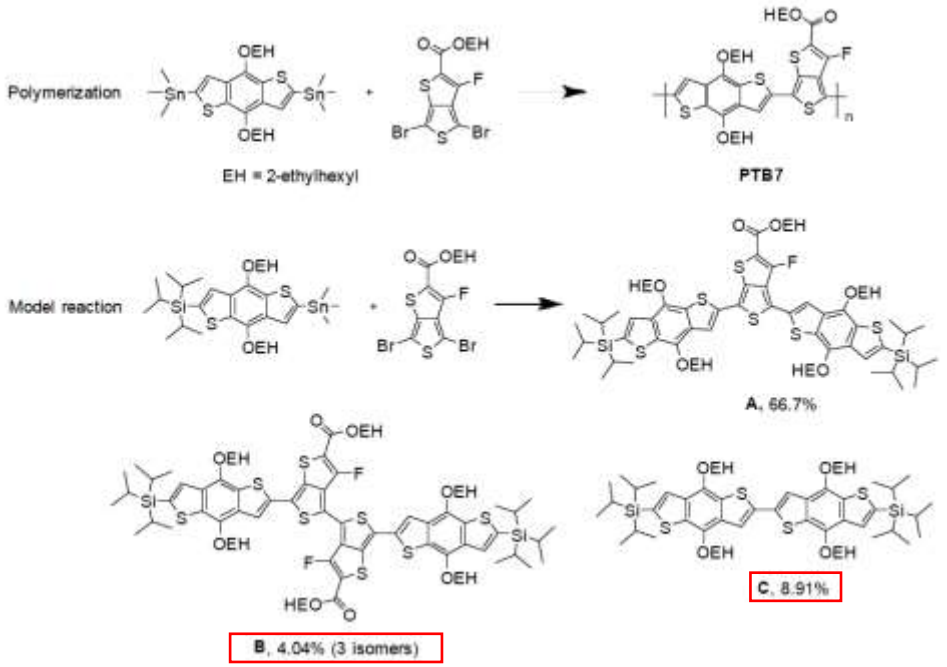


MALDI-ToF MS analysis



PTB7 → combined effect of molar mass and **homocoupling**

model reaction
→ D-D and A-A homocoupling
→ the amount of homocoupling can be substantial
→ not at all surprising this also appears during polymerization



L. Yu *et al.*, *Chem. Mater.* **2015**, *27*, 537

T. Vangerven *et al.*, *Chem. Mater.* **2015**, *27*, 3726 – DOI:10.1021/acs.chemmater.5b00939

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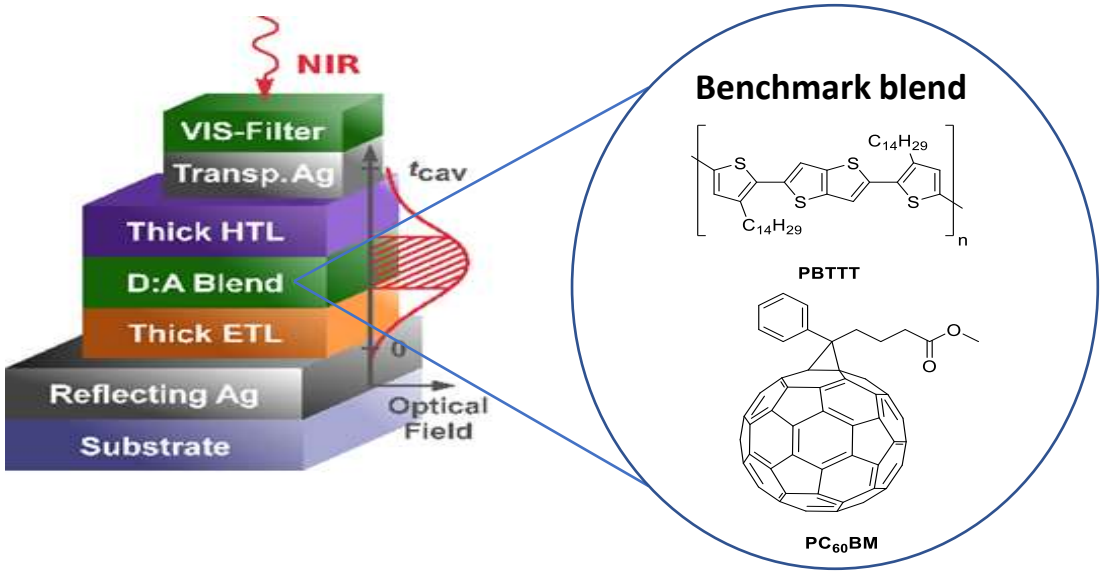
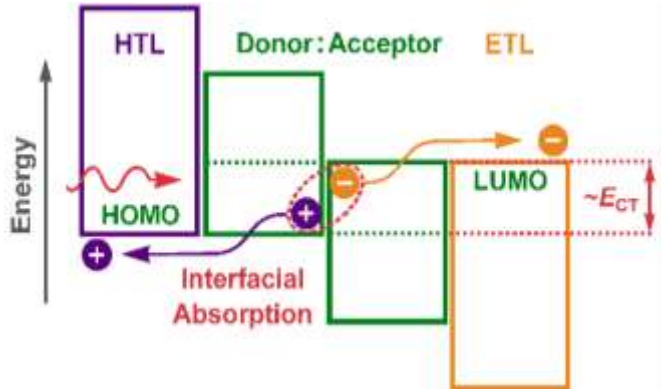
The curious case of PBTTT (a probe for structural perfection)

Organic cavity photodetectors

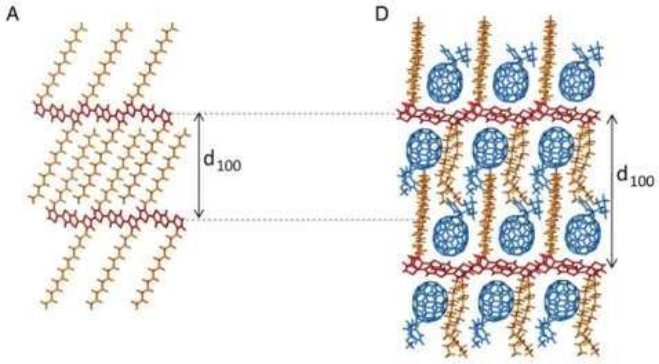


Vandewal *et al.*, *Adv. Mater.* **2017**, *29*, 1702184; *Nat. Commun.* **2017**, *8*, 15421

apply the weak <u>intramolecular</u> D:A absorption for narrow-band NIR light detection



co-crystal formation



McGehee *et al.*, *Adv. Energy Mater.* **2012**, *2*, 1208

PBTTT:$PC_{60}BM$ is a known 'intercalating' donor:acceptor blend

⇩

optimal D:A interface for CT absorption

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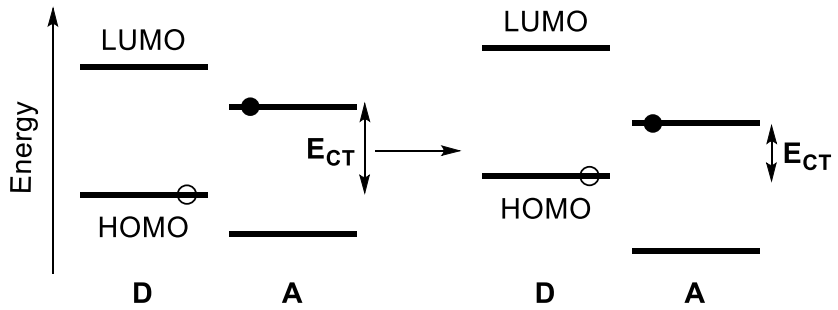
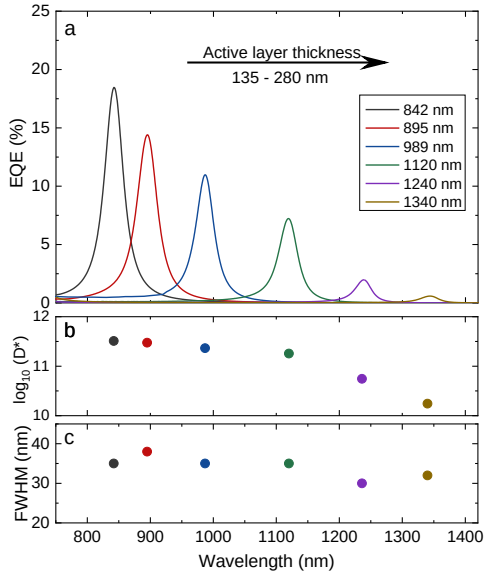
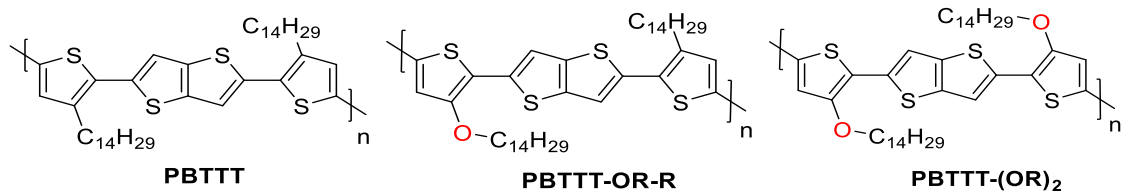
Tuning electronic and morphological properties





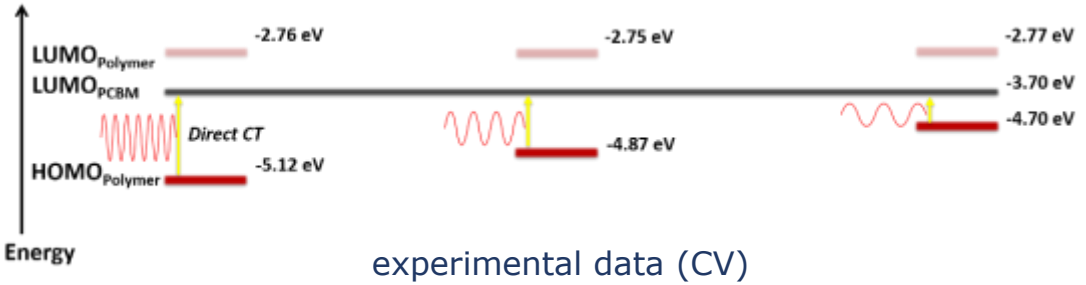
PBTTT-OR-R: extended detection range for narrow-band OPDs wavelength regime 840–1340 nm, FWHMs of 30–38 nm, D^* values of 5×10^{11} – 1.75×10^{10} Jones

Prof. Benoît Champagne



gradual introduction of alkoxy side chains to push up the HOMO level, while aiming to retain intercalation behavior

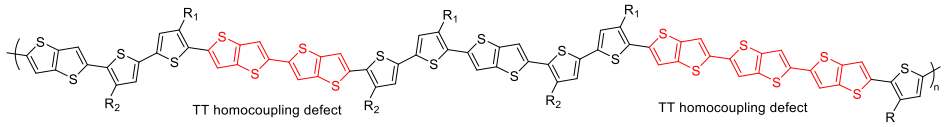
$HOMO_{calc}$	$HOMO_{calc}$	$HOMO_{calc}$
-4.95 eV	-4.88 eV	-4.58 eV

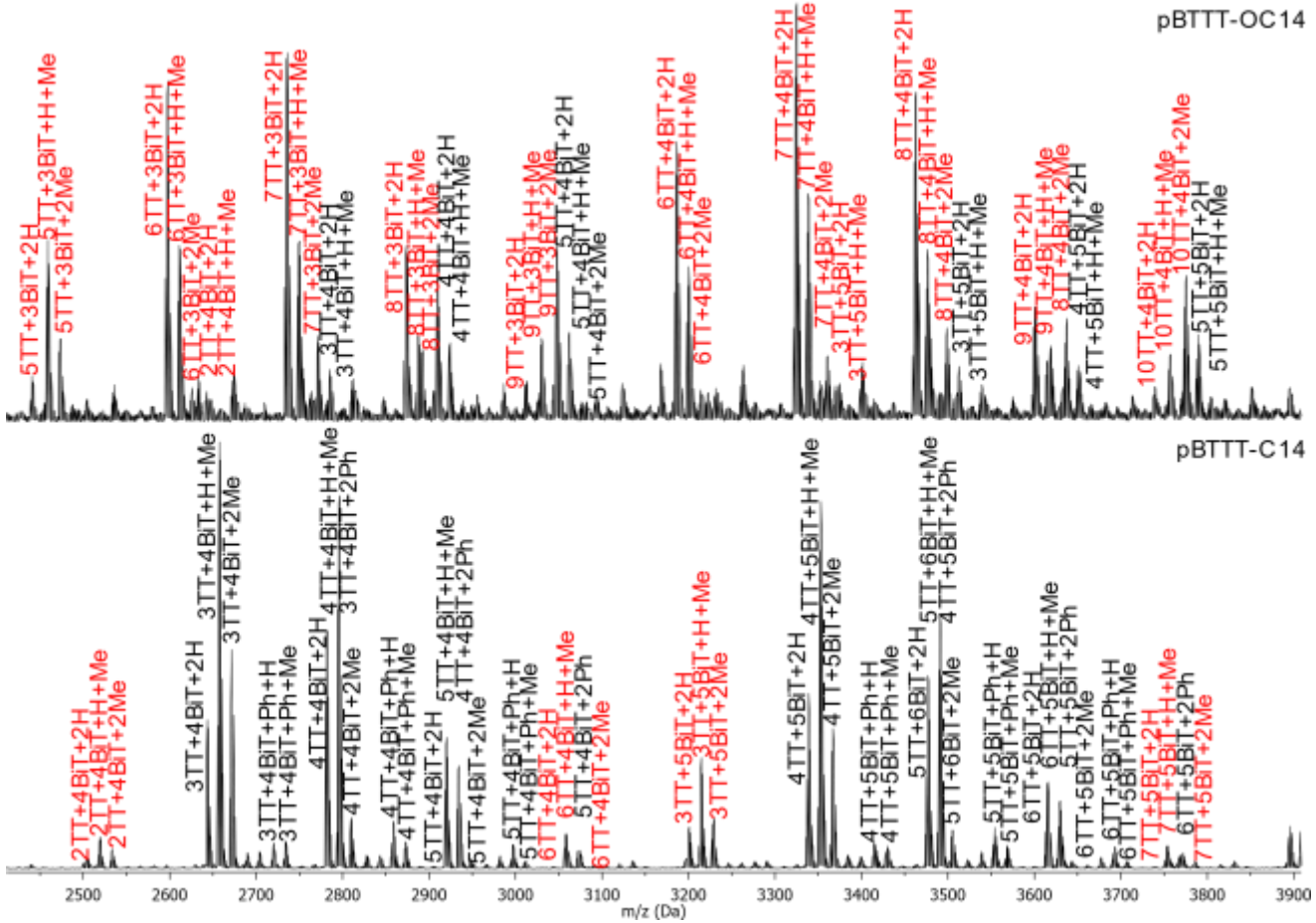


experimental data (CV)

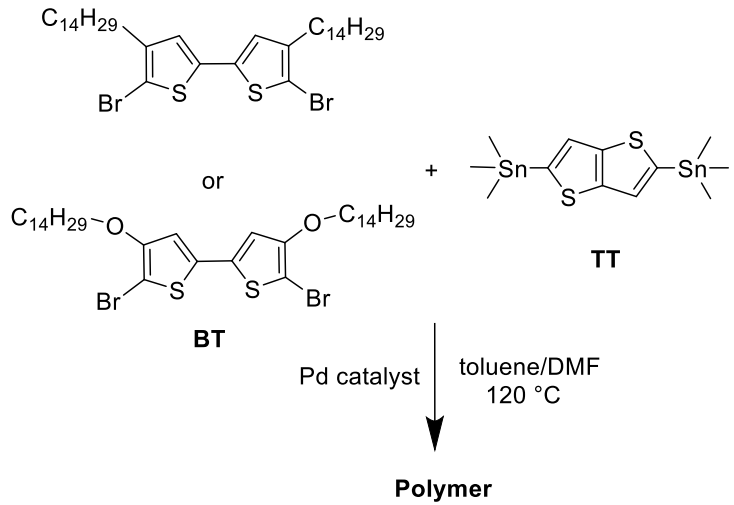
J. Vanderspikken *et al.*, *Adv. Funct. Mater.* **2021**, *31*, 2108146 – DOI:10.1002/adfm.202104060

MALDI-ToF MS analysis





conventional Stille synthesis



extensive homocoupling, especially for PBTTT-$(OR)_2$

⇩

Can this have a detrimental impact on intercalation, CT absorption and blend morphology?

J. Vanderspikken *et al.*, *Adv. Funct. Mater.* **2023**, 2308666 – DOI:10.1002/adfm.202308666

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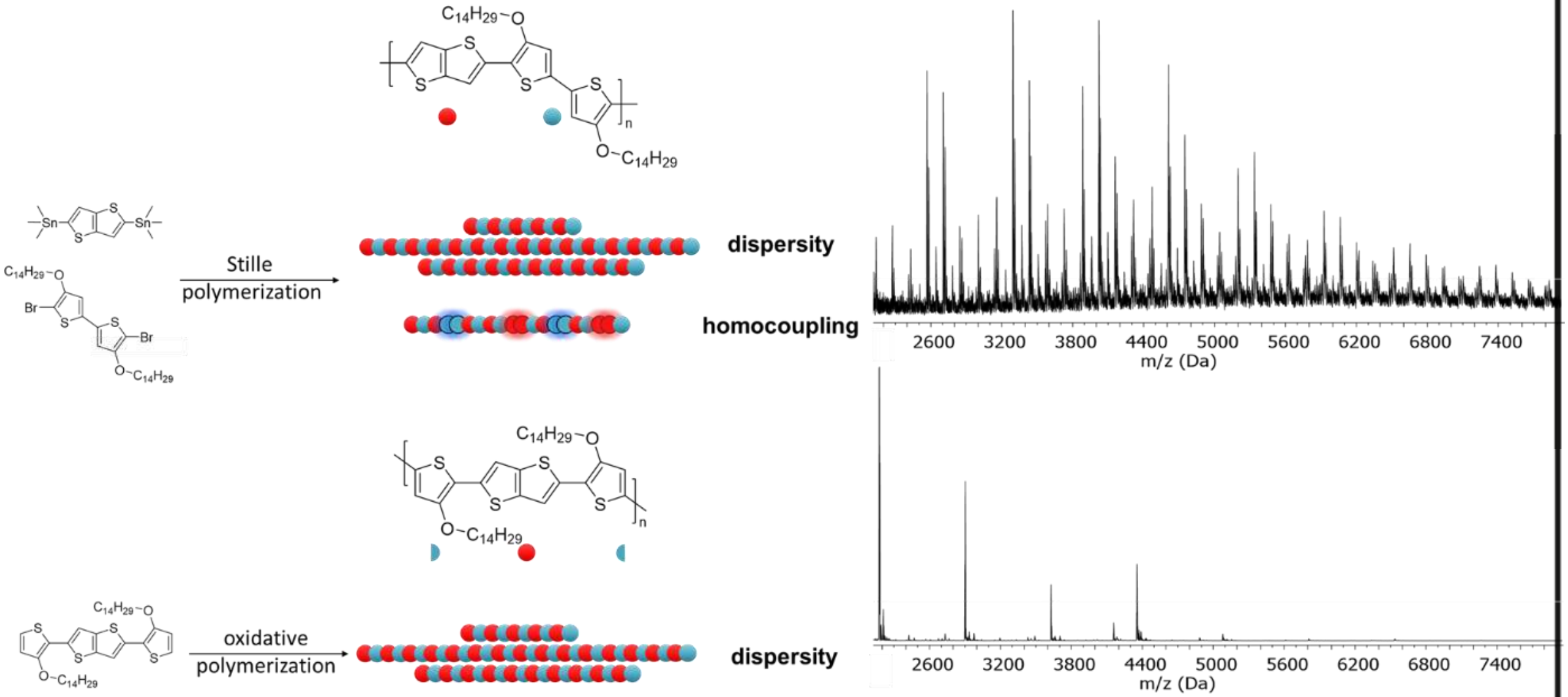
Alternative synthesis method



J. Vanderspikken *et al.*, *Adv. Funct. Mater.* **2023**, 2308666 – DOI:10.1002/adfm.202308666

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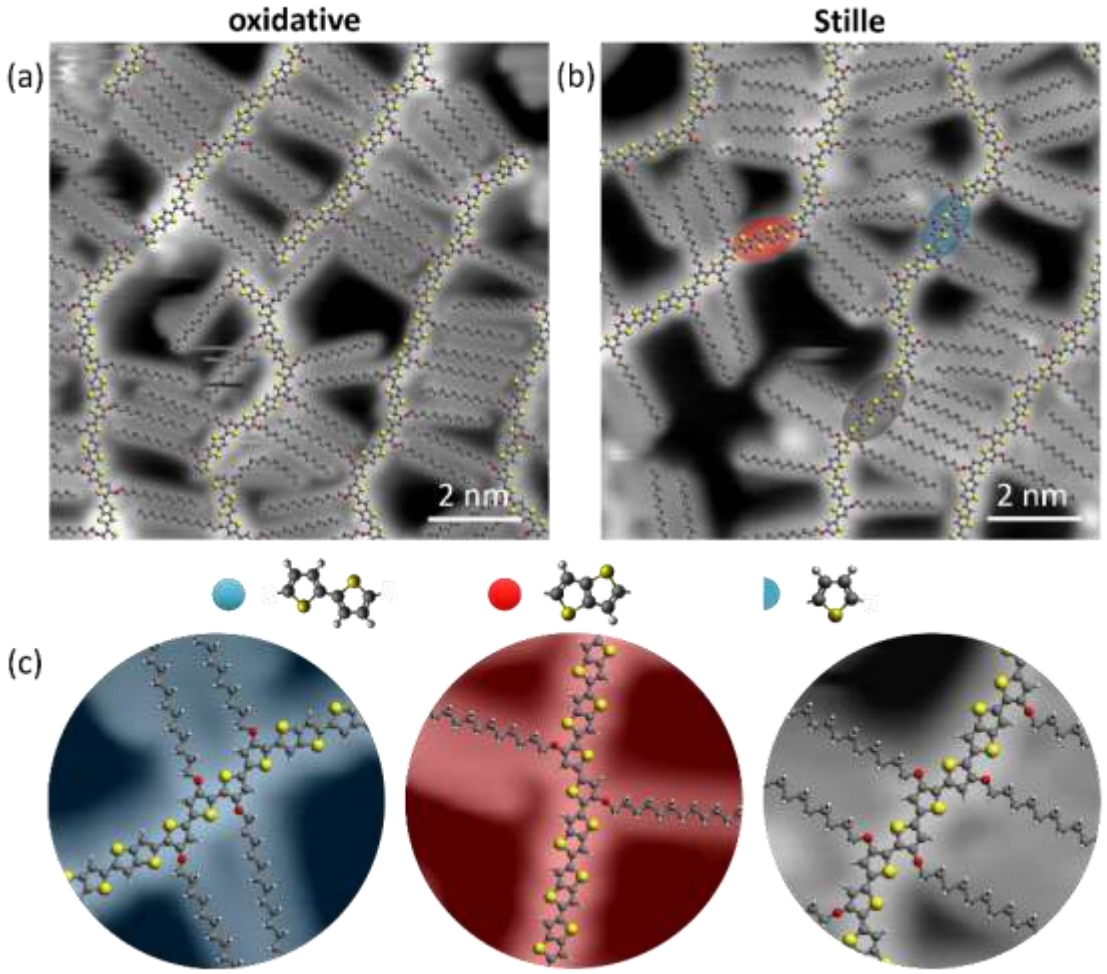
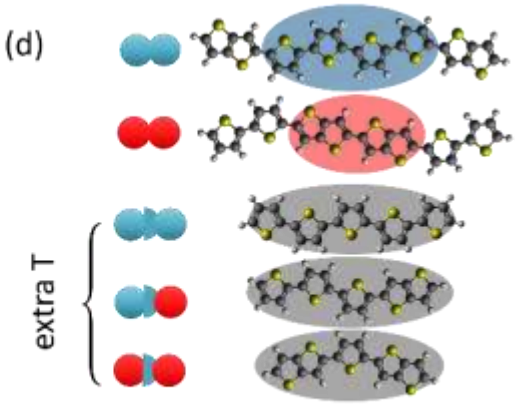
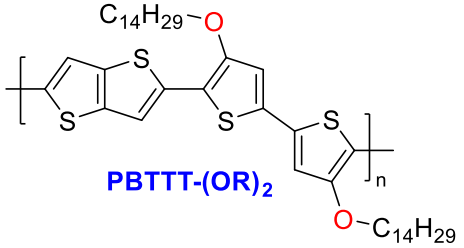
STM analysis





Defect	Count	Frequency
	79	11%
	99	14%
extra T	7	1%
Sum	185	**26%**
	514	**74%**

Monomer	Count	Frequency
	376	49.2%
	381	49.9%
	7	0.9%



UNIVERSITY OF BIRMINGHAM

Prof. Giovanni Costantini

J. Vanderspikken *et al.*, *Adv. Funct. Mater.* **2023**, 2308666 – DOI:10.1002/adfm.202308666

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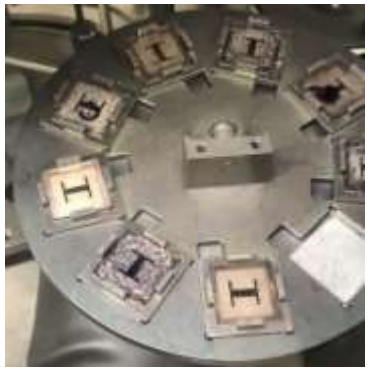
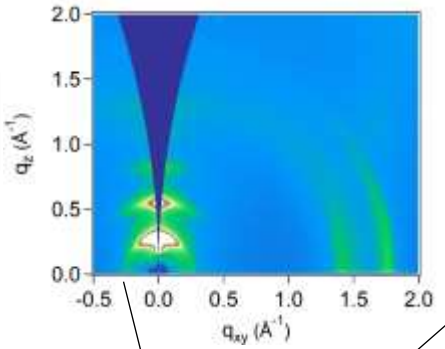
Effect of structural purification on material and device properties

device analysis



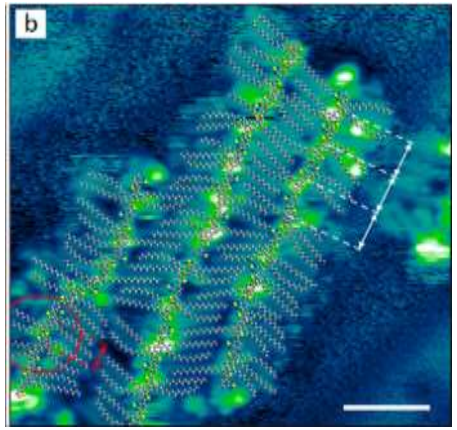
Prof. Koen Vandewal

GIWAXS

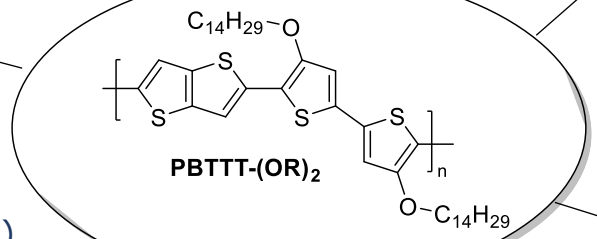


Prof. Alberto Salleo

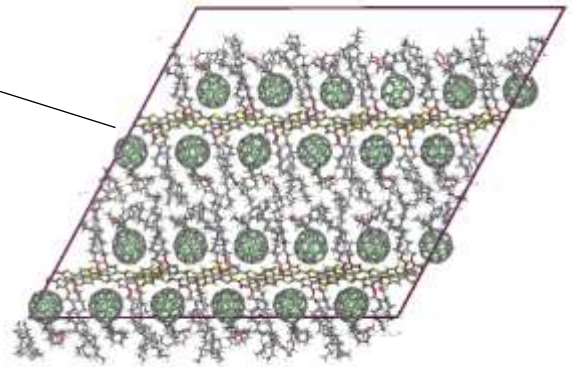
STM analysis



Prof. Giovanni Costantini



molecular mechanics/dynamics



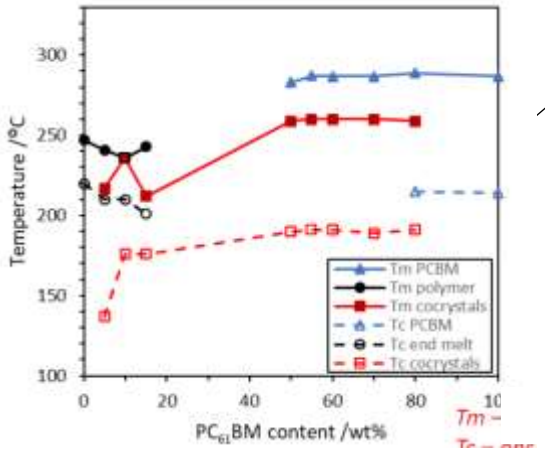
Prof. David Beljonne

Dr. Vincent Lemaur

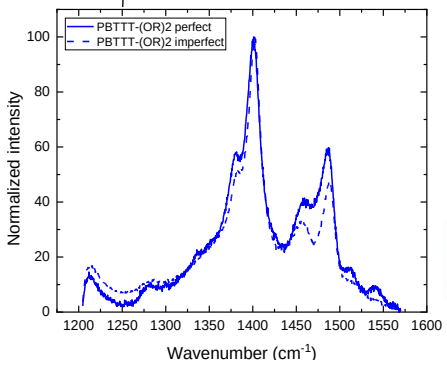
Prof. Em. Bruno Van Mele

Prof. Niko Van den Brande

state diagrams (RHC and T-resolved XRD)



Raman/XPS



Prof. Alberto Salleo

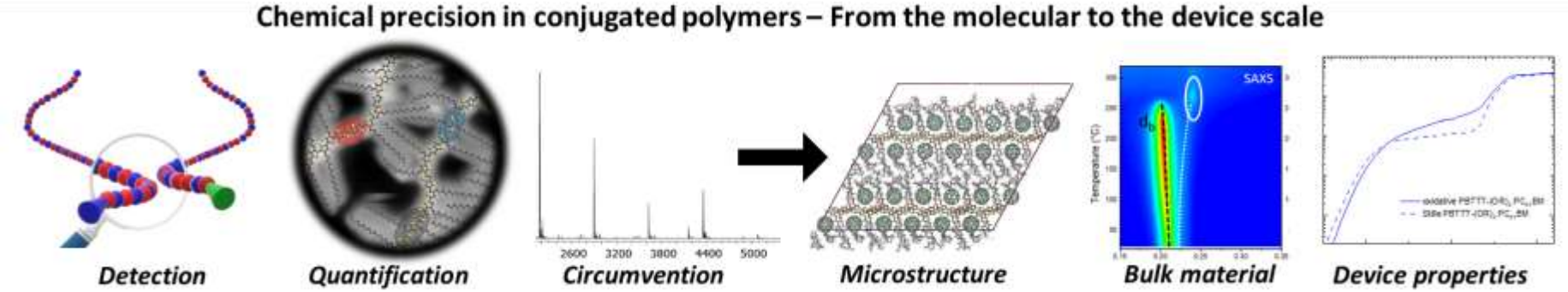
Prof. Bart Goderis

Prof. Erik Nies

J. Vanderspikken *et al.*, manuscripts in progress.

Conclusions

- Homocoupling readily occurs upon performing standard Stille cross-coupling protocols
  - Difficult to detect, especially for push-pull copolymers
  - Mostly detrimental to device (solar cell) performance (although the tolerance to these defects might be case-dependent)
  - Likely occurring quite regularly and plausible cause for many performance/reproducibility issues → still underestimated by the field
  - Of relevance as well to related fields (photodetectors, transistors, …)
- MALDI is a powerful – however, not quantitative (!) – technique for structural elucidation of push-pull type copolymers
- Defect-free cross-coupling conditions have been established now (observation → evaluation → remediation)
- PBTTT is a very useful (semicrystalline) probe to assess the influence of homocoupling (work in progress)



Thank you for your attention !