Congrès Général des 150 ans
de la Société Française de Physique
du 3 au 7 juillet 2023

26ème Congrès Général de la SFP

Auto-organization and doping of ultra-thin films of conducting polymers

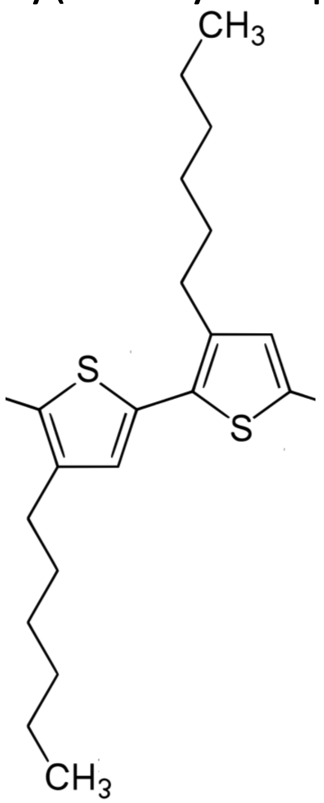
Presented by : Hugo Fernandez
Supervised by : Pr. Sophie Cantin, Dr. Alae El Haitami, Dr. Philippe Fontaine

CERGY PARIS UNIVERSITÉ
LPPI laboratoire de physicochimie des polymères et des interfaces
SIRIUS BEAMLINE
SOLEIL SYNCHROTRON

Context

- **P3HT**

Poly(3-hexylthiophene)



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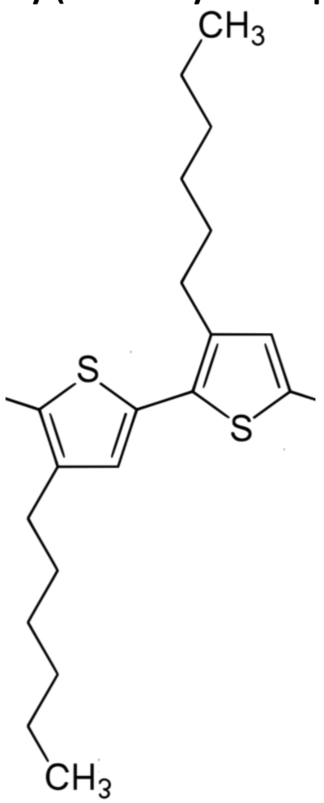


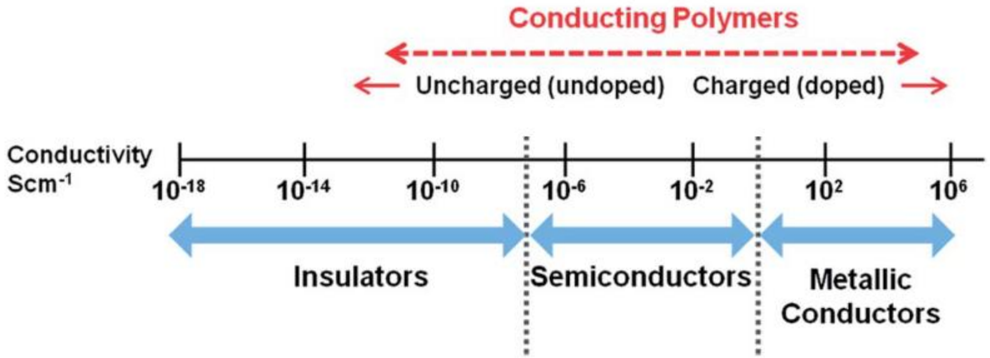
- Conjugated and conductive polymer :

σ can reach 10^3 S/cm **after doping**[1]

- Applications :

Field effect transistor[2]

Photovoltaic cell[3]



Ref. figure: G. Kaur *et al.*, *RSC Adv.*, 5(47), 37553-37567 (2015)

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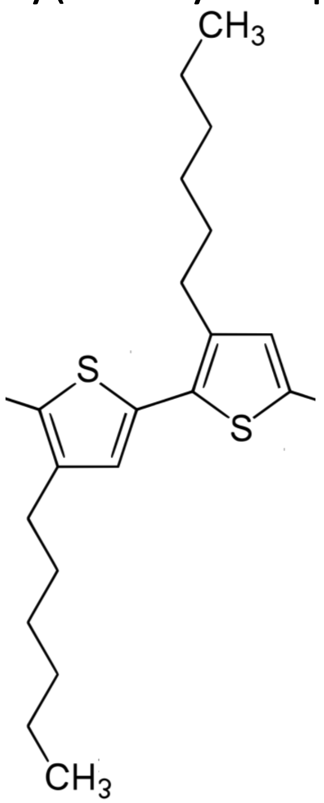

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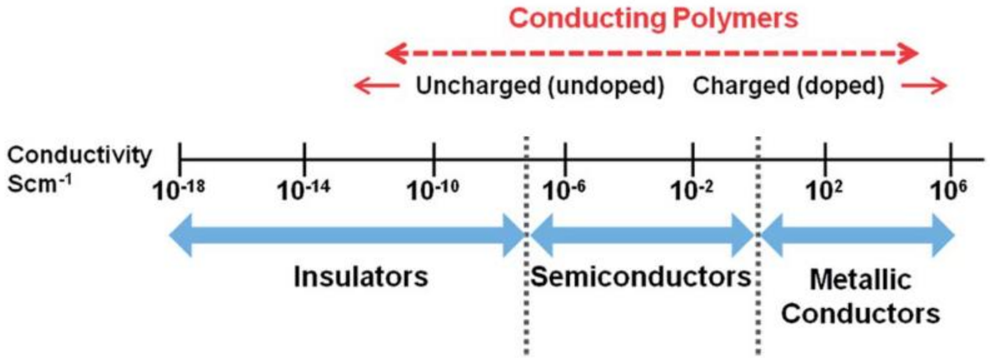

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Properties

⇕

Structure

⇕

Elaboration technique

Objective :

- Elaboration of **ultra-thin and organized** films

with the **Langmuir film technique**

⇨ Link between **structure and conductive properties**

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Langmuir film technique principle

- Elaboration of **film at the air-water interface**

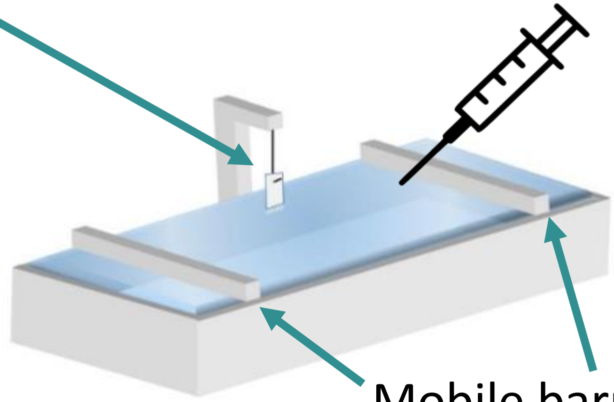
Langmuir film technique principle

- Elaboration of **film at the air-water interface**

$\pi = \gamma_0 - \gamma$

γ_0 = Surface tension of pure water
γ = Surface tension of water with film

Force sensor
⇨ Measurement of
surface pressure (π)



Thermostat
⇨ **Temperature** control

Mobile barriers
⇨ **Area** control

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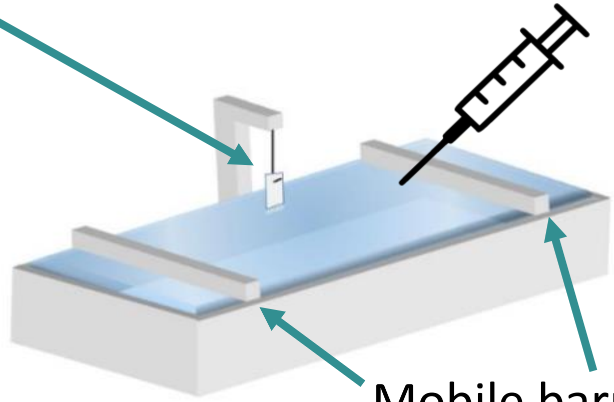

Thermostat
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Mobile barriers
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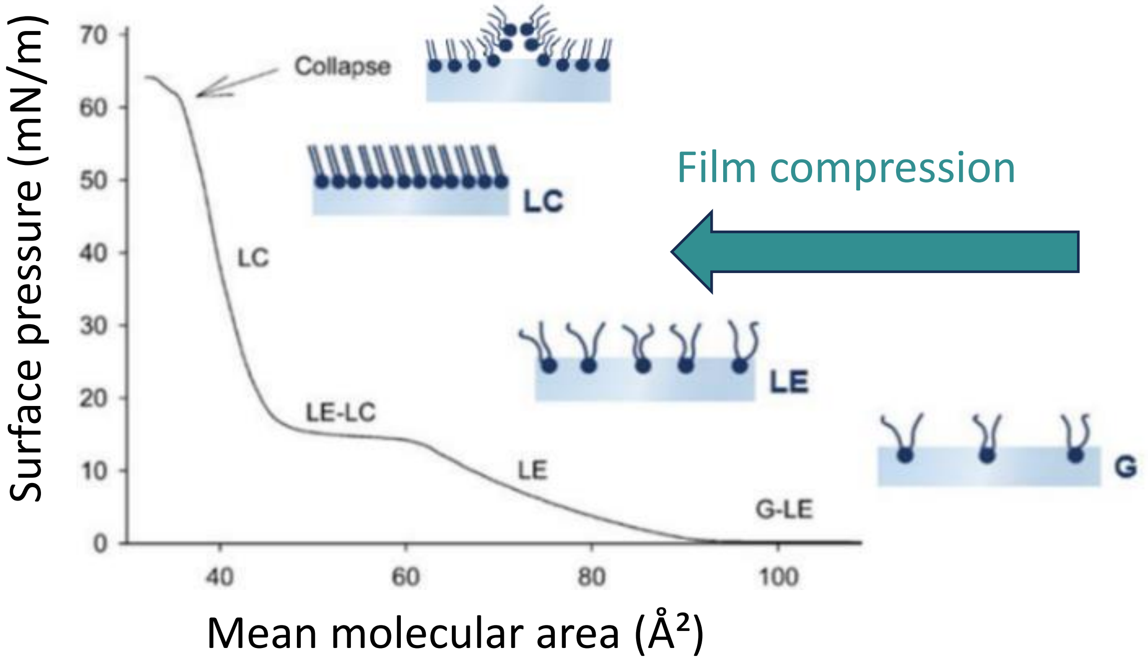
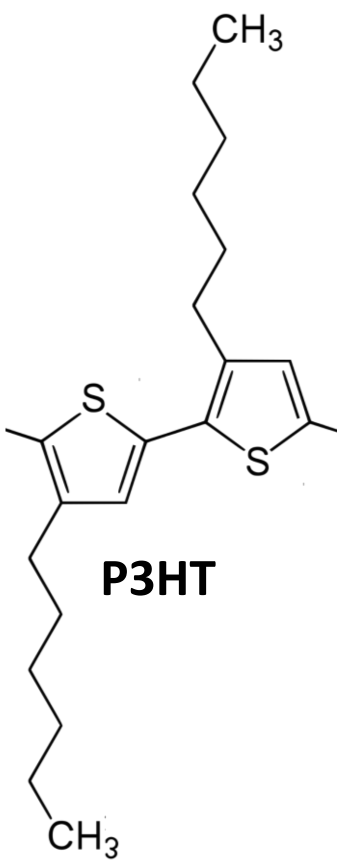
Compression isotherm



⇨ Film **thermodynamic** characterization

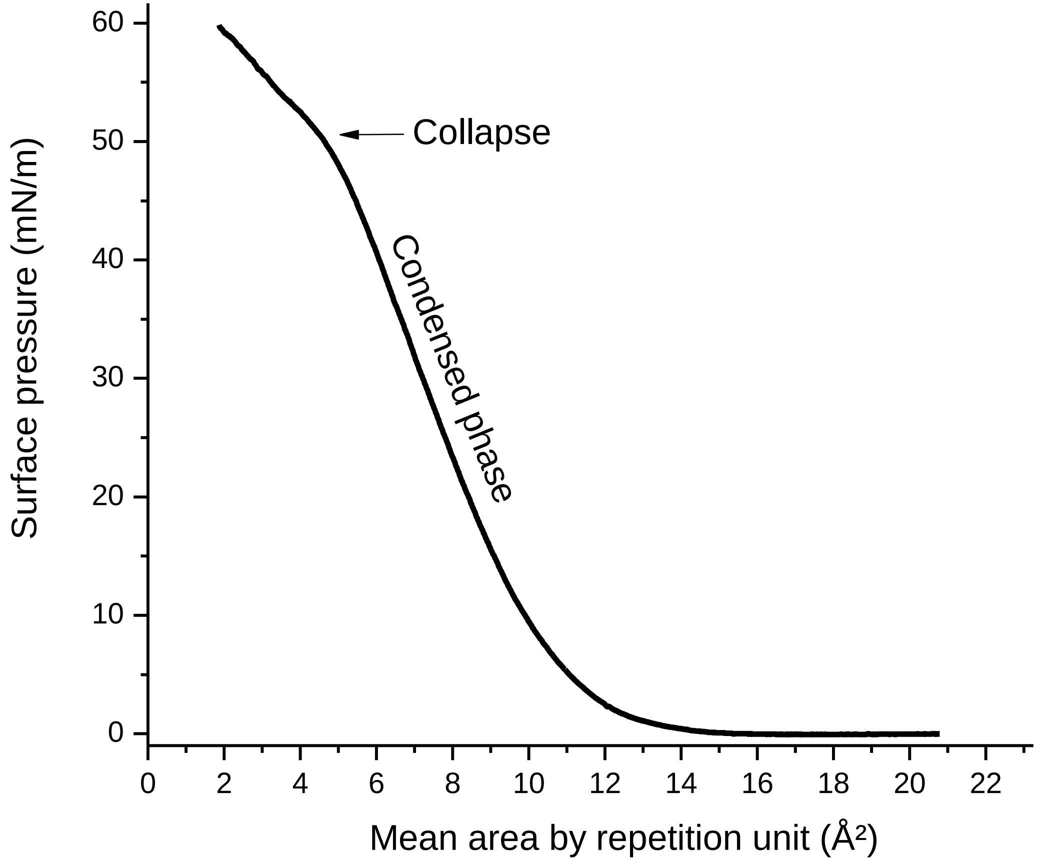
⇨ Detection of **phase transitions**

Thermodynamic and morphology of P3HT film at the air-water interface



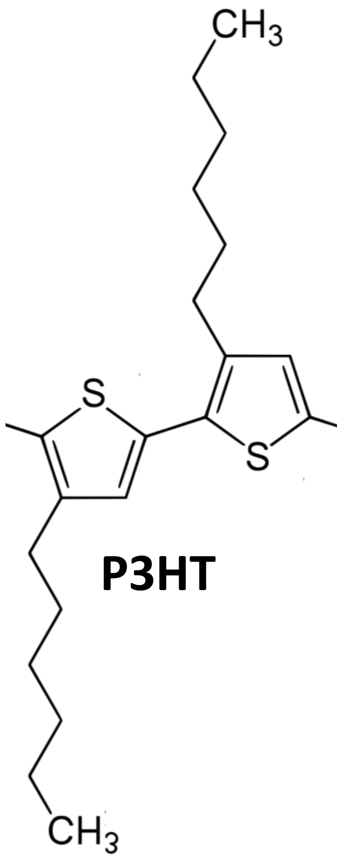
P3HT

- Compression isotherm at 20°C



⇨ **No phase transition detected** at non-zero surface pressure.

Thermodynamic and morphology of P3HT film at the air-water interface



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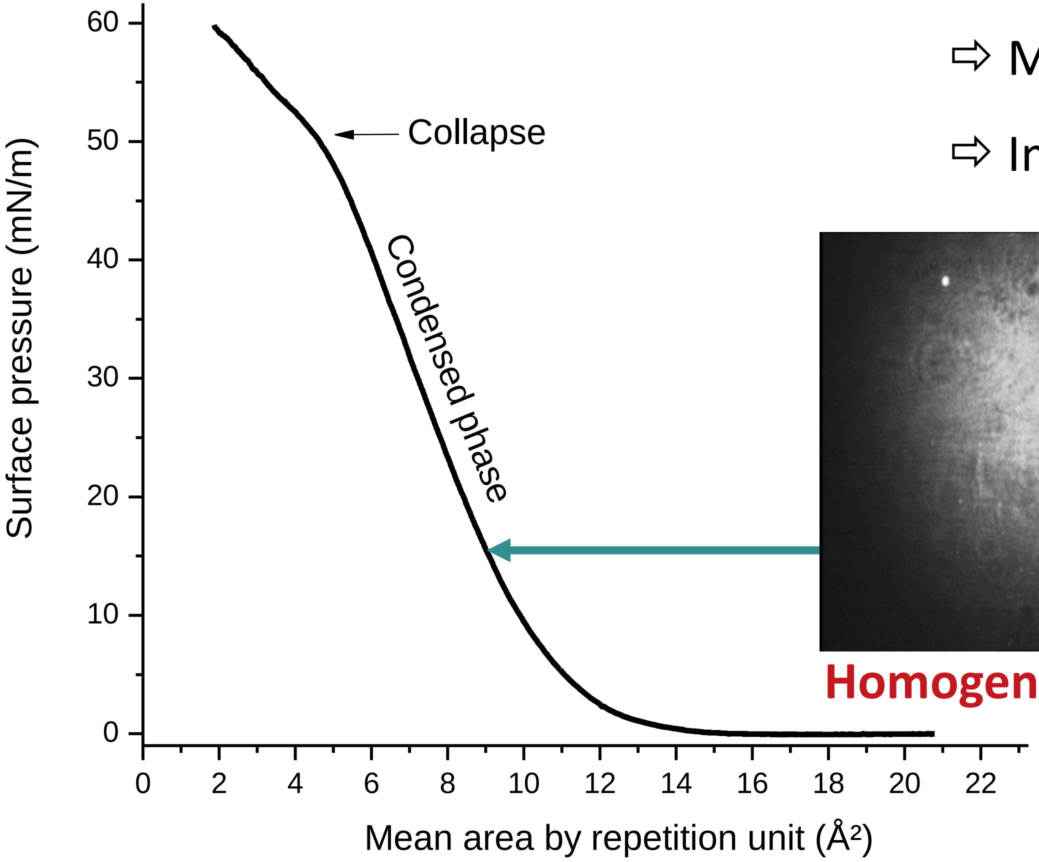
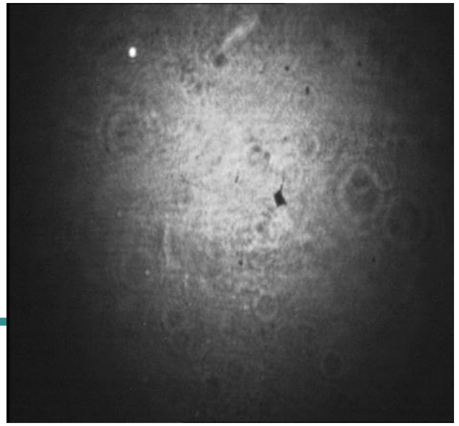


- Brewster angle microscopy (BAM)

⇨ Morphology at the air-water interface

⇨ Image size : 600 x 600 µm²



Homogeneous surface

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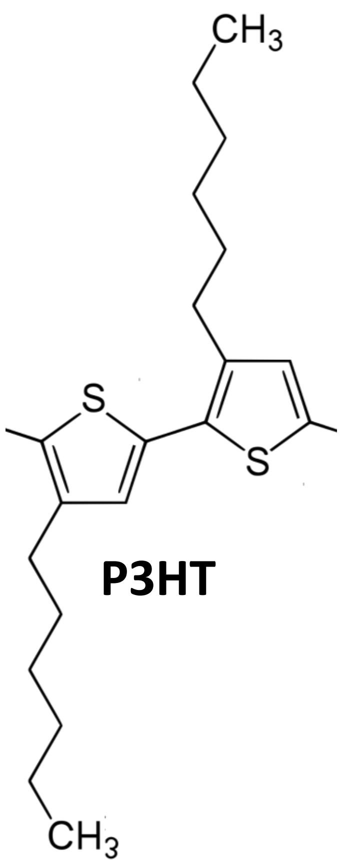

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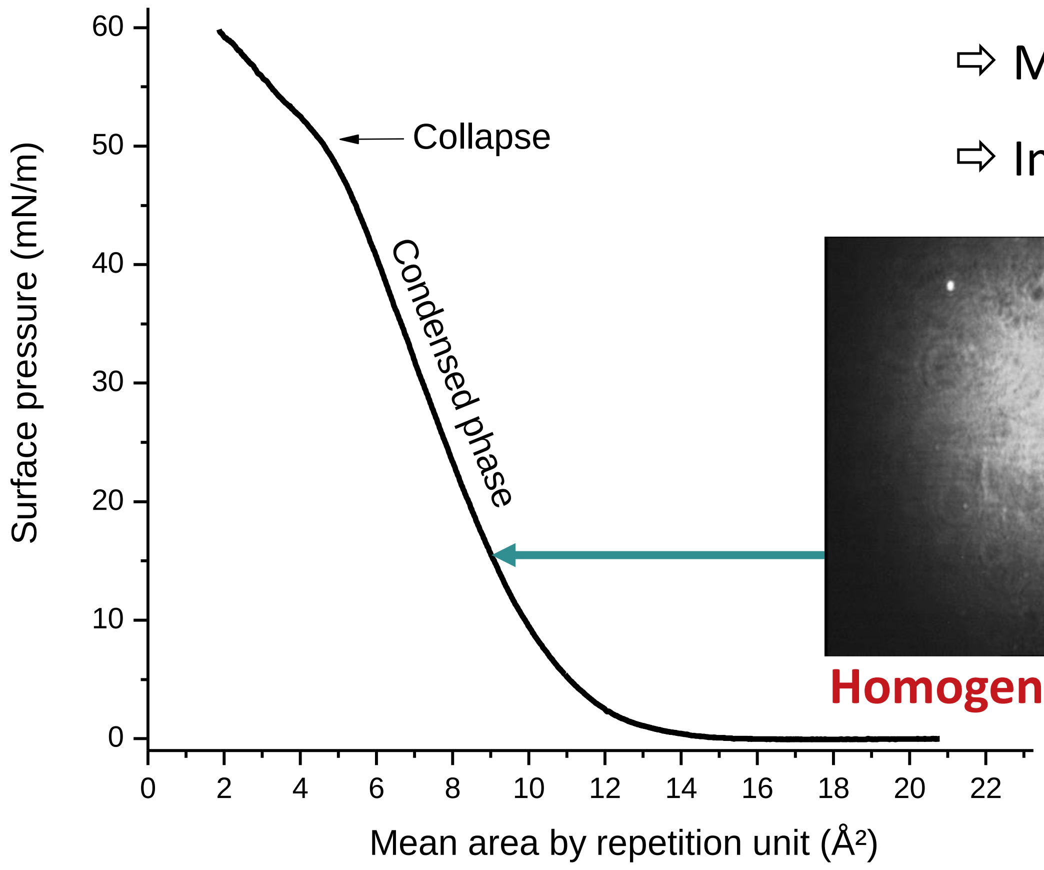

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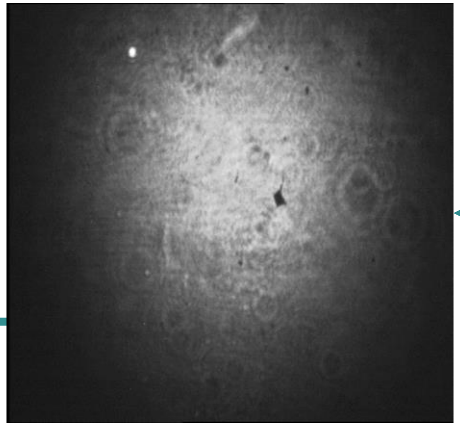

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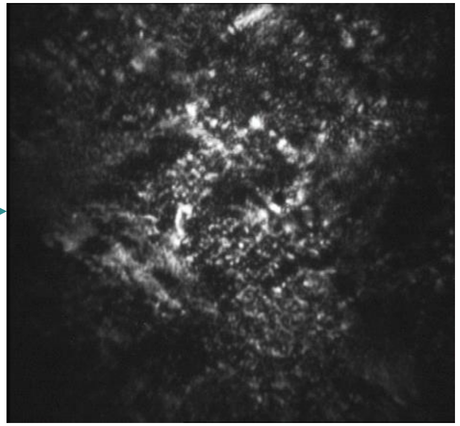


With analyzer :

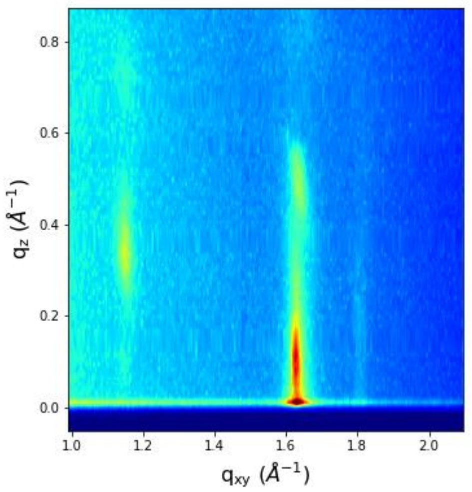
⇨ Optical **anisotropy**

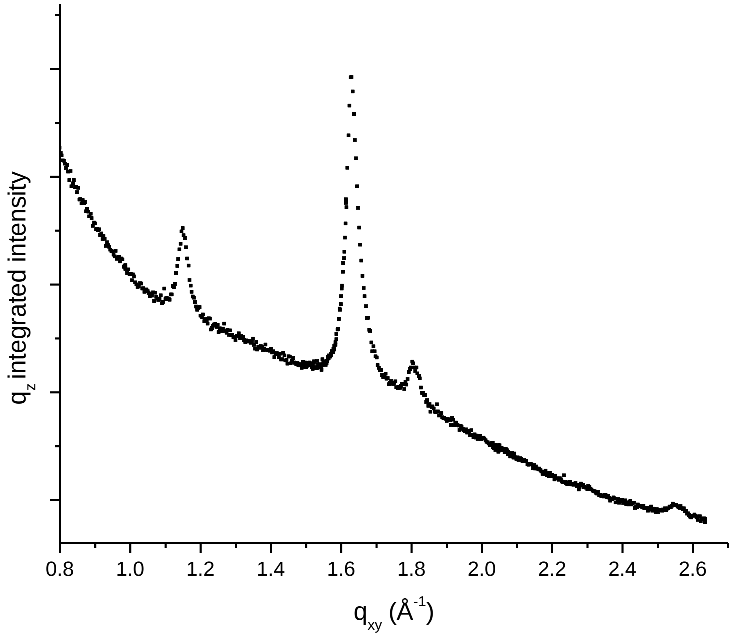
⇨ In-plane **organization**

⇨ **No phase transition detected** at non-zero surface pressure.

In-plane structure of P3HT film at the air-water interface

- Grazing Incidence X-ray Diffraction (GIXD)
- **P3HT** at 5mN/m





Thin peaks (FWHM = 0.05$Å^{-1}$) and good signal-to-noise ratio

⇨ **Long range** positional order

Diffraction rods ⇨ **2D Structure**

(Rings ⇨ 3D Structure)

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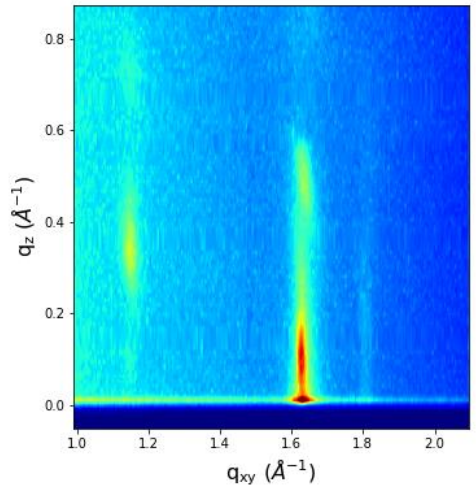
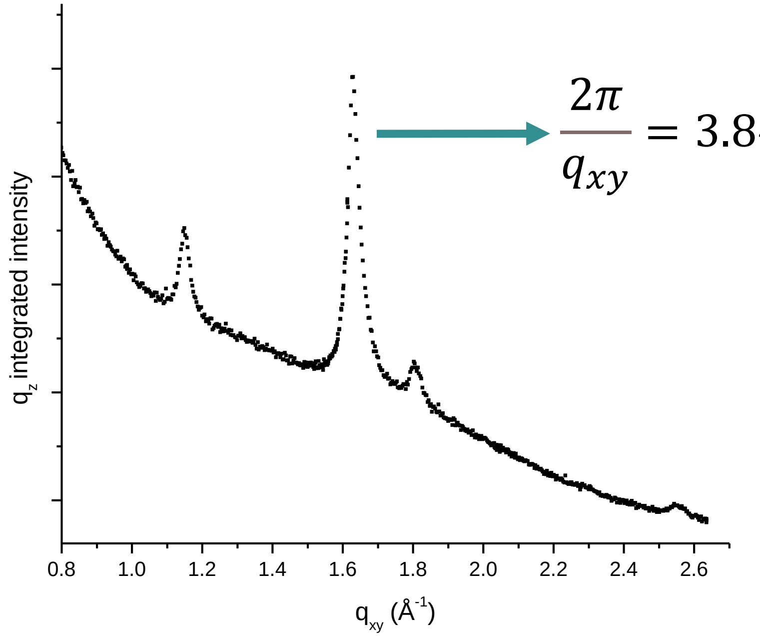
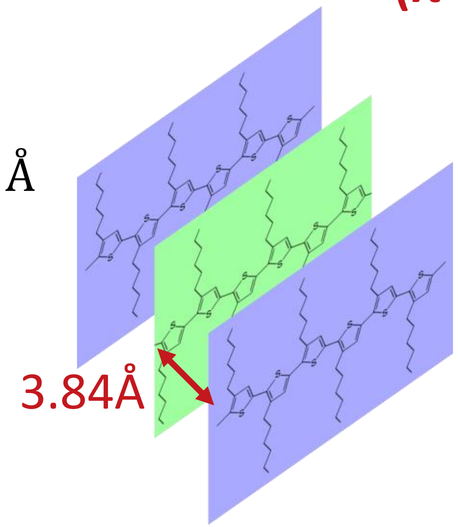
Characteristic length **between thiophenes planes**

(π-π interactions inter-chains)[ref.]





$$\frac{2\pi}{q_{xy}} = 3.84\ \text{Å}$$



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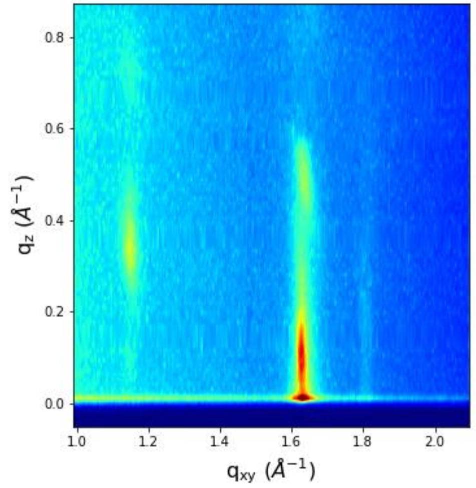

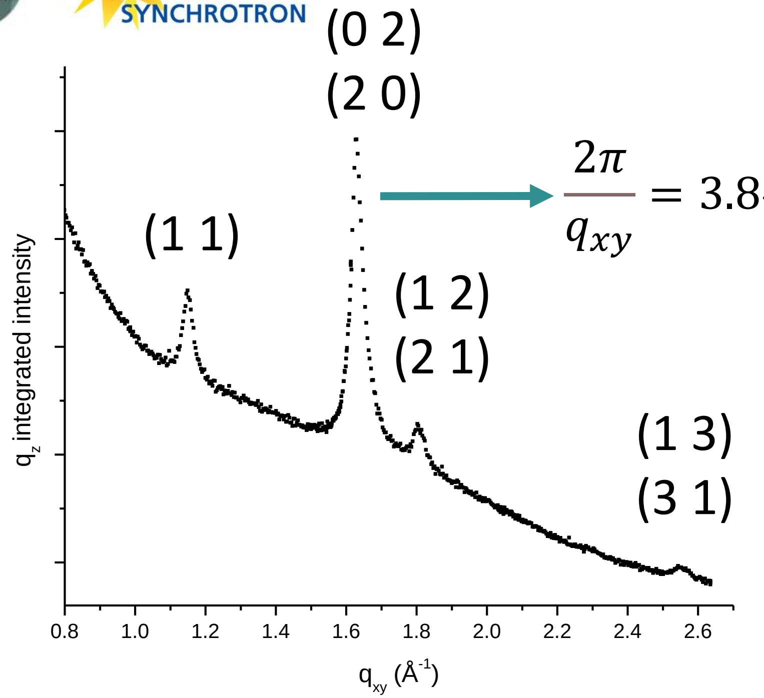

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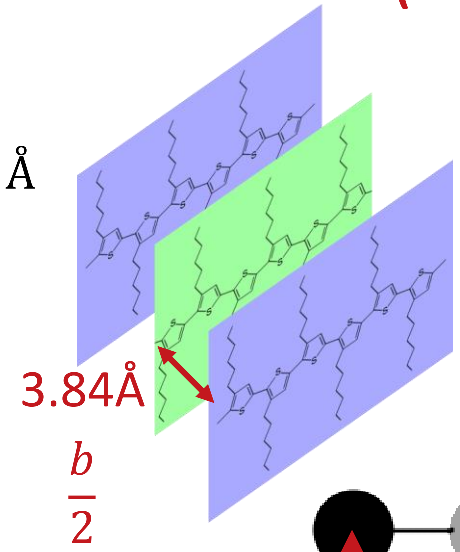

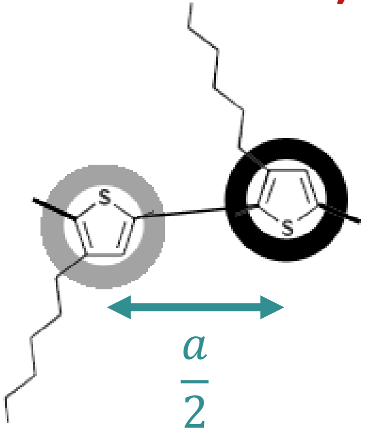

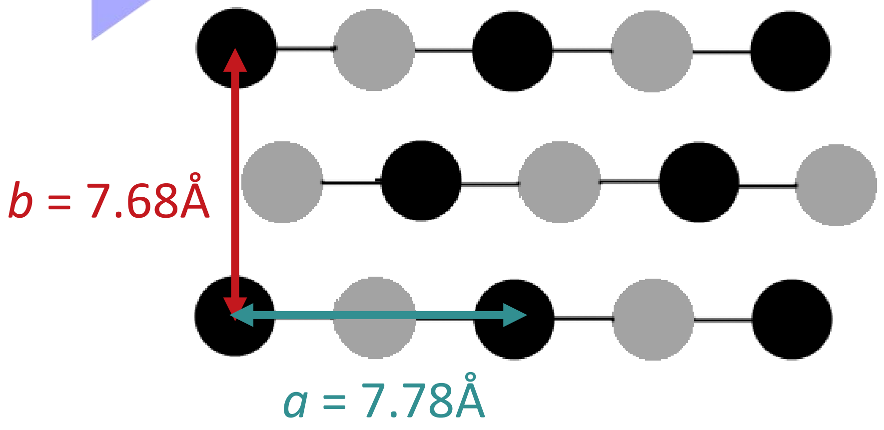

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Existence of (1 2) – (2 1) peak ⇨ **Non-centered lattice**

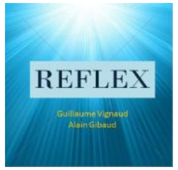
Vertical structure of P3HT film at the air-water interface

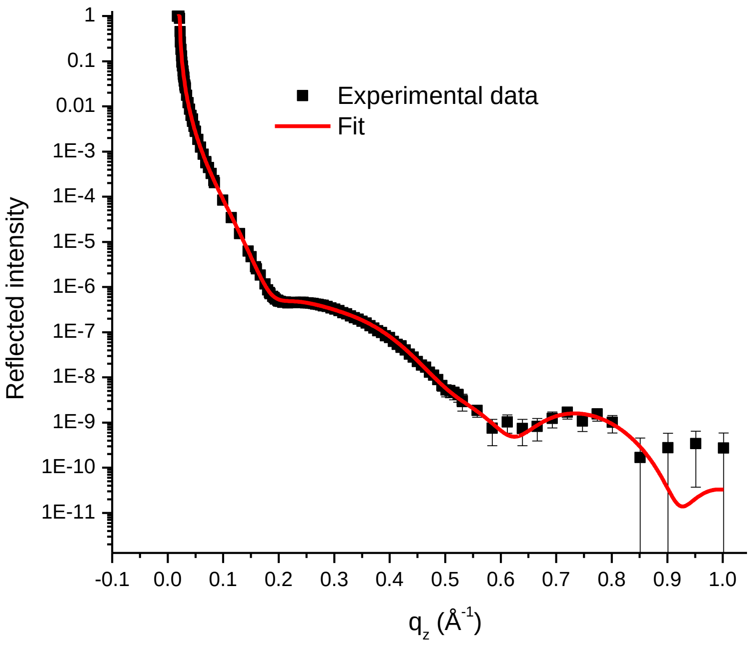
- X-ray reflectivity (XRR)

Fitting software : REFLEX, https://reflex.irdl.fr/Reflex/

PETRA III, P08

- **P3HT** at 5mN/m





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DESY. PETRA III, P08

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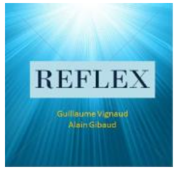

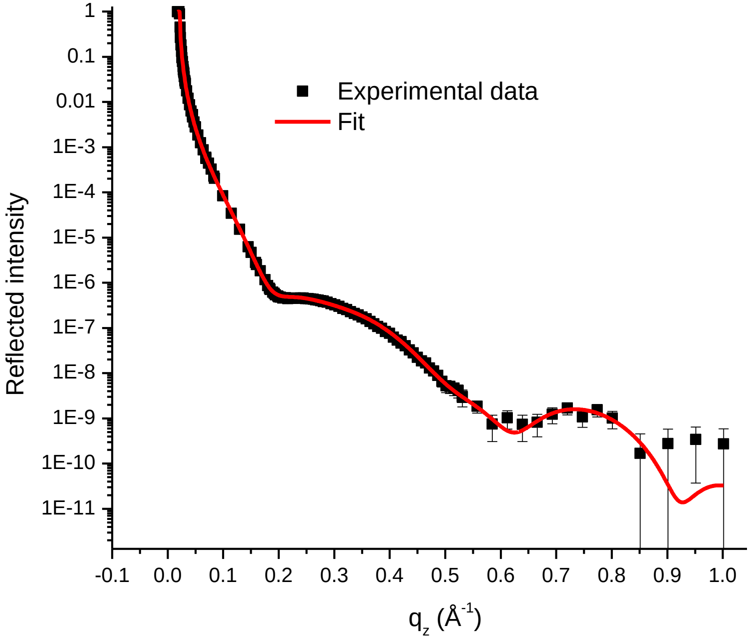

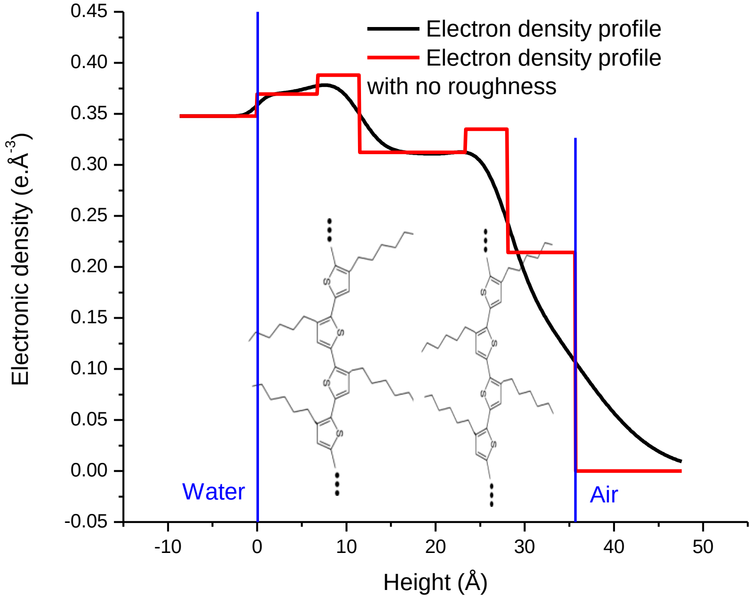

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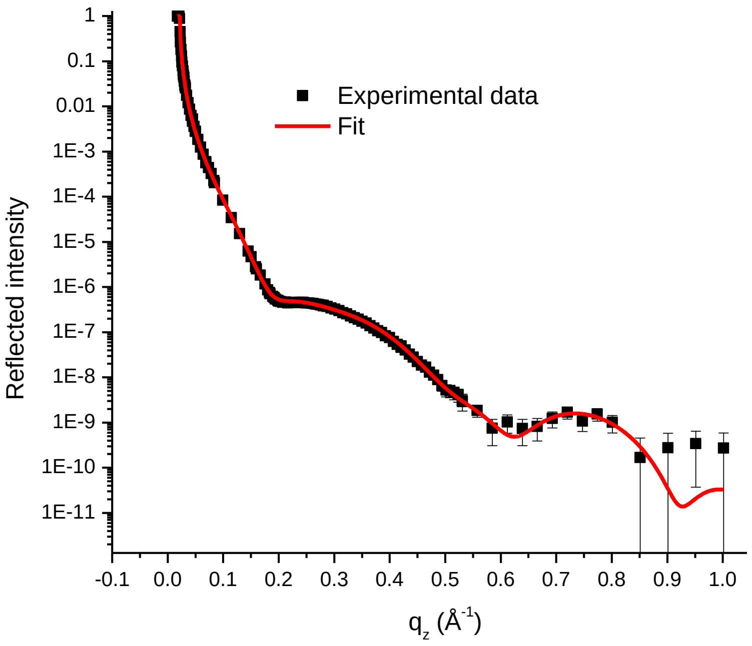
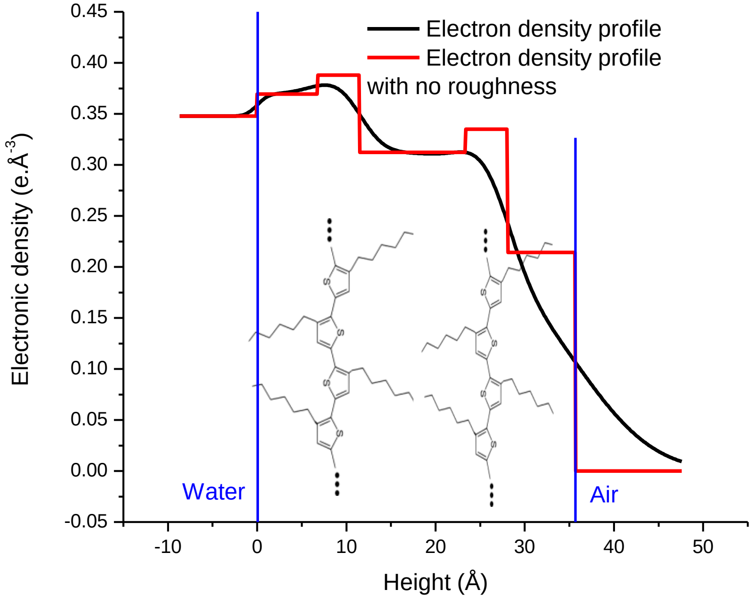
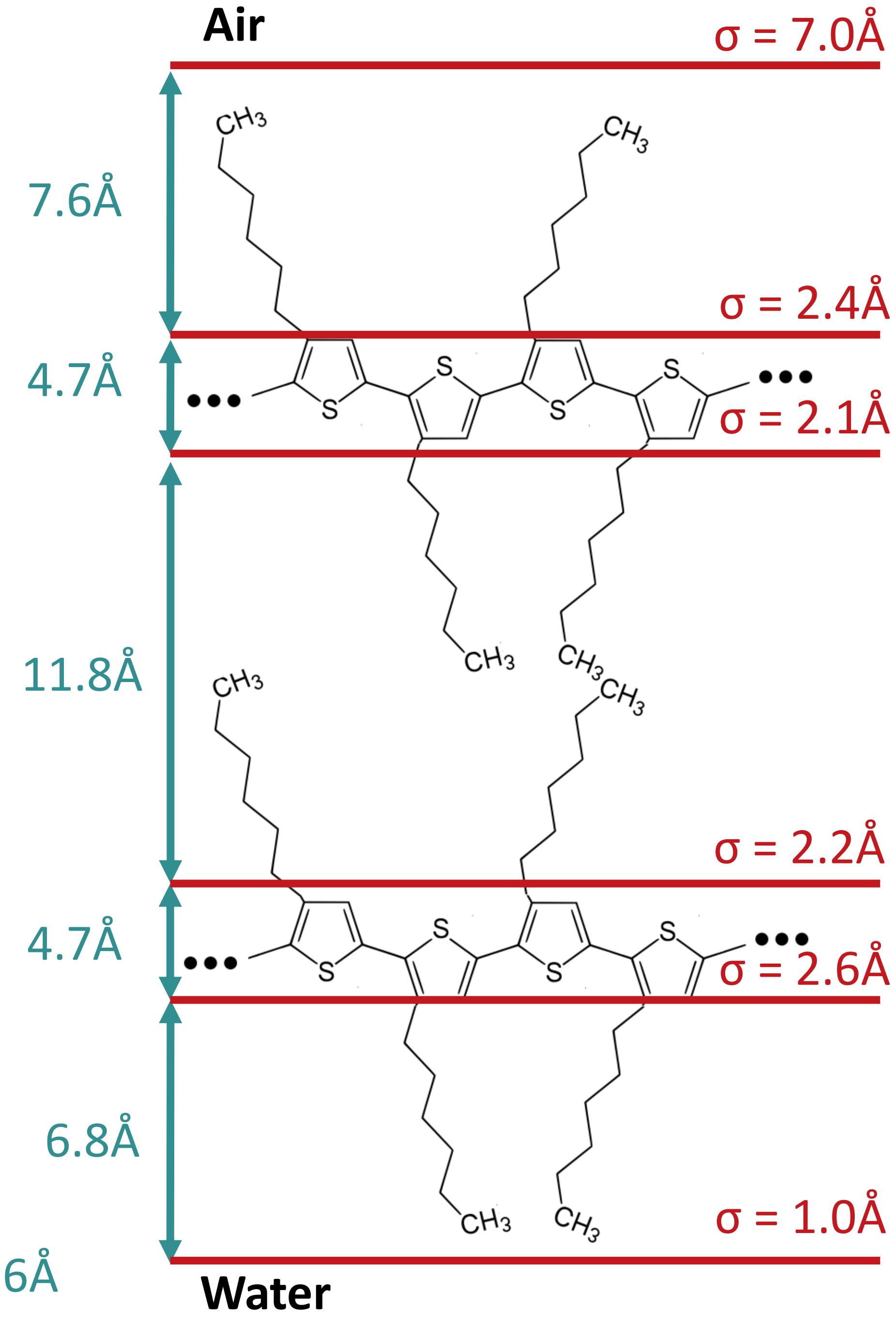






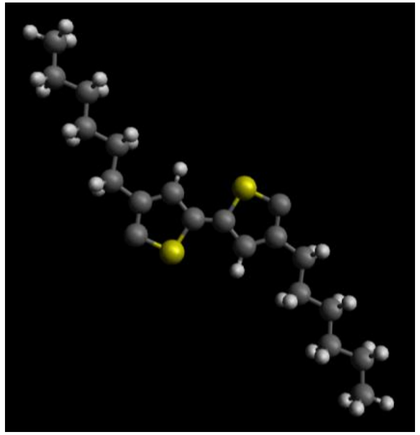
⇨ **Bilayer** with ***edge-on*** orientation

Total thickness = 36Å

More thorough structure determination

- *Avogadro* https://avogadro.cc/

⇨ **Drawing of the repetition unit**



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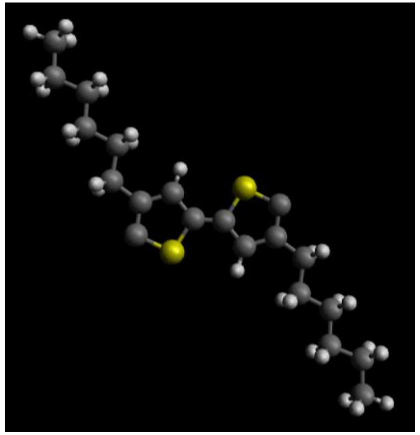
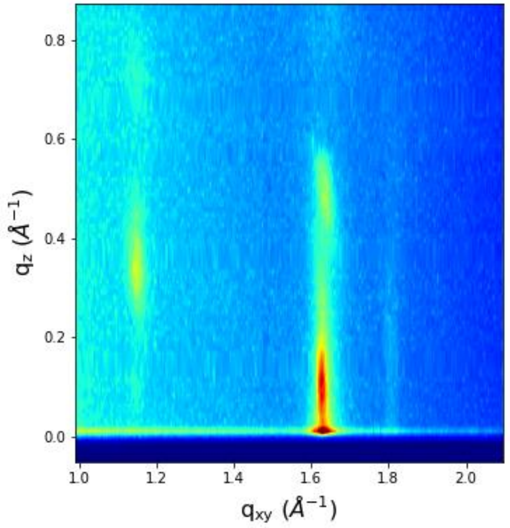


⇨ **Drawing of the repetition unit**

- ***VESTA JP-minerals*** http://www.jp-minerals.org/vesta/en/

⇨ Originally designed to simulate **3D powder diffraction** pattern from known lattice

⇨ Using a **very high *c* parameter** (= 500 Å) ⇨ Simulation of« **2D powder** » diffraction $q_z = \frac{2\pi l}{c}$



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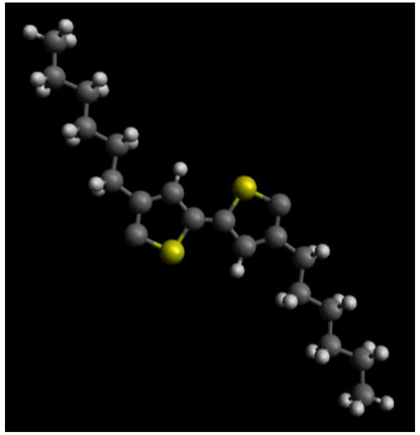

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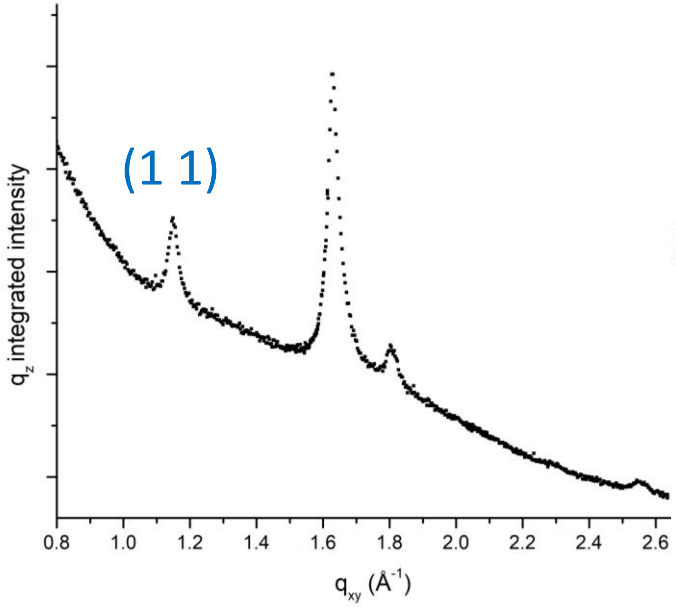
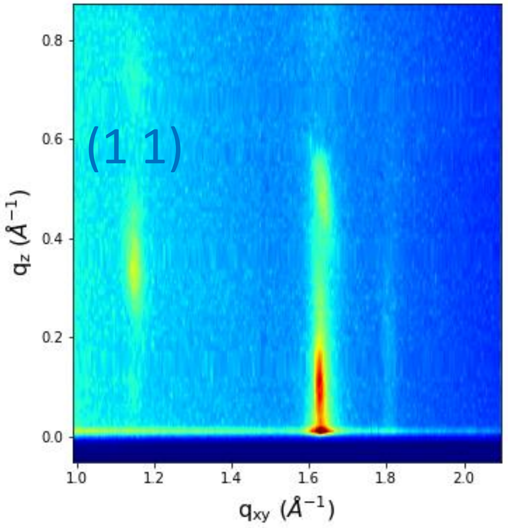
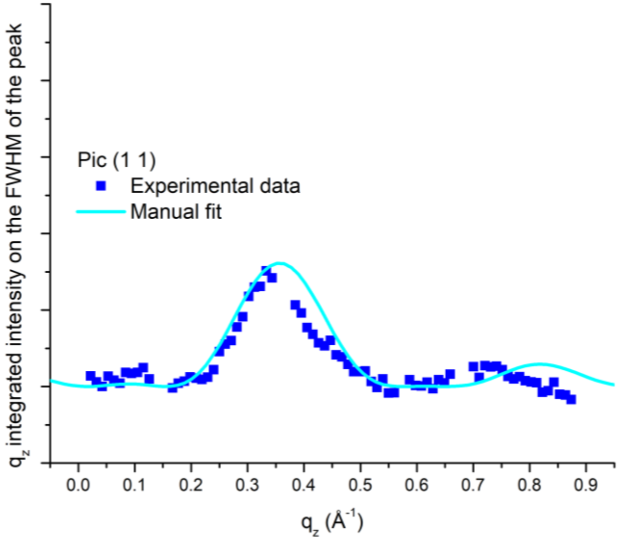
⇨ Vertical section of map ⇨ **Diffraction rods** (Intensity vs q_z with q_{xy} fixed)







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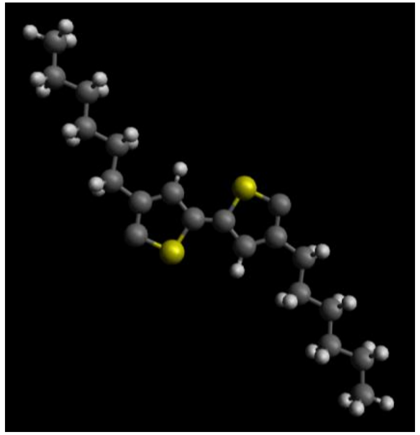

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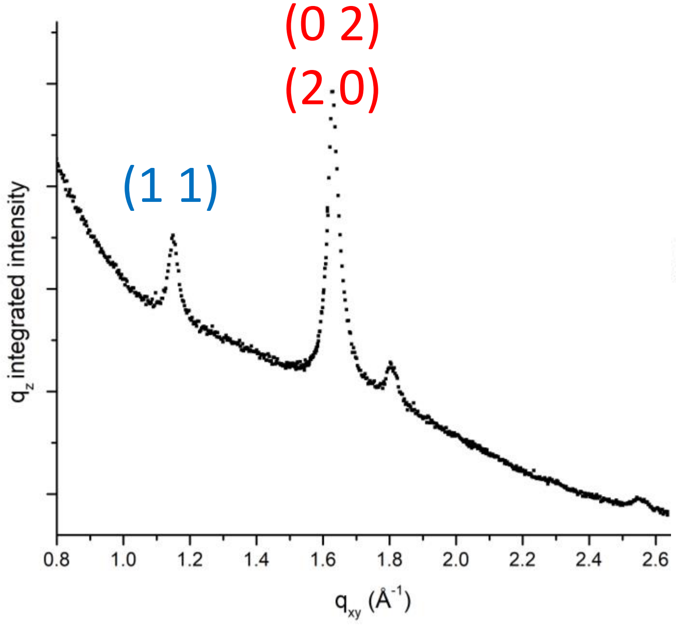
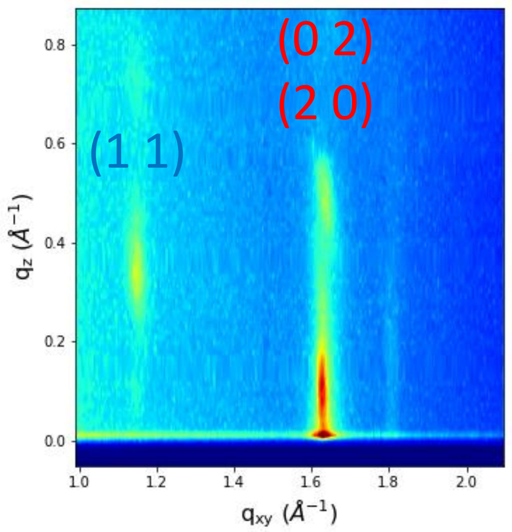
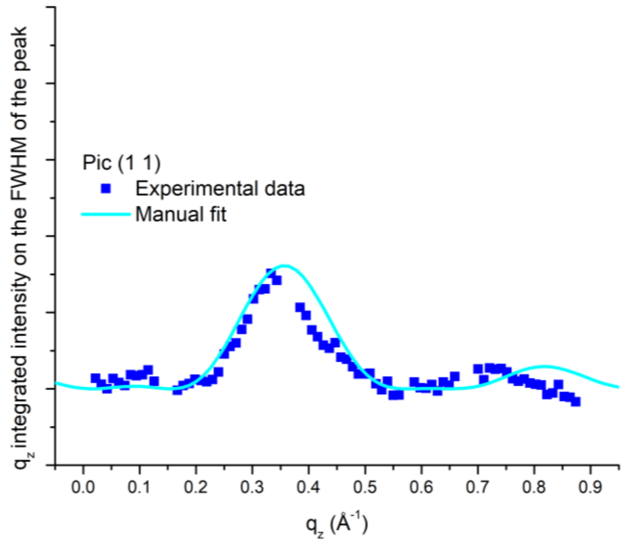
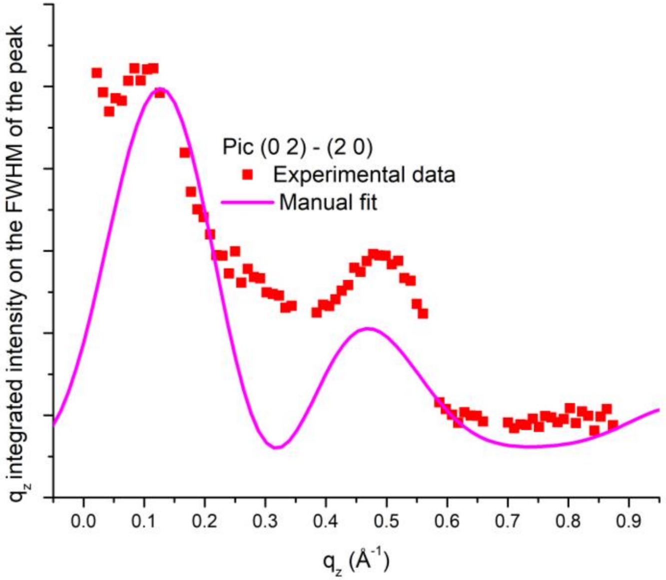
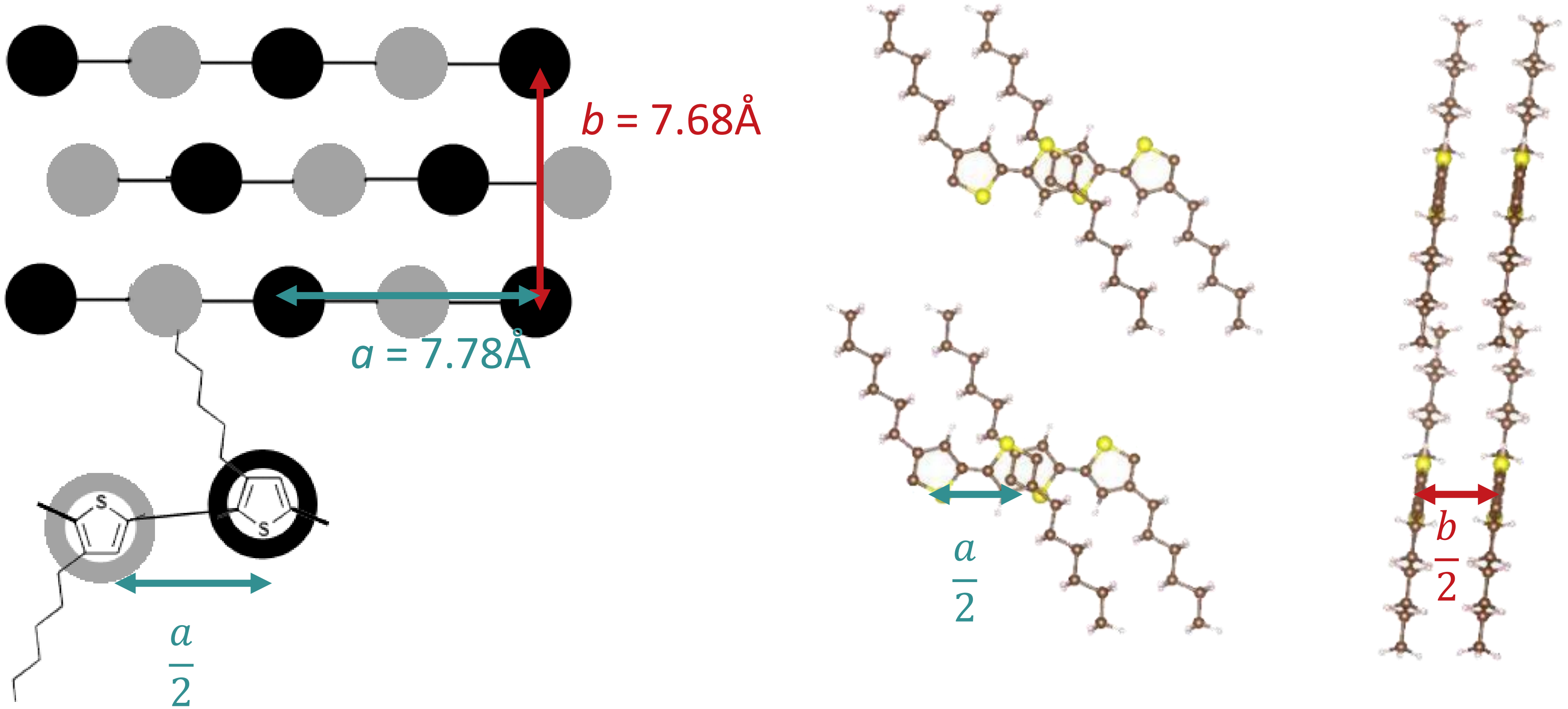








More thorough structure determination at the air-water interface



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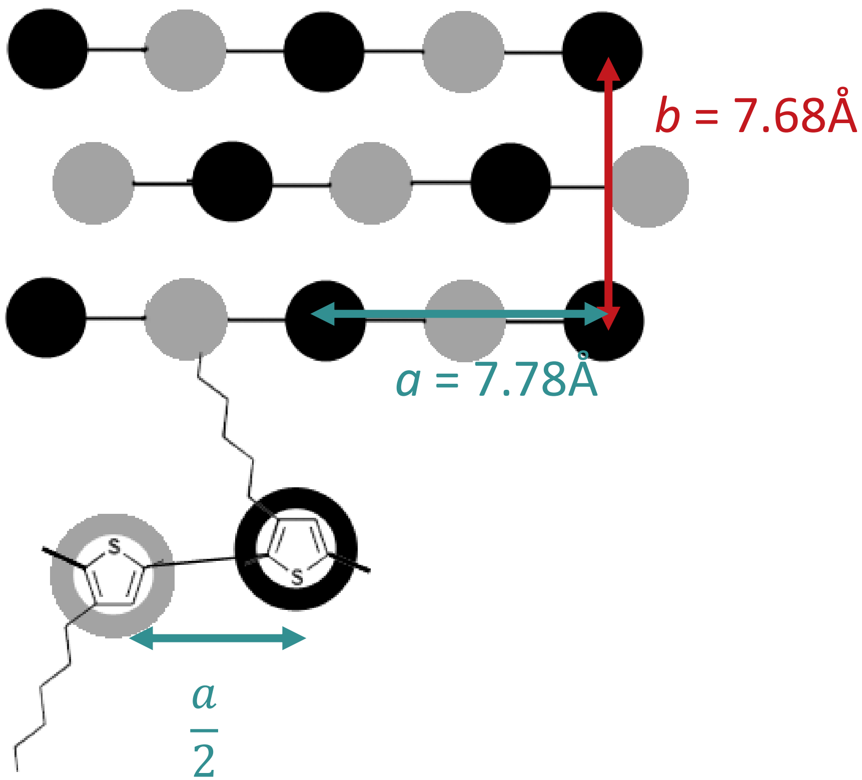

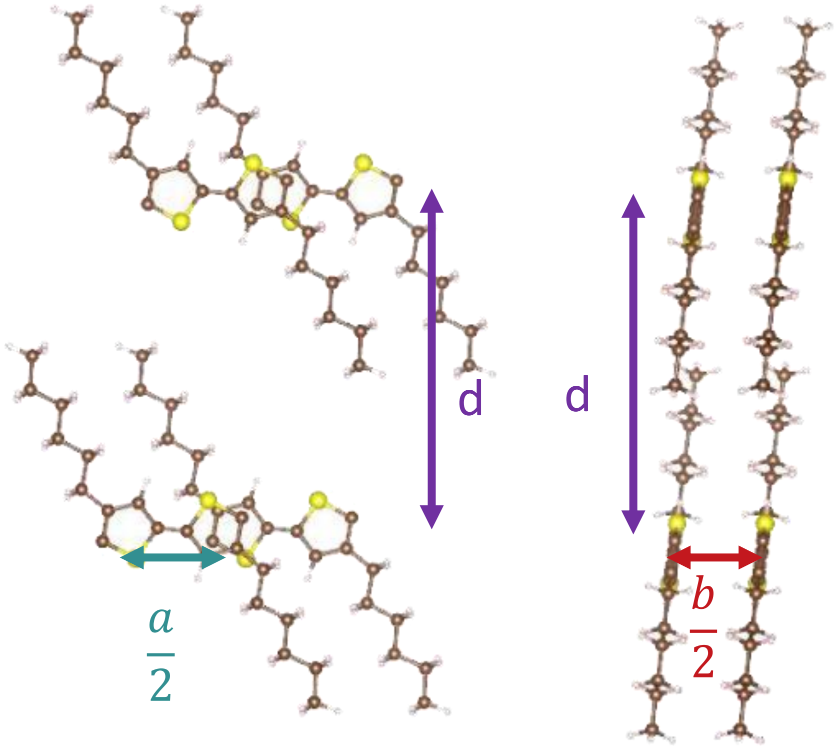

- d = 15Å : vertical distance between thiophene

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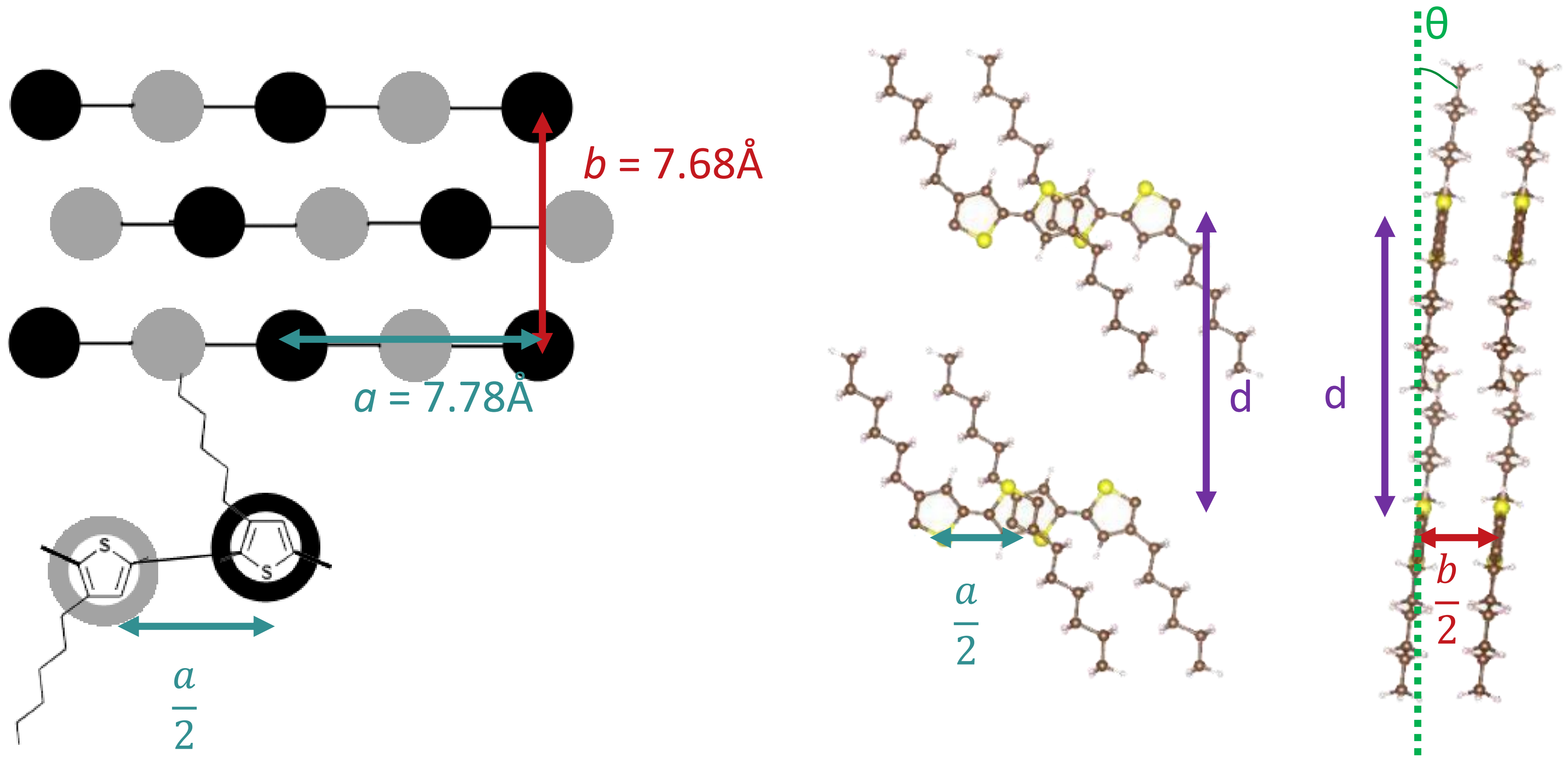

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- θ =13° : tilt along the direction *b* (rotation axis *a*)

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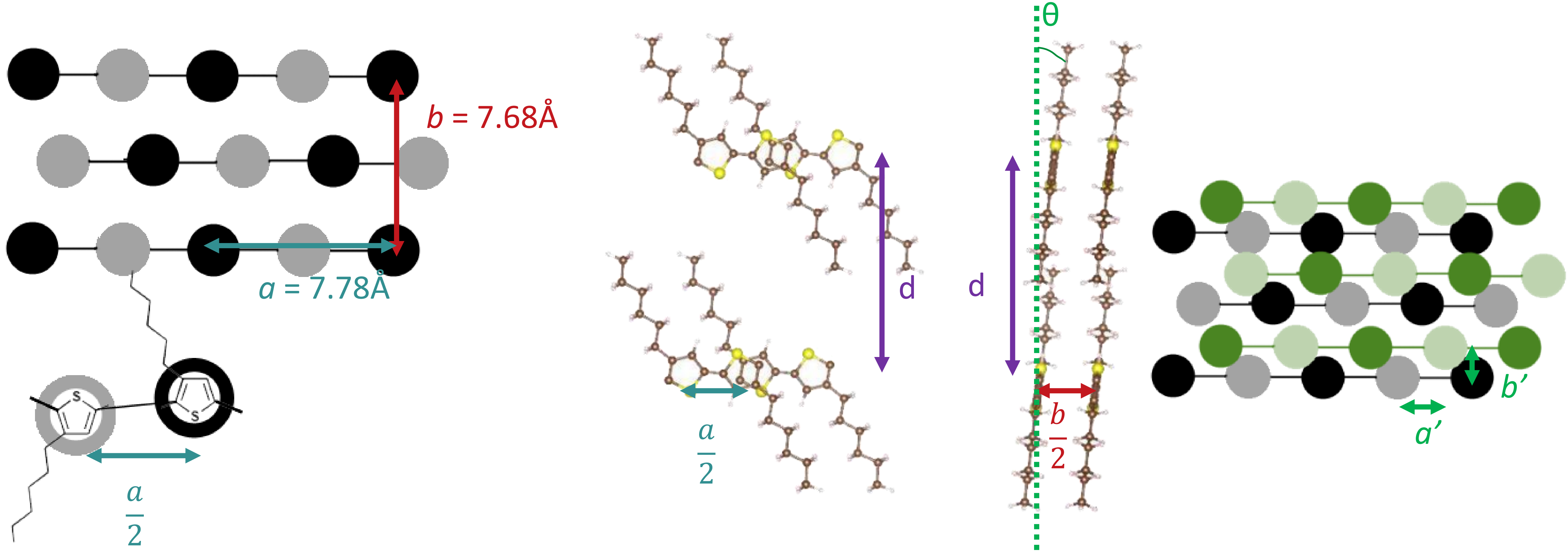

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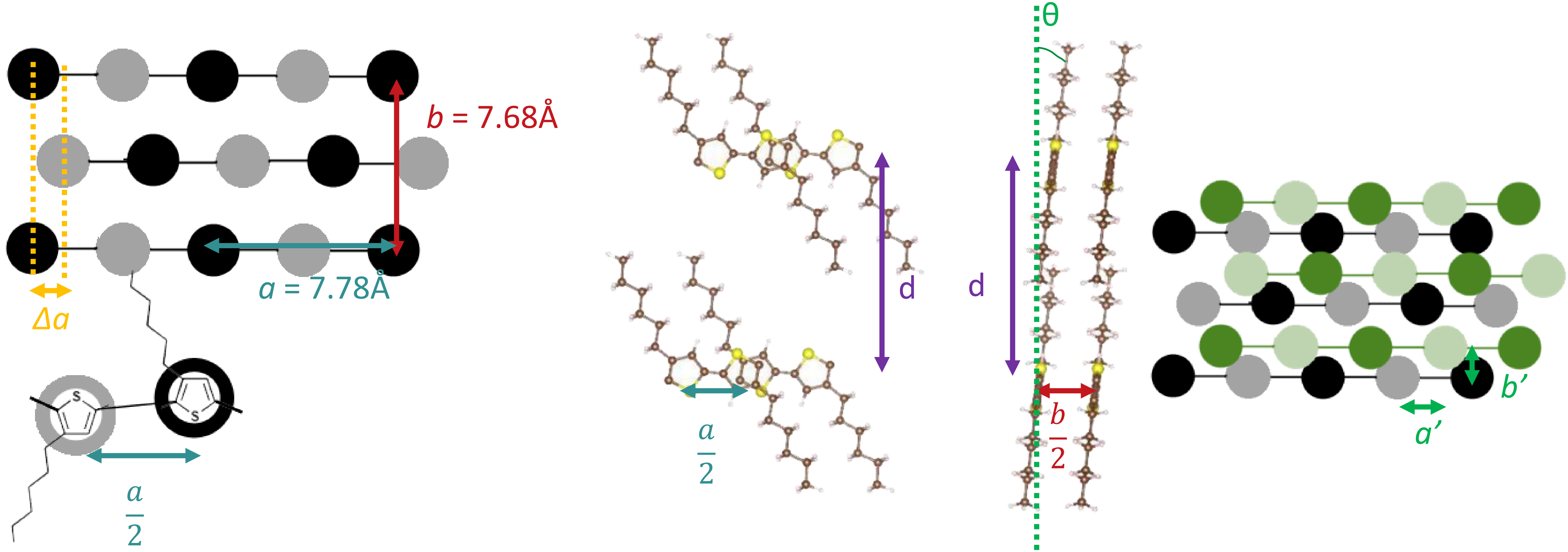

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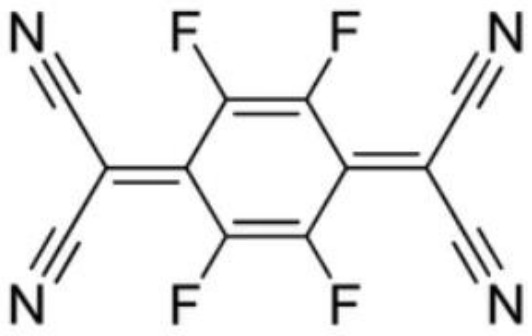
- *a′* = 2Å et *b′* = 1Å : translation of the top layer relative to the bottom layer
- Δ*a* = 1Å: translation of conjugated chain along the *a* direction

In situ film doping

F_4TCNQ

2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane



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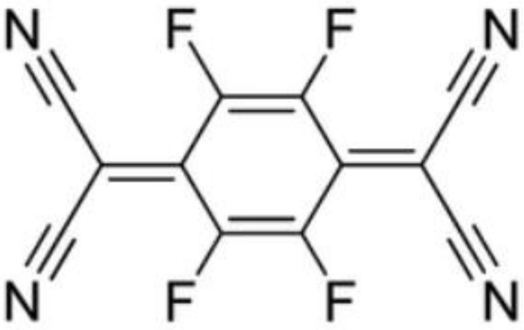
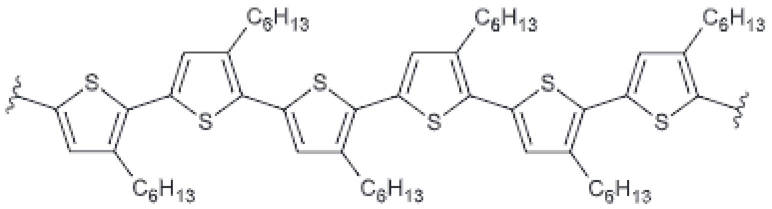
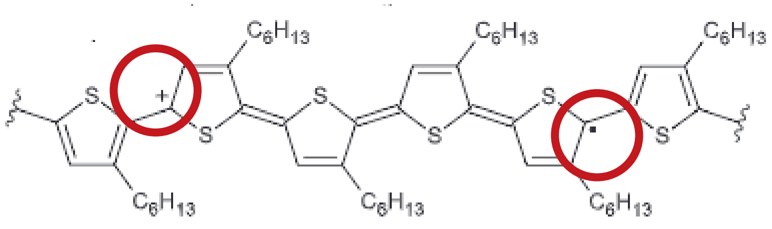




Doping



Neutral P3HT

Doped P3HT

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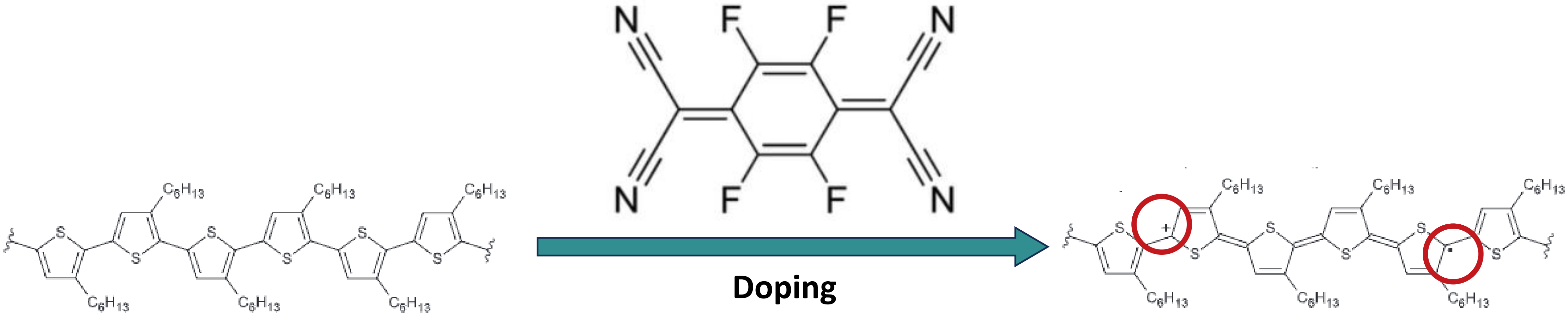
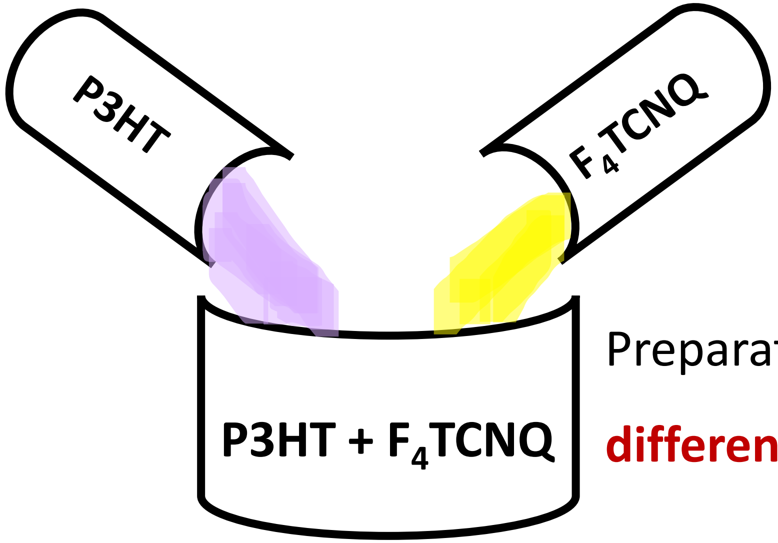
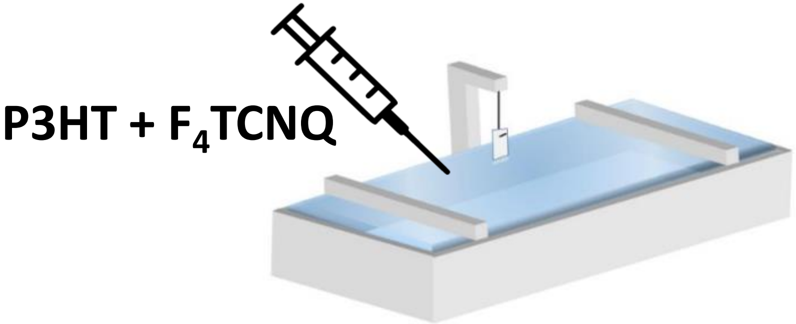


Neutral P3HT **Doped P3HT**



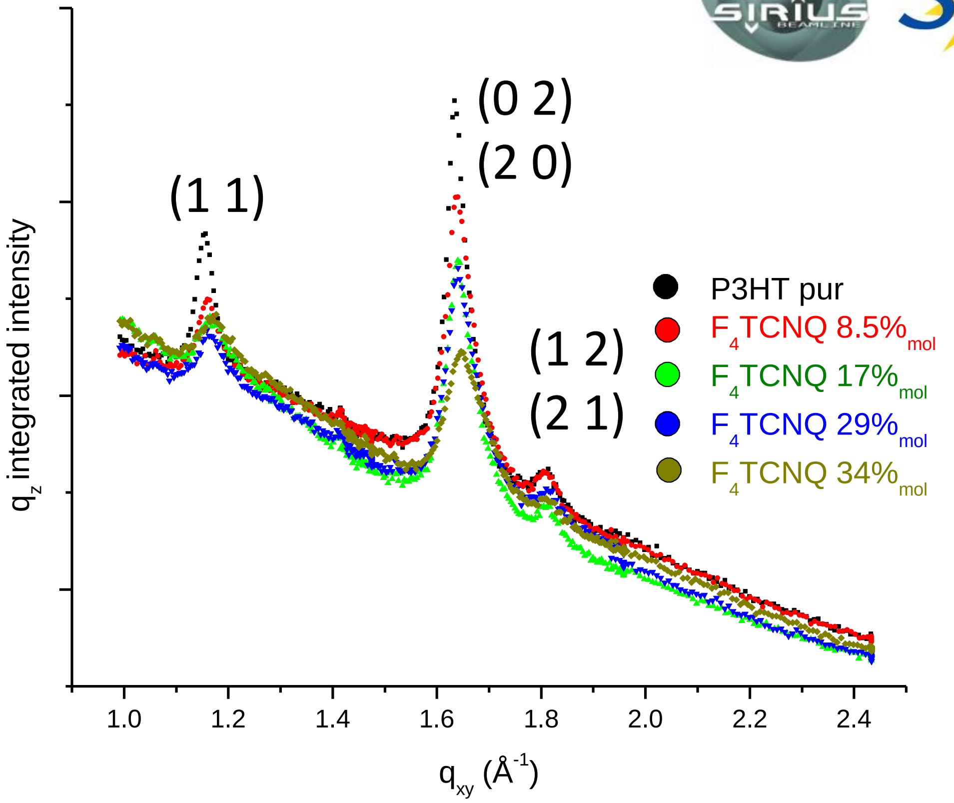
Preparation of mixtures with **different proportions**



Structure determination at the air-water interface

In-plane structure of P3HT+F_4TCNQ films at the air-water interface

- Grazing Incidence X-ray Diffraction (GIXD)
- **P3HT+F_4TCNQ** at 5mN/m



- Peak **intensity diminution**

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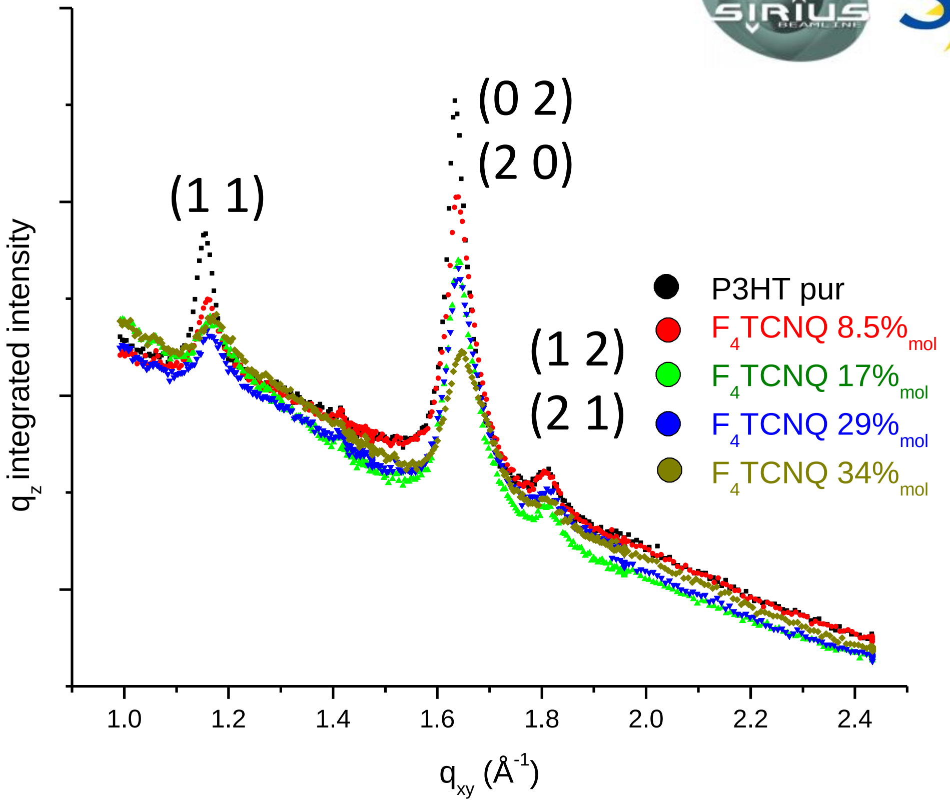
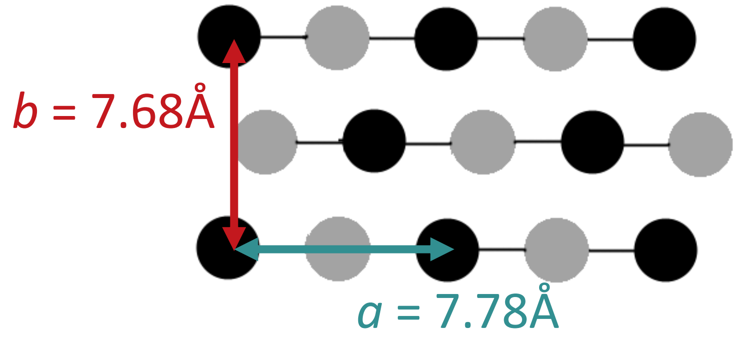
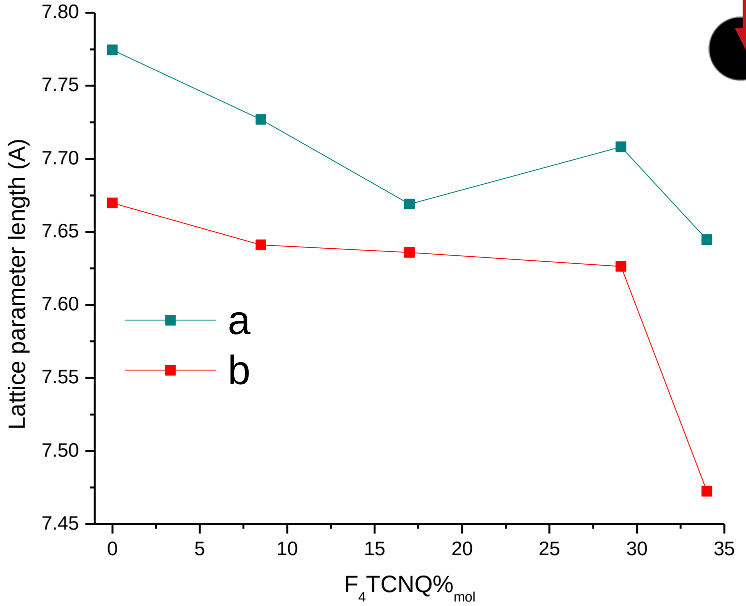






- Peak **intensity diminution**

- Slight **lattice contraction**

⇨ **F_4TCNQ does not intercalate into the plane**

Also observed in thicker film of 200nm thickness (spin-coating)

Ref. : D. T. Scholes *et al.*, *Adv. Funct. Mater.*, 27(44), 1702654 (2017)

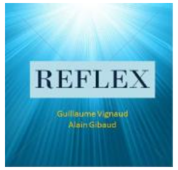
Vertical structure of P3HT+F_4TCNQ films at the air-water interface

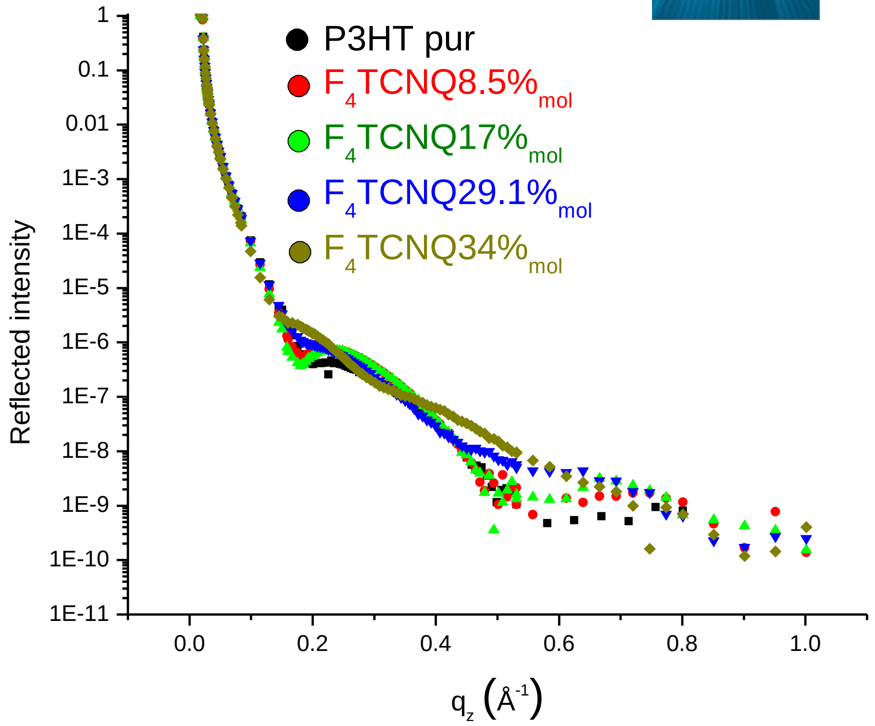
- X-ray reflectivity (XRR)

PETRA III, P08

Fitting software : REFLEX, https://reflex.irdl.fr/Reflex/

- **P3HT+F_4TCNQ** at 5mN/m





Slight **shift** of 1st minimum **towards smaller q_z**

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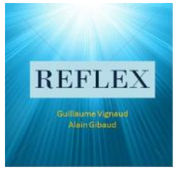

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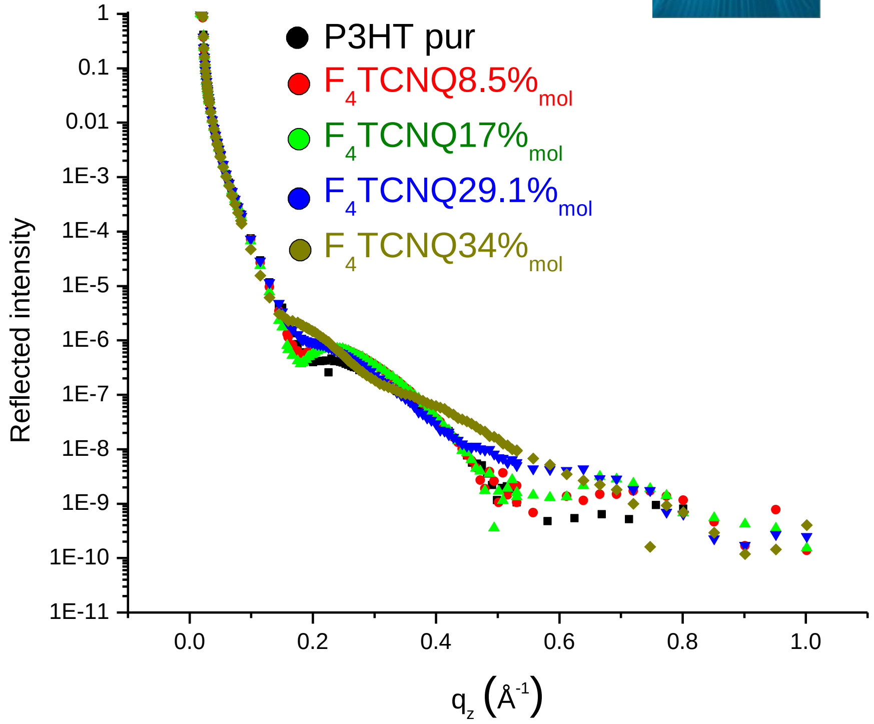

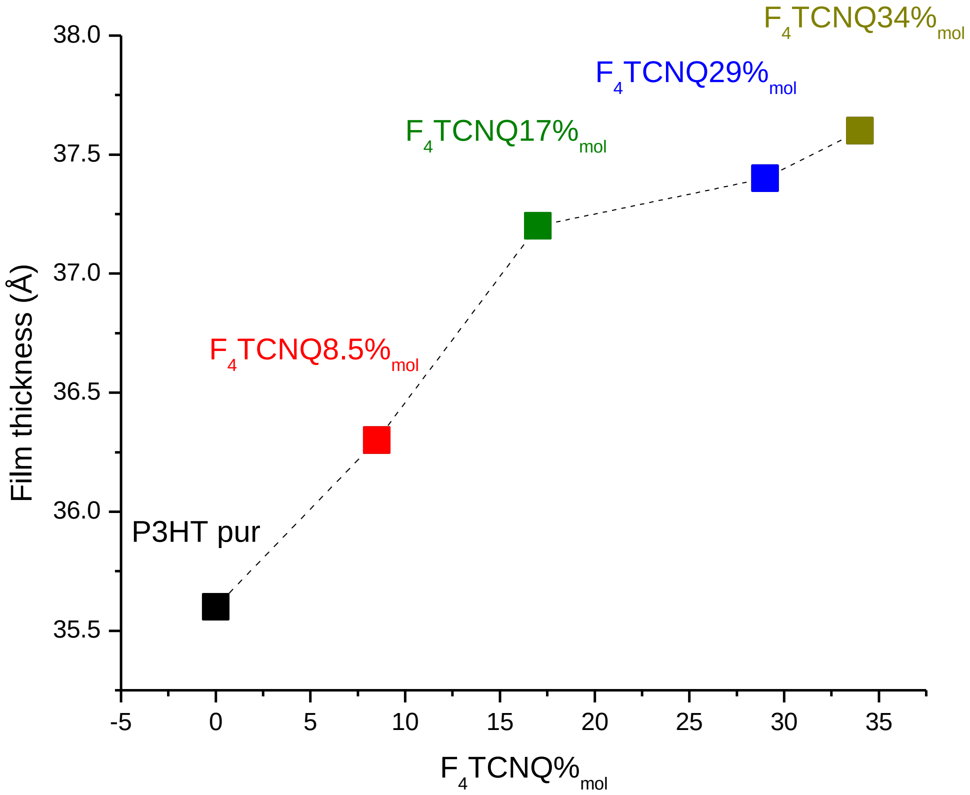

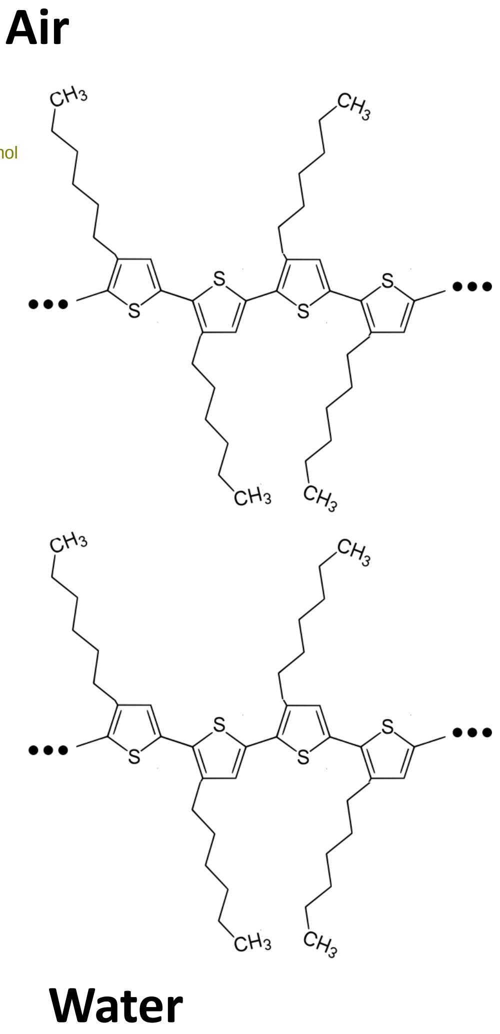

Slight **shift** of 1st minimum **towards smaller q_z** ⇨ Film **slightly thicker** (+2Å)

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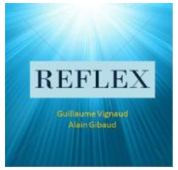

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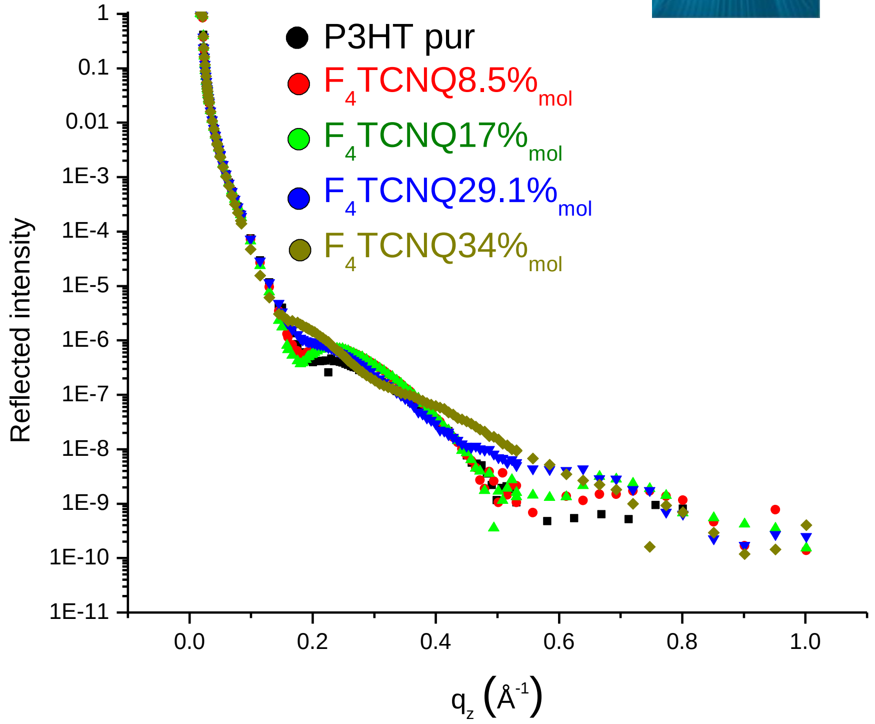
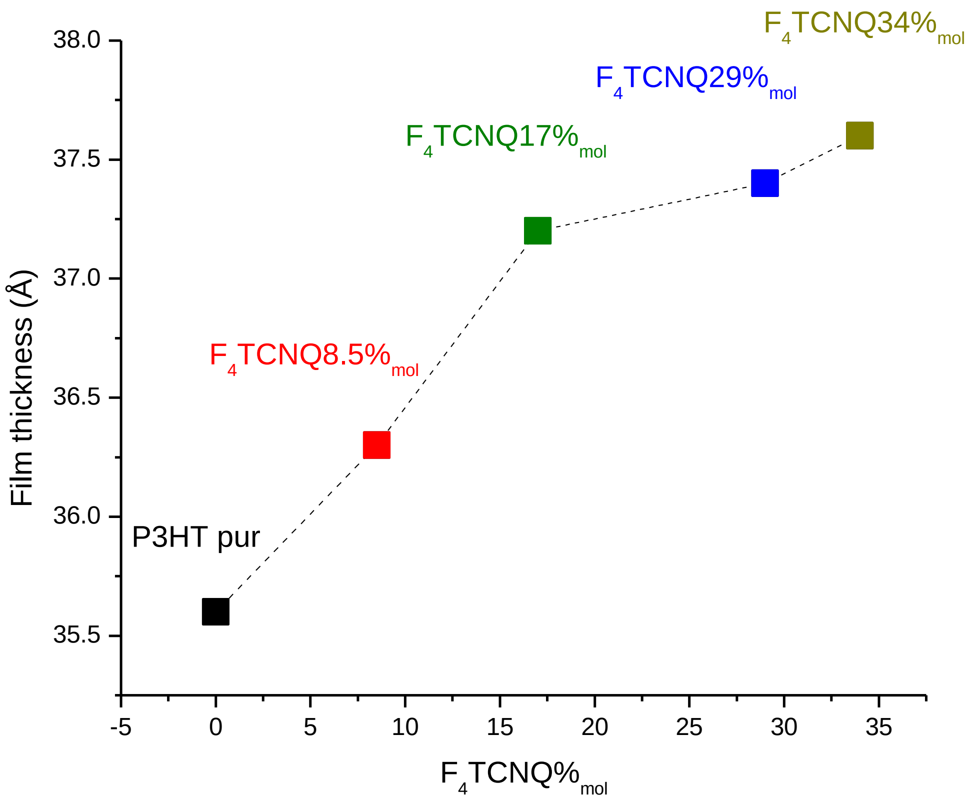
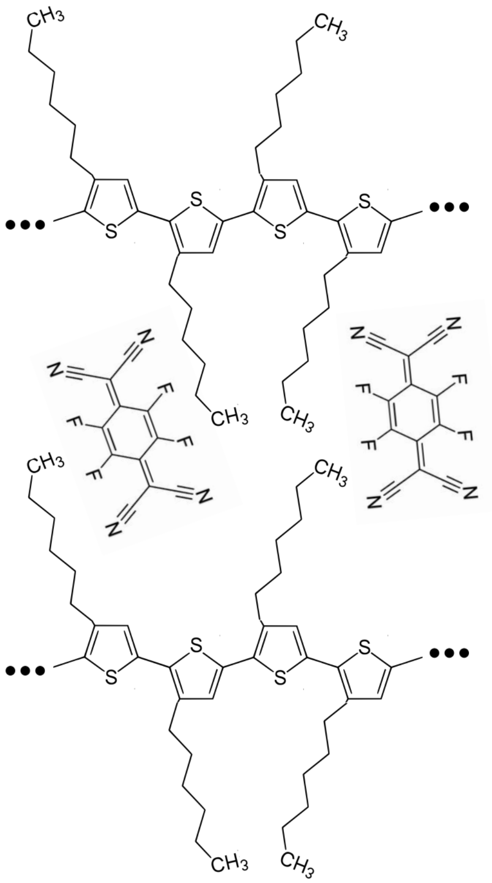




Air



Water

Slight **shift** of 1st minimum **towards smaller q_z** ⇨ Film **slightly thicker** (+2Å)

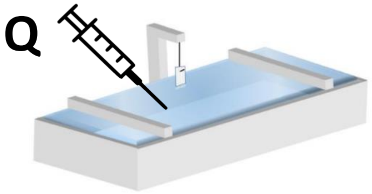
⇨ **Insertion** of **F_4TCNQ between the two layers**

Also observed in spin-coated films. Ref. : D. T. Scholes *et al.*, *Adv. Funct. Mater.*, 27(44), 1702654 (2017)

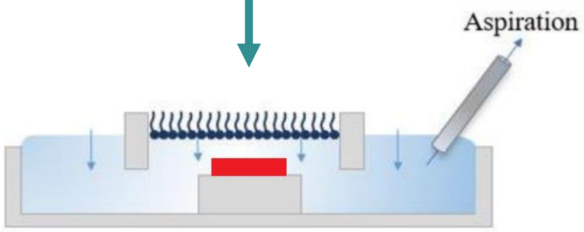
Electronic conductivity determination

- *In situ* doping, directly at the **air-water interface**

P3HT + F_4TCNQ



Inverted Langmuir-Schaeffer technique
at 5 mN/m



$R_\square$ measurement and **electronic conductivity** determination

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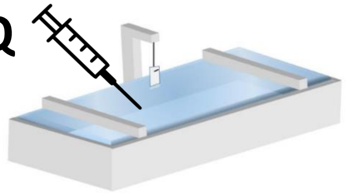

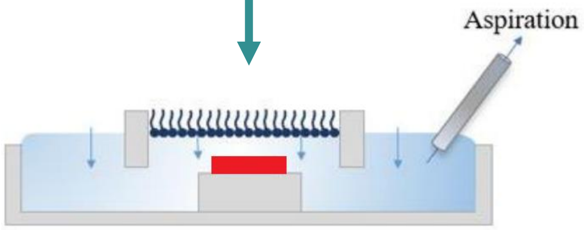

Inverted Langmuir-Schaeffer technique
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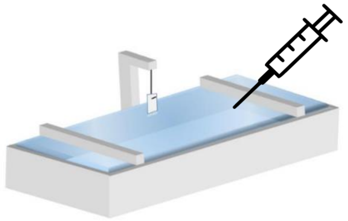
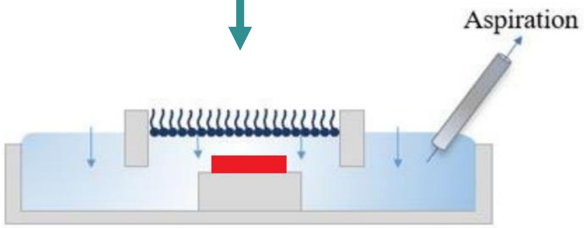
- ***Ex situ*** doping, **after** the film **transfer**

P3HT





Inverted Langmuir-Schaeffer technique
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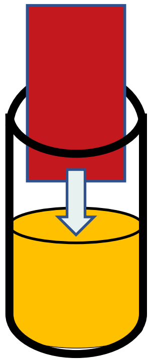
***Ex situ* doping**
Dipping 15min in F_4TCNQ solution
0,1g/L or 0,36mM
(solvent : acetonitrile)



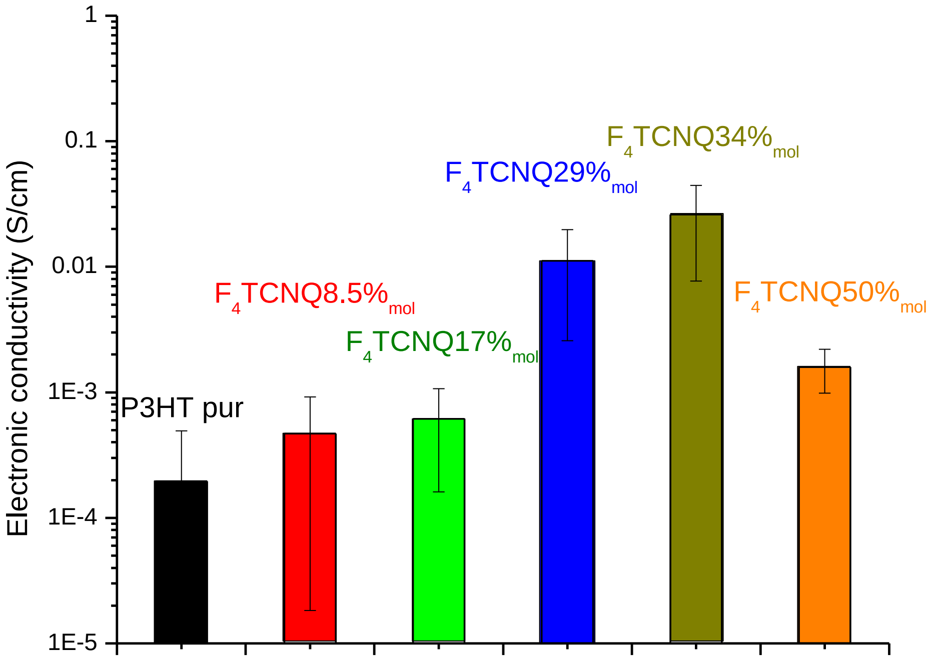
$R_{\square}$ measurement and **electronic conductivity** determination

Electronic conductivity determination

- **P3HT+F_4TCNQ** at 5mN/m

Effect of **F_4TCNQ amount**

In situ doping



Optimum F_4TCNQ amount ⇨ F_4TCNQ34%$_{mol}$

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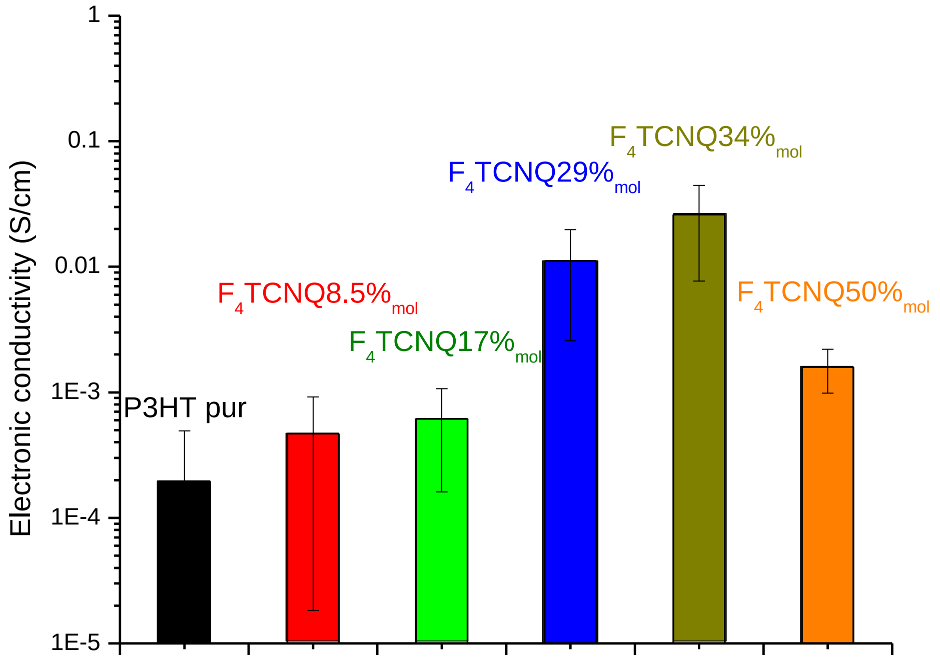

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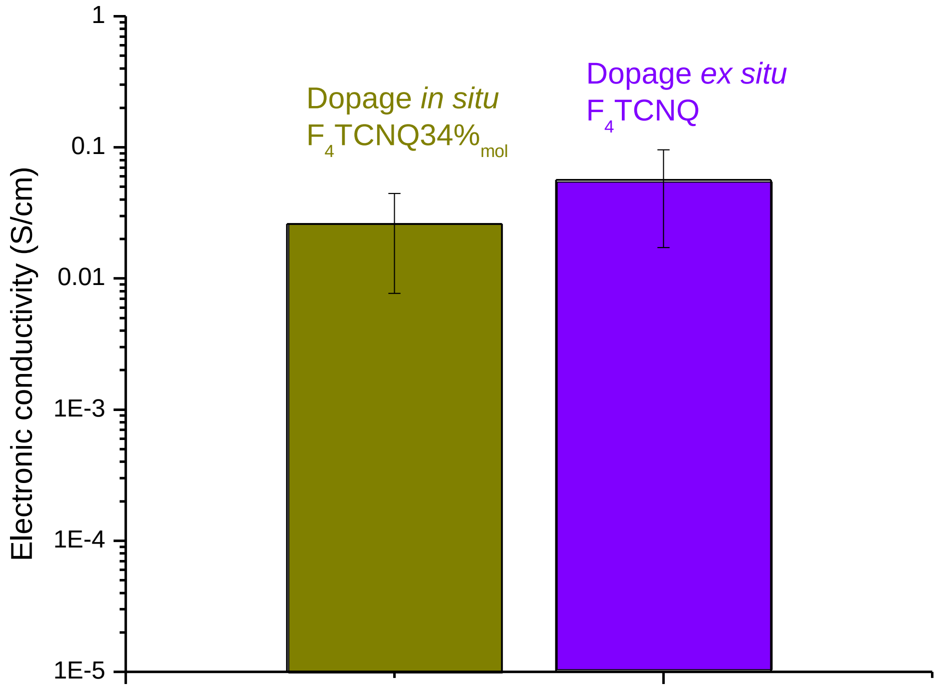
in situ *vs* ***ex situ*** doping



⇨ Electronic conductivity of the **same order of magnitude**

Conclusions

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⇨ **Bilayer** with ***edge-on*** orientation, **rectangular non-centered lattice**

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⇨ Film **slightly thicker**

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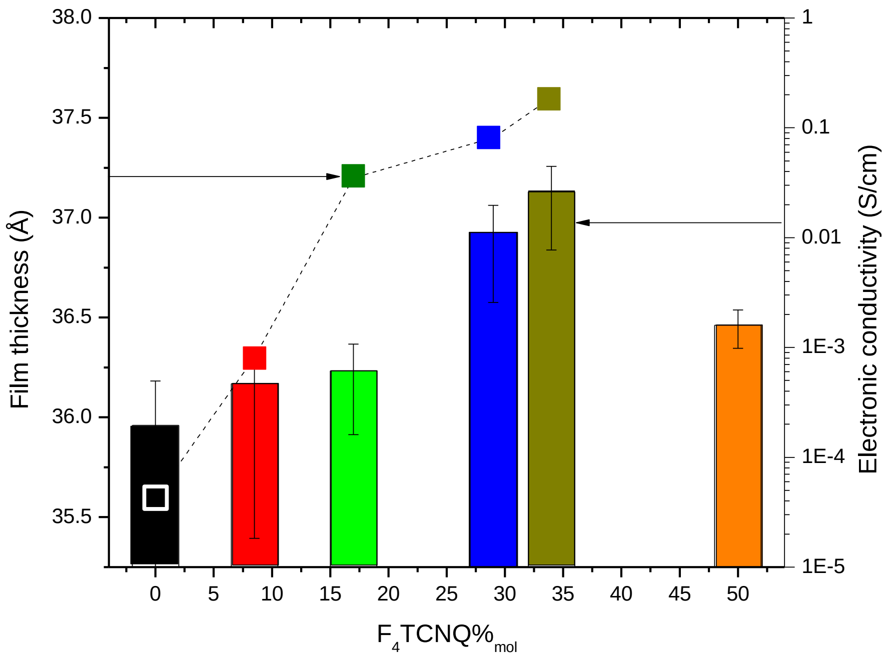

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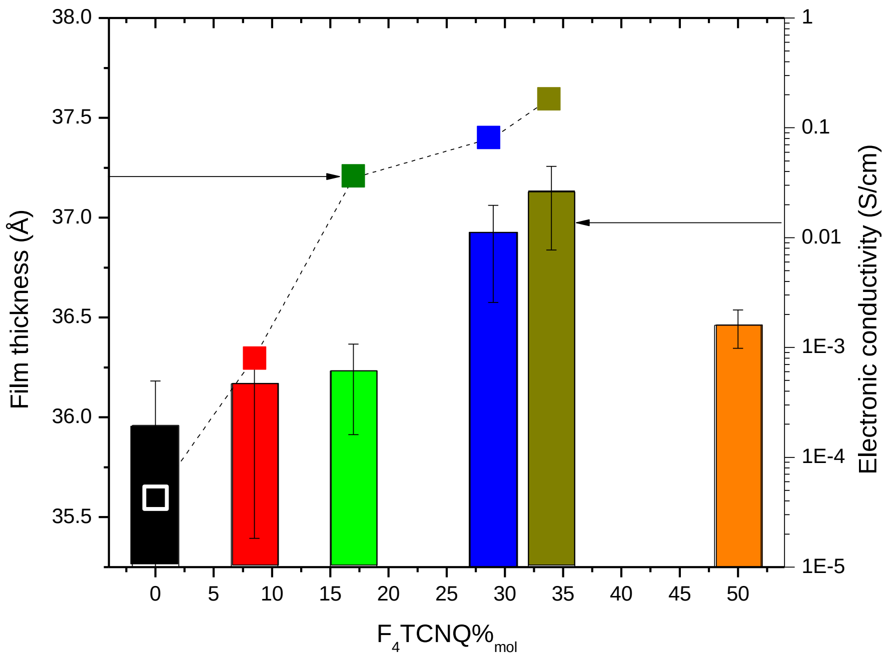
⇨ Electronic conductivity of the **same order of magnitude** between ***in situ*** and ***ex situ* doping**



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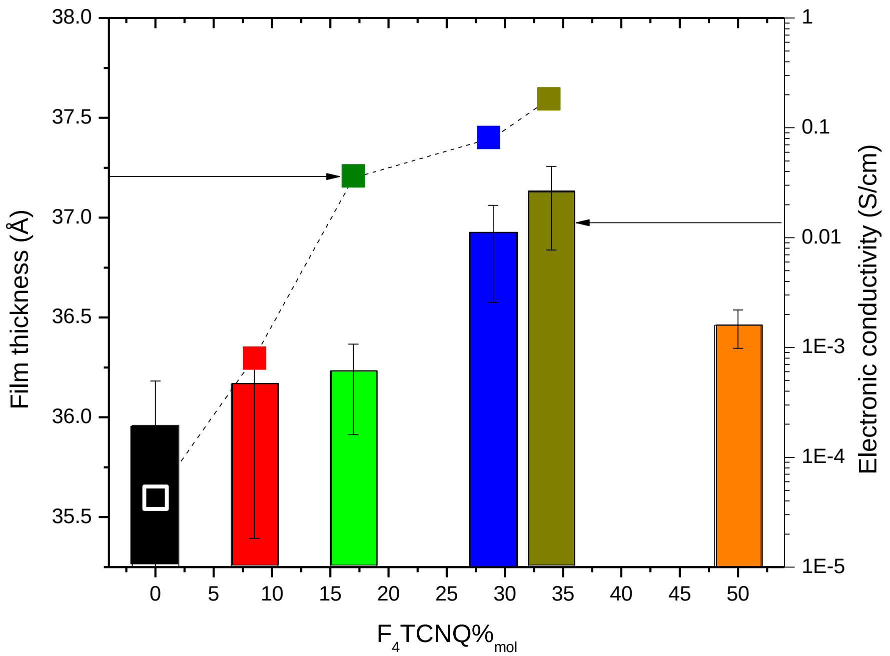

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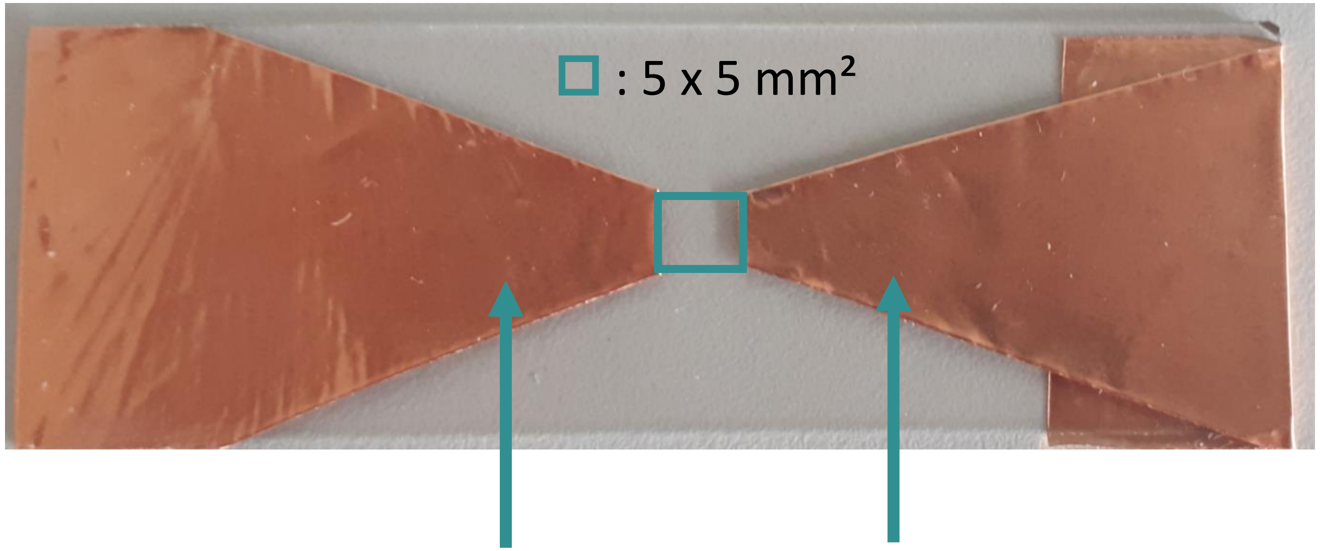
- **Perspectives** : Study the **P3HT** film **structure** after ***ex situ* doping** with **F_4TCNQ**

Thanks for your attention

Presented by : Hugo Fernandez
Supervised by : Pr. Sophie Cantin, Dr. Alae El Haitami, Dr. Philippe Fontaine

CY Cergy Paris Université
LPPI laboratoire de physicochimie des polymères et des interfaces
SIRIUS Beamline
SOLEIL Synchrotron

Protocol : electronic conductivity determination



Copper electrodes

- ⇨ Application of voltage U, measurement of I
- ⇨ Ohm's law : calculation of $R_{\square} = \frac{U}{I}$
- ⇨ Calculation of **electronic conductivity** (S/cm)

$$\frac{1}{\text{film thickness} \,.\, R_{\square}}$$