

Oriented thermoelectric polymers: fabrication, structure and transport properties

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Master of Science 1 – Magister of Fundamental Physics

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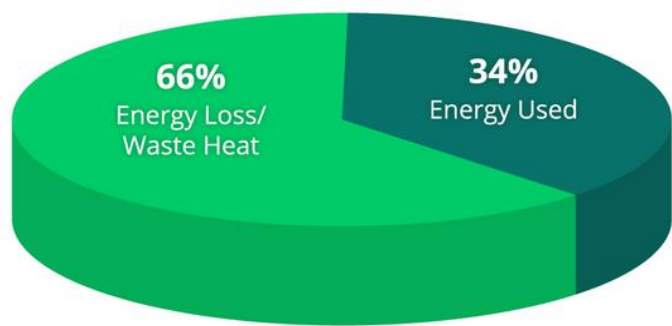


SYCOMMOR

Mondial energy consumption



PRIMARY ENERGY

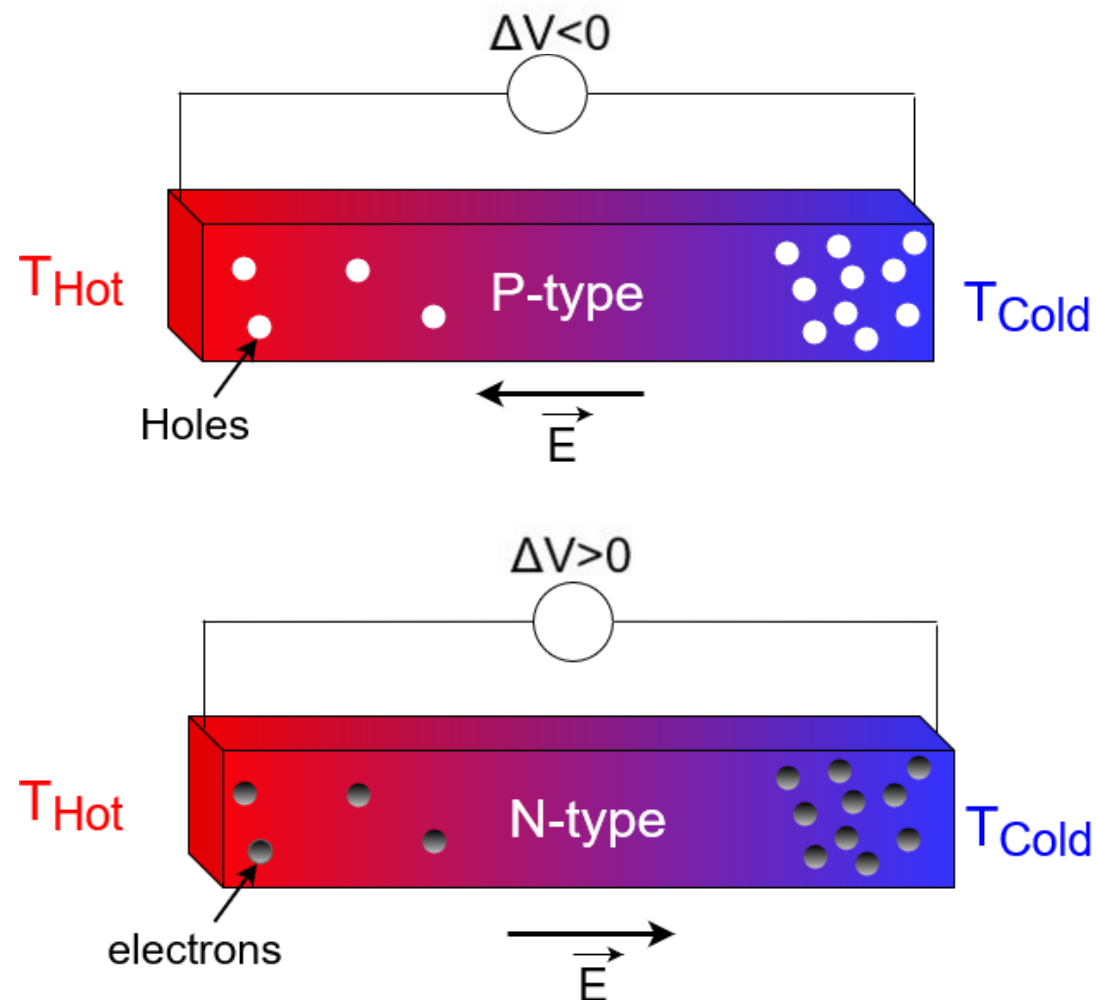


THERMOELECTRICS

ELECTRICAL ENERGY

RETRIVAL

Thermoelectric materials Seebeck effect



A survey on waste heat recovery: Electric power generation and potential prospects within Pakistan

Thermoelectric figure of merit

Seebeck coefficient
(V.K⁻¹)

$$S = \frac{-\Delta V}{\Delta T}$$

Energy conversion efficiency

Electrical conductivity
(S.m⁻¹)

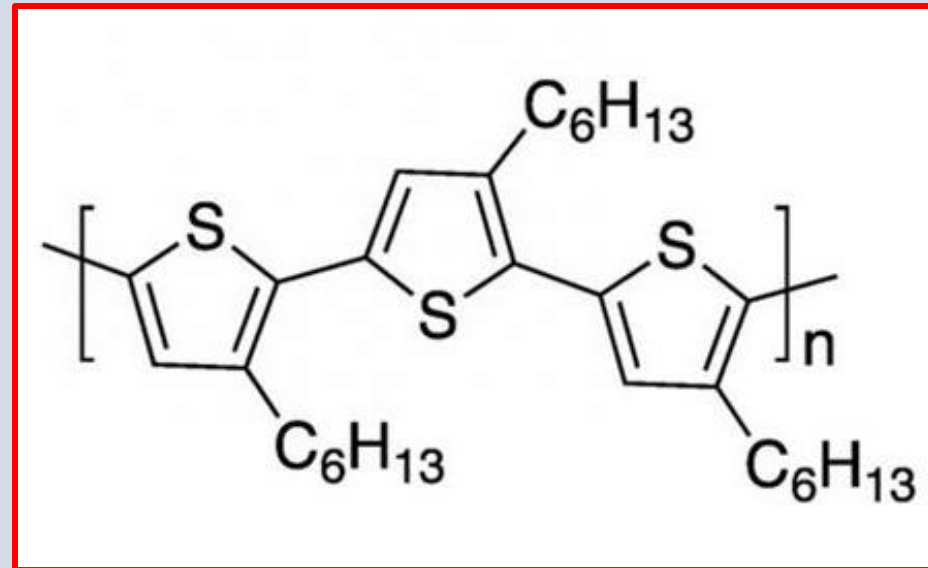
$$zT = \frac{S^2 \sigma}{\kappa} T$$

The diagram shows the equation $zT = \frac{S^2 \sigma}{\kappa} T$ enclosed in a red rectangular box. A dashed blue box highlights the term $S^2 \sigma$, which is labeled "Power factor".

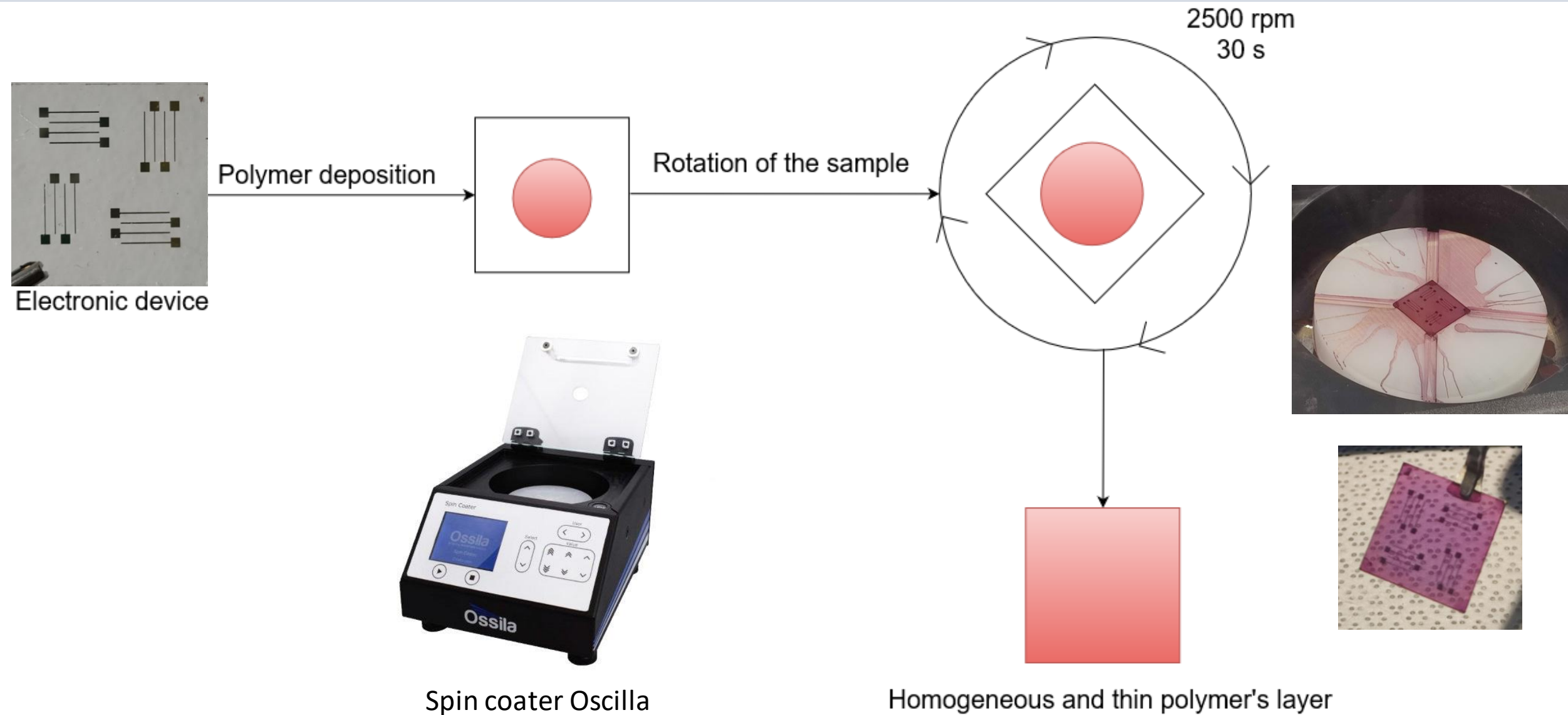
Thermal conductivity
(W.m⁻¹.K⁻¹)
(fixed by the material)

Average temperature
(K)

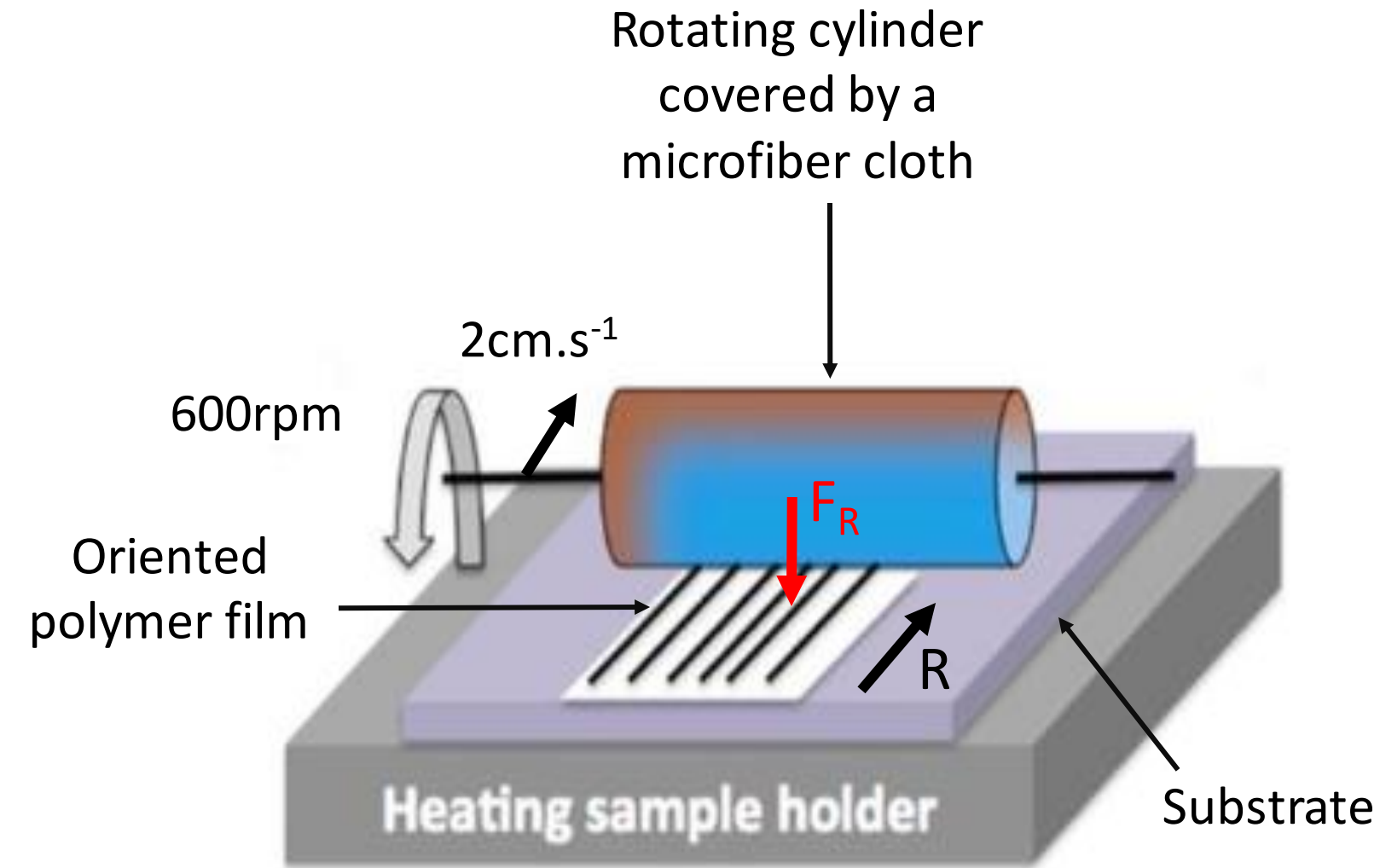
Fabrication of a P₃HT polymer film and increase of its charge transport



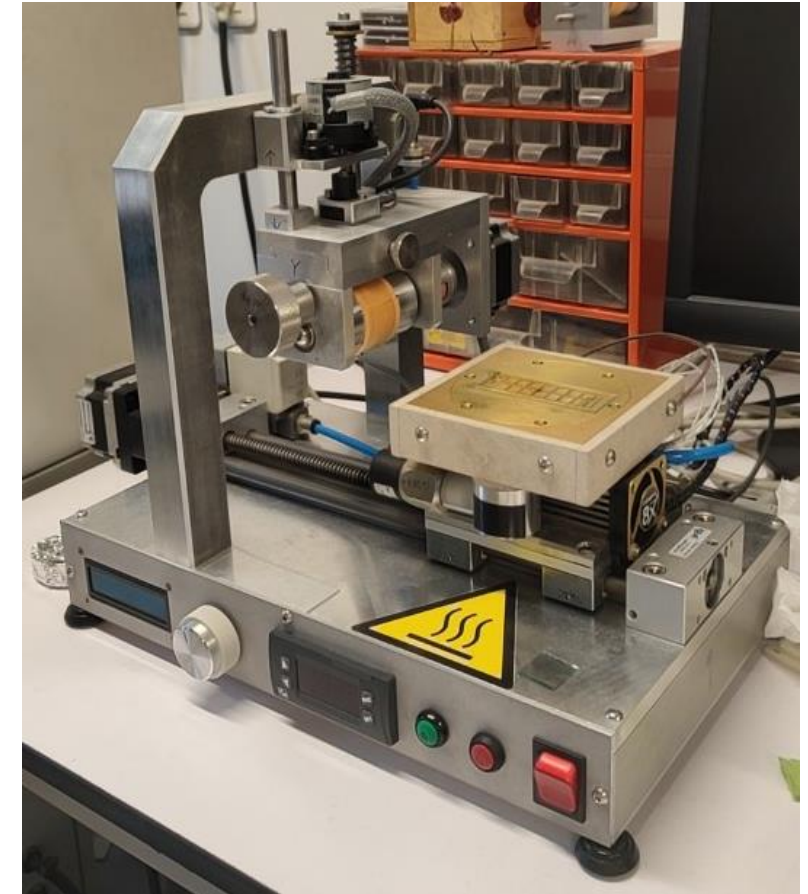
Spin coating method



High temperature rubbing method

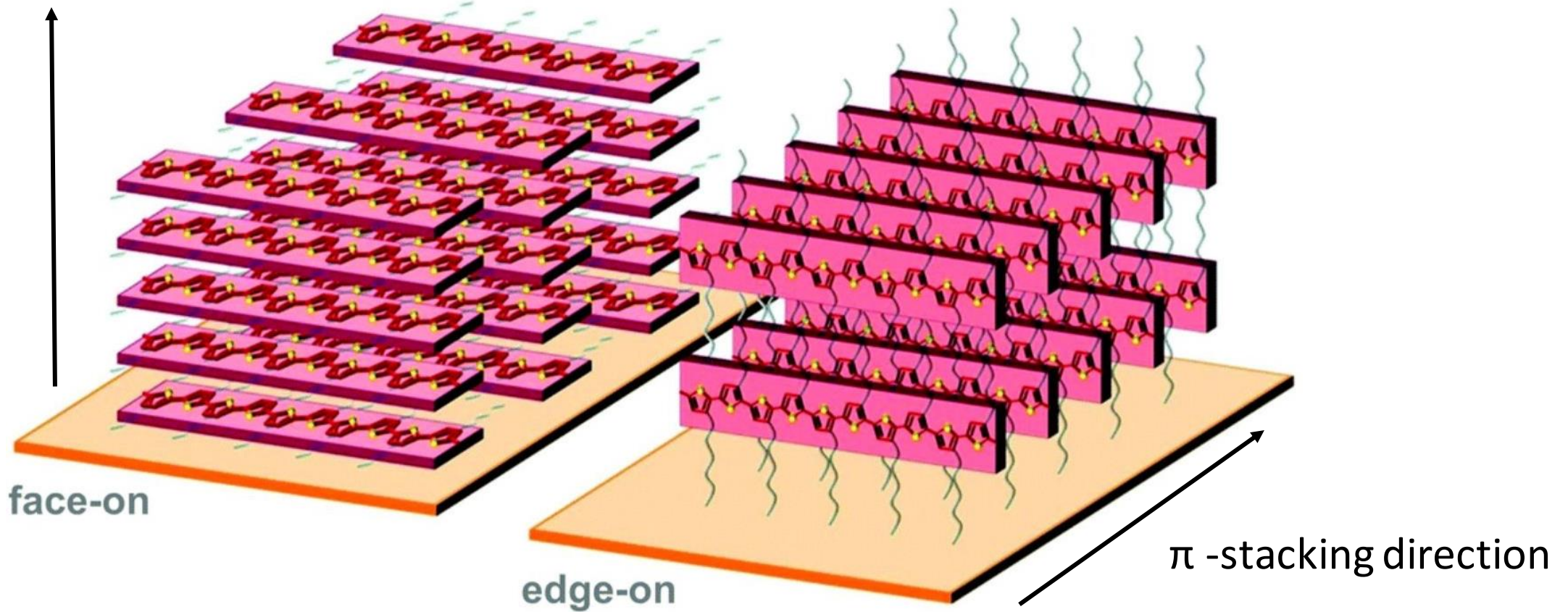


(Guchait et al., 2023)



High temperature rubbing method

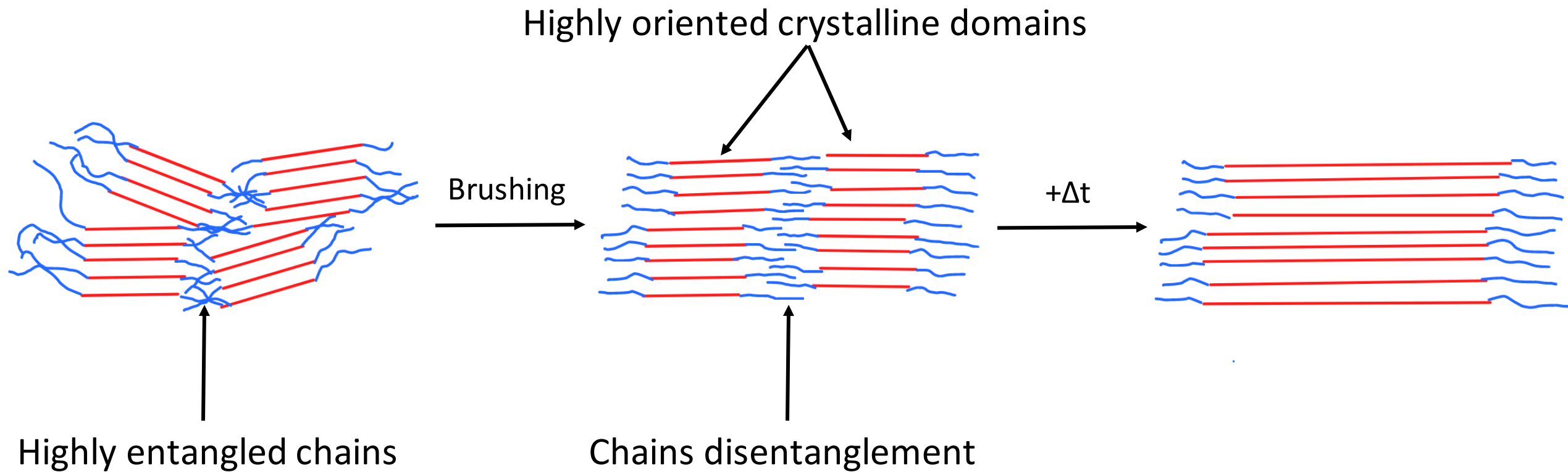
π -stacking direction



(Kroon et al., 2016)

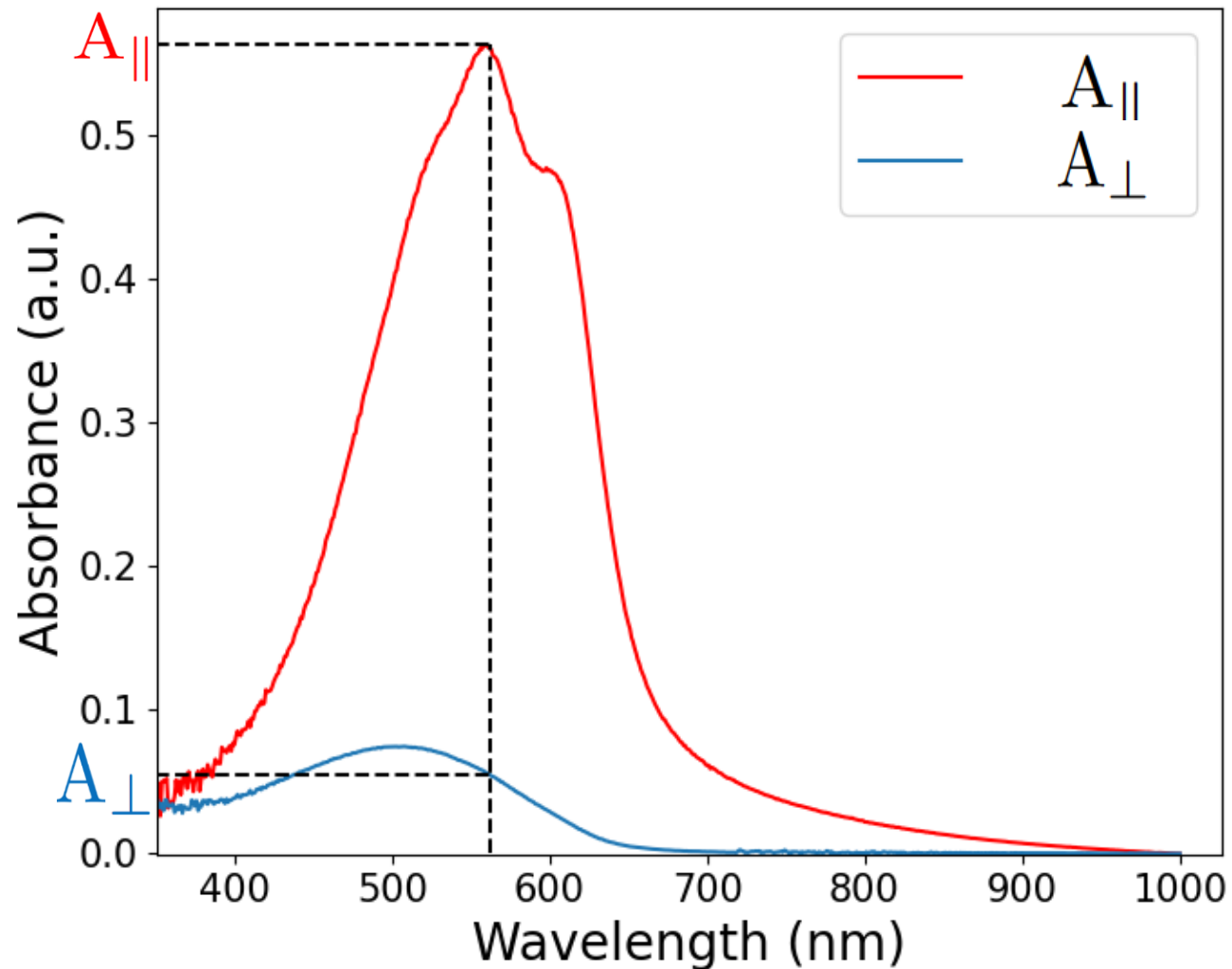
High temperature rubbing method

Crystalline domains / Amorphous domains



UV-Vis spectroscopy

P₃HT film brushed at T_R=150°C and F_R=8.8N



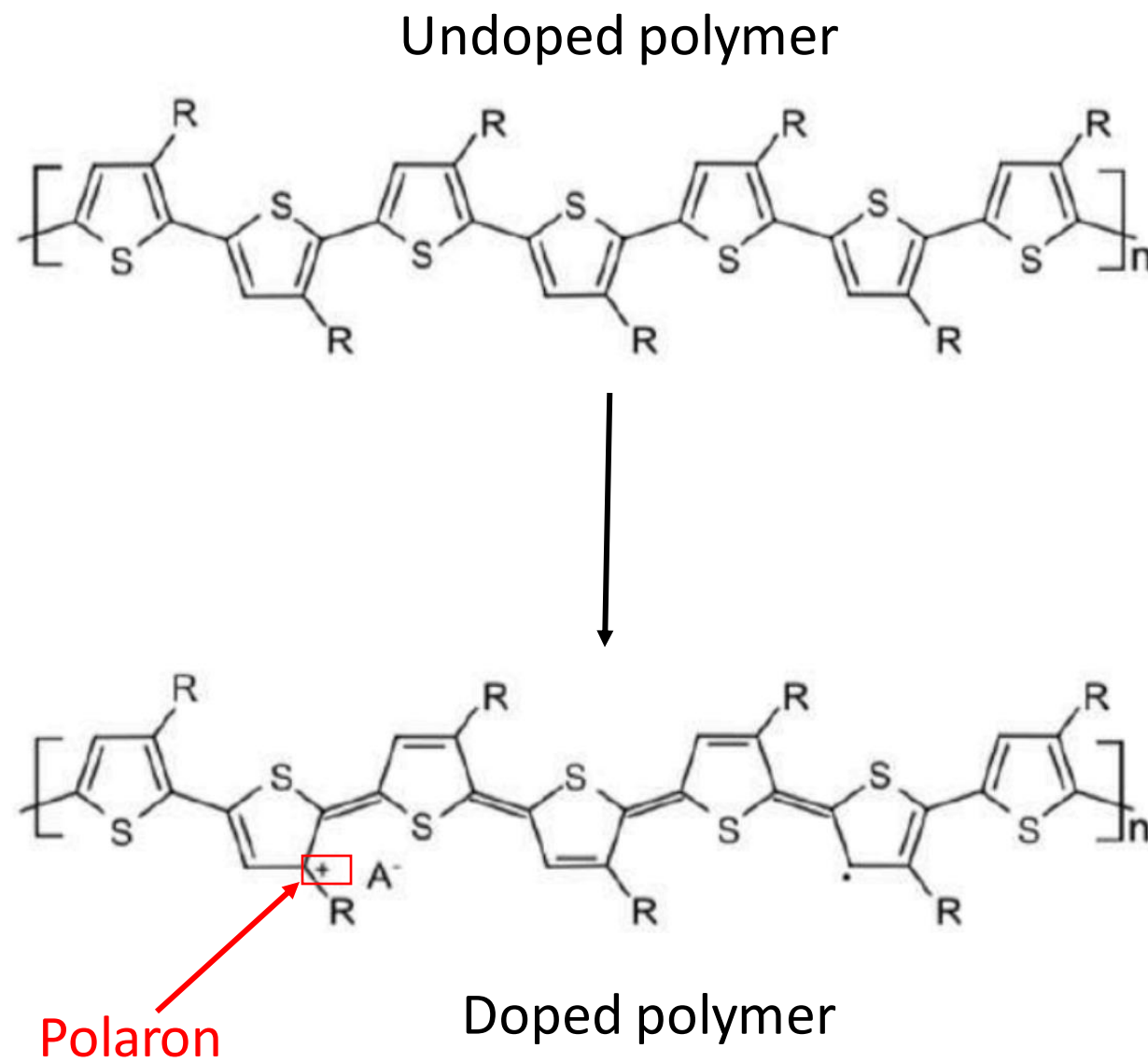
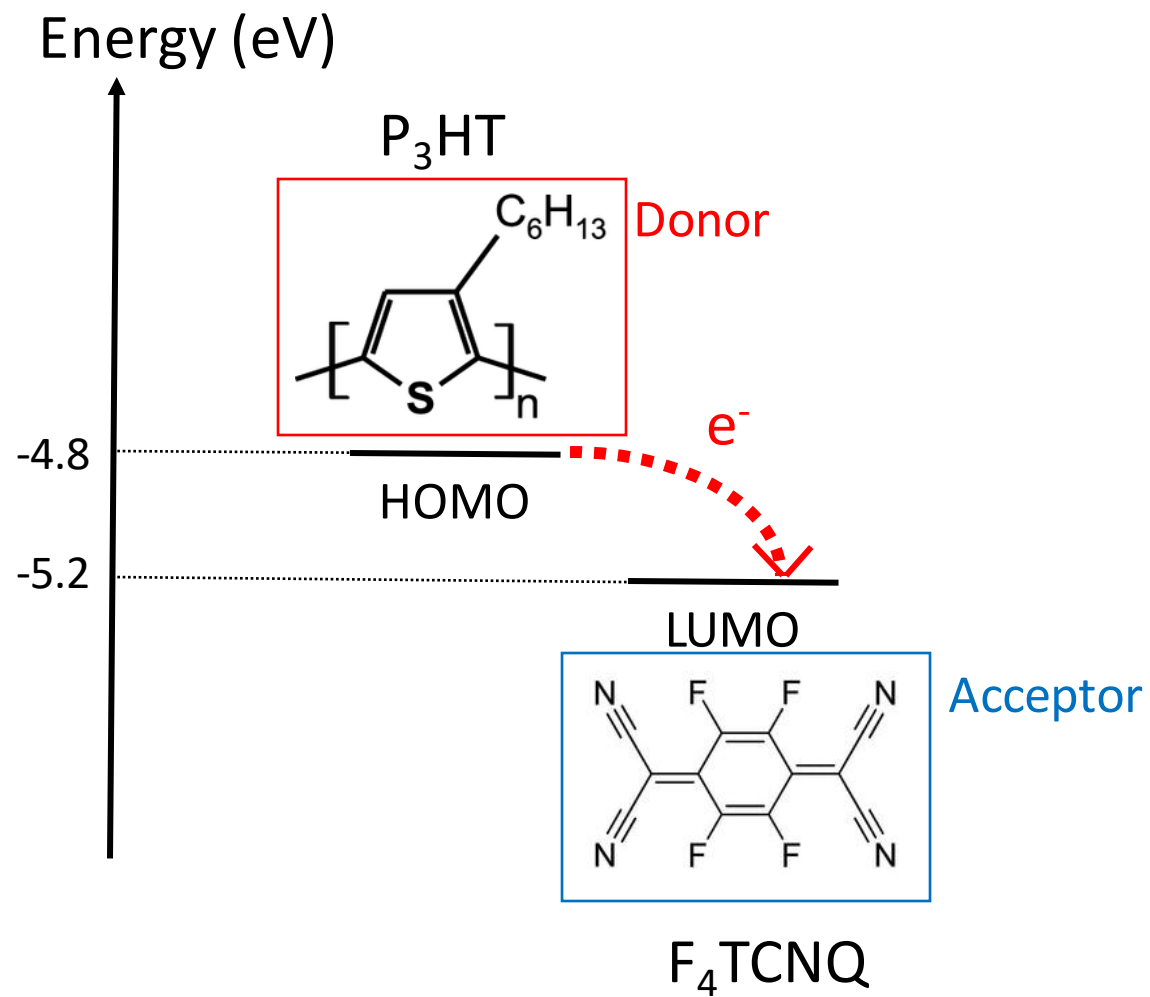
Cary 5000 spectrometer

Dichroic ratio

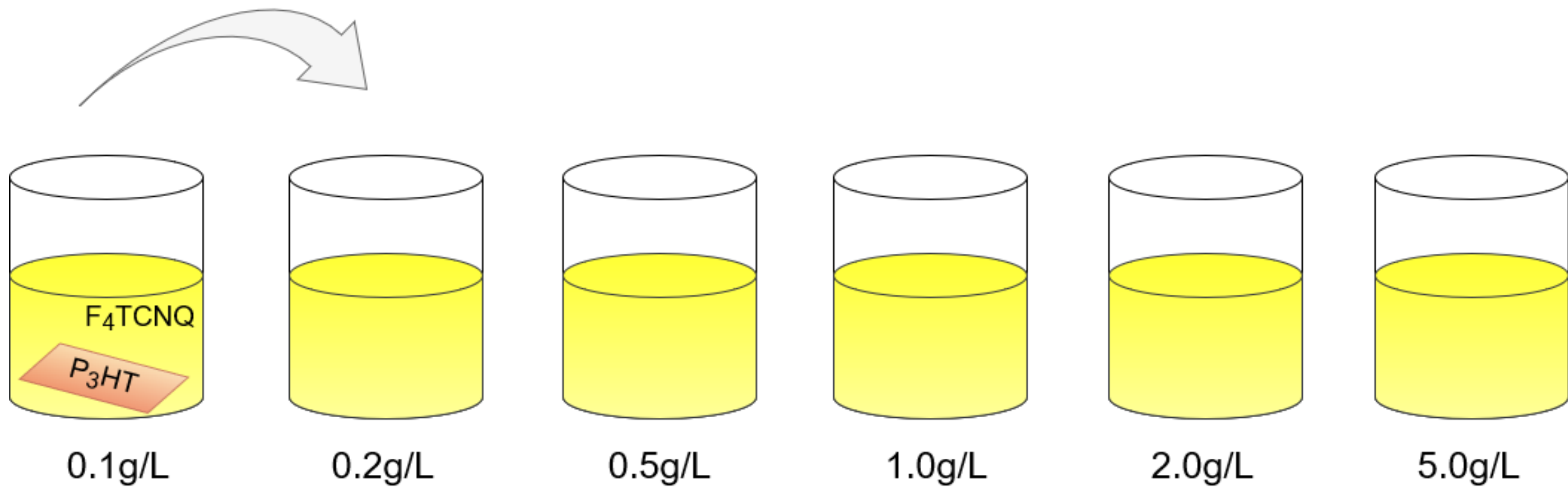
$$DR = \frac{A_{||}}{A_{\perp}} = 10.2$$

$$e = \left(\frac{A_{||} + A_{\perp}}{2} \right) \times \text{coef} = 47.1\text{nm}$$

Redox doping



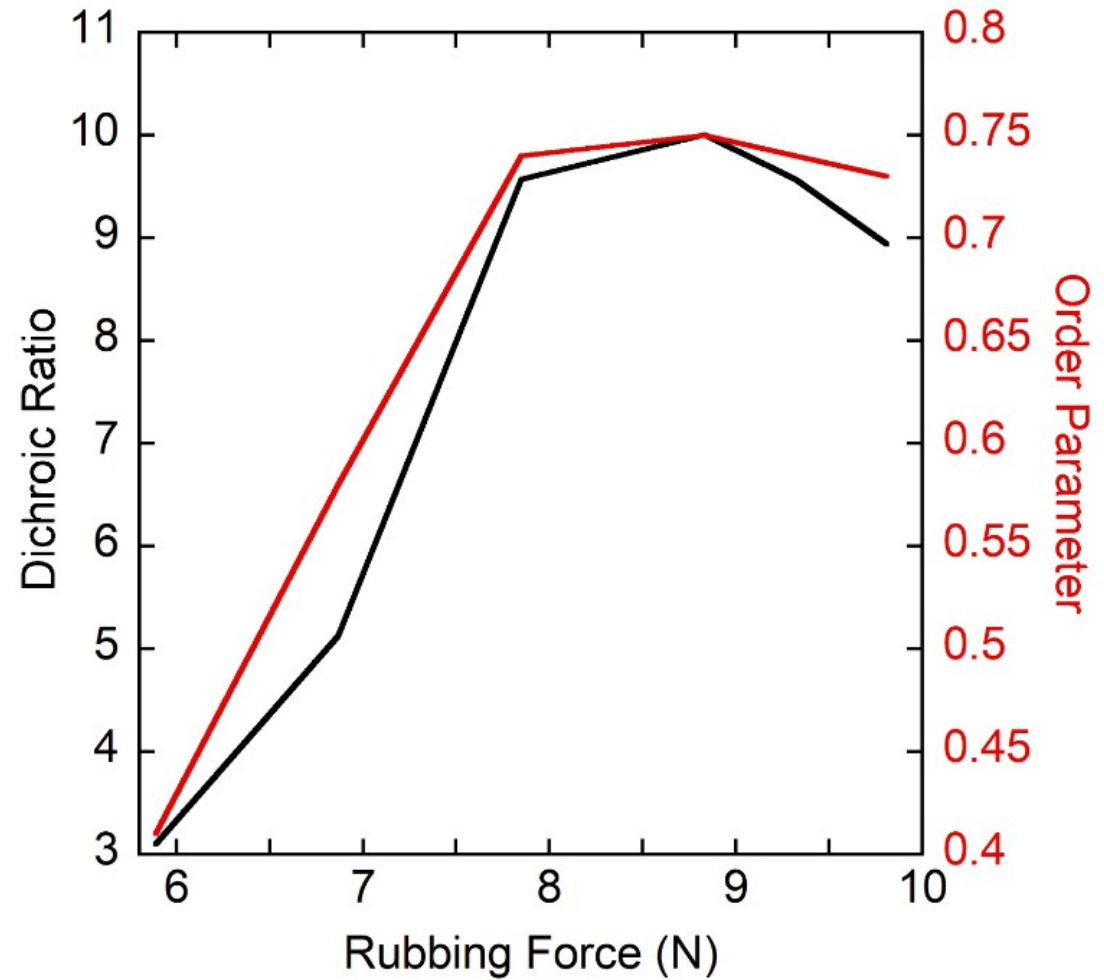
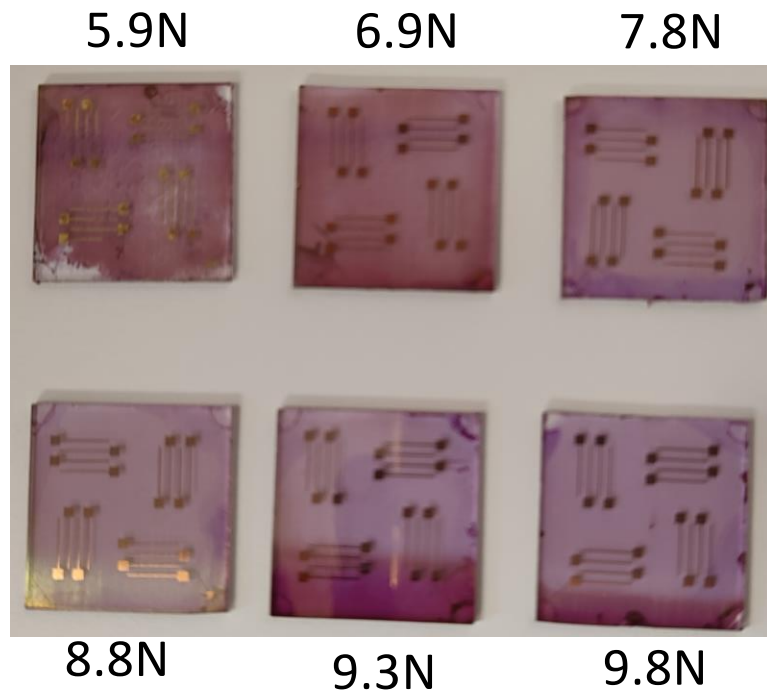
Incremental Concentration Doping



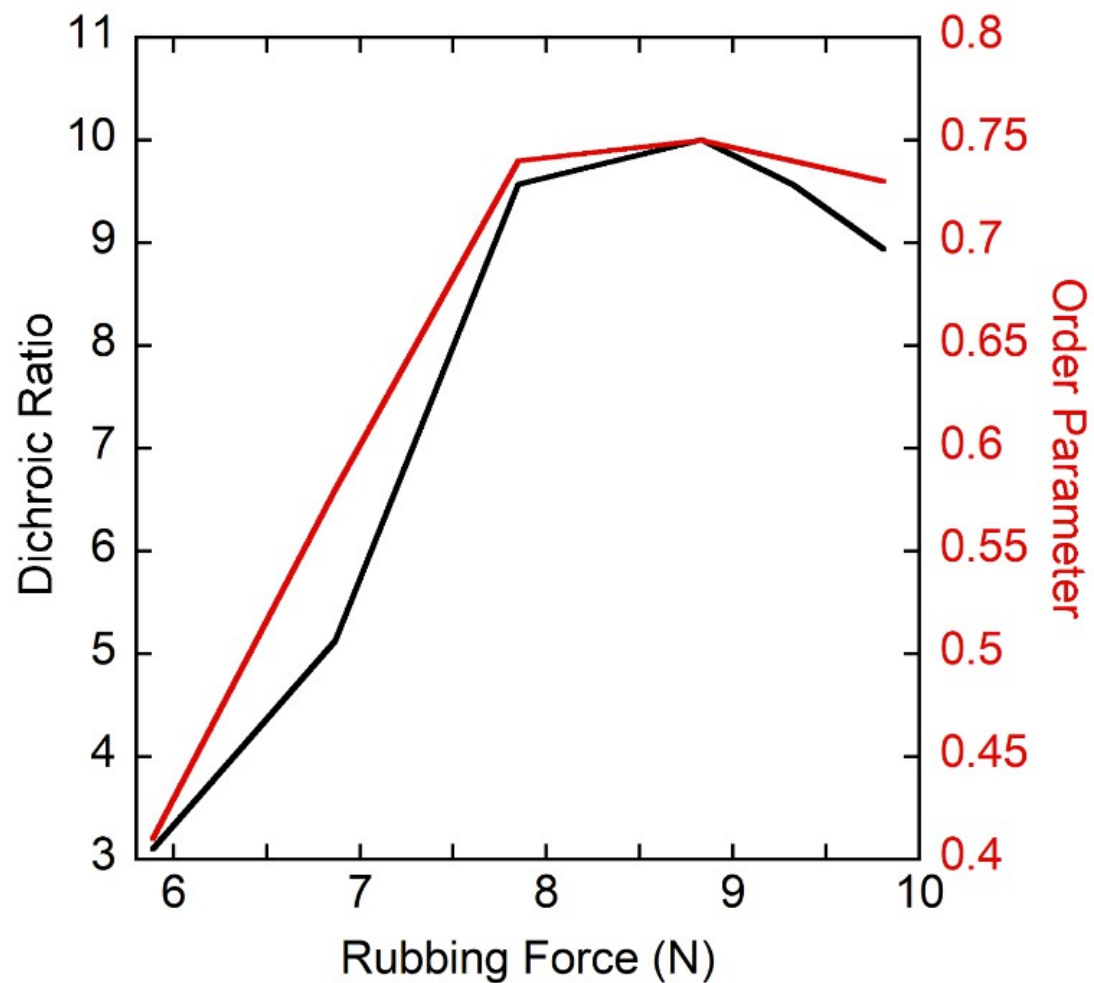
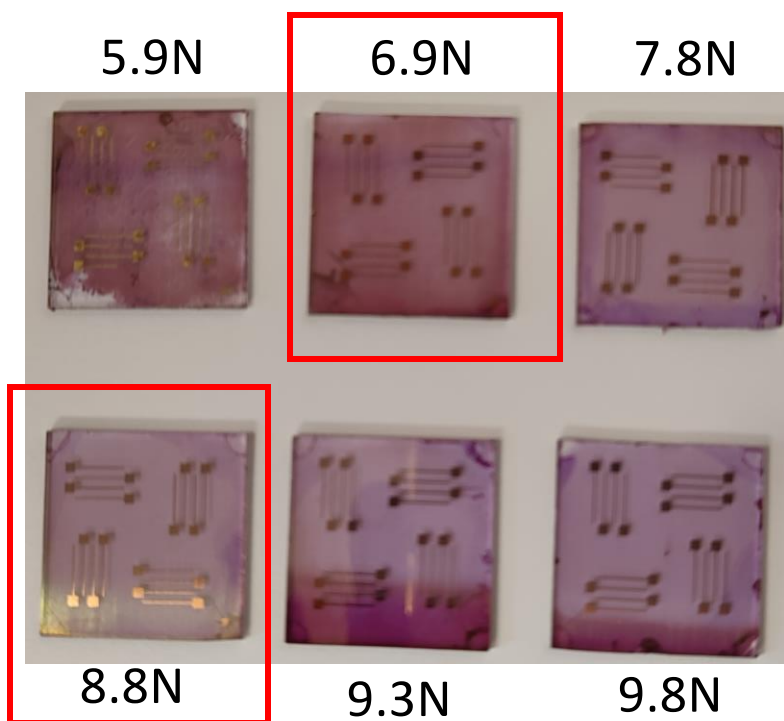
Experimental Results :

Influence of the Rubbing Force
on the thermoelectric parameters

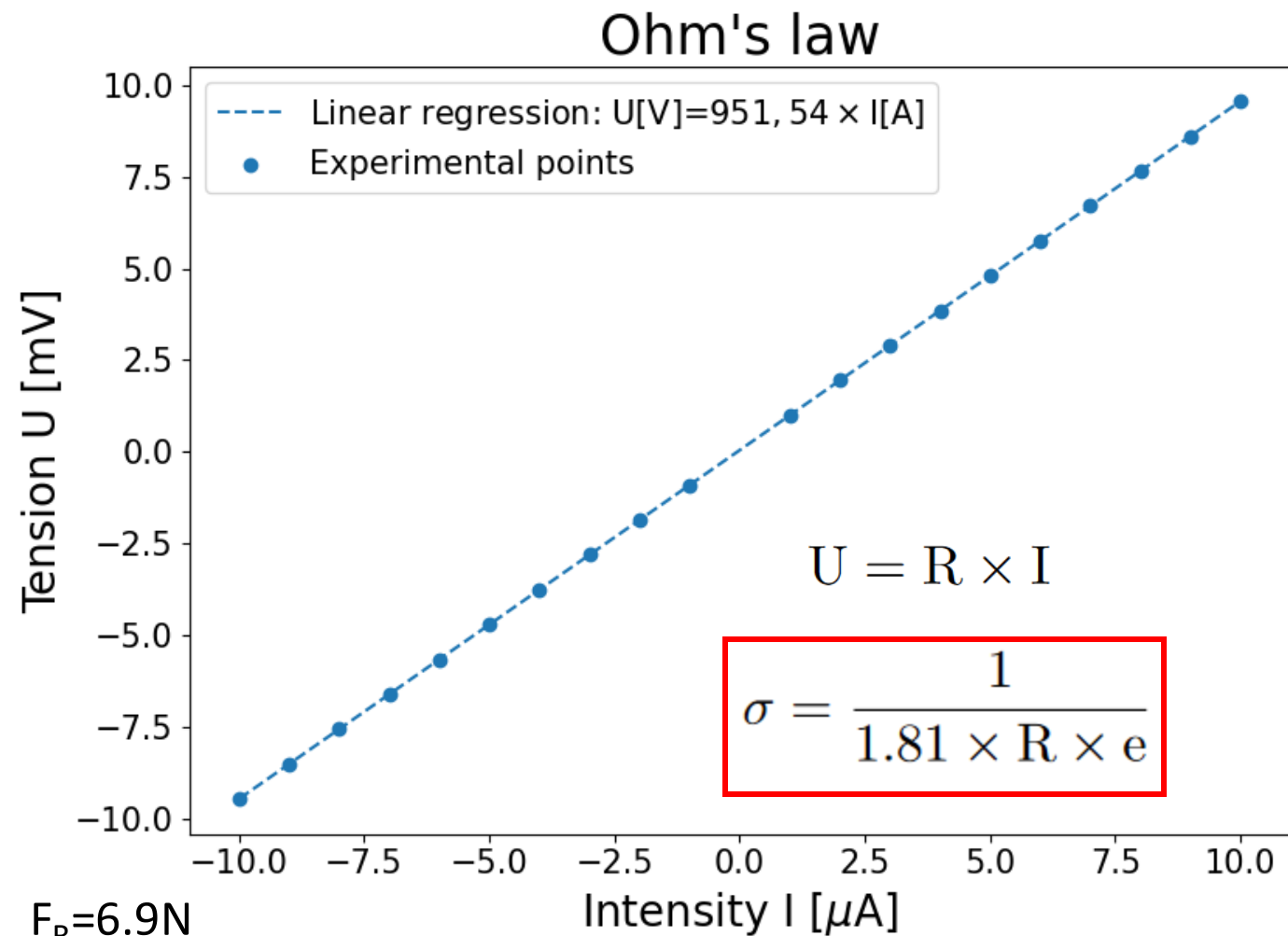
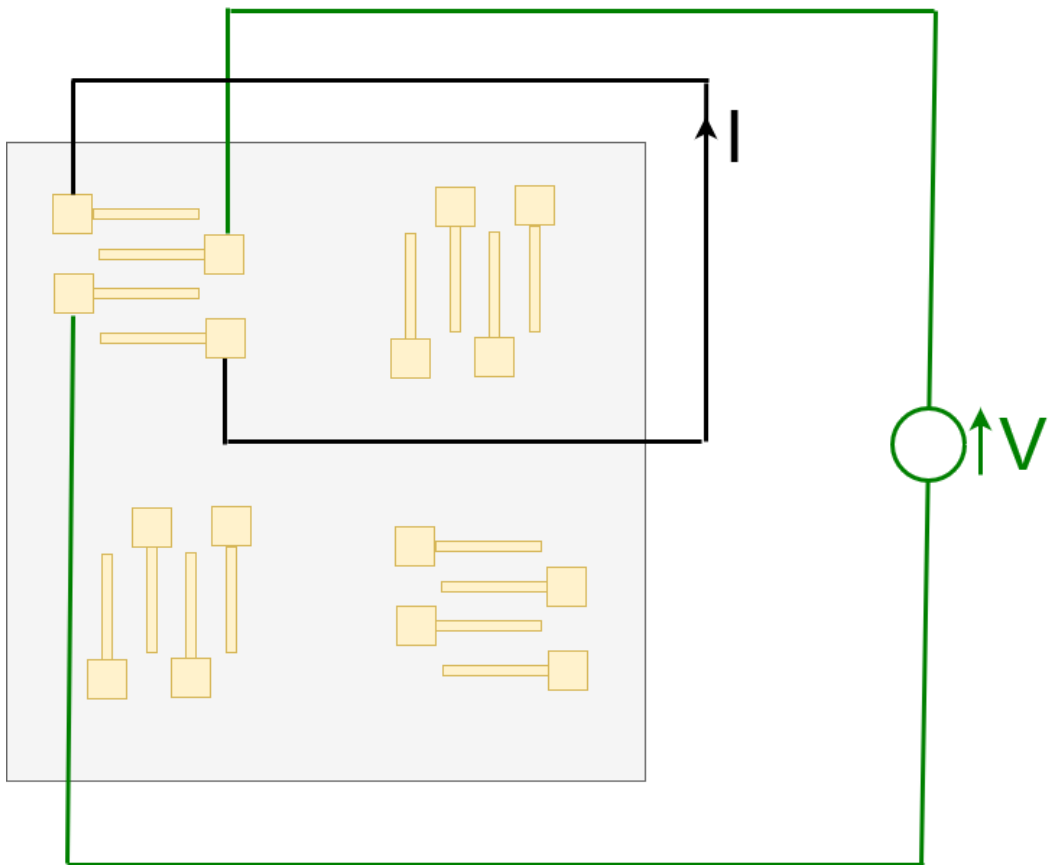
Dichroic ratio (DR)



Dichroic ratio (DR)



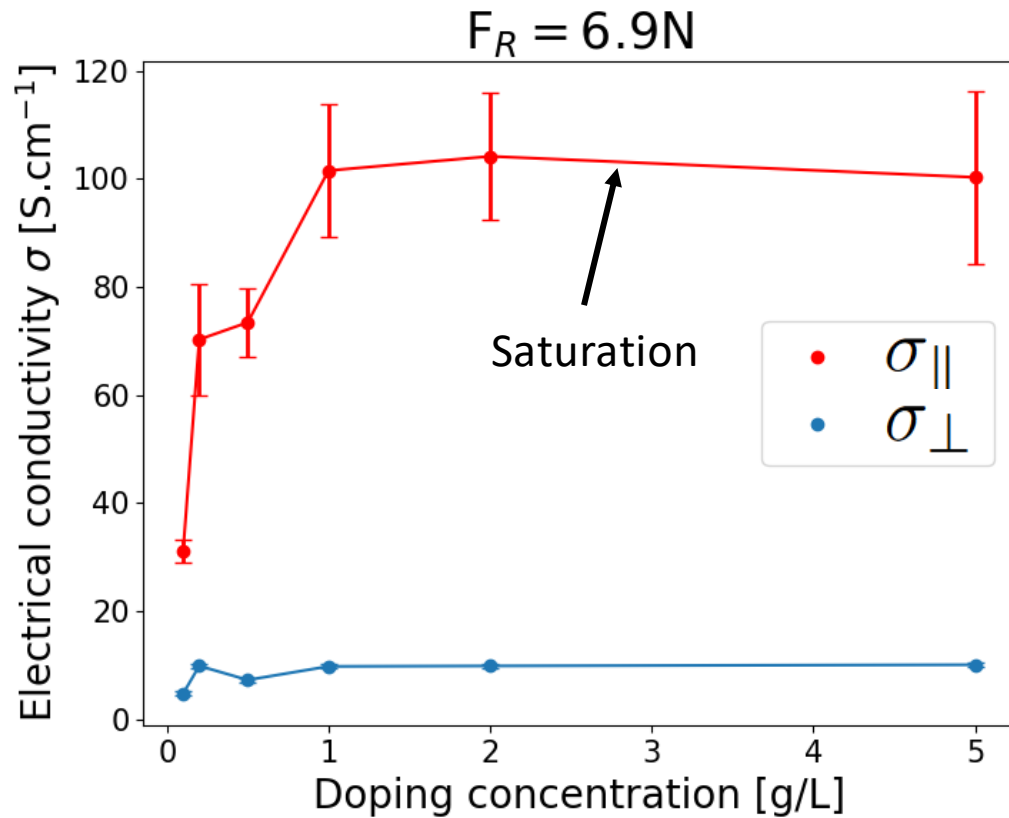
Electrical conductivity (σ)



$F_R=6.9N$
 $[F_4TCNQ]=0.5 \text{ g/L}$
 $e=71,5nm$

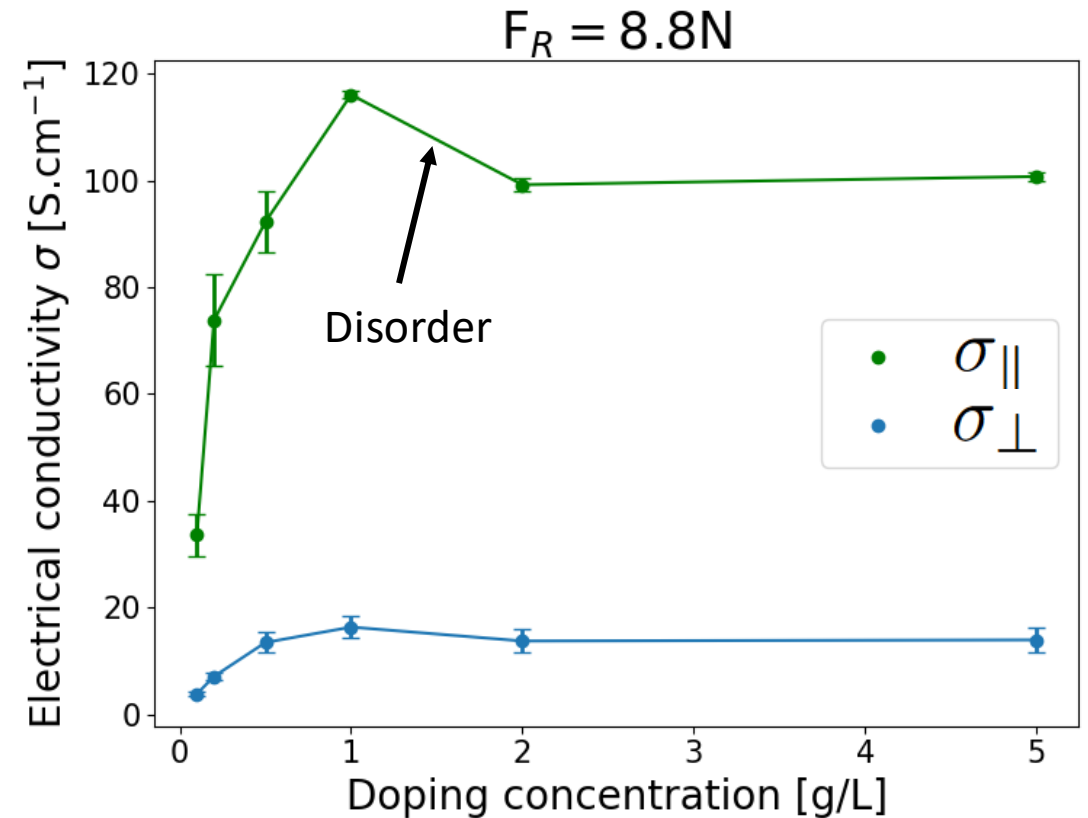
Electrical conductivity (σ)

$e=71,5\text{nm}$



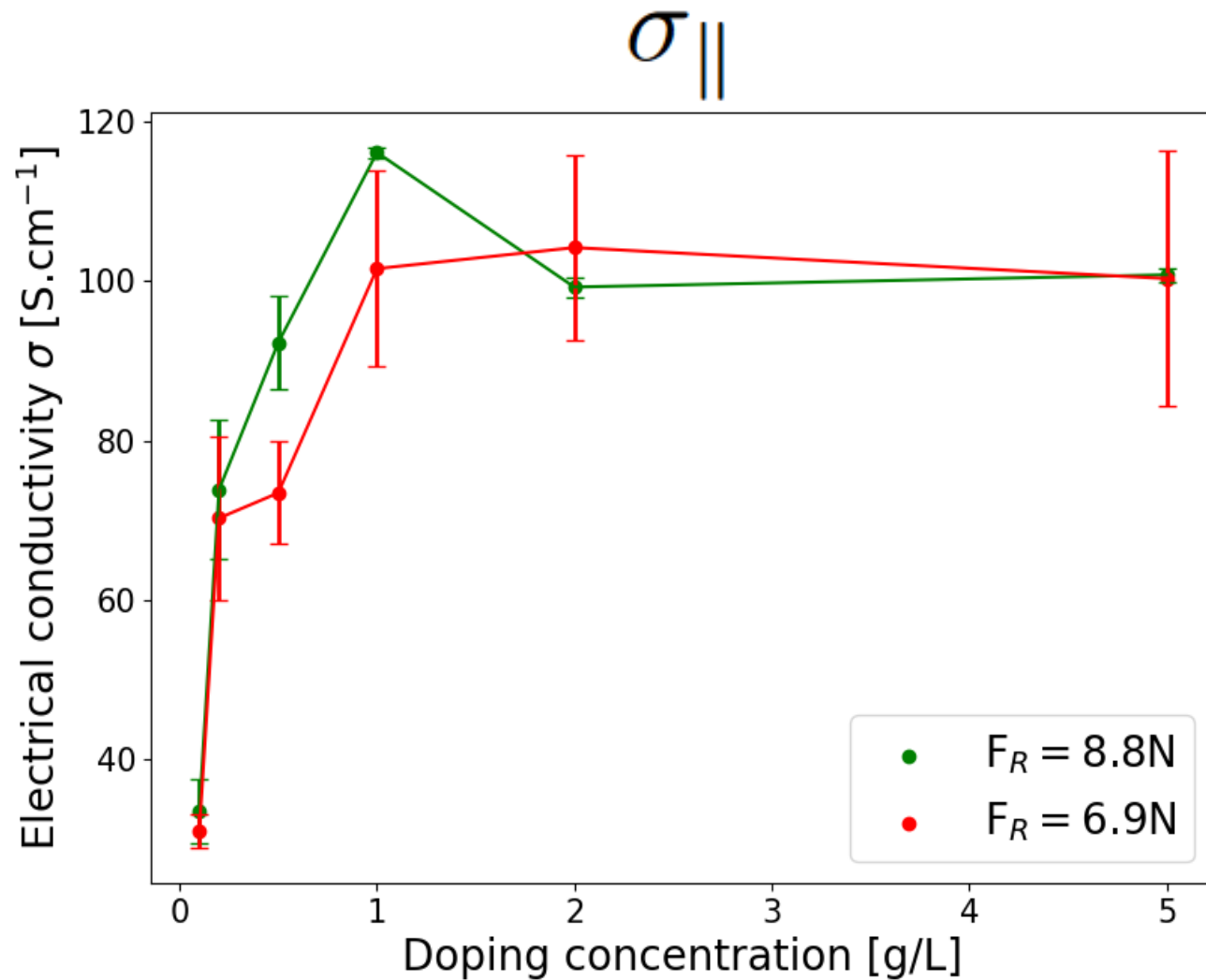
$$\frac{\sigma_{\parallel}}{\sigma_{\perp}} = 10.5$$

$e=47,1\text{nm}$



$$\frac{\sigma_{\parallel}}{\sigma_{\perp}} = 10.4$$

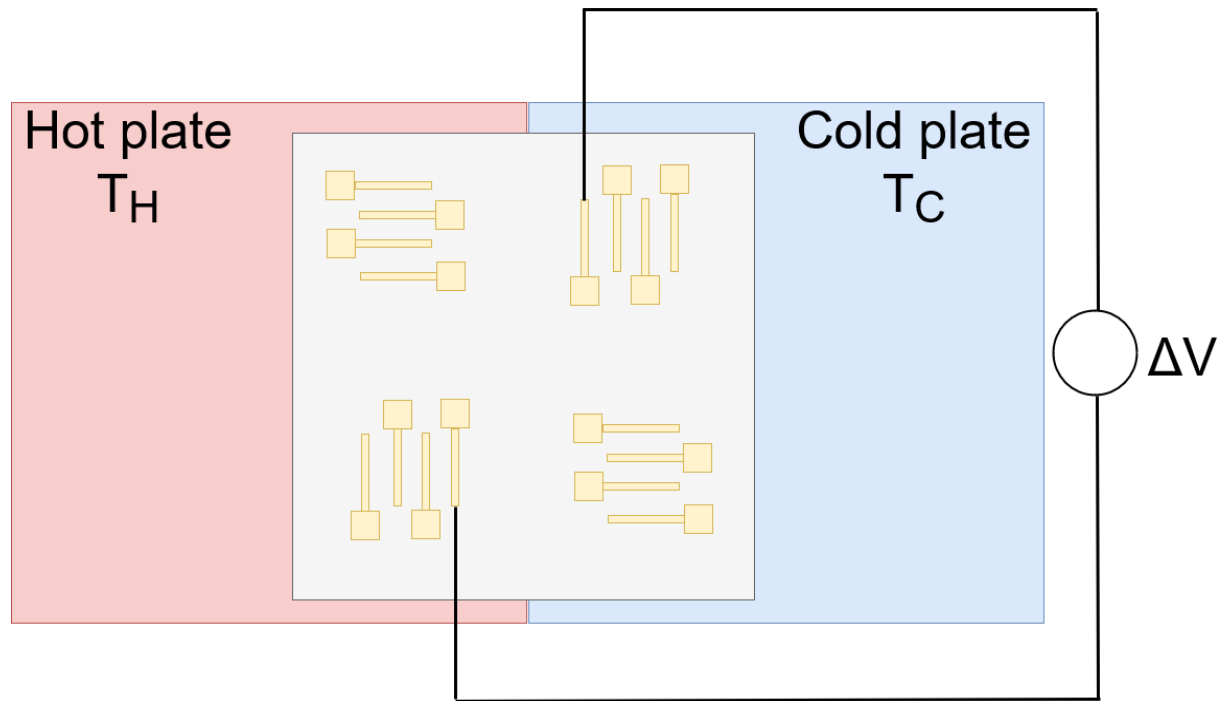
Electrical conductivity (σ)



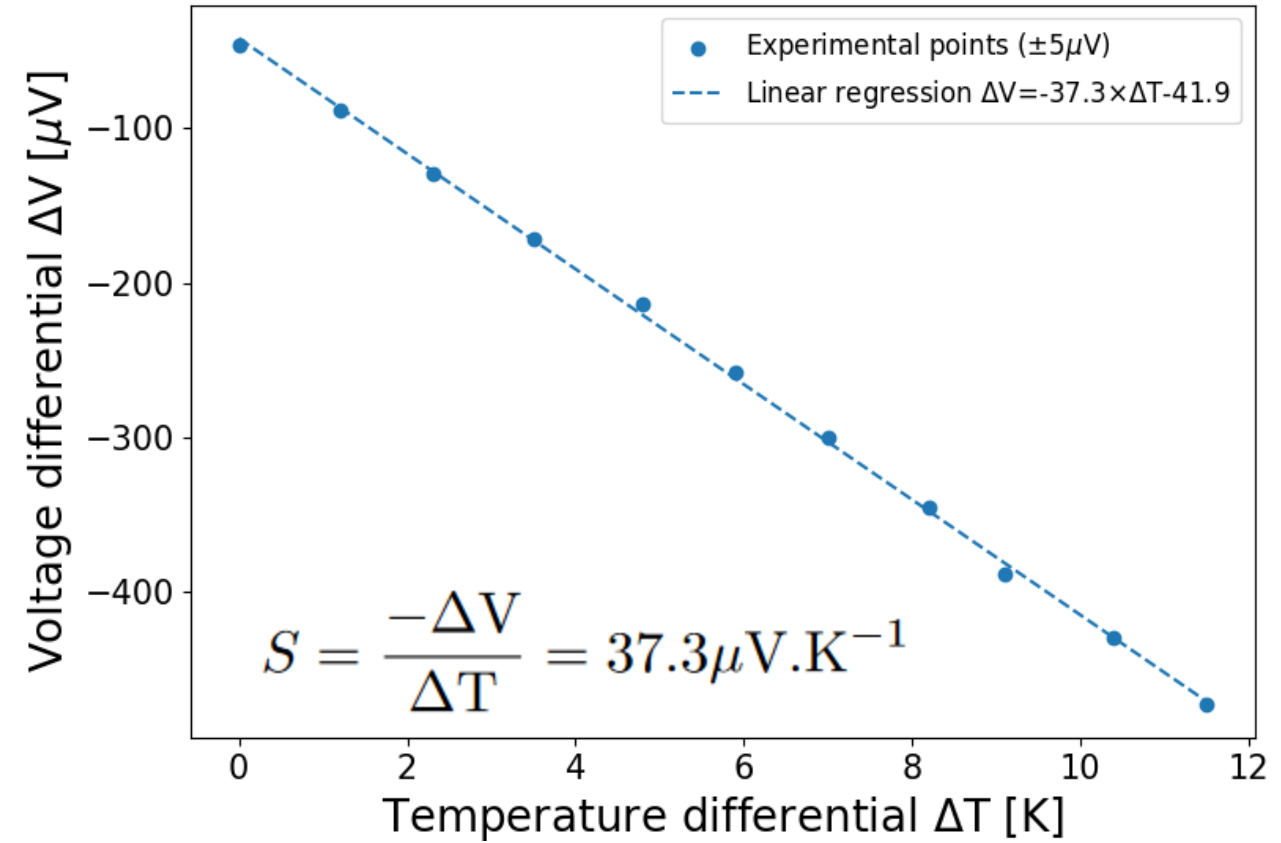
$\nearrow [\text{F}_4\text{TCNQ}^-] \Rightarrow \nearrow \sigma$

$\nearrow F_R \Rightarrow \nearrow \sigma$

Seebeck coefficient (S)



Seebeck's law

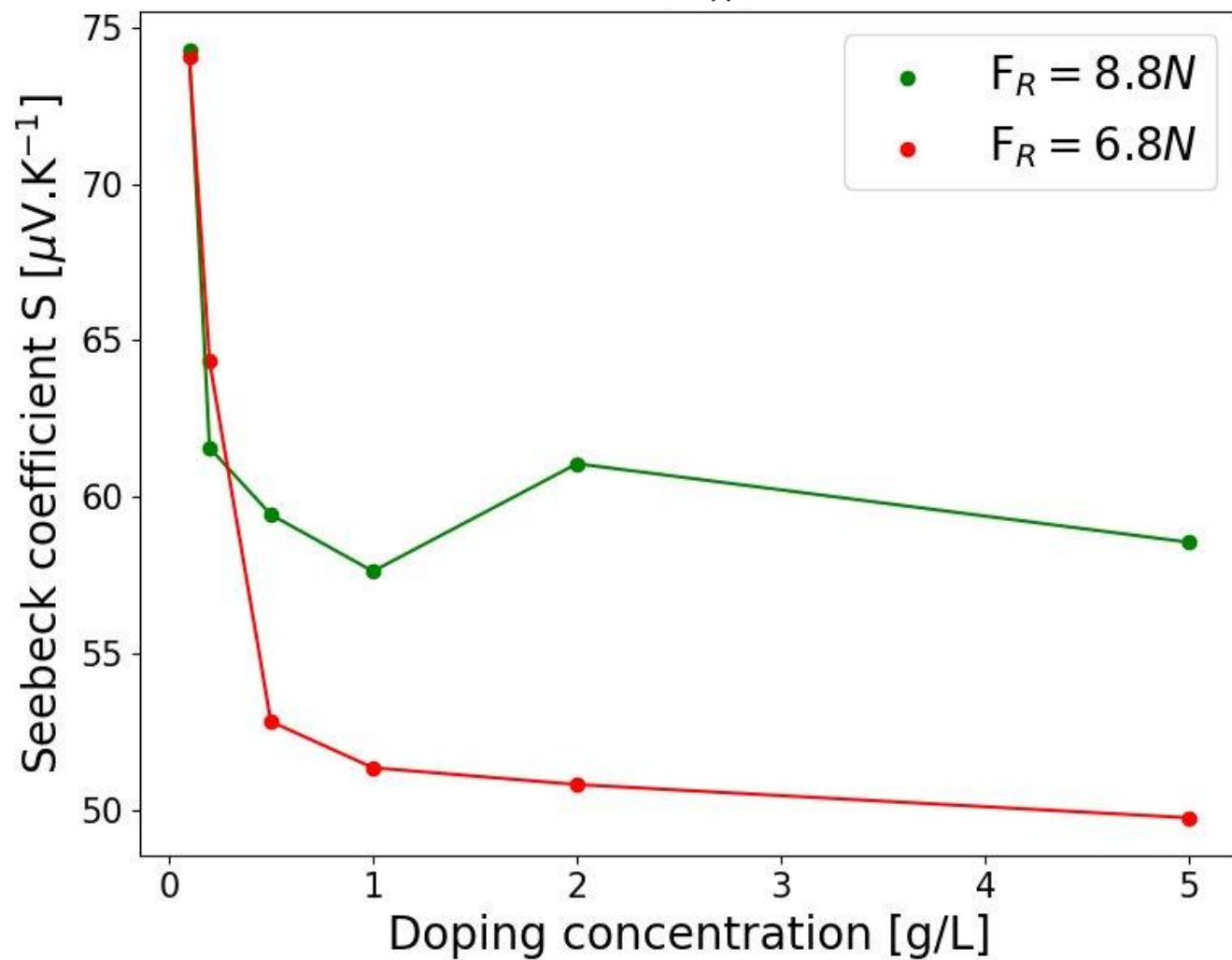


$F_R = 6.9 N$

$[F_4TCNQ] = 0.5 \text{ g/L}$

Seebeck coefficient (S)

$S_{||}$

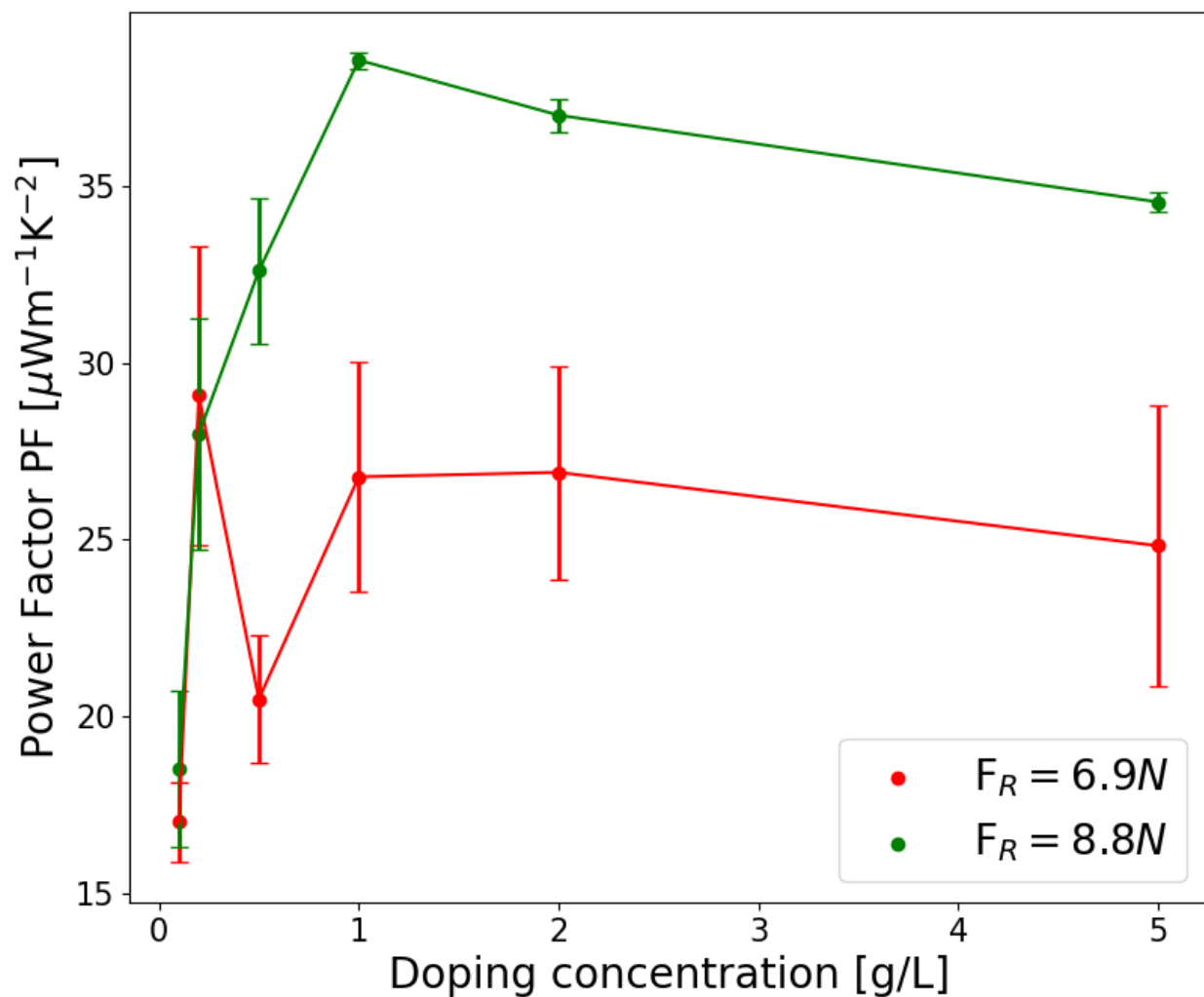


$\nearrow [F_4\text{TCNQ}^-] \Rightarrow \searrow S$

$\nearrow F_R \Rightarrow \nearrow S$

Power factor (PF)

PF_{\parallel}



$\nearrow [F_4\text{TCNQ}^-] \Rightarrow \nearrow \text{PF}$

$\nearrow F_R \Rightarrow \nearrow \text{PF}$

$[F_4\text{TCNQ}^-] = 1\text{g/L}$

$PF_{\text{max}} = 38.6\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$

$PF = 26.8\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$

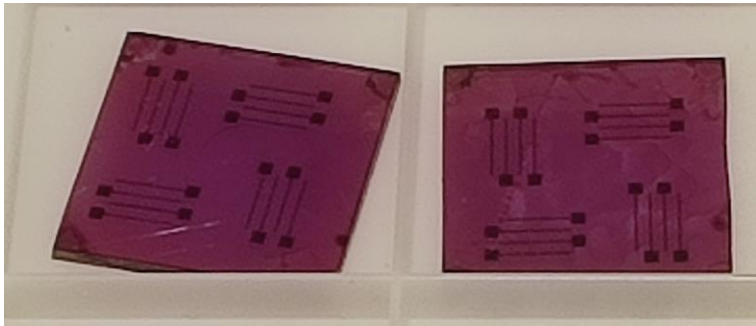
+44%

Conclusion

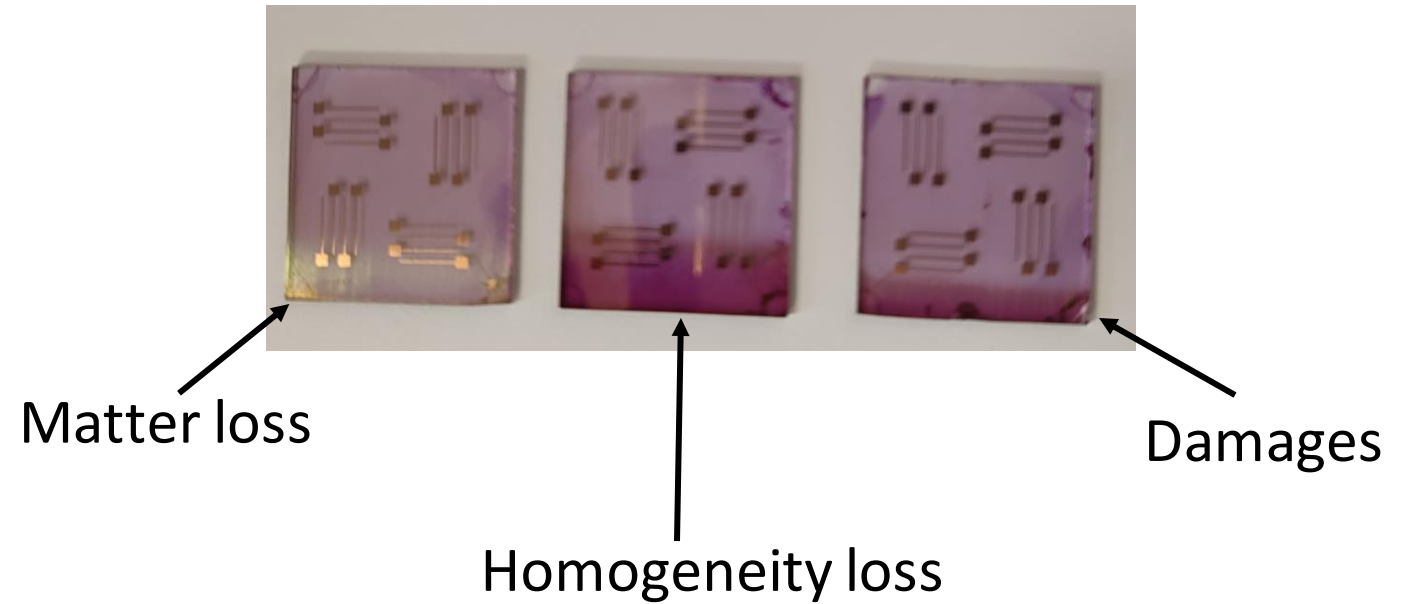
$\nearrow F_R \Rightarrow \nearrow DR$ and $\nearrow PF$

\nearrow alignment $\Rightarrow \nearrow$ charges transport $\Rightarrow \nearrow PF$

Before brushing



After brushing



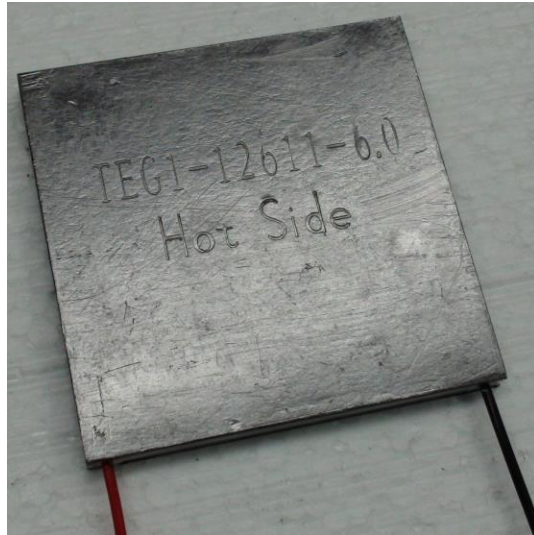
$\nearrow [F_4TCNQ^-] \Rightarrow \nearrow PF$

Bibliography

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- Zhong, Y., Untilova, V., Muller, D., Guchait, S., Kiefer, C., Herrmann, L., Zimmermann, N., Brosset, M., Heiser, T., & Brinkmann, M. (2022). Optimizing chain alignment and preserving the pristine structure of single-ether based PBTTT helps improve thermoelectric properties in sequentially doped thin films. In *Journal of Materials Chemistry C* (Vol. 10, Issue 42, pp. 15883–15896). Royal Society of Chemistry (RSC). <https://doi.org/10.1039/d2tc03600b>
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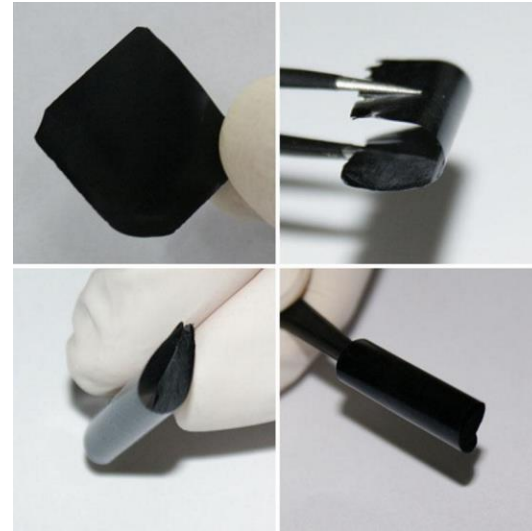
Annexes

Thermoelectric materials



Bi_2Te_3 :

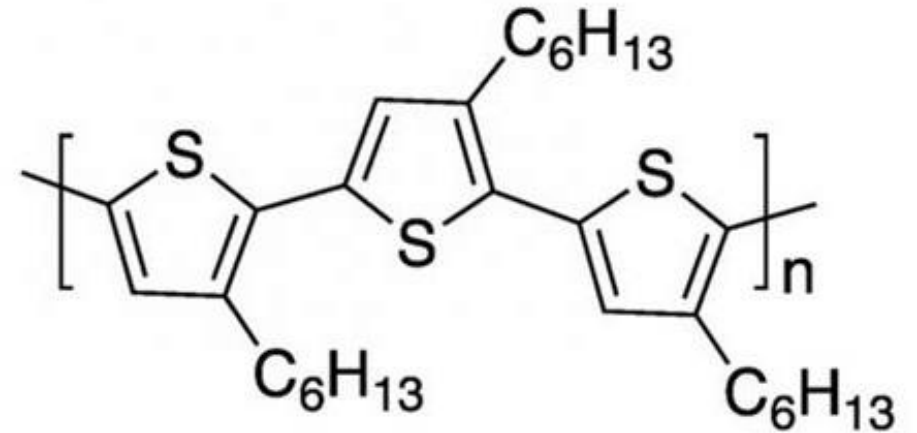
- $zT \approx 1.0$
- Stiff
- Expensive
- Toxic elements



PEDOT : PSS films :

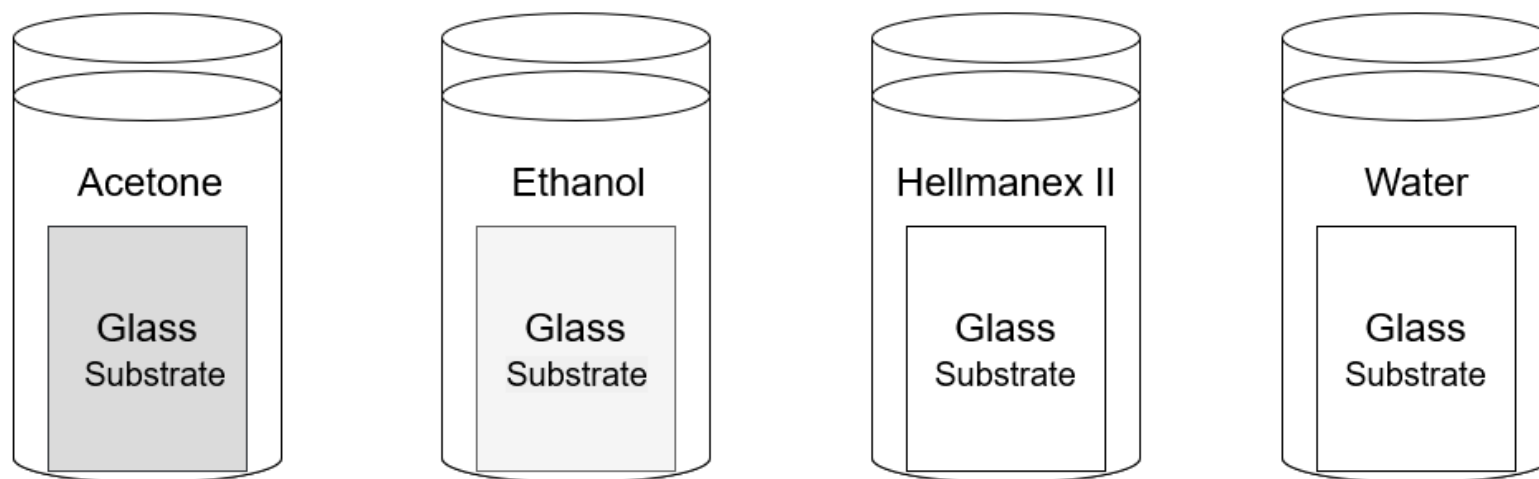
- $zT \approx 0.4$
- Flexible
- Complex geometry
- Untoxic elements

P_3HT : p-type semiconductor



Poly (3-hexylthiophène-2,5-diyl)

Cleaning process



Ultrasonic Cleaner

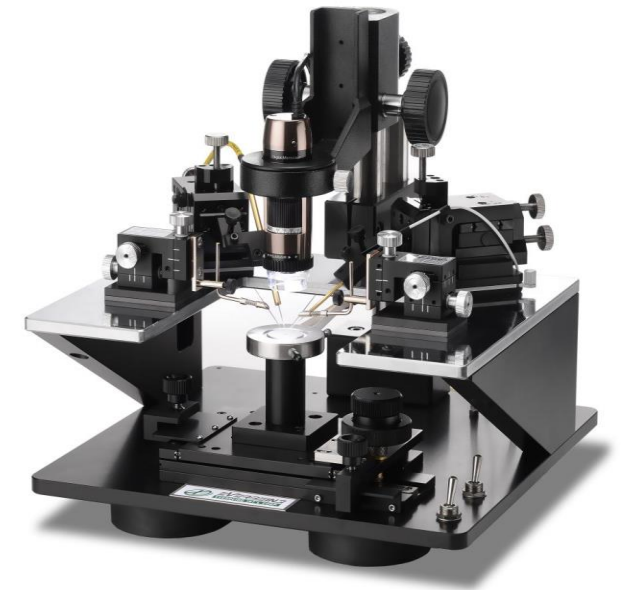
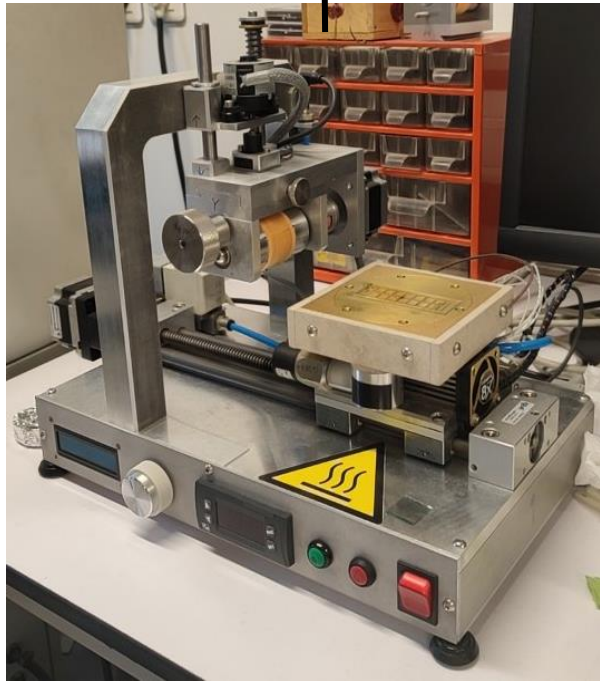


Ultrasonic Cleaner



UV-Ozone Cleaner

Glove Box

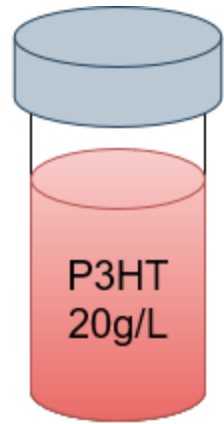


Glove box

High temperature rubbing instrument

Probe-station

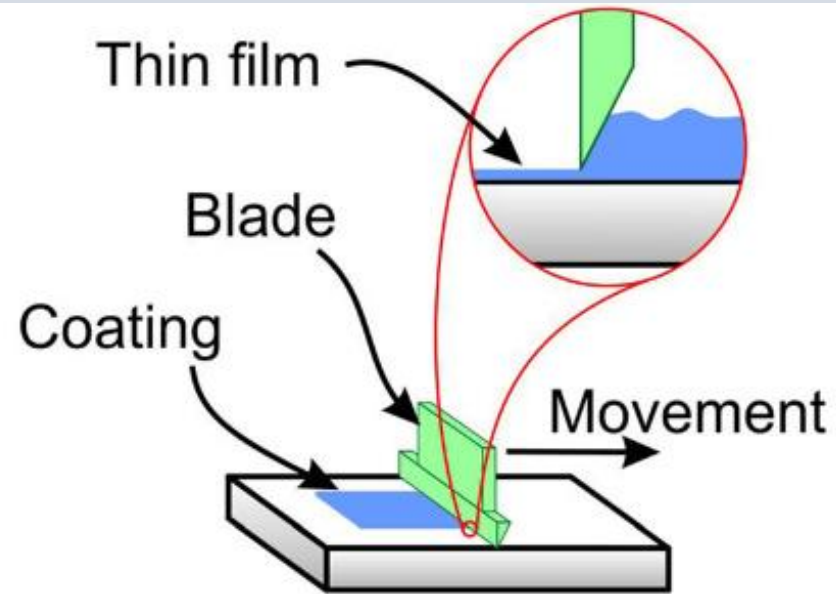
Doctor Blade Method



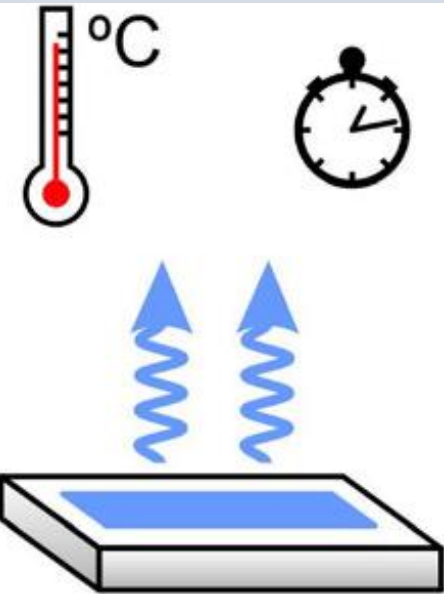
Surface
preparation



Step 1

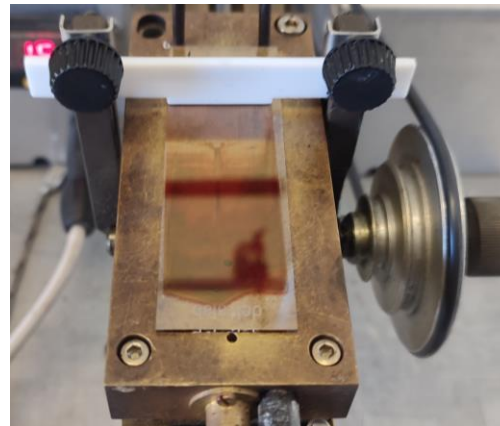
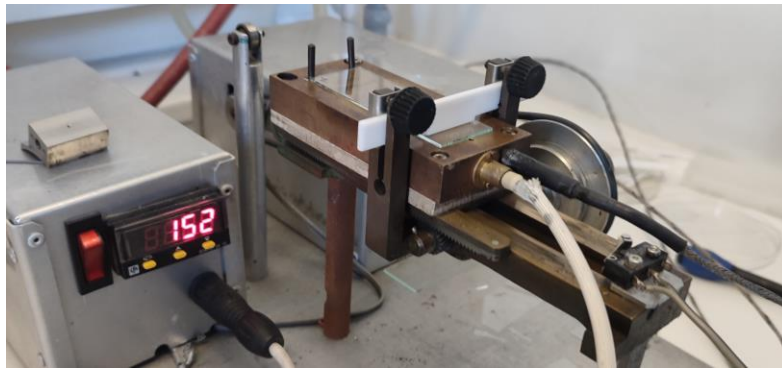


Step 2

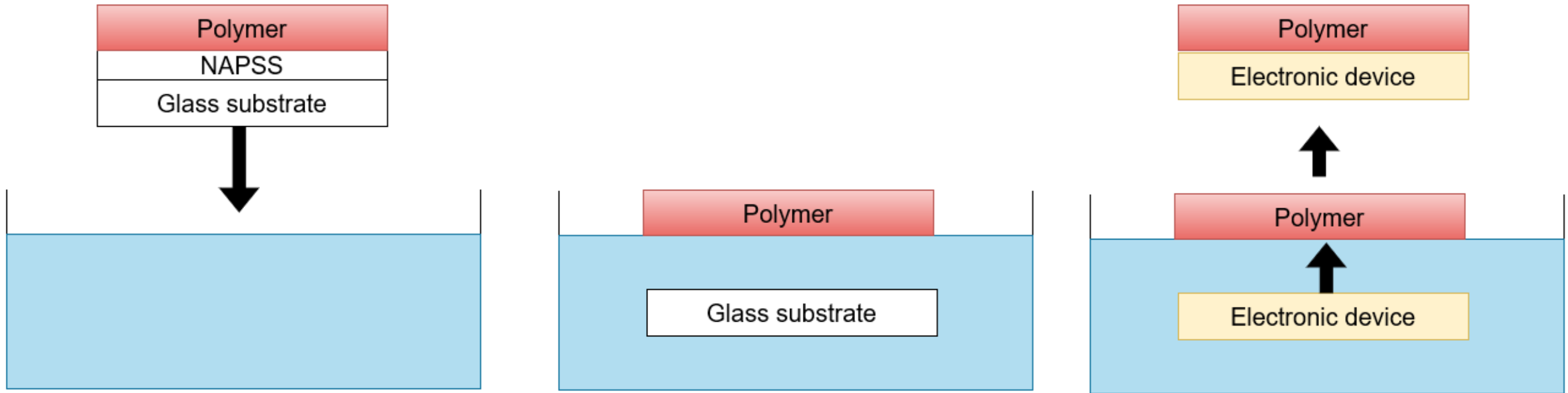


Step 3

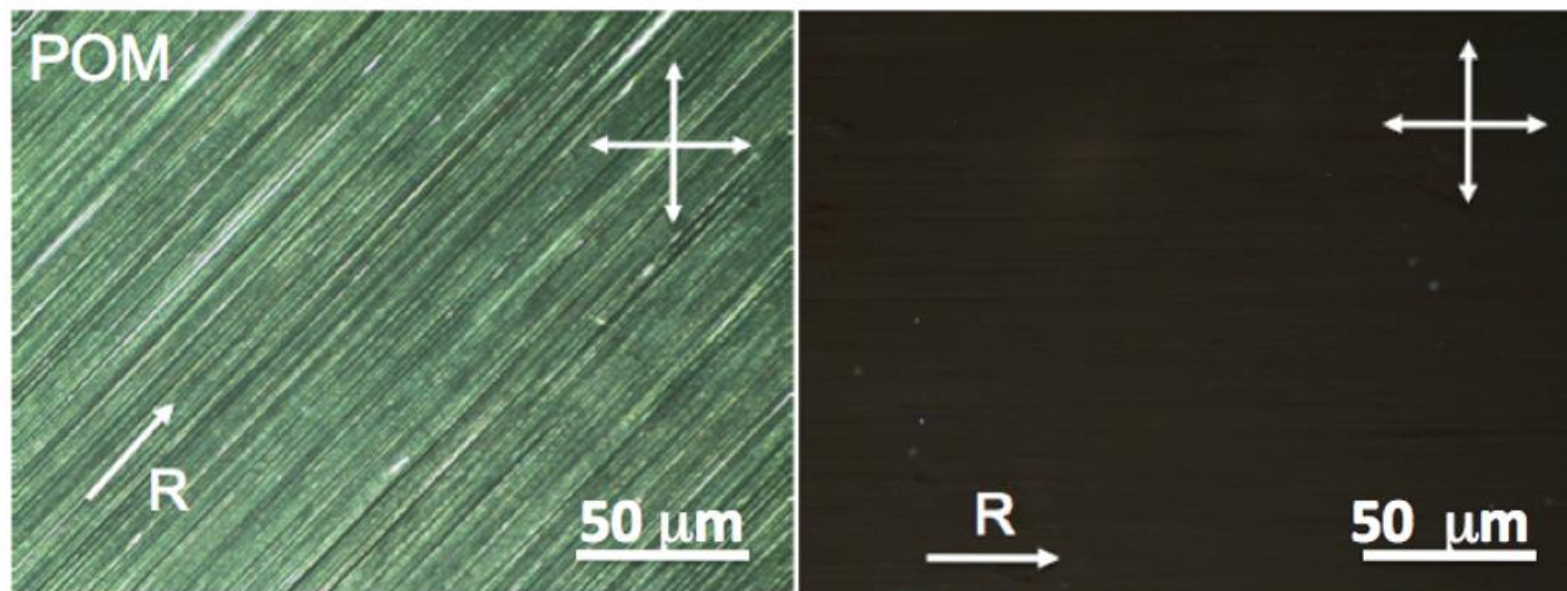
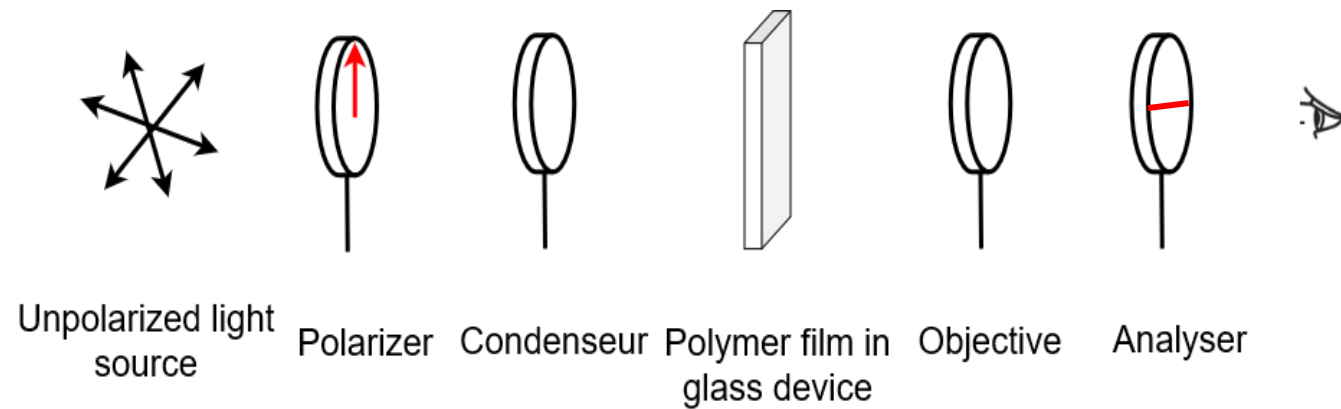
(Guchait et al., 2023)



"Floating" process

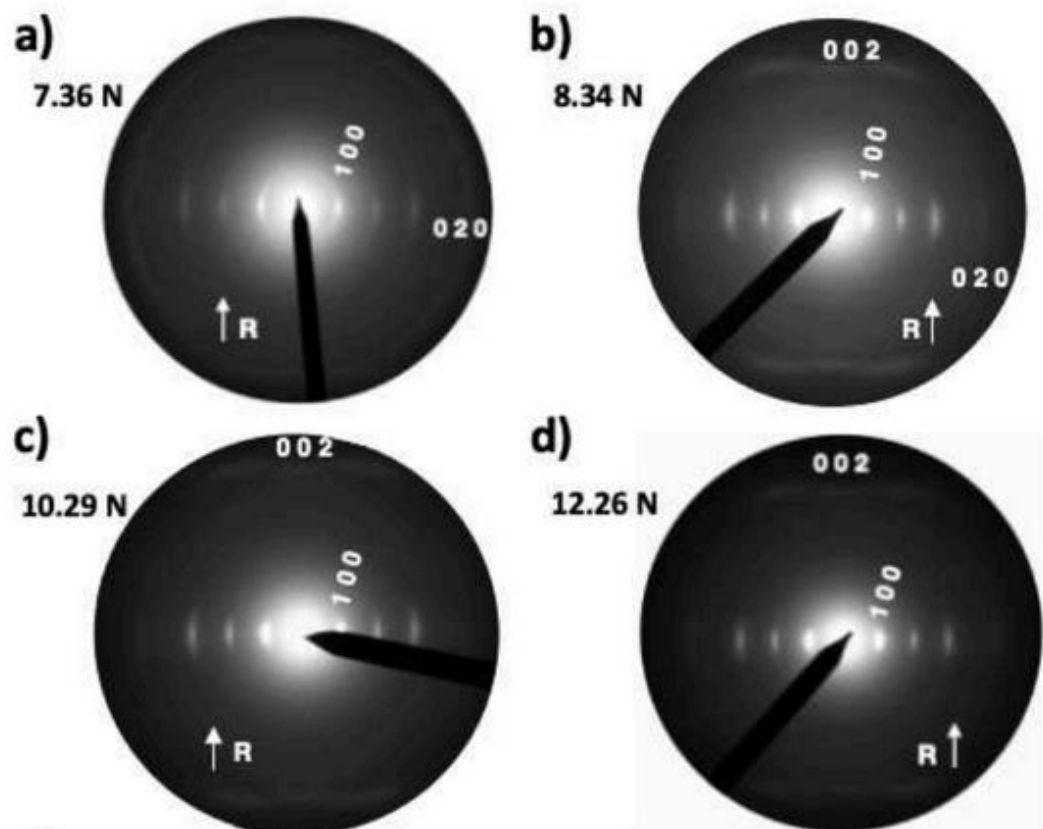


Polarized optic microscopy

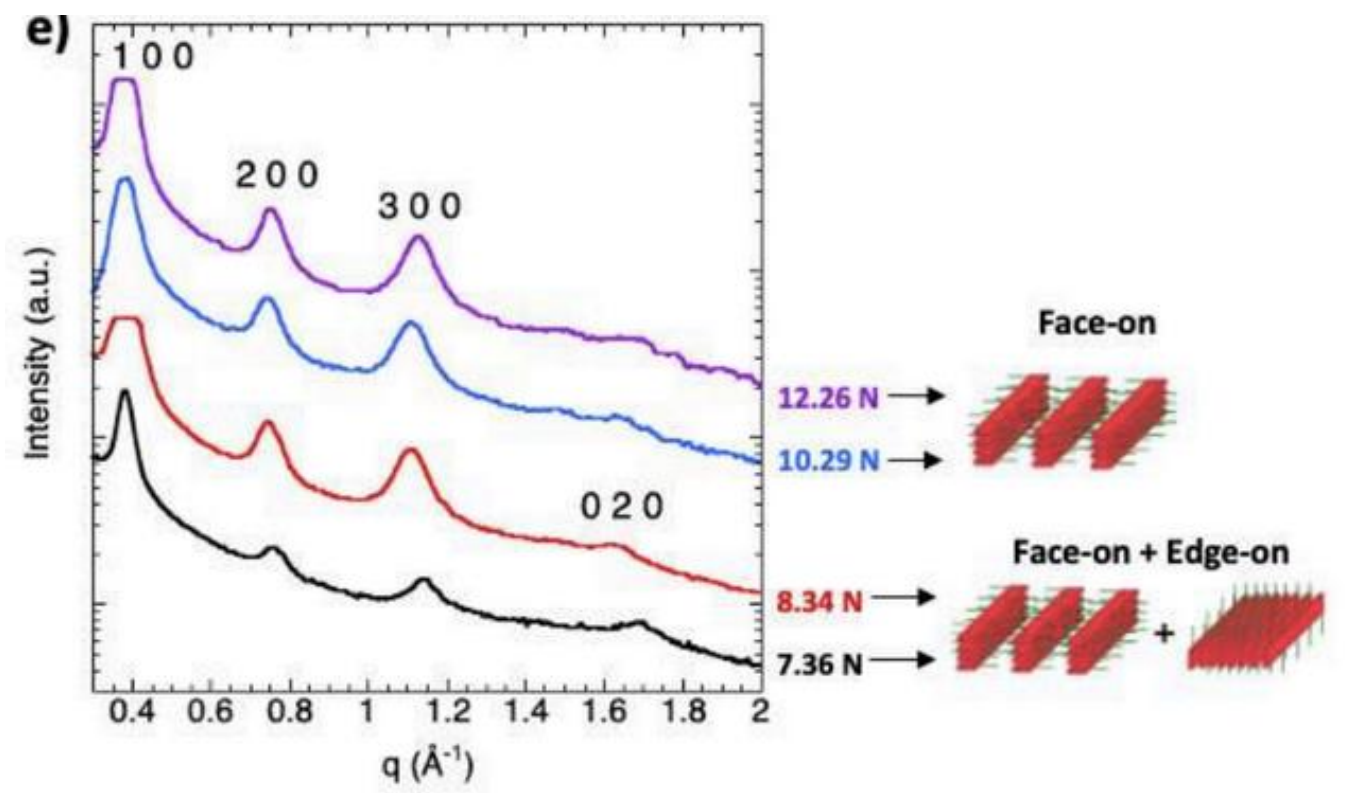


Birefringent high oriented P₃HT film

High temperature rubbing method

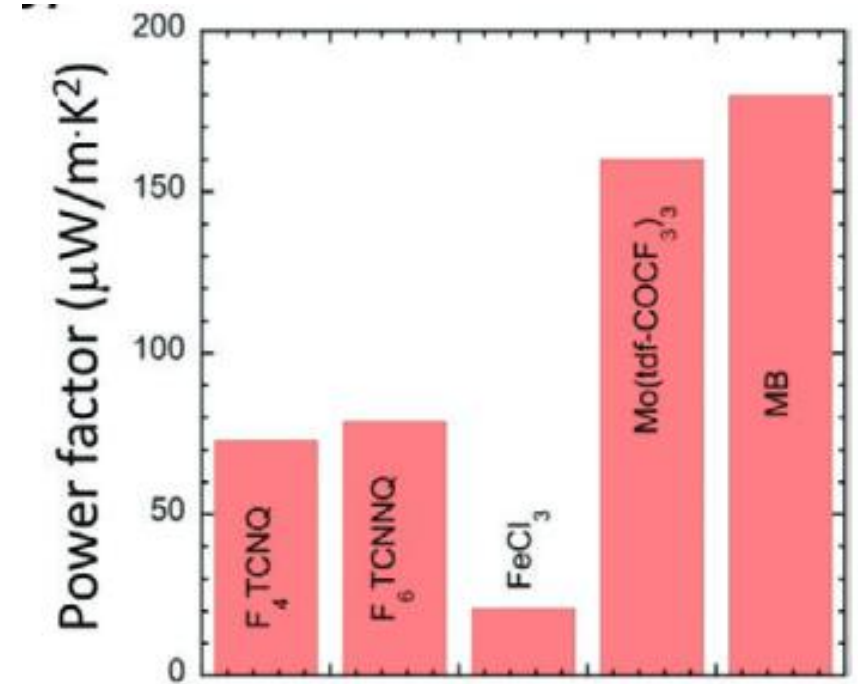
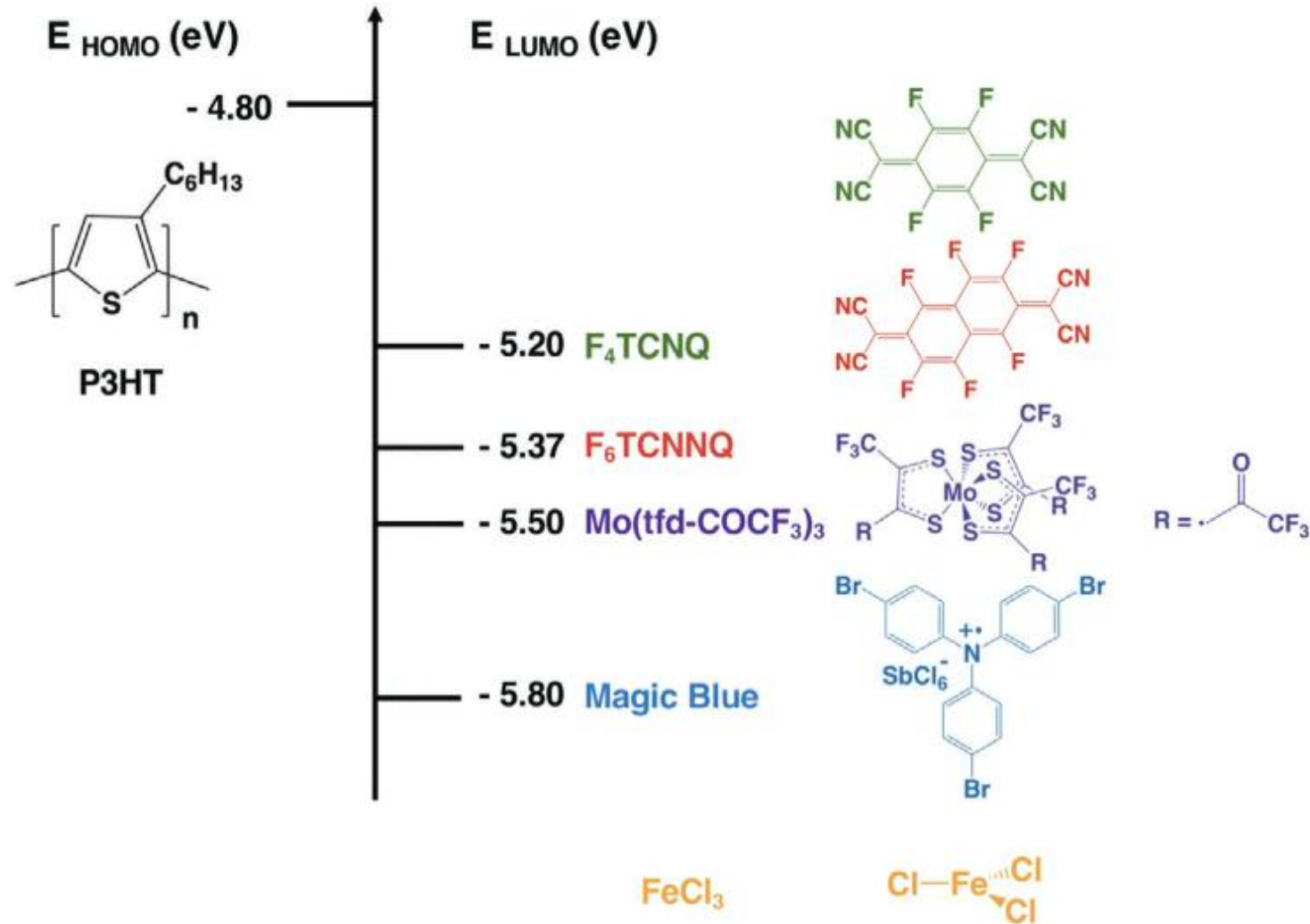


ED patterns of oriented P₃HT films prepared at different rubbing forces (Tr=150°C)



Intensity profile along the equator of the ED patterns

Dopants overview

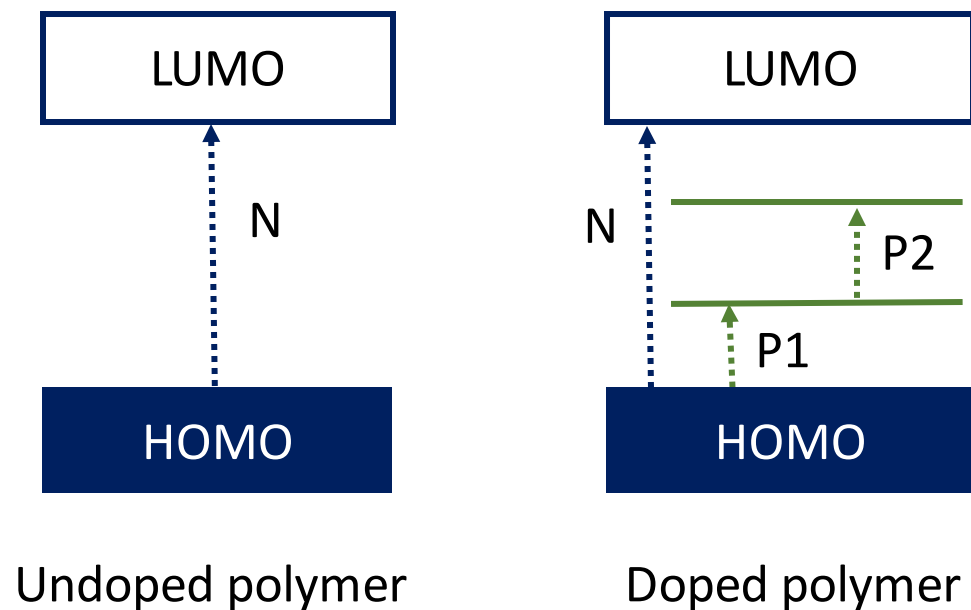


Maximum values of the power factor PF// measured

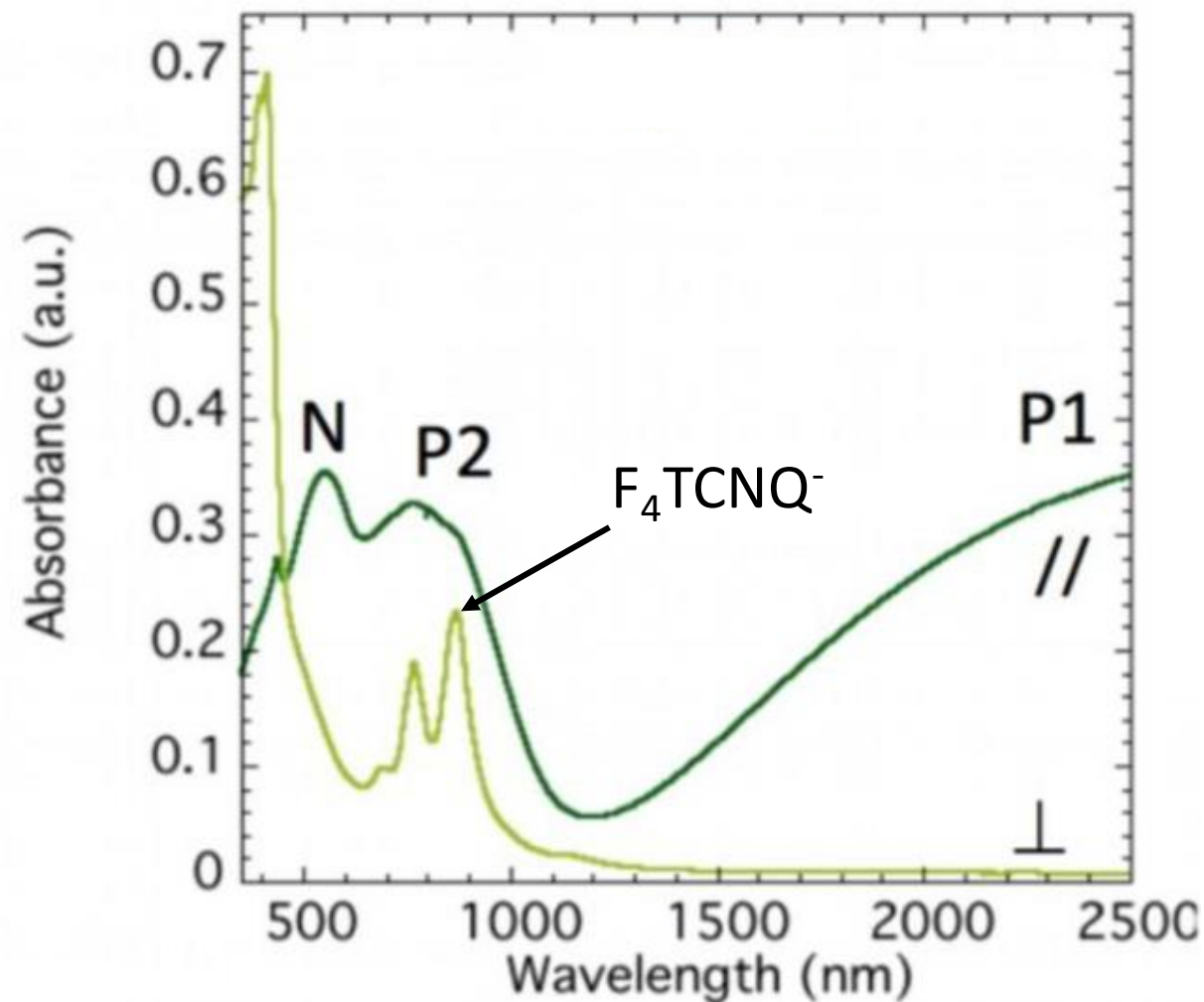
(Guchait et al., 2023)

(Guchait et al., 2023)

Polaronic absorption bands



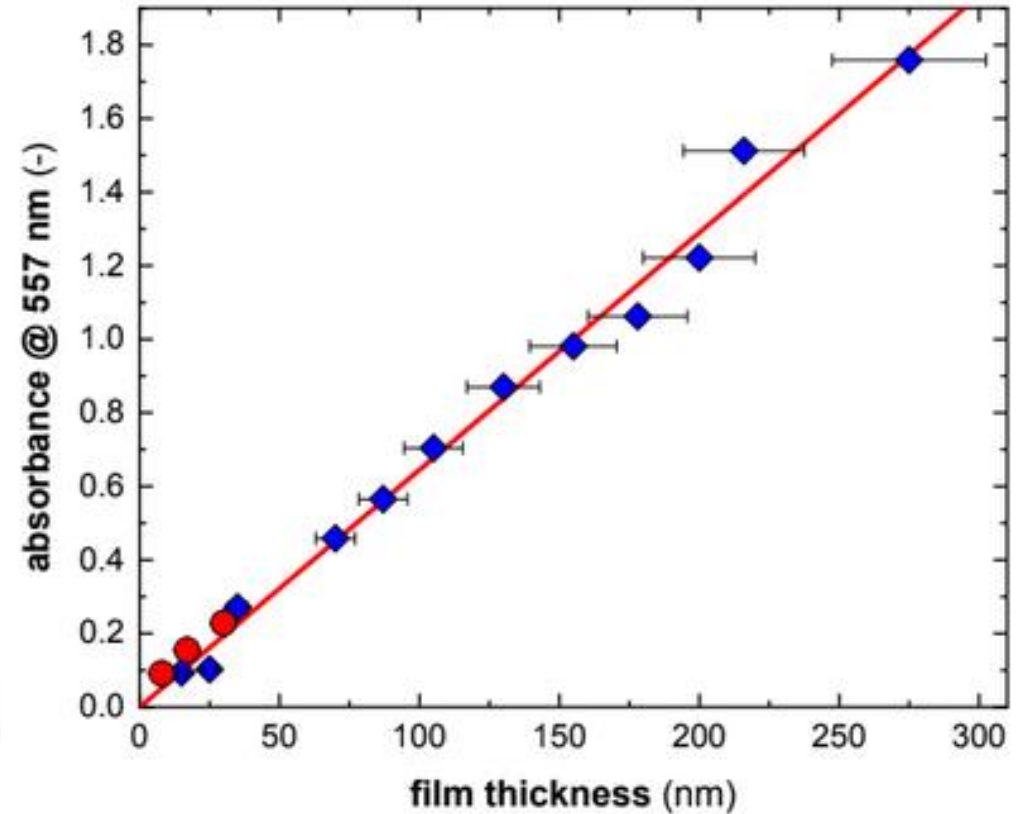
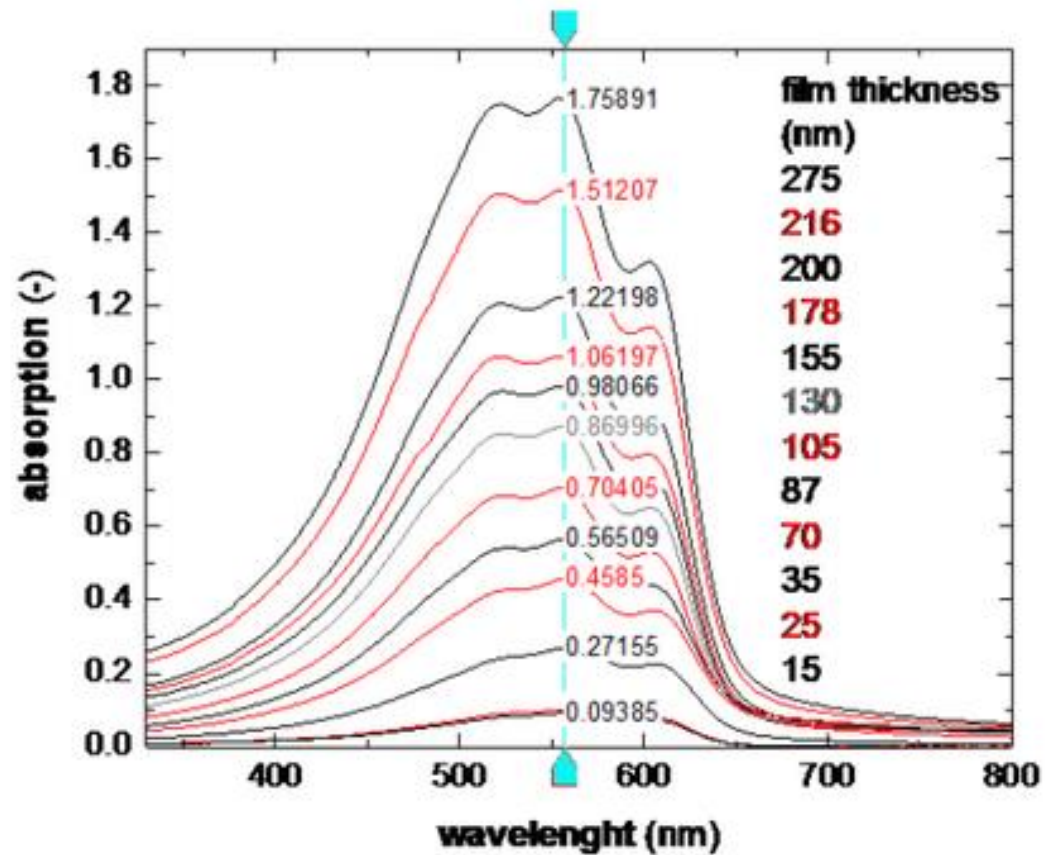
UV-Vis absorption spectra of a doped P₃HT film



DOI: [10.1021/acs.macromol.1c00554](https://doi.org/10.1021/acs.macromol.1c00554)

Calibrated coefficient

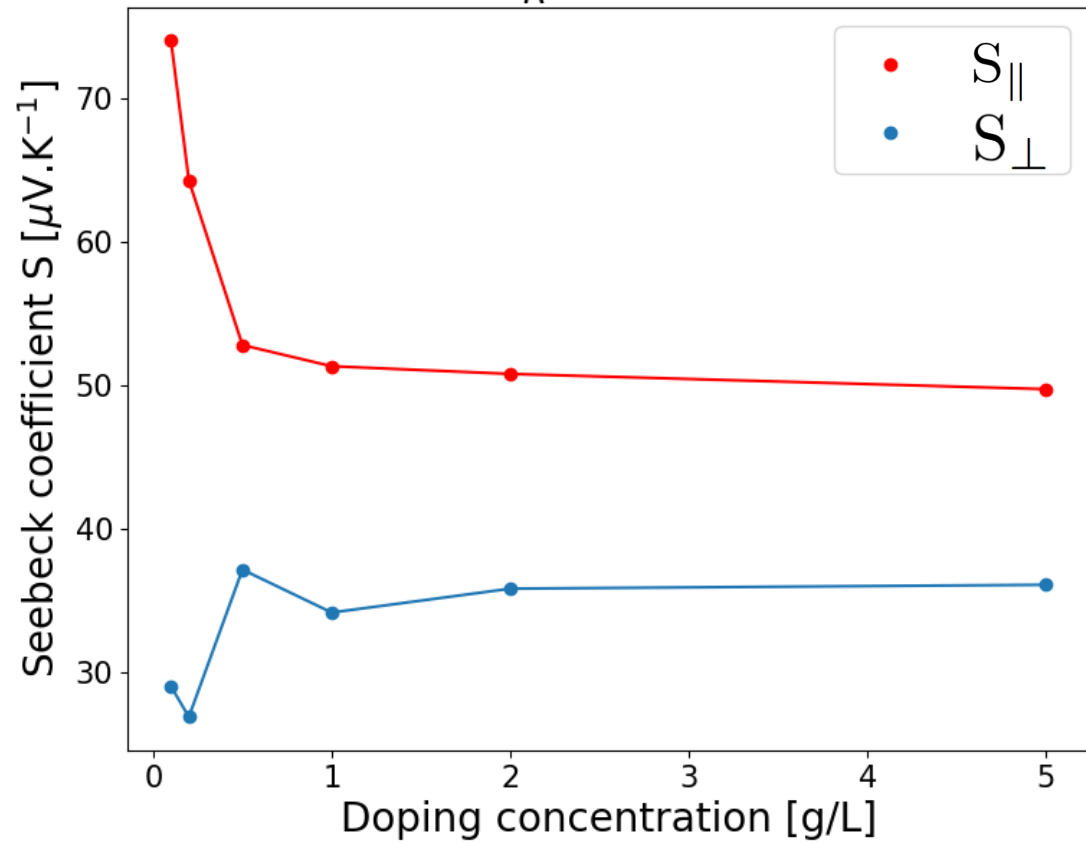
P₃HT films



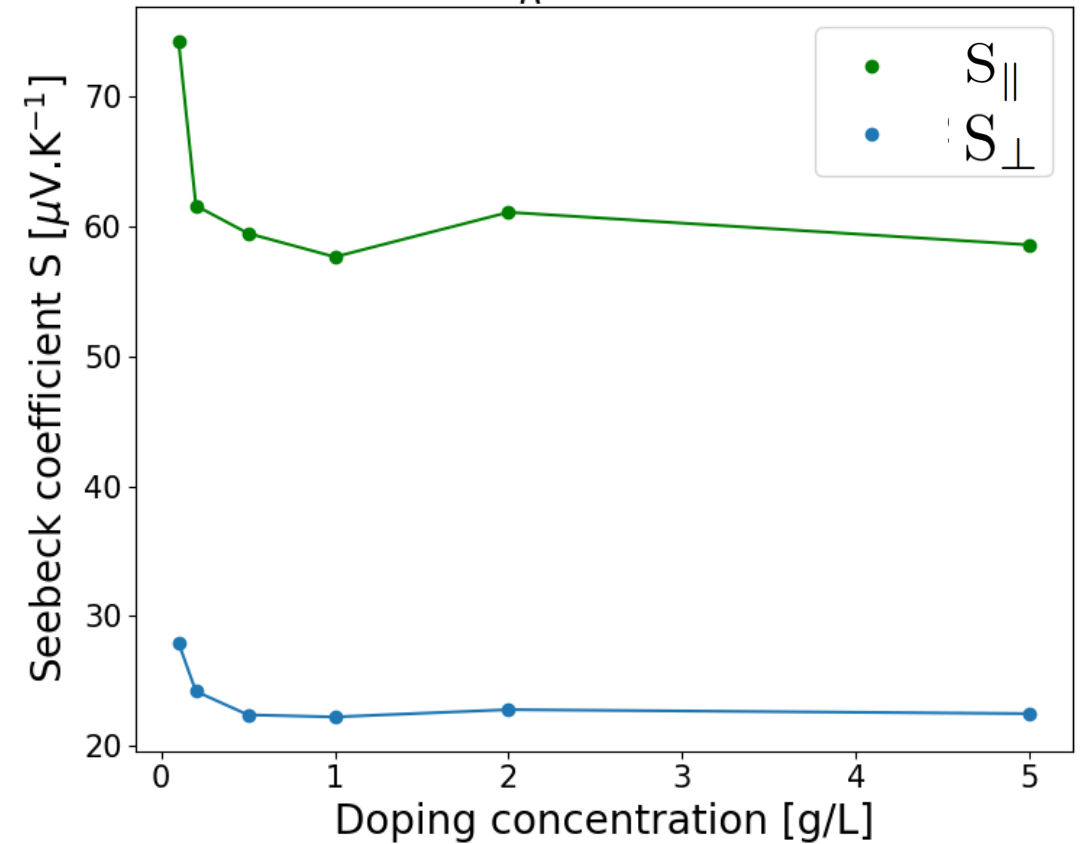
DOI: <https://doi.org/10.1002/aenm.201900266>

Seebeck coefficient (S)

$F_R = 6.9\text{N}$

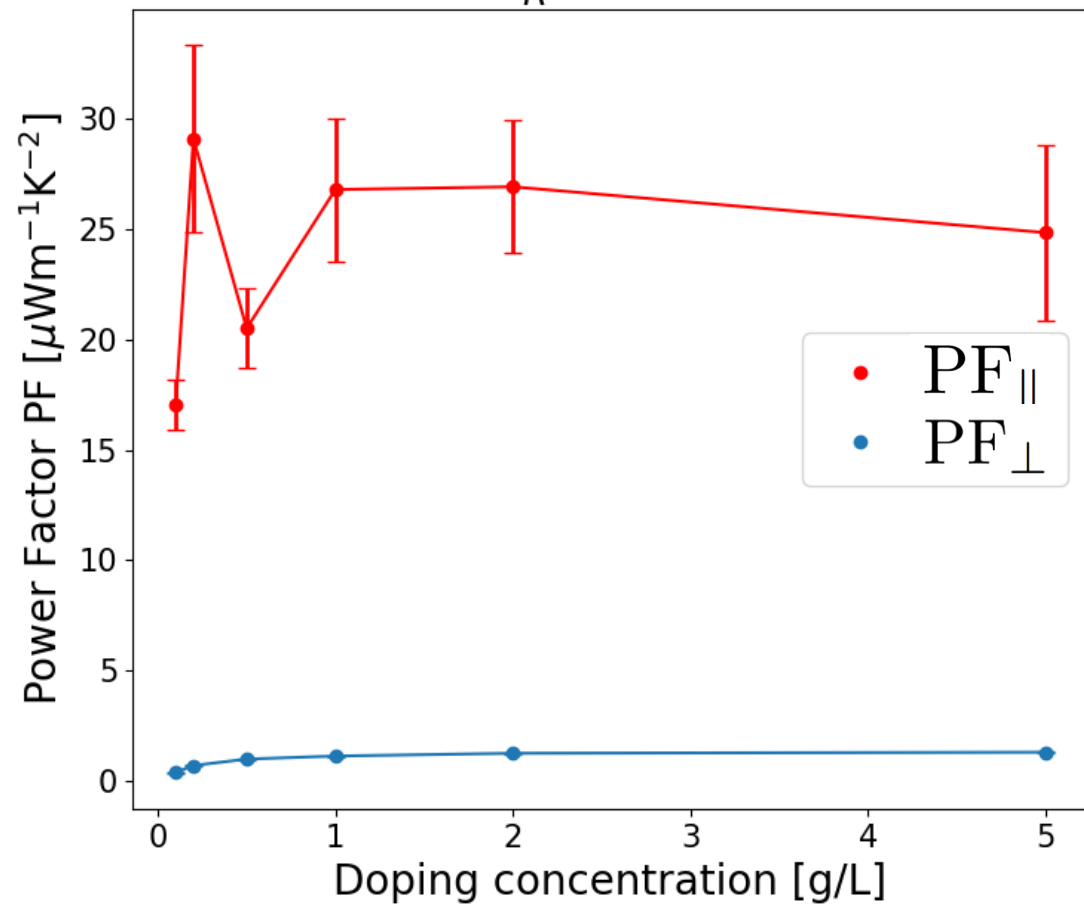


$F_R = 8.8\text{N}$

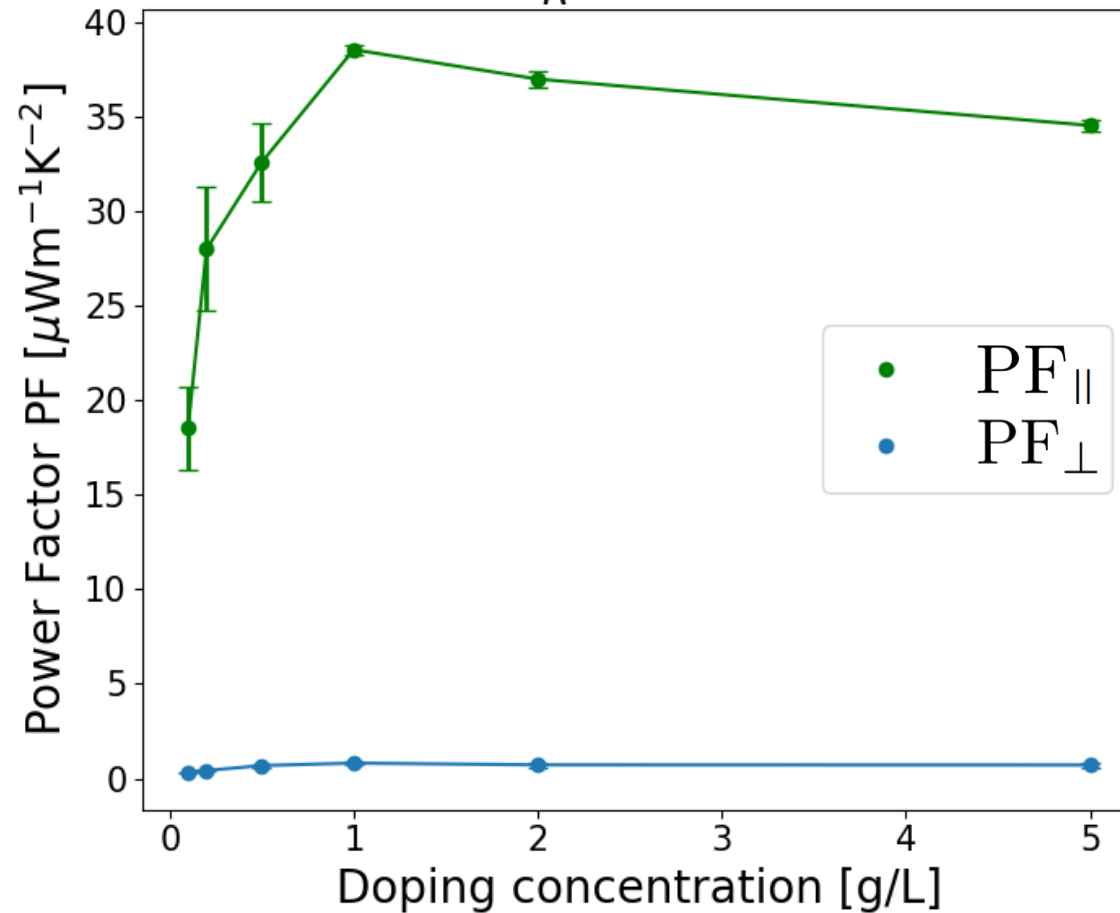


Power factor (PF)

$F_R = 6.9\text{N}$

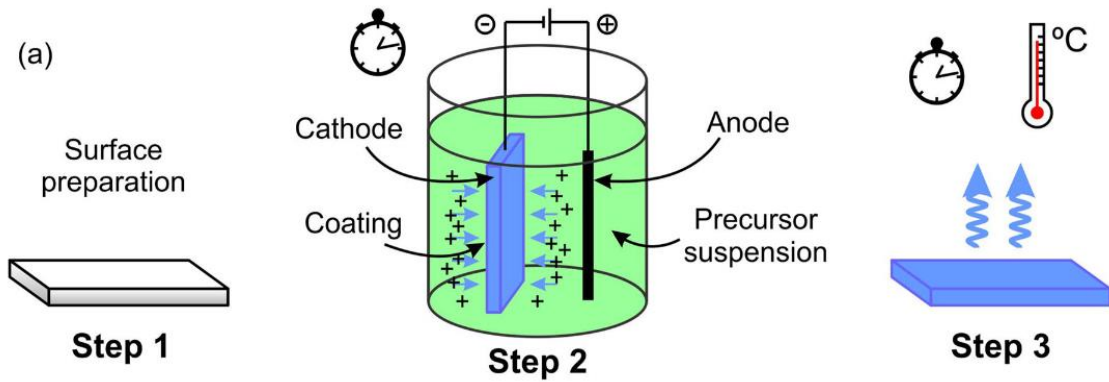


$F_R = 8.8\text{N}$

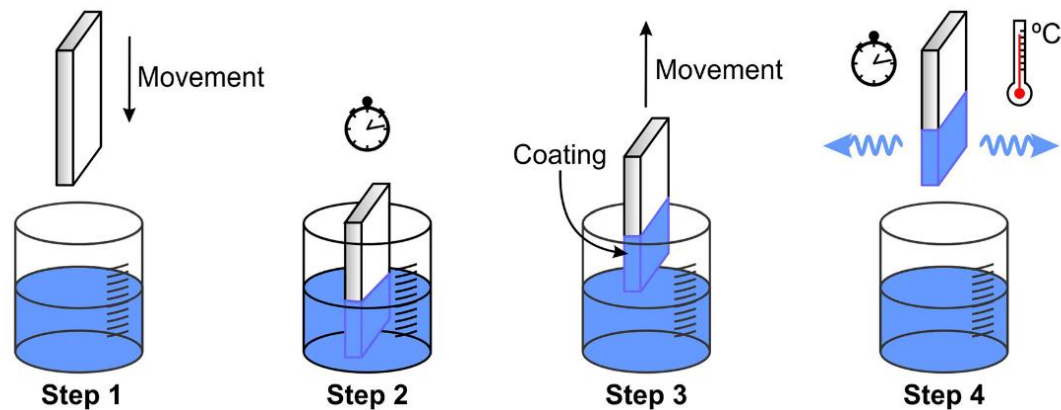
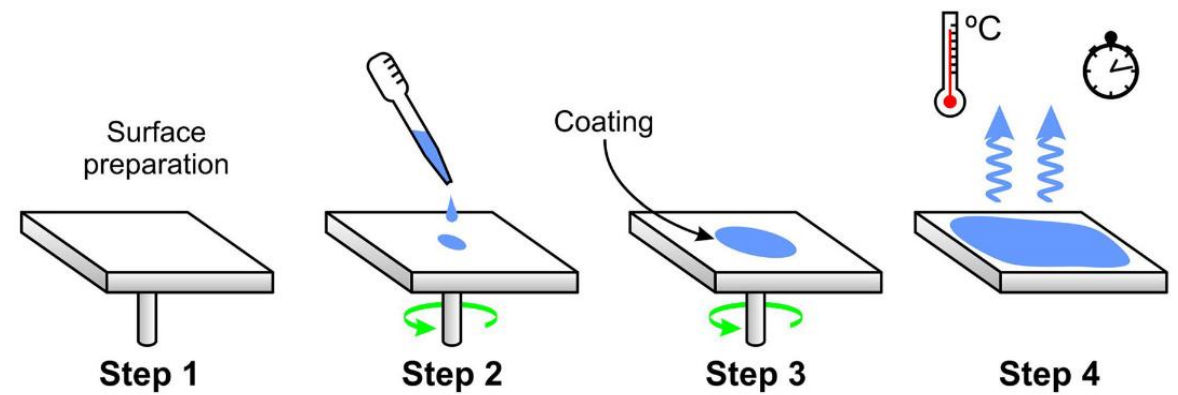


Deposition methods

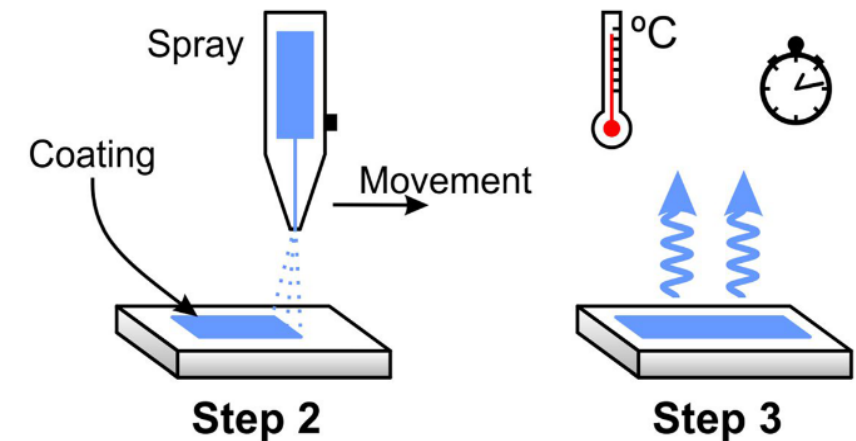
Electrolytic deposition method



Spin-coating method



Dip-coating method



Spray-coating