Experimental and numerical study of an oCVD process for the deposition of PEDOT thin films

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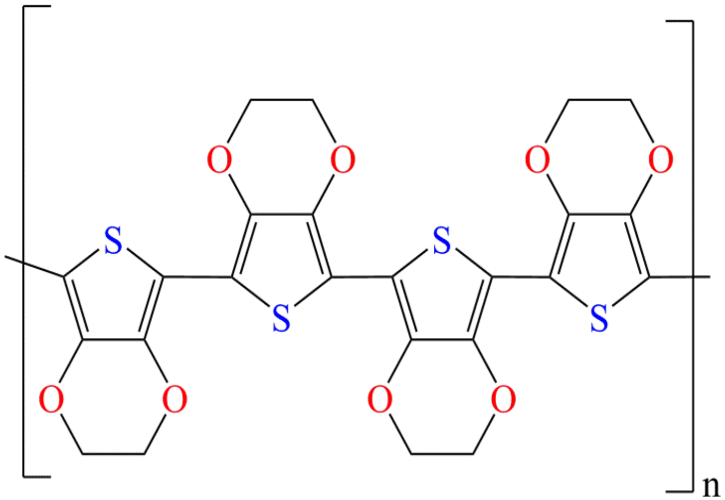
State-of-the-art about PEDOT thin films



PEDOT polymer
Numerous applications in organic devices
Conductivity : 0.1 to 5000 S/cm

Deposition processes of PEDOT film:

- Spin-coating (aqueous suspension)
- Sequential dip-coating (liquid solution)
- Electrochemical polymerization (electrolyte)

Drawbacks:

- ❑ High contamination with solvent residuals
- ❑ Low diffusivity in substrates with complex 3D structure
- ❑ Solvent-substrate compatibility
- ❑ Conductive substrate (Electrochemical polymerization)

A new process by Gleason's group since 2007 → **Gas phase (CVD)** → **Oxidative chemical vapor deposition (oCVD)**

Oxidative chemical vapor deposition (oCVD)

Advantages:

- No contamination due to solvent
- High diffusion in gas phase under vacuum
  - Uniform concentration distribution
    - Uniform thickness
- Working at ambient temperature
  - Suitable for temperature-sensitive substrates
- Depositing on any substrate
  - Porous materials, fibers, 3D objects, paper, membrane, textile…

However:

- The links between process parameters and film properties are not well understood.
- A post-deposition rinsing is necessary to remove by-products and unreacted materials to improve conductivity.

Dedicated studies are necessary targeting process optimization for the production of highly conductive PEDOT

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Aim of the project

Combine experimental and numerical studies to correlate film properties to deposition conditions

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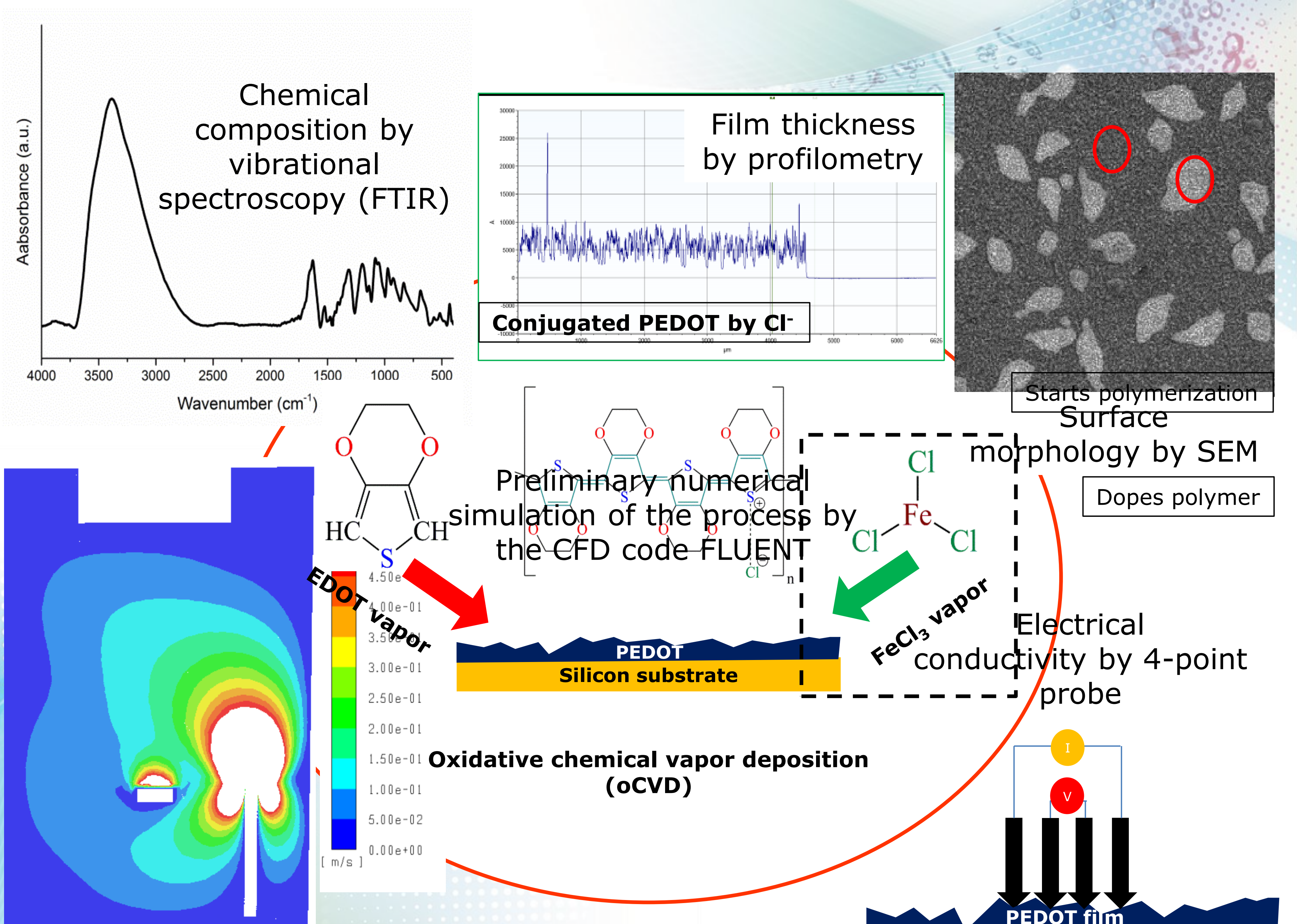

Chemical composition by vibrational spectroscopy (FTIR)
Aabsorbance (a.u.)
Wavenumber (cm-1)
4000 3500 3000 2500 2000 1500 1000 500
Film thickness by profilometry
Conjugated PEDOT by Cl-
Starts polymerization
Surface morphology by SEM
Dopes polymer
Preliminary numerical simulation of the process by the CFD code FLUENT
EDOT vapor
FeCl3 vapor
PEDOT
Silicon substrate
Oxidative chemical vapor deposition (oCVD)
Electrical conductivity by 4-point probe
PEDOT film
4.50e
4.00e-01
3.50e
3.00e-01
2.50e-01
2.00e-01
1.50e-01
1.00e-01
5.00e-02
0.00e+00
[m/s]

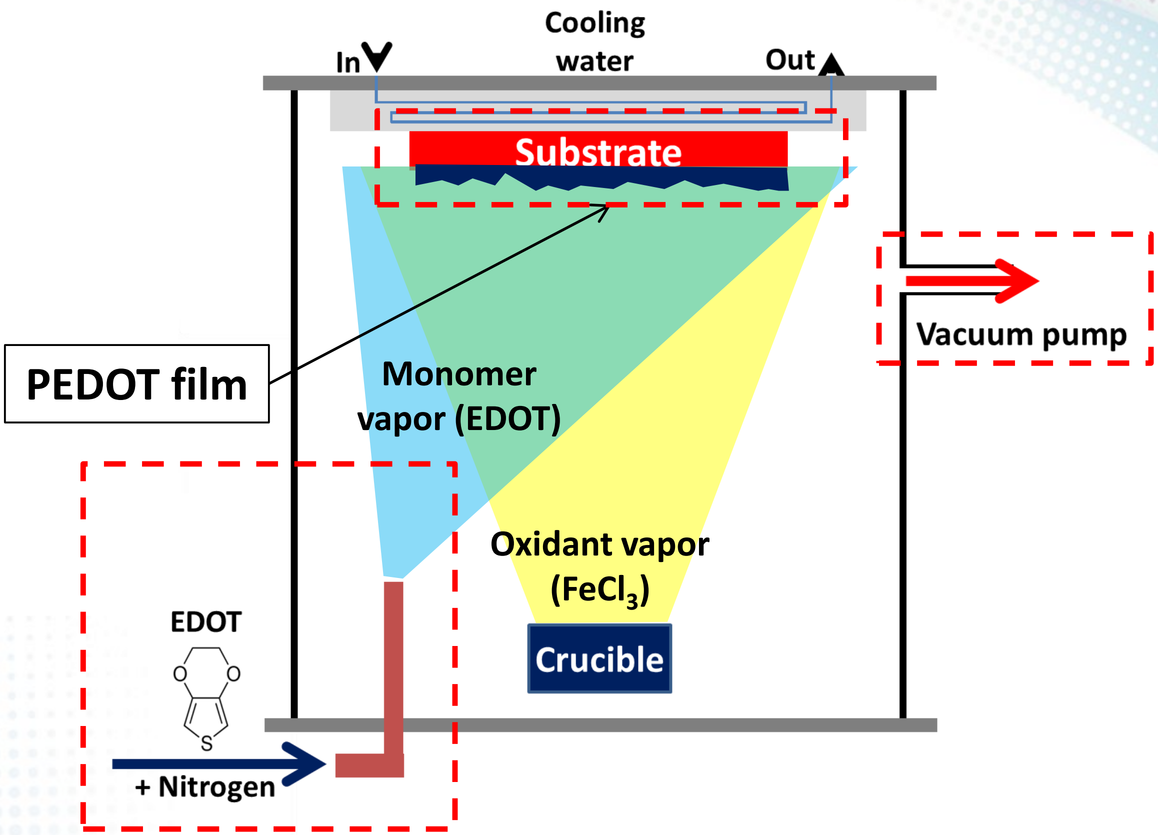
Schematic view of the oCVD reactor

Deposition conditions

- Deposition duration: 30 min
- Total pressure: 100 mTorr
- Substrate temperature kept at 20°C
- Constant EDOT flow rate through a jar kept at 70°C
- Constant Nitrogen flow rate sent after the jar to carry EDOT vapor

Post-treatment after deposition

Rinsing in MeOH and drying in air



Substrate: Silicon wafers with diameter of 10 cm

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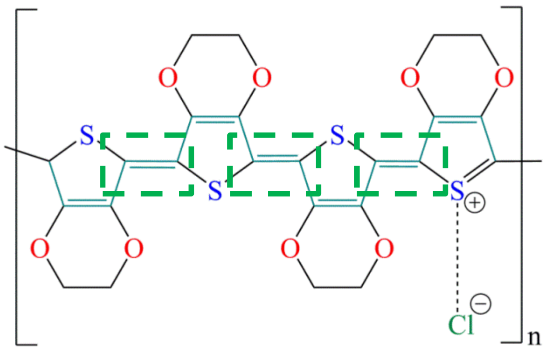
Studying the effect of the $FeCl_3$/EDOT ratio
How to change this ratio?
Constant EDOT flow rate, varying $FeCl_3$ flow rate

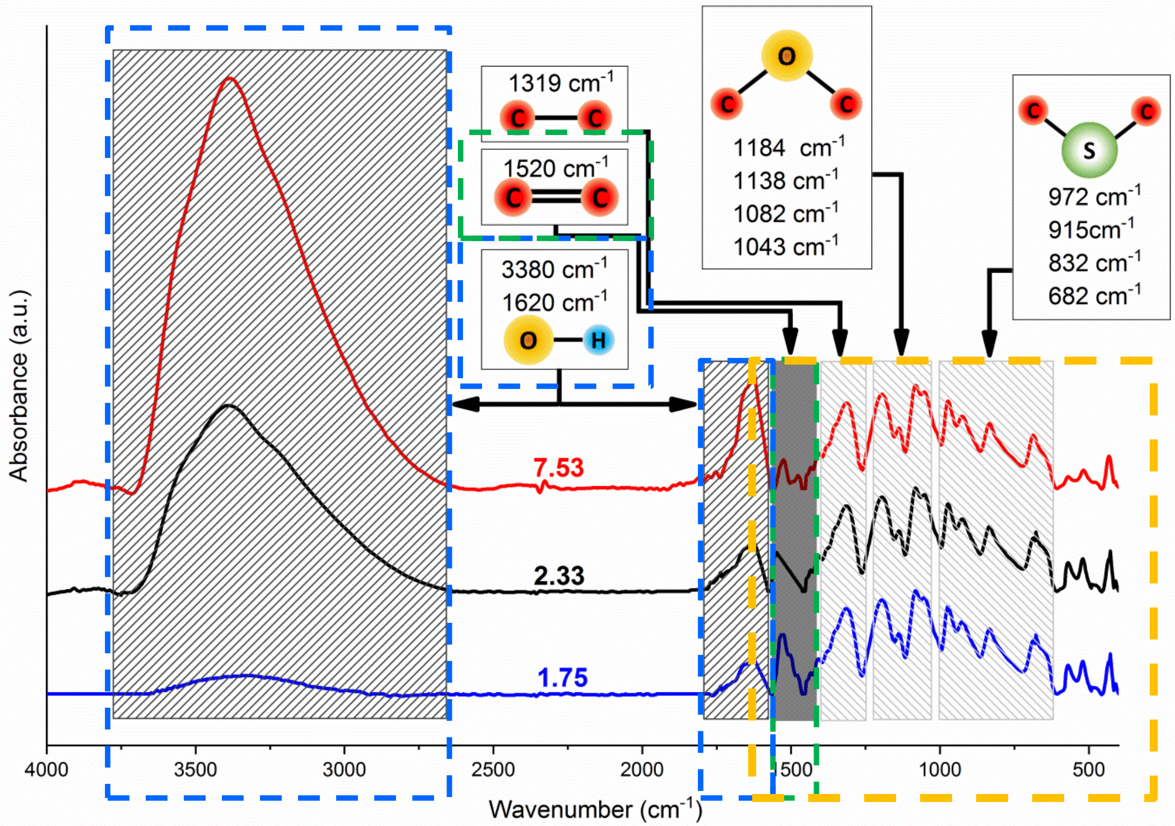
$FeCl_3$ crucible temperature	$FeCl_3$/EDOT inlet molar ratio
175°C	1.75
200°C	2.33
240°C	7.53

Let us go to the results…

Influence of the inlet $FeCl_3$/EDOT ratio on vibrational spectrometry response of the films



PEDOT polymer backbone (Doped with Chlorine)

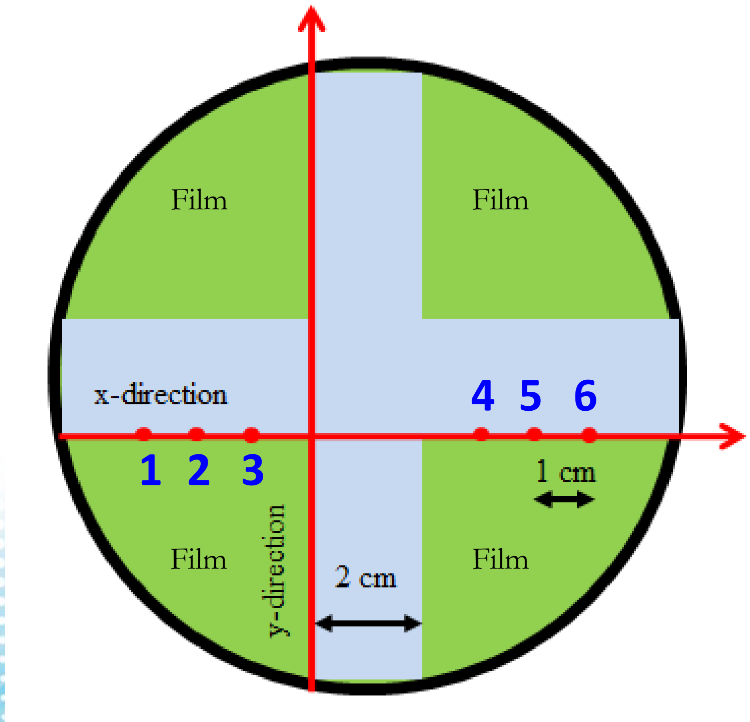


FTIR spectra for the three $FeCl_3$/EDOT ratios

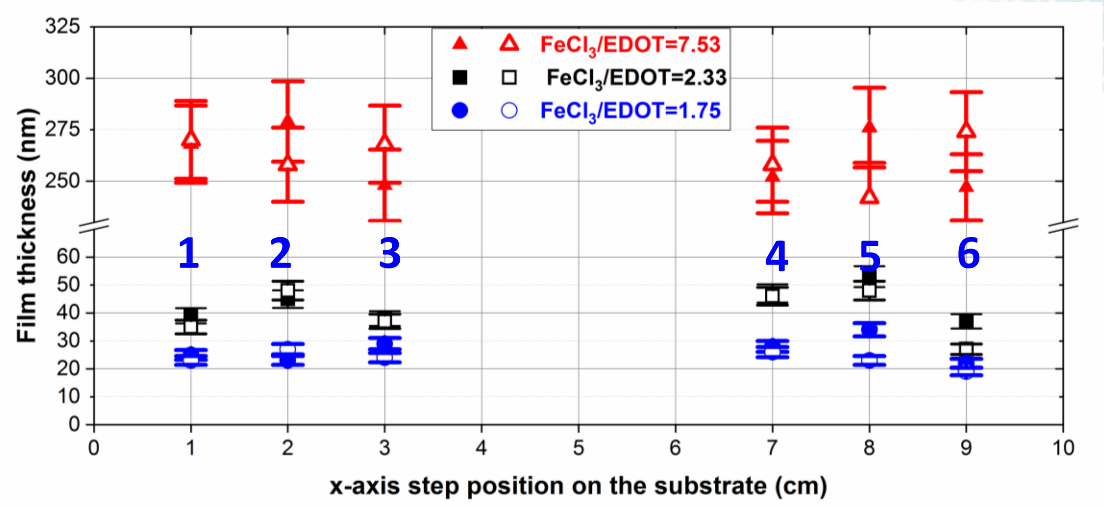
- **The deposited films are PEDOT**
- **Hygroscopic behavior of $FeCl_3$ or presence of iron oxides**
- **Increasing the $FeCl_3$/EDOT ratio:**

→ Higher intensity of OH peaks
→ Lower intensity of **asymmetric stretching of C=C inter-ring** bonds, which could decrease the conductivity

Influence of the inlet $FeCl_3$/EDOT ratio on local film thickness (profilometry)



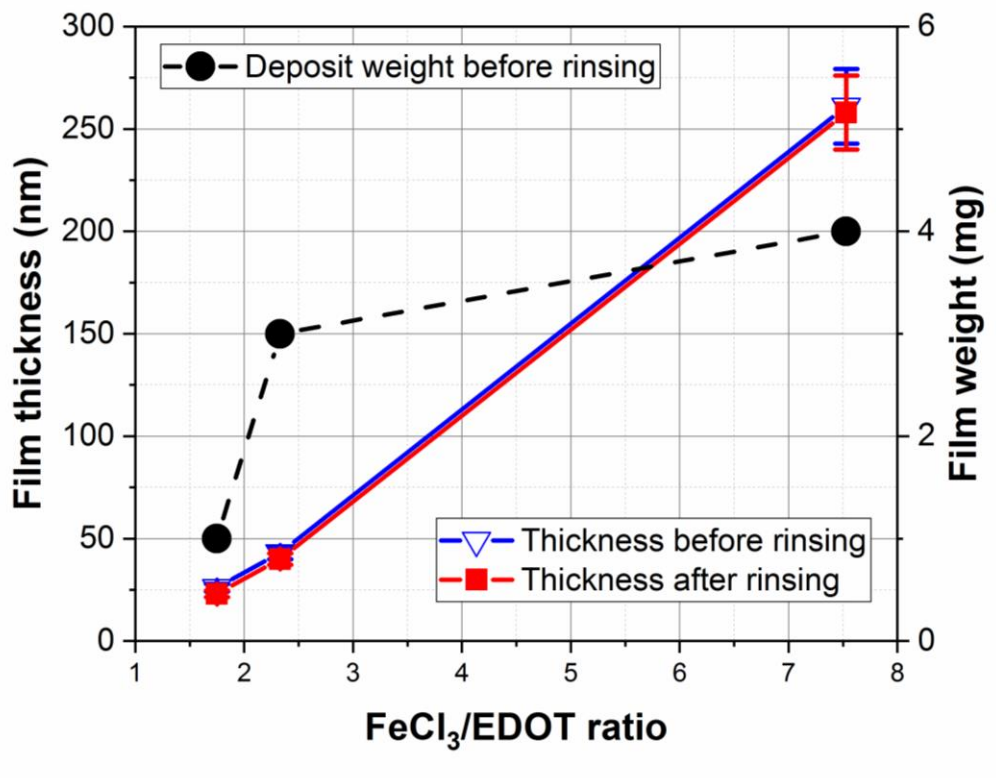
Thickness measurement points on the silicon wafer



Full points: before rinsing, empty points: after rinsing

Uniform thickness on 10 cm silicon wafers before and after rinsing

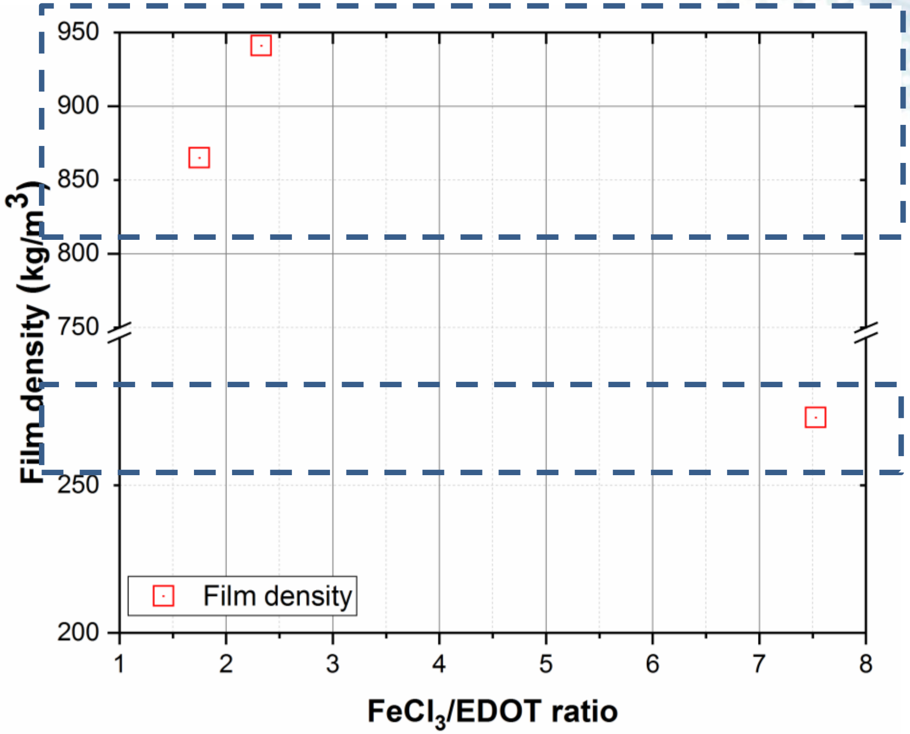
Influence of the inlet $FeCl_3$/EDOT ratio on average thickness (profilometry) and film weight



- Seemingly linear increase of the thickness with the $FeCl_3$/EDOT ratio.
- Rinsing with MeOH does not change the thickness
- Non-linear increase for the film weight with the $FeCl_3$/EDOT ratio, probably due to changes in film composition or porosity.

Influence of the inlet $FeCl_3$/EDOT ratio on the film apparent density (profilometry and deposit weight)

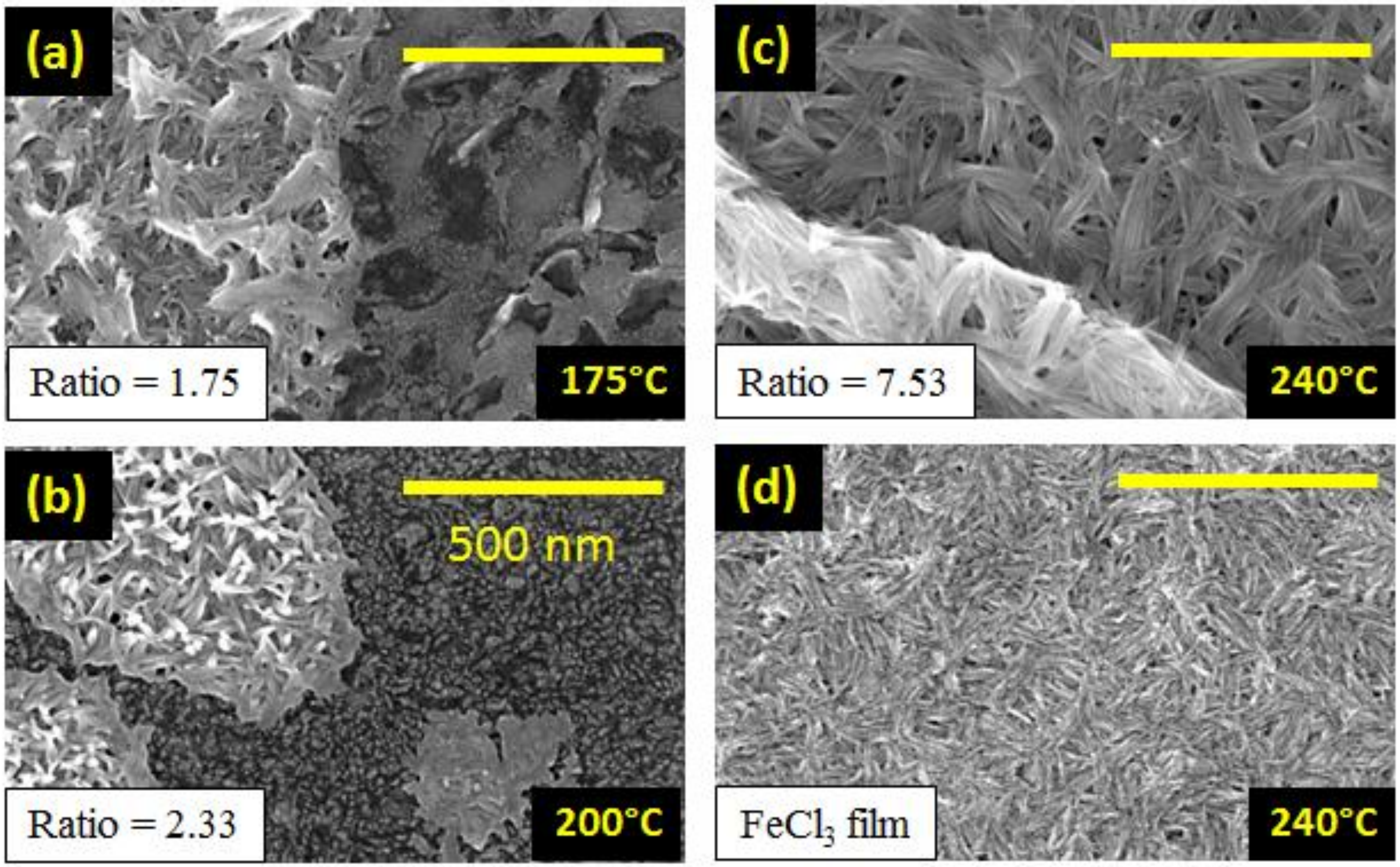
$$\rho = \frac{deposit\ mass}{film\ thickness \times coated\ area}$$



Significant change in apparent density for the highest $FeCl_3$/EDOT ratio

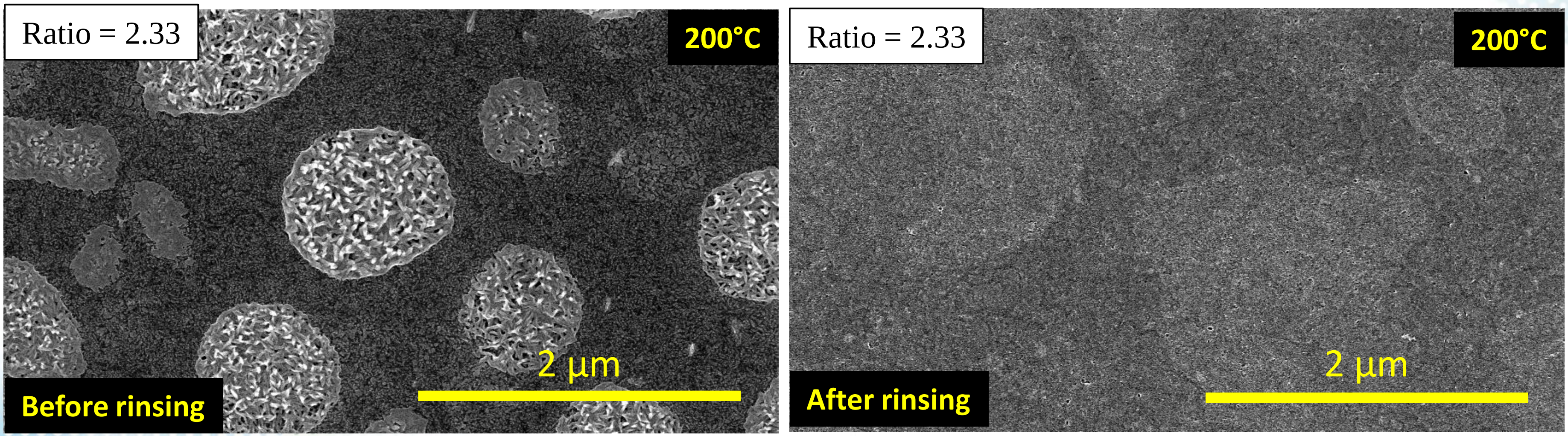
→ As the three films contain PEDOT, the different evolution for thickness and deposited mass probably comes from film porosity variation.

Influence of the inlet $FeCl_3$/EDOT ratio on the film morphology before rinsing (SEM)



- **Porous films**
- **Two different morphologies depending on the $FeCl_3$/EDOT ratio**
- **For the highest ratio: deposit morphology close to that of sublimated $FeCl_3$**
- **Zones of different compositions measured by EDX**

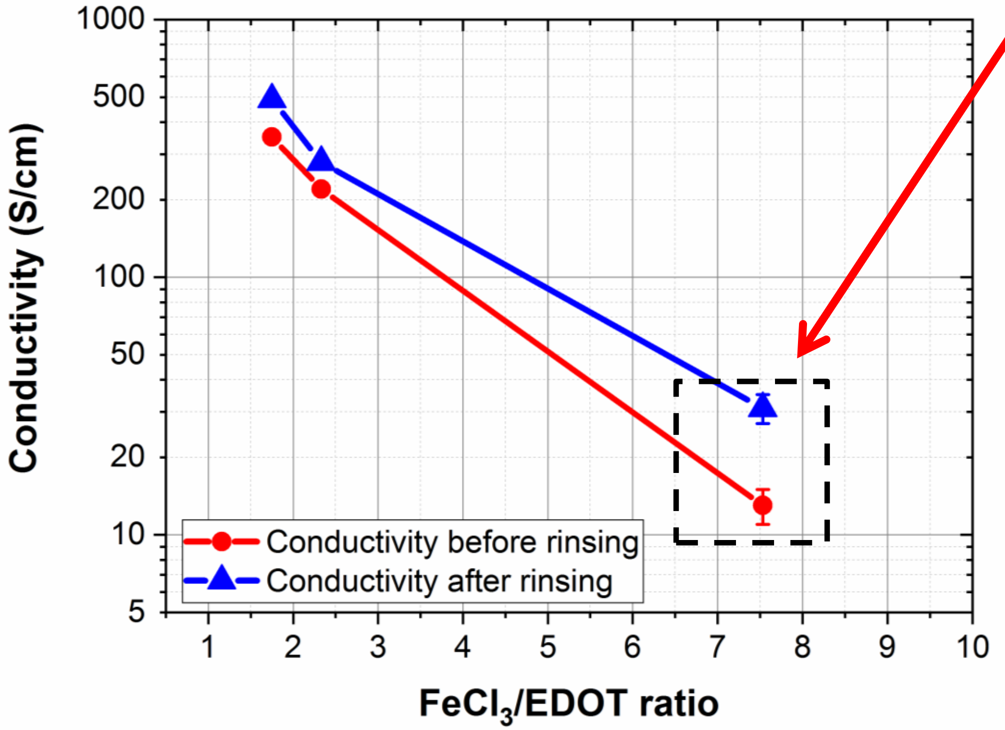
Influence of the inlet $FeCl_3$/EDOT ratio on the film morphology (SEM) before and after rinsing



- **Bright zones disappeared after rinsing**
- **Rinsing in MeOH removes impurities**

Influence of the inlet $FeCl_3$/EDOT ratio on the film electrical conductivity (4-point probe)

One order of magnitude decrease

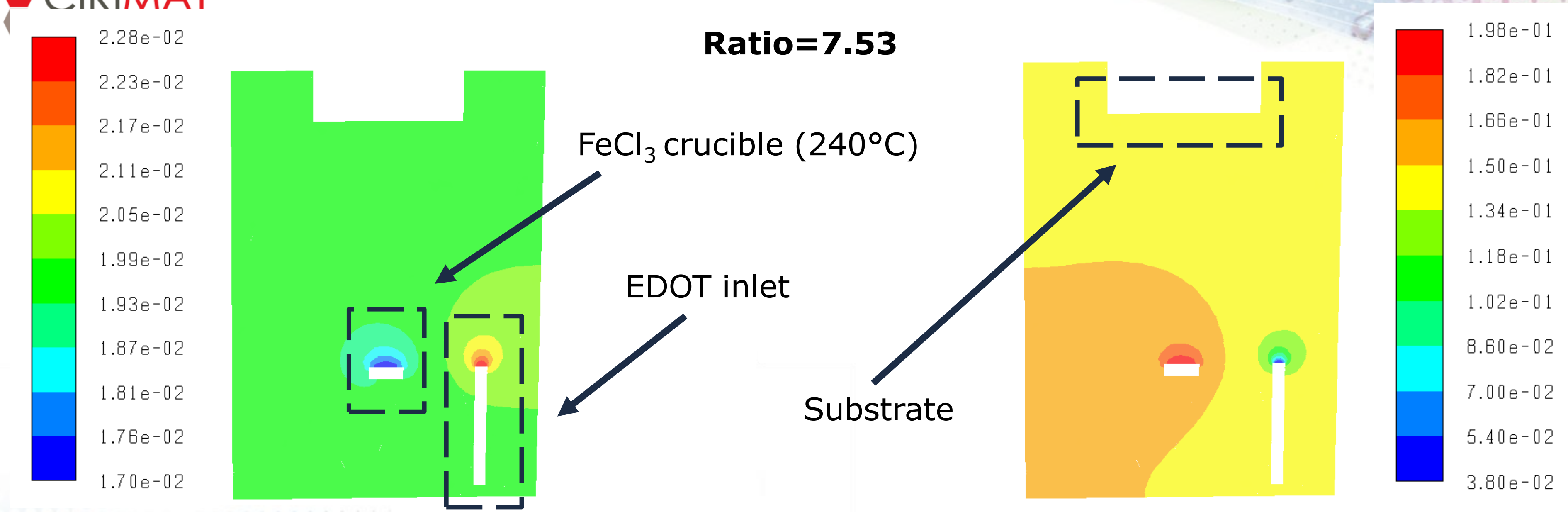


- Decrease of the conductivity when the $FeCl_3$/EDOT increases.
  - Conjugation length decreases
- Rinsing with MeOH improves the conductivity slightly.

Im and Gleason, (2007)
3 sccm EDOT and 320°C for $FeCl_3$
at T_{sub}=20°C: 0.05 S/cm

In accordance with FTIR observations

Simulation results
Vertical cross view of the reactor
(Simulation results without considering surface reaction)



EDOT mole fraction distribution ***$FeCl_3$ mole fraction distribution***

- Uniform concentration all over the reactor for both EDOT and $FeCl_3$, due to high gas diffusion coefficients

In accordance with experimental observation of uniform film thickness

Simulation results
Influence of the inlet $FeCl_3$/EDOT ratio on flux near the substrate (Preliminary simulation results)

Inlet $FeCl_3$/EDOT ratio	Experimental deposition rate/Calculated total reactant flux (%)
1.75	1.07
2.33	1.33
7.53	1.20

- **Only one percent of the flux of reactants reaching the substrate is responsible for the deposit → strong kinetic limitation.**

Conclusions

- Deposition of PEDOT thin film of uniform thickness on 10 cm Si substrates at ambient temperature

- Sending more $FeCl_3$ into the reactor:
  - Increases the film thickness
  - Changes in a coherent way the film morphology, porosity and composition
  - Decrease the amounts of C=C bonds and logically the conductivity

- Rinsing with MeOH
  - Slightly improves the conductivity

- Simulation results
  - Uniform concentration and weak contribution of reactants to the deposition
  - Strong kinetic limitation

The $FeCl_3$/EDOT ratio and more largely all the deposition parameters must be controlled to produce highly conductive PEDOT.

Perspectives

Optimize all contributing parameters in the deposition process to produce PEDOT with the best physical properties (in progress)

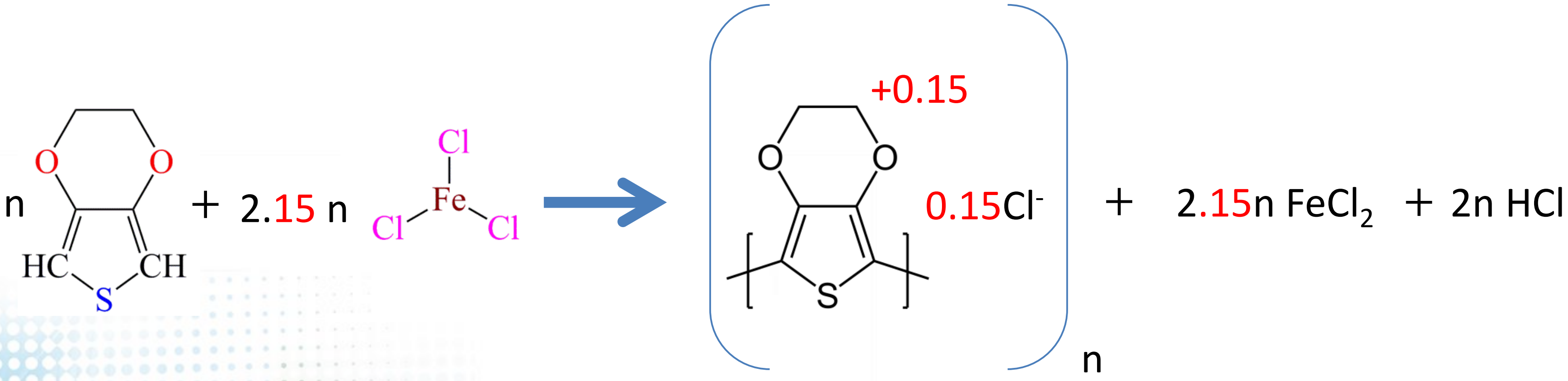
Measure in real time the deposition rate with an *in situ* quartz microbalance (in progress)

Develop apparent kinetic laws for reaction rates to be implemented in the reactor model (in progress)

Study films on complex substrates for applications in organic electronics

Thank you!

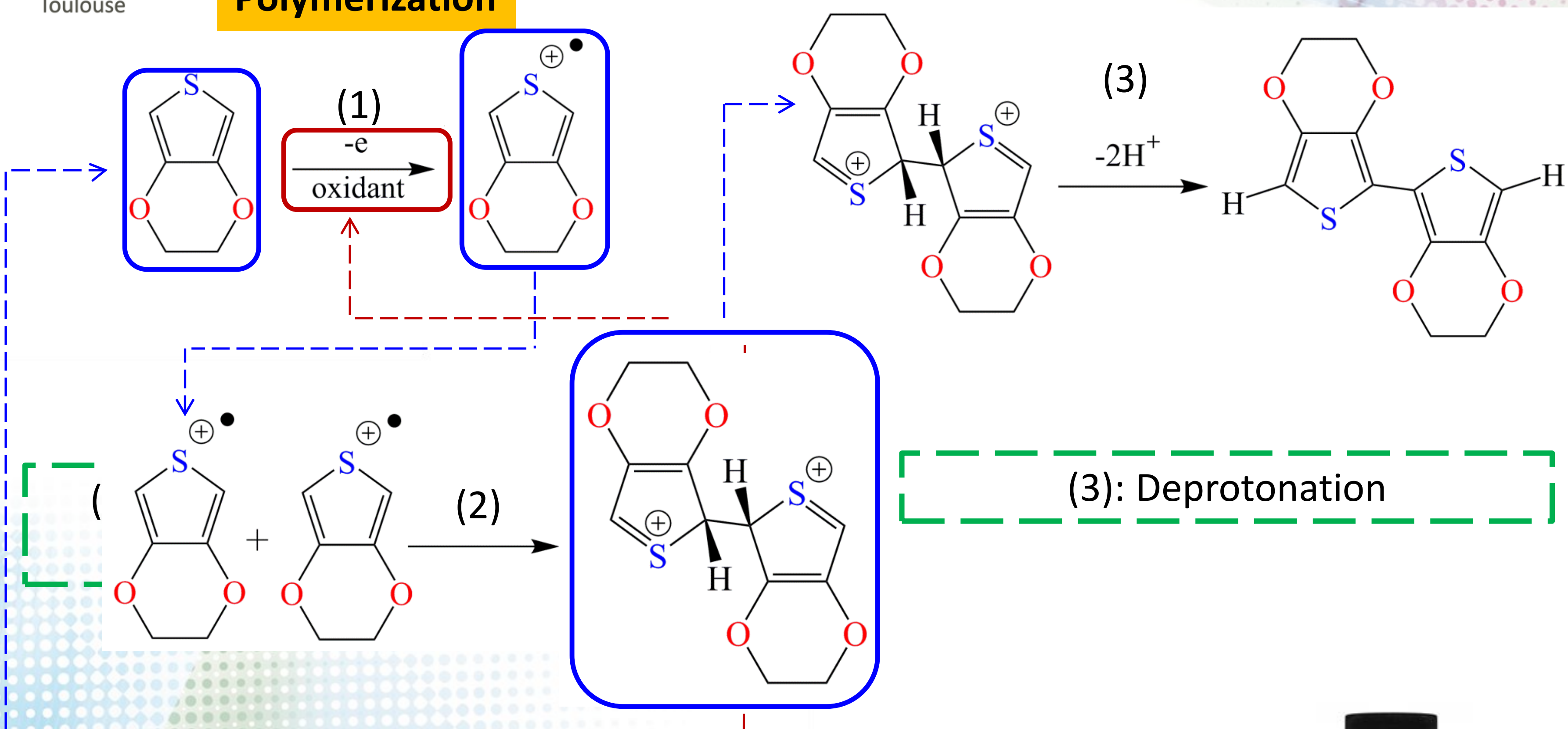
Our proposition based on other polymers:



With 0.15 as the ratio of Cl/S, we are considering that for each 7 EDOT units, there is one Cl with negative charge. Therefore, the M_w=2+(0.15*35+140)=147.25

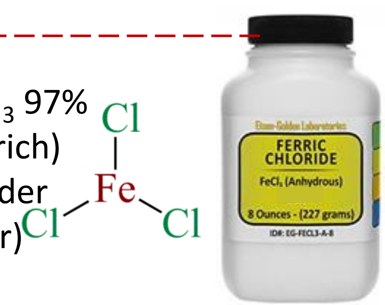
Proposed polymerization mechanism in the literature for PEDOT by oCVD [6]

Polymerization



Monomer: EDOT 97%
(Sigma-Aldrich)
Colorless or yellow liquid

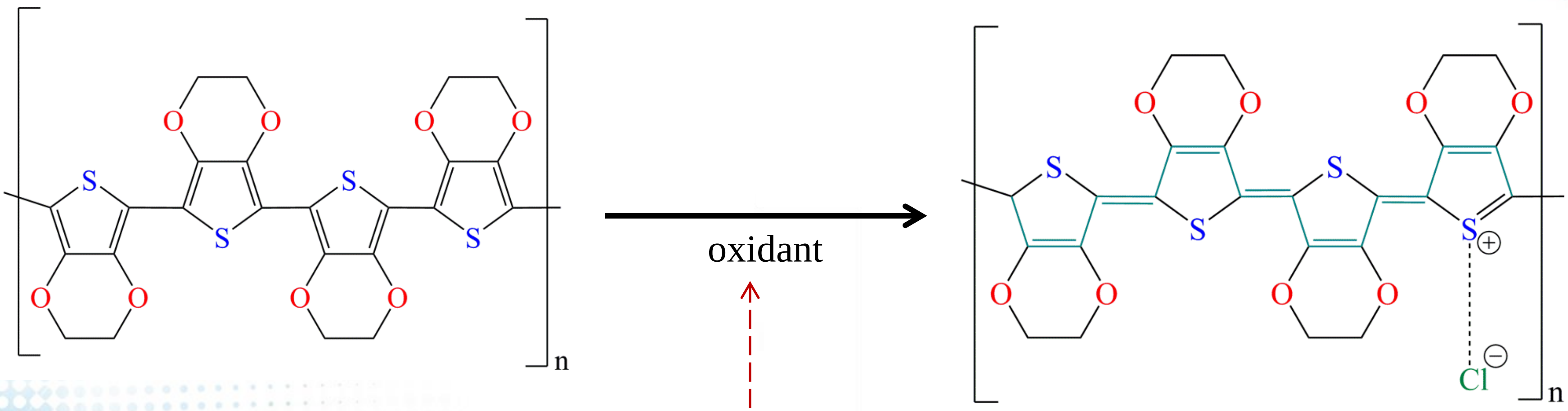
Oxidant: $FeCl_3$ 97%
(Sigma-Aldrich)
Black powder
(Insulator)



Proposed polymerization mechanism in the literature for PEDOT by oCVD [6]

Doping

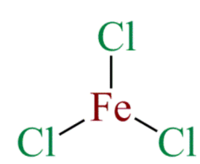
(4): Chlorine doping of polymer backbone



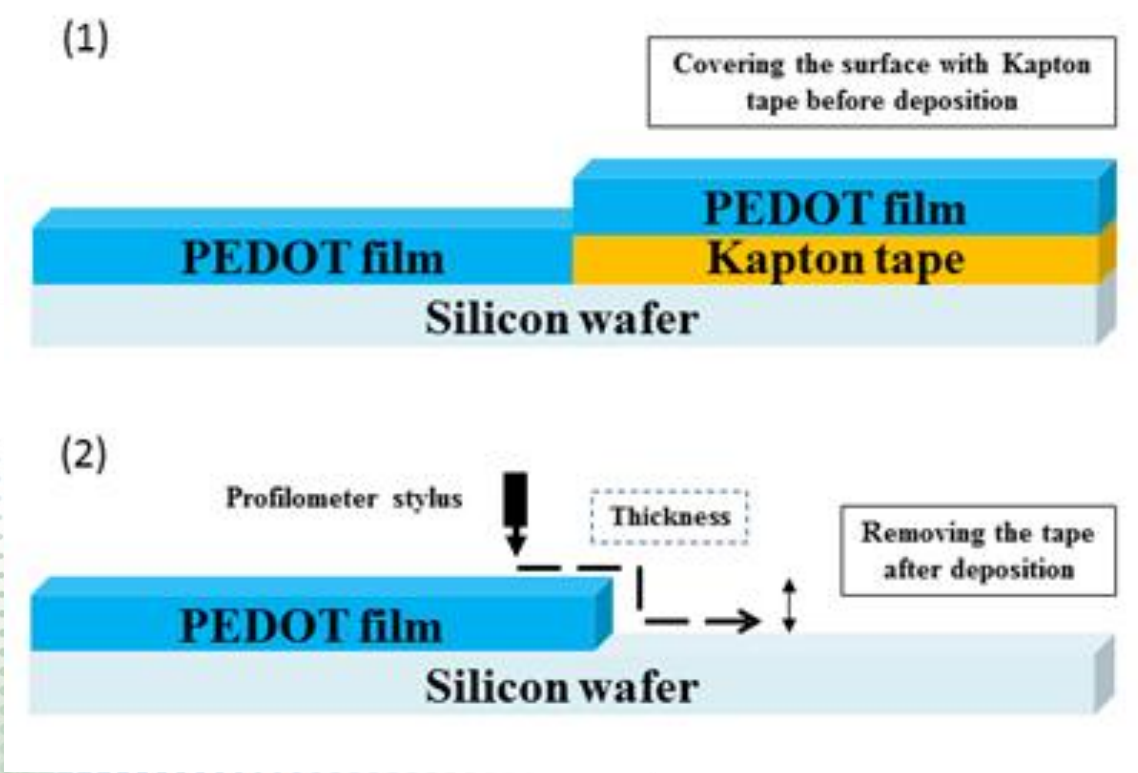
Undoped PEDOT
(Insulator)

Doped PEDOT
(Conductive)

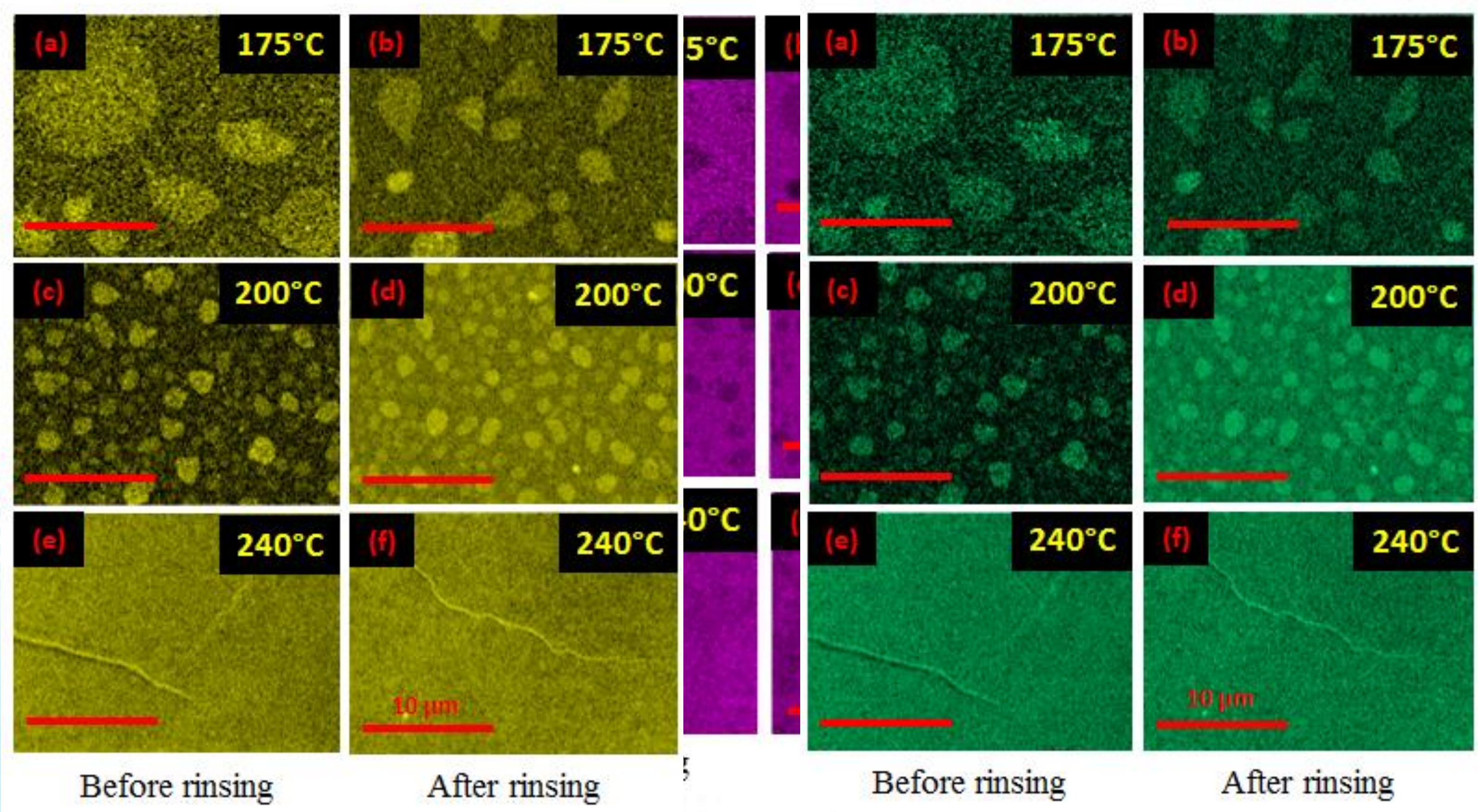
- Presence of Chlorine in the backbone
- Presence of C=C inter-ring bond in the backbone (conjugation and conductivity)
- Removal of C-H bond in the thiophene ring due to the polymerization



Influence of inlet $FeCl_3$/EDOT ratio

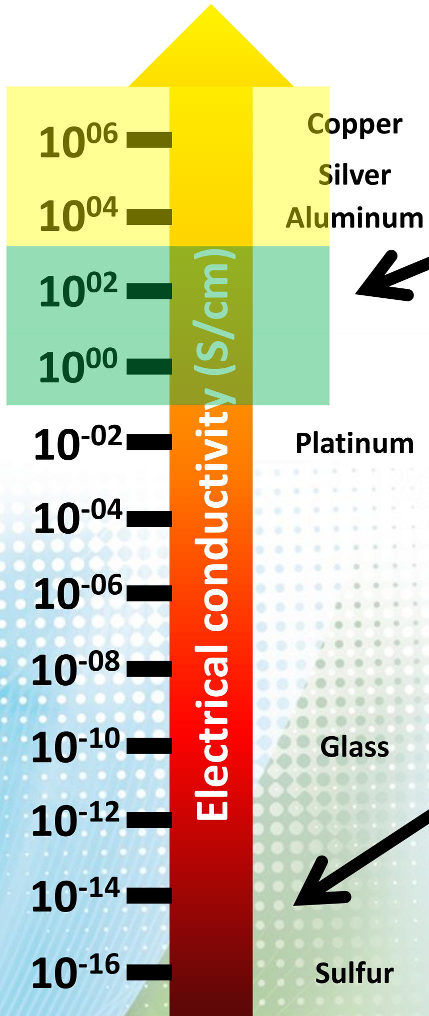


Thickness measurement procedure on the substrate



EDX analysis of surface for Oxygen EDX analysis of surface for Silicon EDX analysis of surface for Iron

CONDUCTIVE POLYMERS

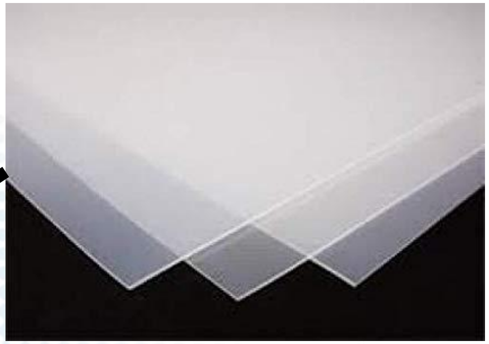


Conductive polymers are organic polymers (containing Carbon) that conduct electricity.

Such compounds may have metallic conductivity (10^{6} S/cm) or can be semiconductors (10^{-3} to 10^{4} S/cm).

Their electrical properties can be fine-tuned during the synthesis process.

Conductive polymers
Doped
(Semi conductors: 10^{-1} to 10^{3} S/cm)



Neutral polymers
Undoped
(Insulators: 10^{-14} S/cm)

Why conductive polymers and not metals?

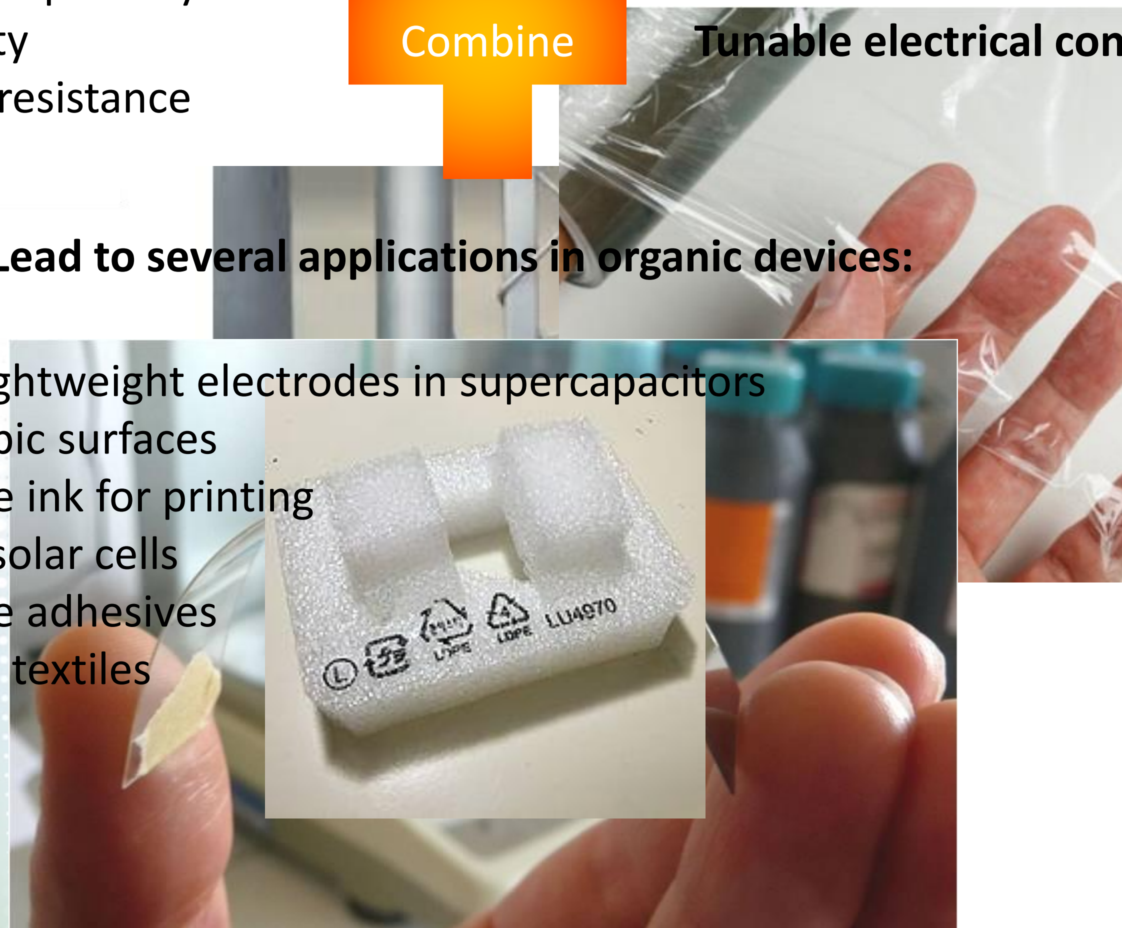
Polymeric properties

- Optical transparency
- Low density
- Corrosion resistance
- Flexibility

Combine

Tunable electrical conductivity

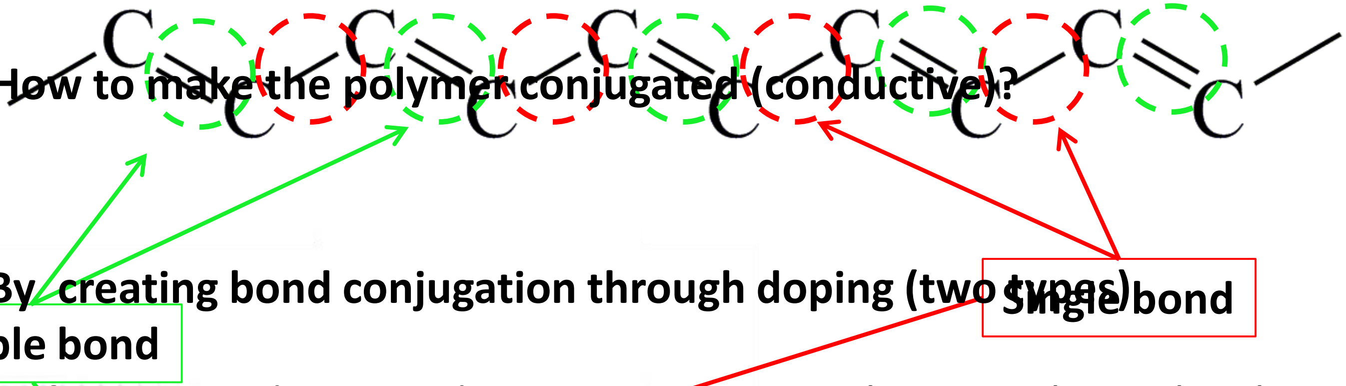
Lead to several applications in organic devices:



- Flexible, lightweight electrodes in supercapacitors
- Hydrophobic surfaces
- Conductive ink for printing
- P-layer in solar cells
- Conductive adhesives
- Functional textiles

Theory:

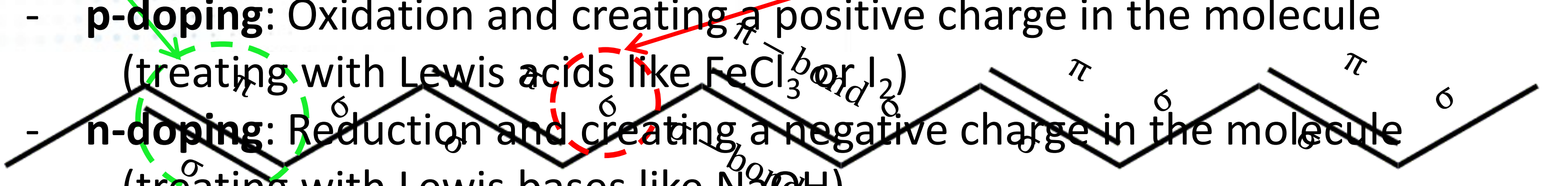
Electrical conductivity in polymers comes from the presence of **conjugated bond structure** through **doping** that permits **pi-orbital overlap** along the **alternating double and single-bonds** in the polymer backbone.



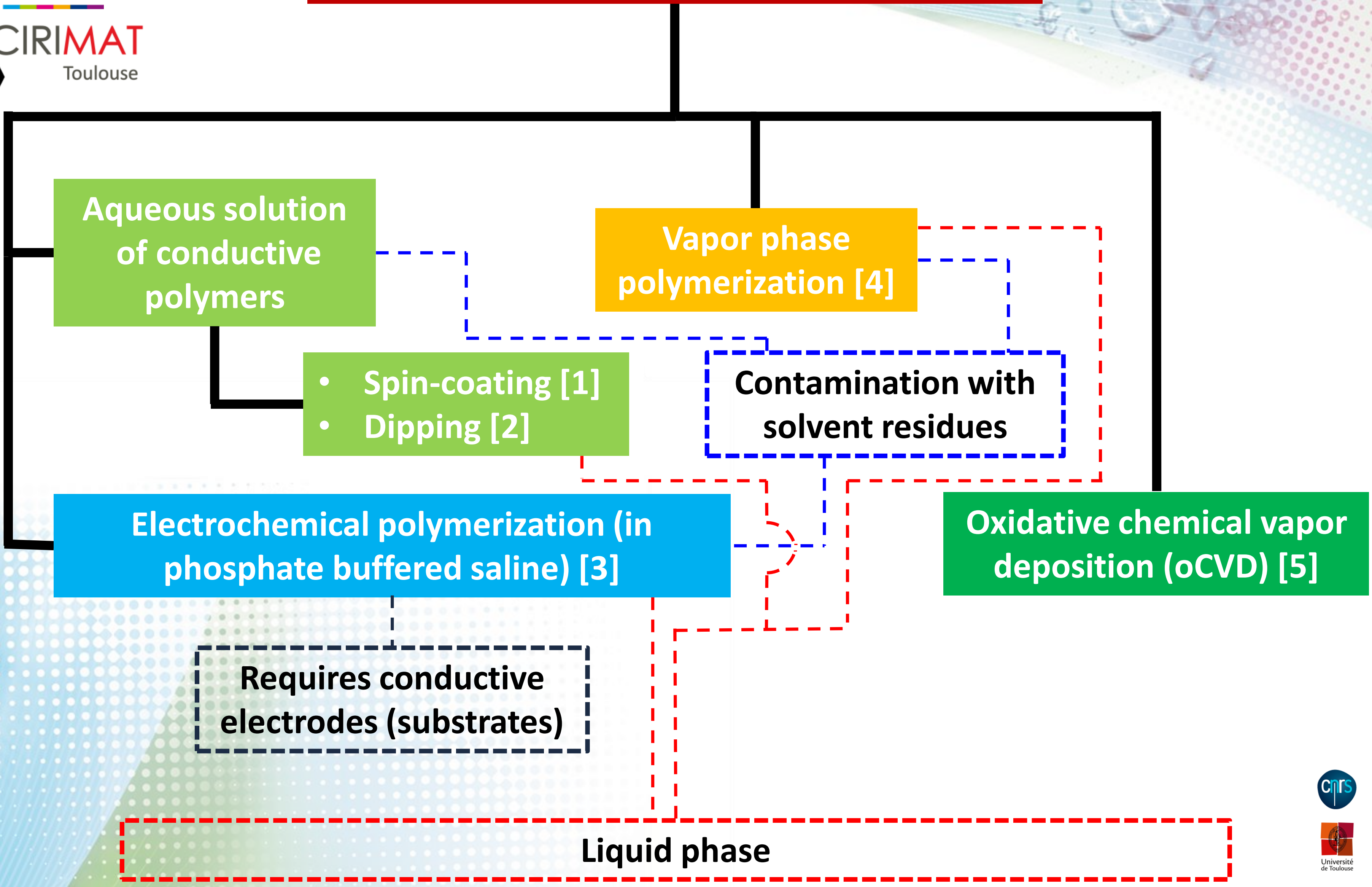
Q: How to make the polymer conjugated (conductive)?

A: By creating bond conjugation through doping (two types)

- **p-doping**: Oxidation and creating a positive charge in the molecule (treating with Lewis acids like $FeCl_3$ or I_2)
- **n-doping**: Reduction and creating a negative charge in the molecule (treating with Lewis bases like NaOH)



How to deposit a layer of PEDOT on a surface?



Influence of the inlet $FeCl_3$/EDOT ratio on flux near substrate (Preliminary simulation results)

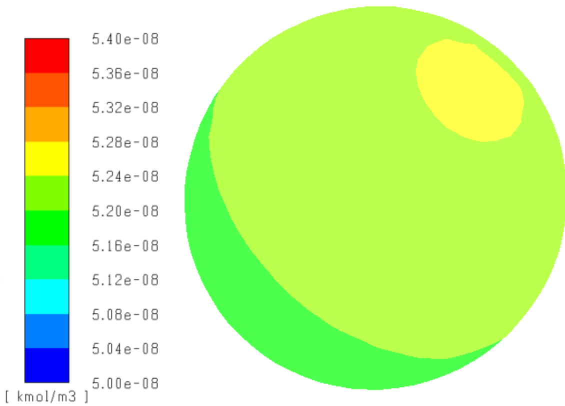
Inlet $FeCl_3$/EDOT ratio	Simulations by FLUENT: Flux near substrate ($kg/m^2.s$)		Simulations by FLUENT: Sum of EDOT+ $FeCl_3$ fluxes near substrate ($kg/m^2.s$)	Experiments: Experimental deposition rate ($kg/m^2.s$)	Experimental deposition rate/Calculated total reactant flux (%)
	$FeCl_3$	EDOT			
1.75	Increases with the ratio	Constant	1.17E-06	1.25E-08	1.07
2.33			1.89E-06	2.52E-08	1.33
7.53			3.30E-06	3.97E-08	1.20

- Only one percent of the flux of reactants reaching the substrate is responsible for the deposit → strong kinetic limitation.
- The deposition rate is clearly dependent of the $FeCl_3$ flux toward the substrate (limiting reactant).

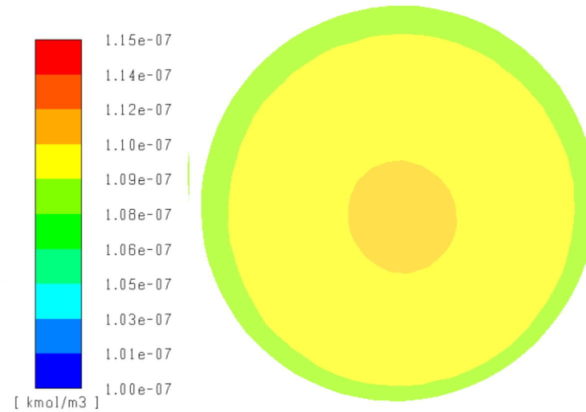
Vertical cross view of the reactor

(Simulation results without considering surface reaction)

Ratio=7.53



EDOT concentration distribution



$FeCl_3$ concentration distribution

Less than 3% variation over substrate

- Uniform concentration all over the reactor for both EDOT and $FeCl_3$, due to high diffusion coefficients

In accordance with experimental observation of uniform film thickness