RegioneLombardia

# DALLA SCIENZA DEI MATERIALI ALLA BIOMEDICINA MOLECOLARE

**Percorsi scientifico-formativi per giovani ricercatori**

# MATERIALI PER ENERGETICA E DRUG DELIVERY

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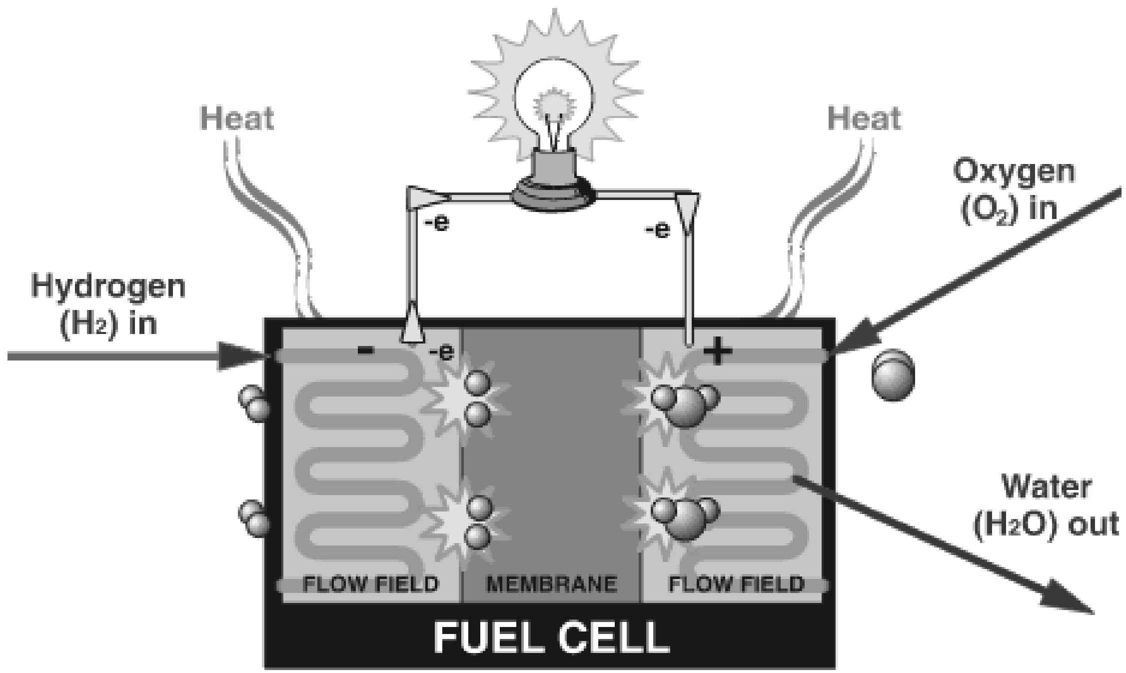
# Summary

- Materials for polymer fuel cells
- Highly functionalized nanotubes for drug delivery

# Polymer fuel cell (PEMFC)



## Aim

To obtain membranes able to operate at temperatures around 120°C, under low or no humidification.

## Choice

Acid-doped polybenzimidazoles (PBI) -based membranes are particularly appealing, chiefly because of their high proton conductivity at low humidification.

## Problems

Leaching of the free acid in presence of water:

- causes a drop of proton conductivity during operation;
- limits the use of PBI-based membranes at temperatures higher than 150°C.

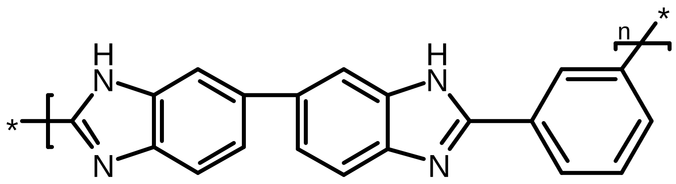
## Strategies

1. Synthesis of new PBI-based polymers, with a higher number of basic N-groups with respect to commercial PBI (Celanese);
2. Preparation of PBI-based composite membranes:
   - nanoscale $SiO_2$;
   - silica functionalised with acid or basic moieties.

**Experimental**

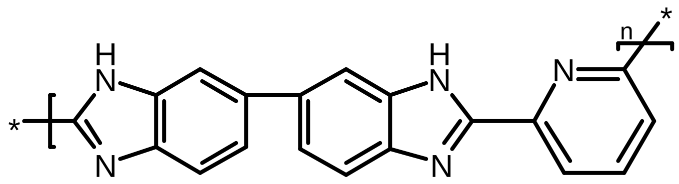
- Membrane preparation by solvent casting (MSA/TFA mixture)
- Doping with $H_3PO_4$ (75 wt%)
- Leaching: elution test by washing with water/MeOH (1.0 M) at 80$^{o}$C up to the complete removal of free acid (ICP)
- Conductivity measurements before and after leaching as a function of:
  - humidity at 120$^{o}$C (RH: 20÷70%);
  - temperature at RH=50% (T: 60-120$^{o}$C)

# 1. Development of new PBI-based polymers



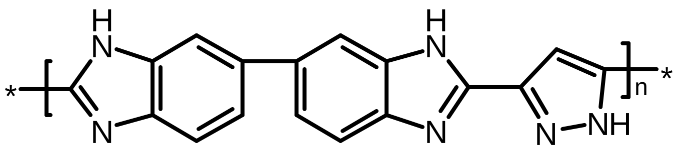
**Poly-2,2’-(m-phenilene)-5,5’-bibenzimidazole**

**PBI_4N**



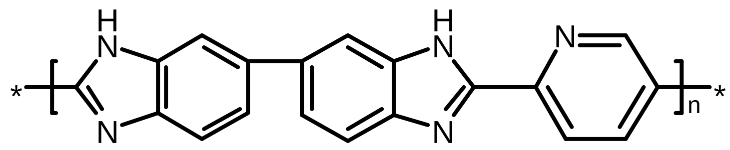
**Poly-2,2’-(2,6-pyridine)-5,5’-bibenzimidazole**

**PBI_5N_2,6**



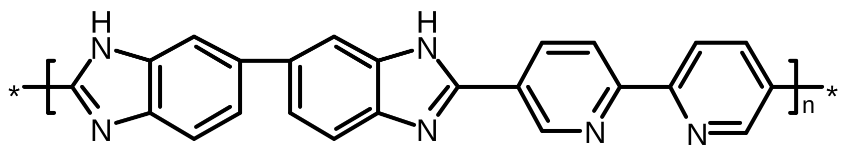
**Poly-2,2’-(3,5-pyrazole)-5,5’-bibenzimidazole**

**PBI_6N_pyra**



**Poly-2,2’-(2,5-pyridine)-5,5’-bibenzimidazole**

**PBI_5N_2,5**

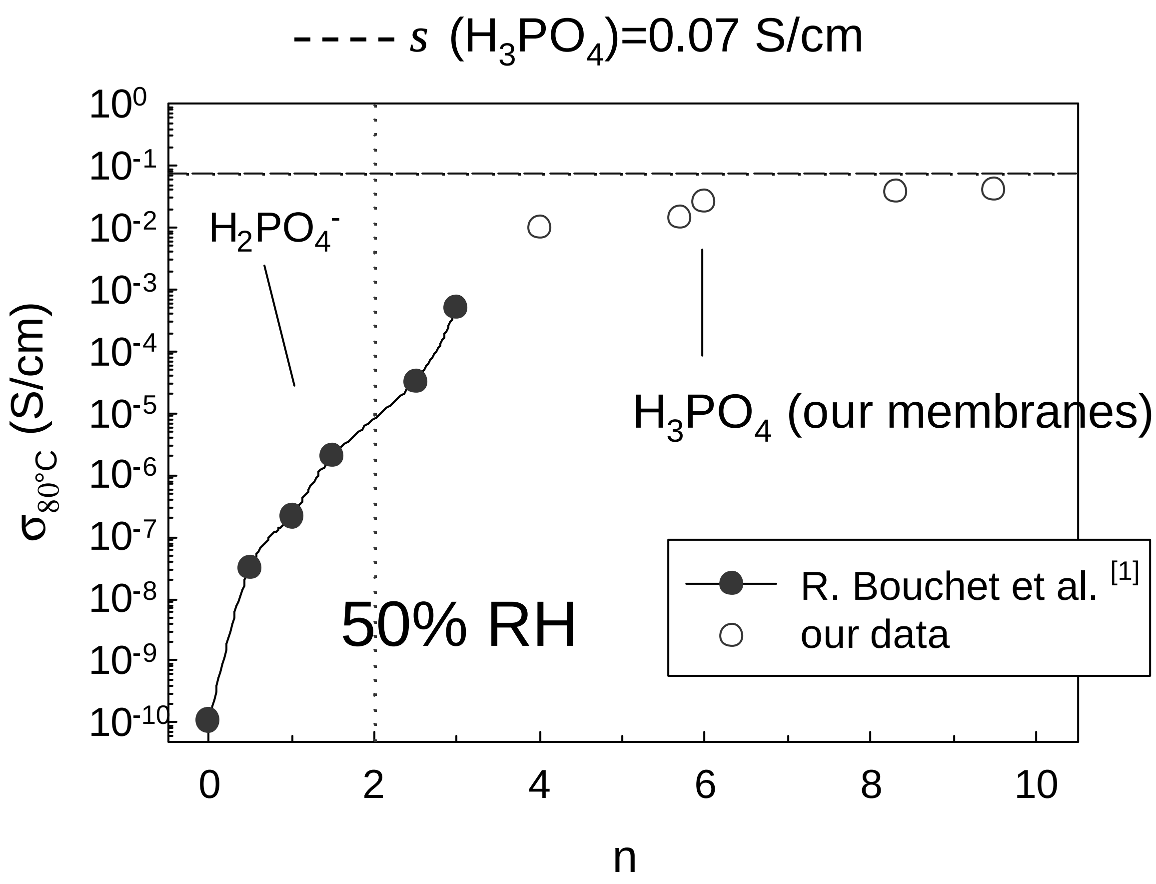


**PBI_6N_bipy**

**Poly-2,2’-(2,2’-bypyridine)-5,5’-bibenzimidazole**

# 1. Development of new PBI-based polymers

## The conductivity before leaching




n = $H_3PO_4$/ monomer unit

**For high *n* the *polymer behaviour* is like that of concentrated $H_3PO_4$**


1. R. Bouchet, et al. Solid State Ionics 118 (1999) 287.

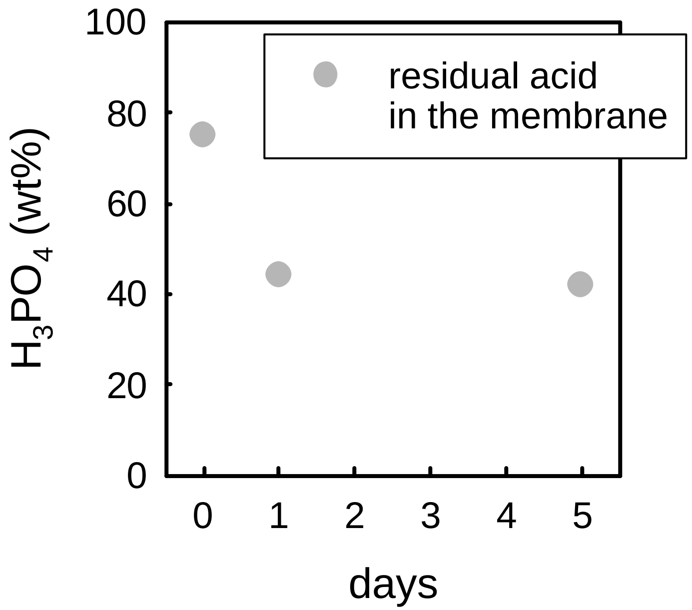
# 1. Development of new PBI-based polymers

## The acid doping level before and after leaching

| Polymer | $n_{doping}$ | $n_{residual}$ |
|---|---|---|
| PBI_4N | 4.0 | 2.0 |
| PBI_5N 2,5 | 6.0 | 2.2 |
| PBI_5N 2,6 | 9.5 | 4.5 |
| PBI_6N_bipyri | 5.7 | 2.6 |
| PBI_pyra | 8.0 | 3.0 |

**The acid doping is not proportional to the N number!**

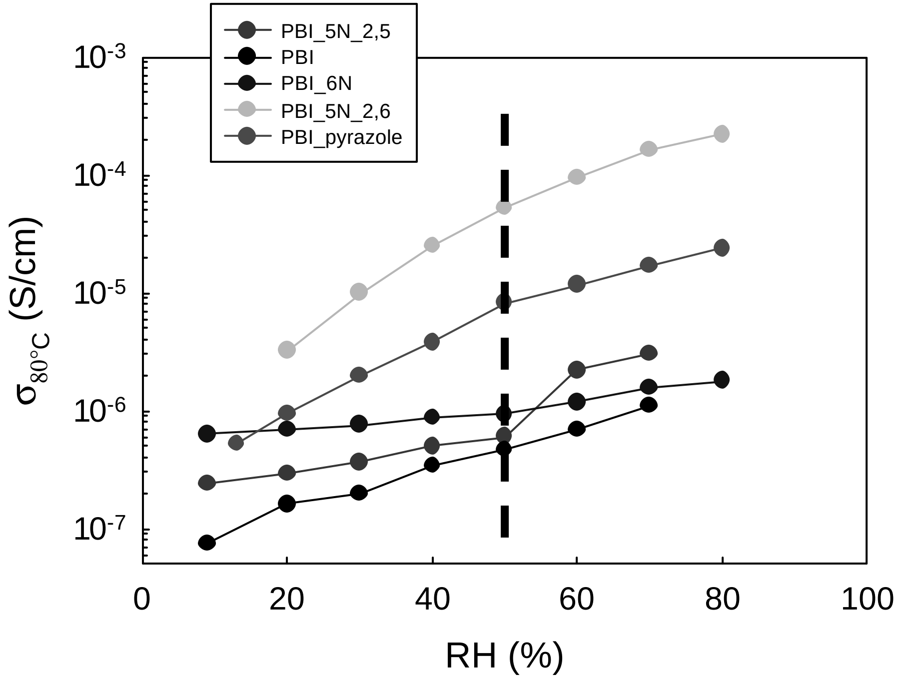
**Phosphate leaching in PBI_5N 2,6**

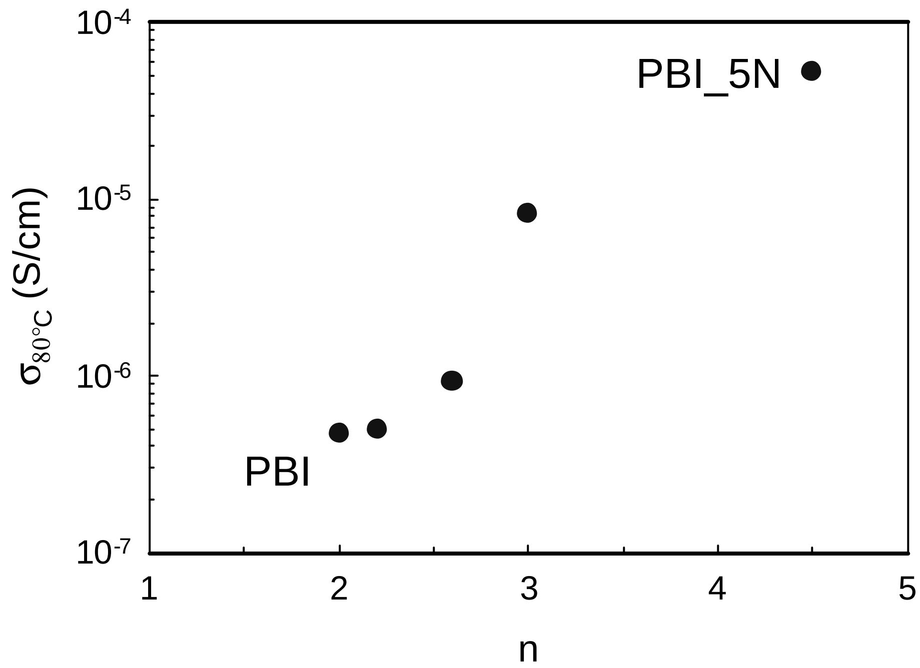



**ICP analysis**

# 1. Development of new PBI-based polymers

## The conductivity after leaching



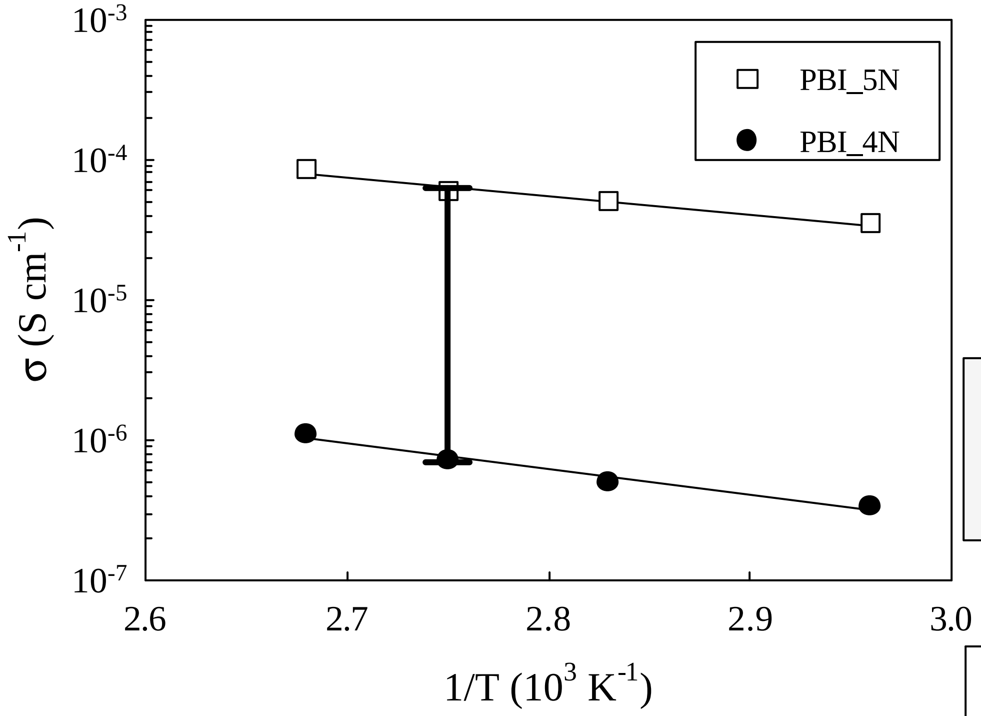




**Sigmoidal behaviour: N-N interspacing, monomer basicity, percolation?**

# 1. Development of new PBI-based polymers

## PBI_5N vs Celanese-like PBI

RH=50%




Factor $10^2$

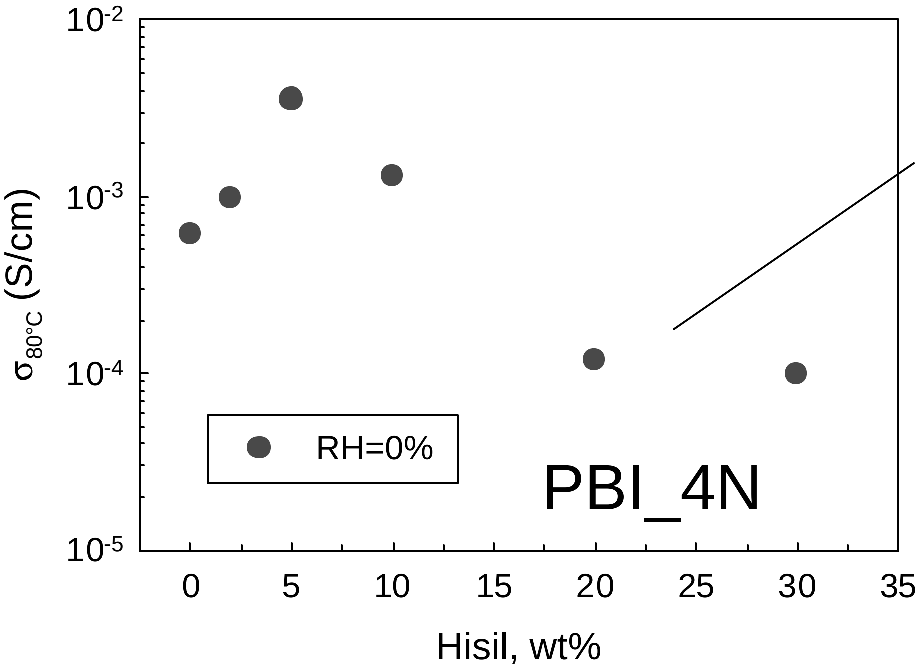
**PBI_5N 2,6**

**σ (50%R.H.@120°C)= 0.2 mS/cm**

| Membrane | $E_a$ (eV) as doped | $E_a$ (eV) after leaching |
|---|---|---|
| PBI_4N | 0.27 | 0.39 |
| PBI_5N 2,6 | 0.25 | 0.29 |

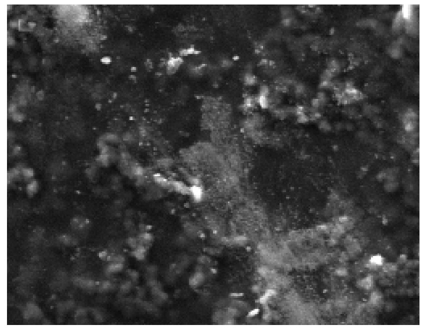
# 2. Composite PBI-based membranes

## a) The first approach: commercial nanosized $SiO_2$ (Hi-Sil)

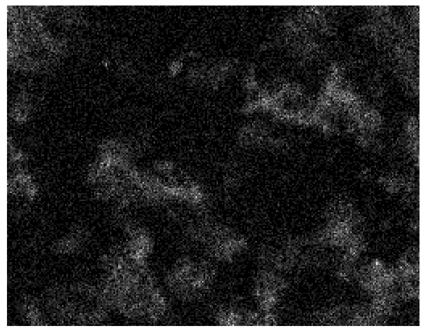



Dilution

**PBI_4N + 10 wt% HiSil backscattered**



**Si map**



Not homogeneous

148 µm ×116 µm

**Hi-Sil** — **Surface area= 210 $m^2$/g**

**Particle size= 21 nm**

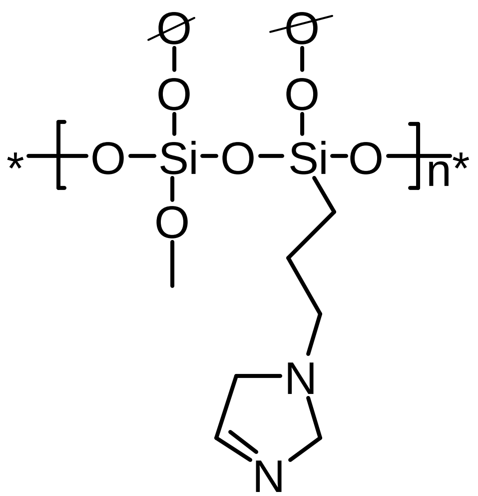
**[OH-groups]= 8-12/$nm^2$**

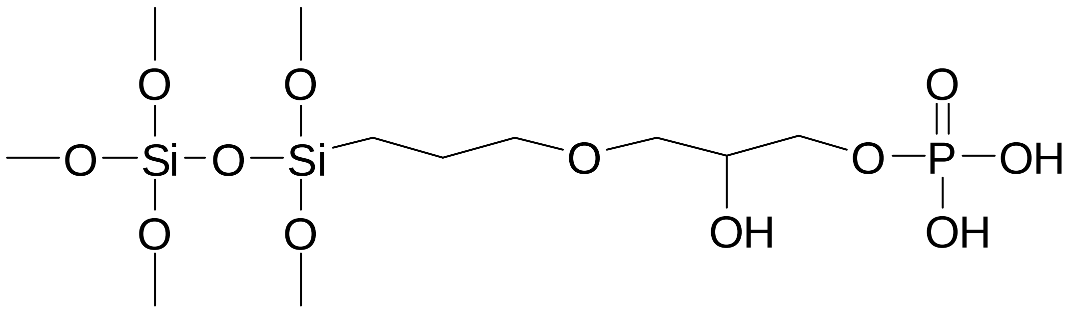
## 2. Composite PBI-based membranes

## b) Synthesis of new functionalised silica via sol-gel routes

**Basic filler $SiO_2$ _ Im**

**Acid filler $SiO_2$ _ $H_2PO_4$**





Ø = OH; Si-O

Imidazole: 3.6 mmol/g

Specific area:3.5 $m^2$/g

## 2. Composite PBI-based membranes

## b) Synthesis of new functionalised silica via sol-gel route

# Ideas:

### $SiO_2$ _ Im

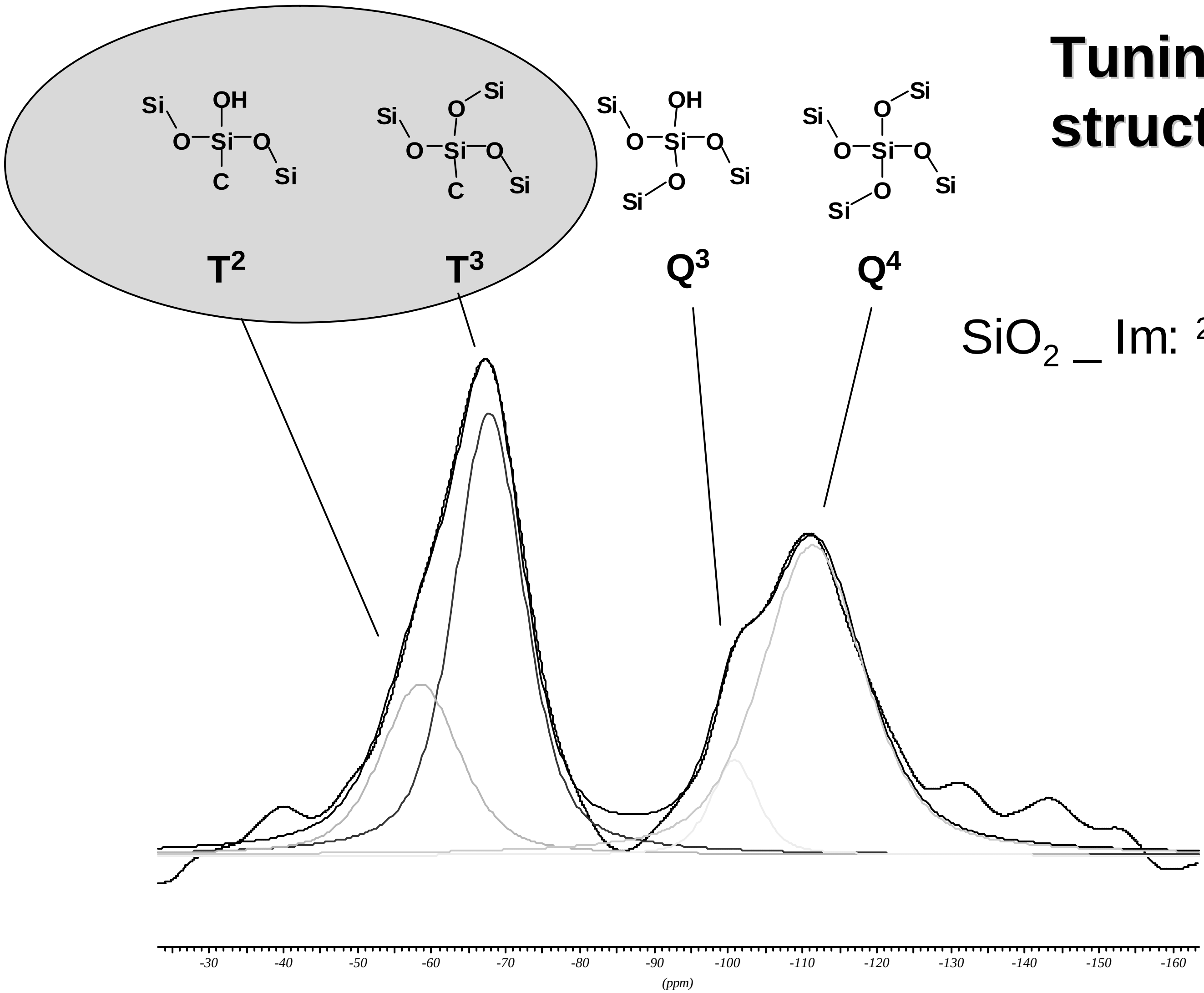
**The presence of highly basic units, similar to BI, could improve the acid retention of the membrane and in the mean time the filler/polymer compatibility**

### $SiO_2$ _ $H_2PO_4$

**The presence of covalently bonded acid units could partially balance the loss of free acid**

# 2.  Composite PBI-based membranes

## Tuning the filler structure




SiO$_2$ _ Im: $^{29}$Si MAS-NMR

# 2. Composite PBI-based membranes

## Fillers distribution in the membrane: SEM_EDX analysis

Si-map

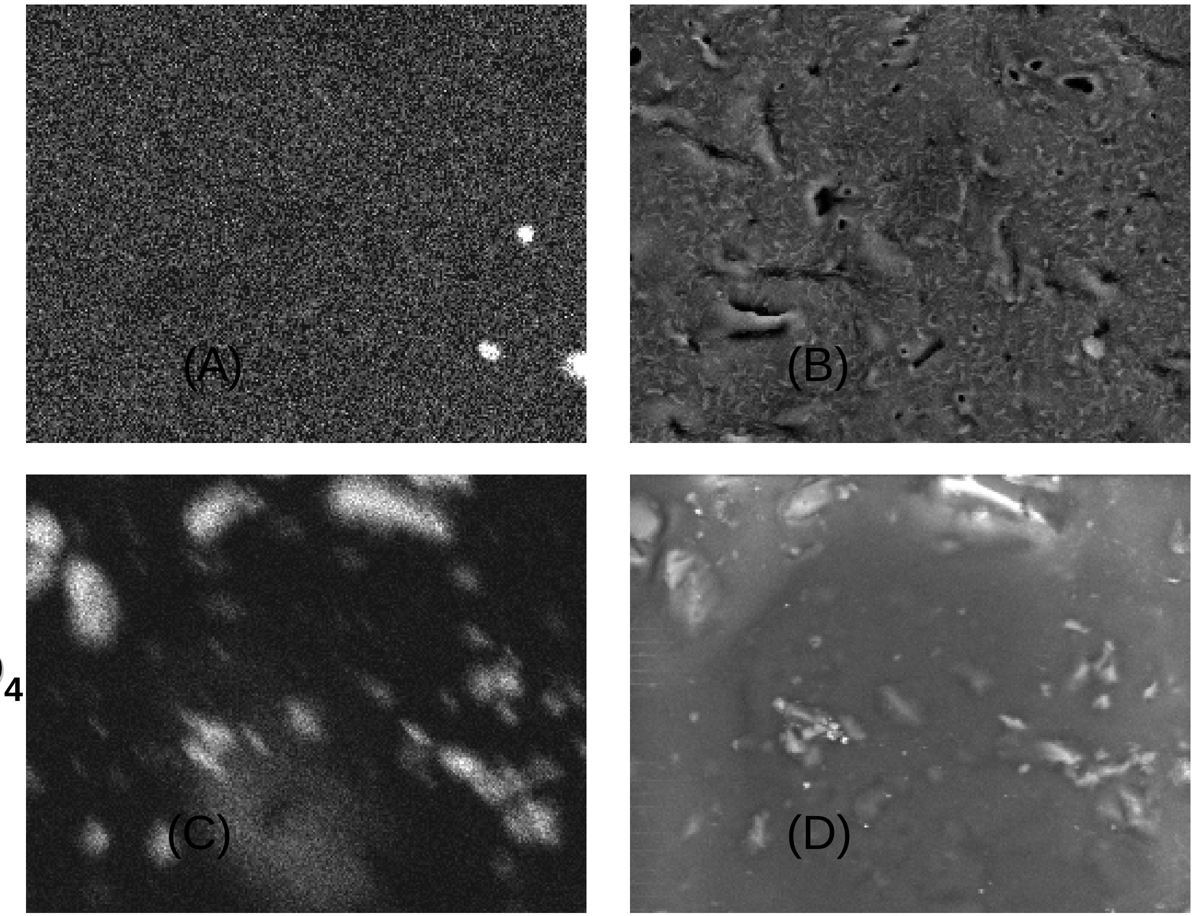
Back-scattered

**PBI + 30 wt% $SiO_2$ _ Im**

Homogeneous

**PBI + 30 wt% $SiO_2$ _ $H_2PO_4$**

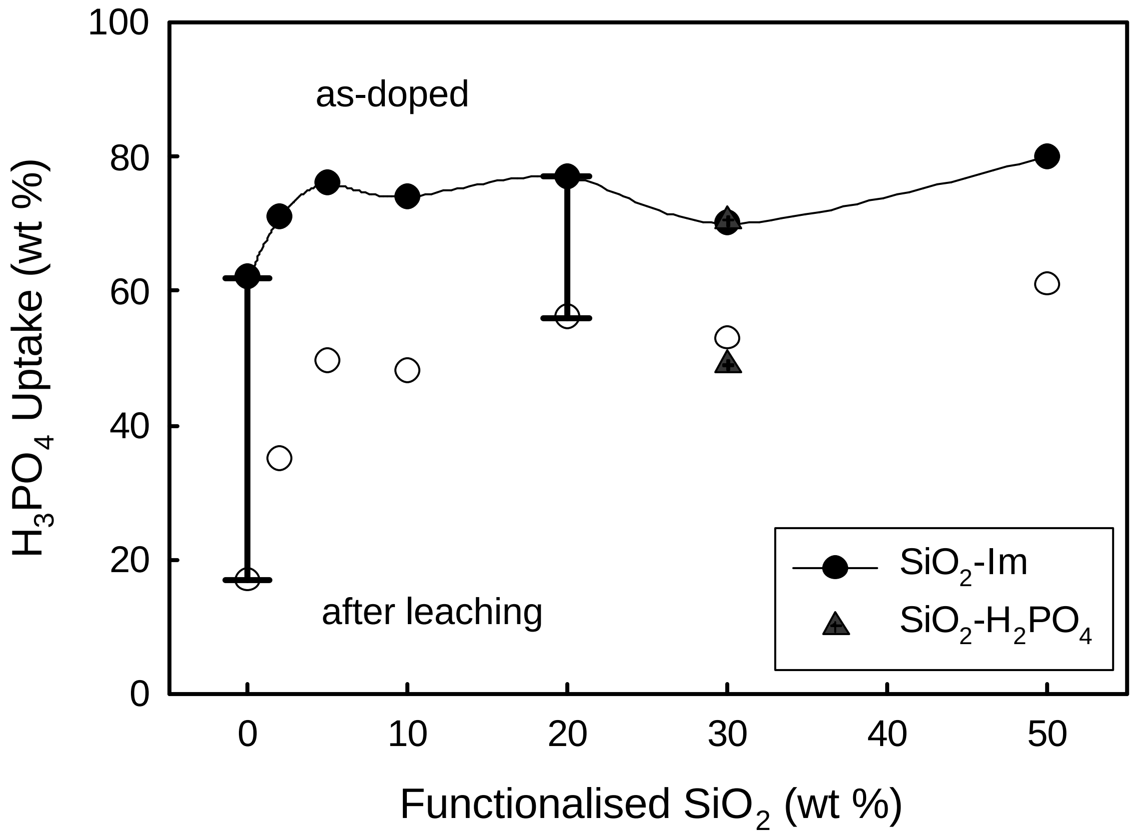
100 µm



# 2. Composite PBI-based membranes

## Effects of the fillers on the acid leaching

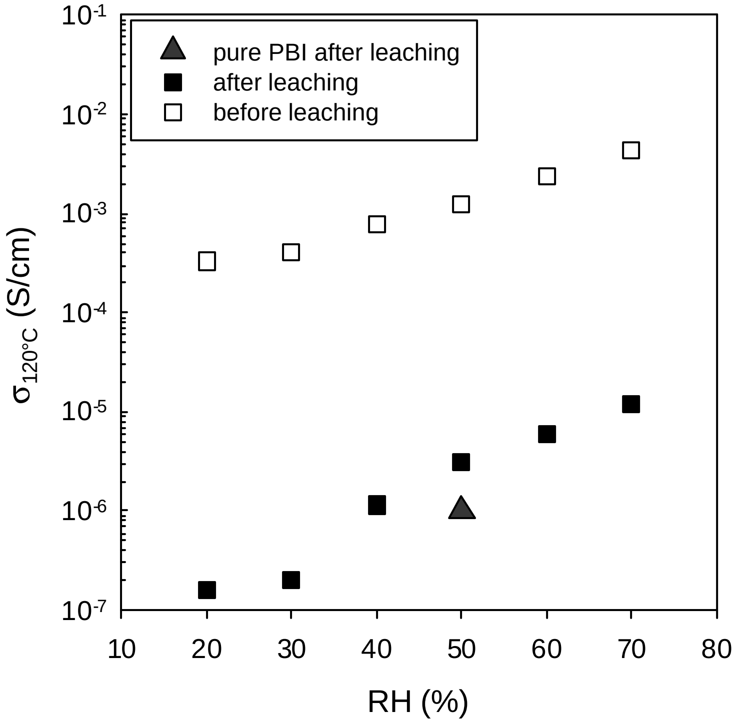
### PBI_4N – X wt% filler



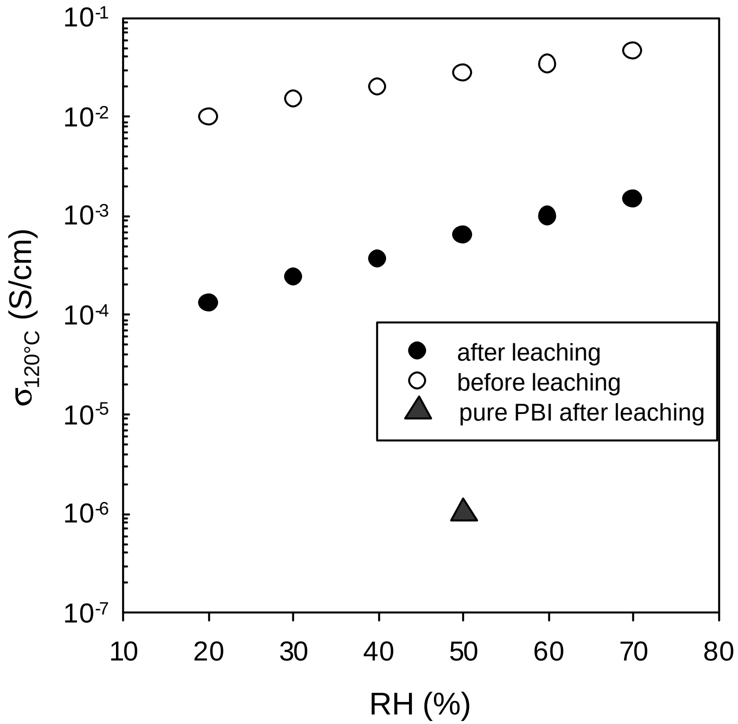

~50% reduction of the acid leaching!

# 2. Composite PBI-based membranes
# Filler effects on the proton conductivity

## PBI + 30 wt% $SiO_2$ _ $H_2PO_4$

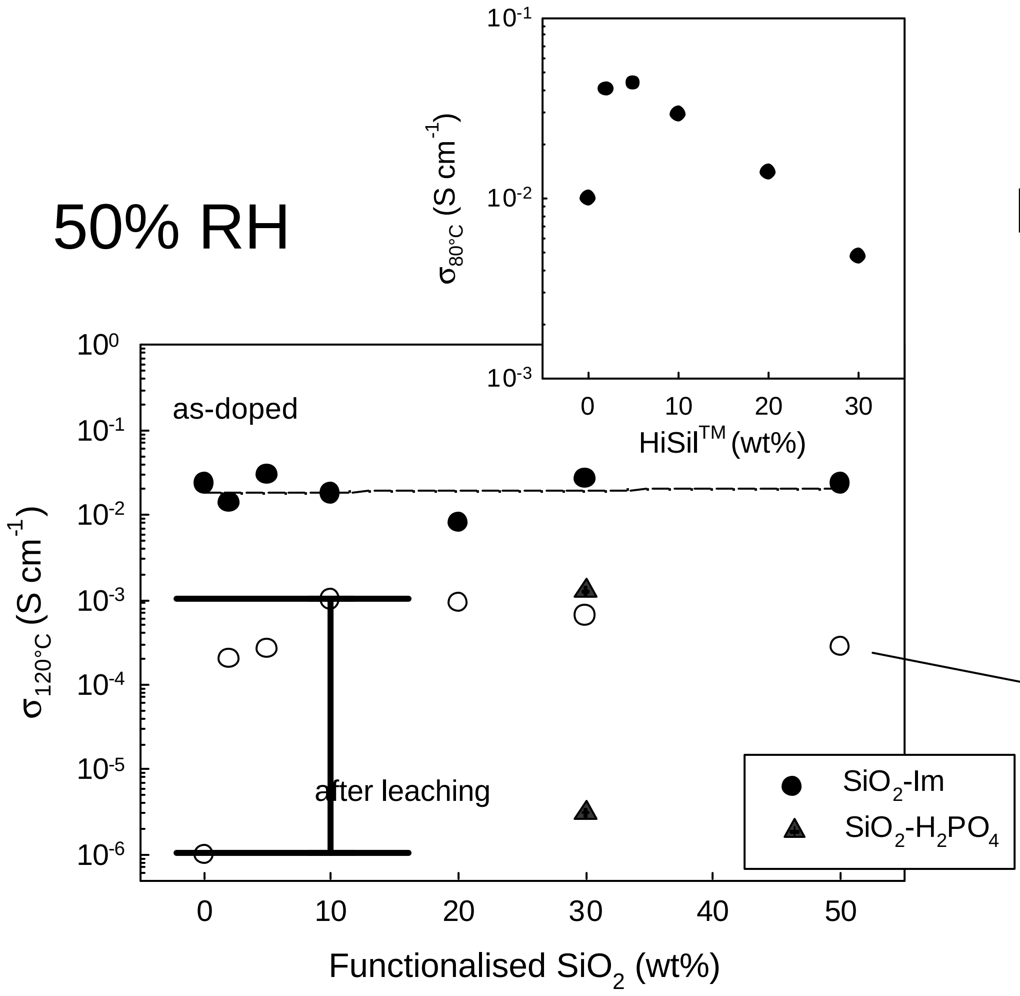



## PBI + 30 wt% $SiO_2$ _ Im



# 2. Composite PBI-based membranes

50% RH




**PBI – X wt% $SiO_2$ _ Im**

Factor $10^3$!

No dilution!
Active filler

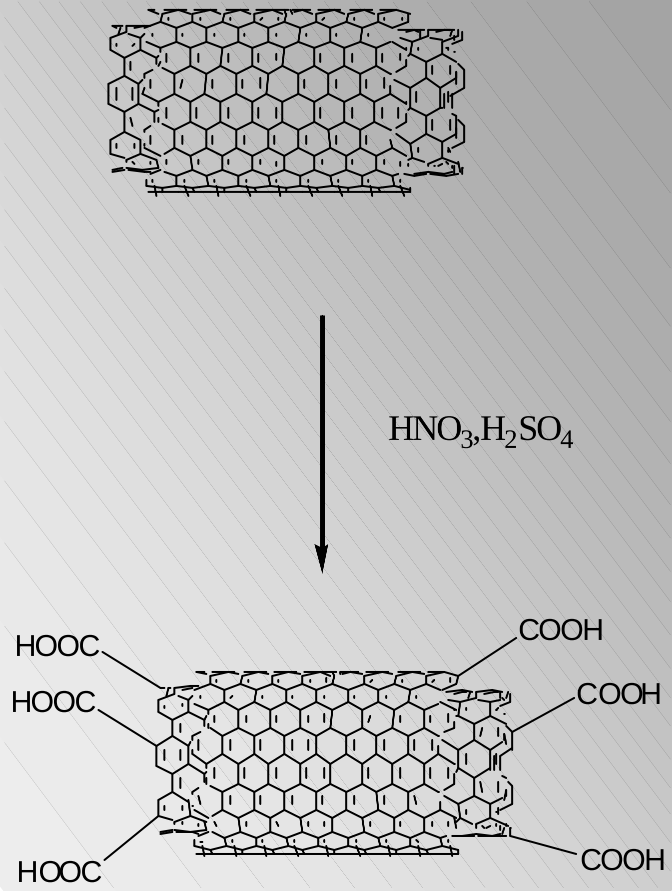
# Conclusions

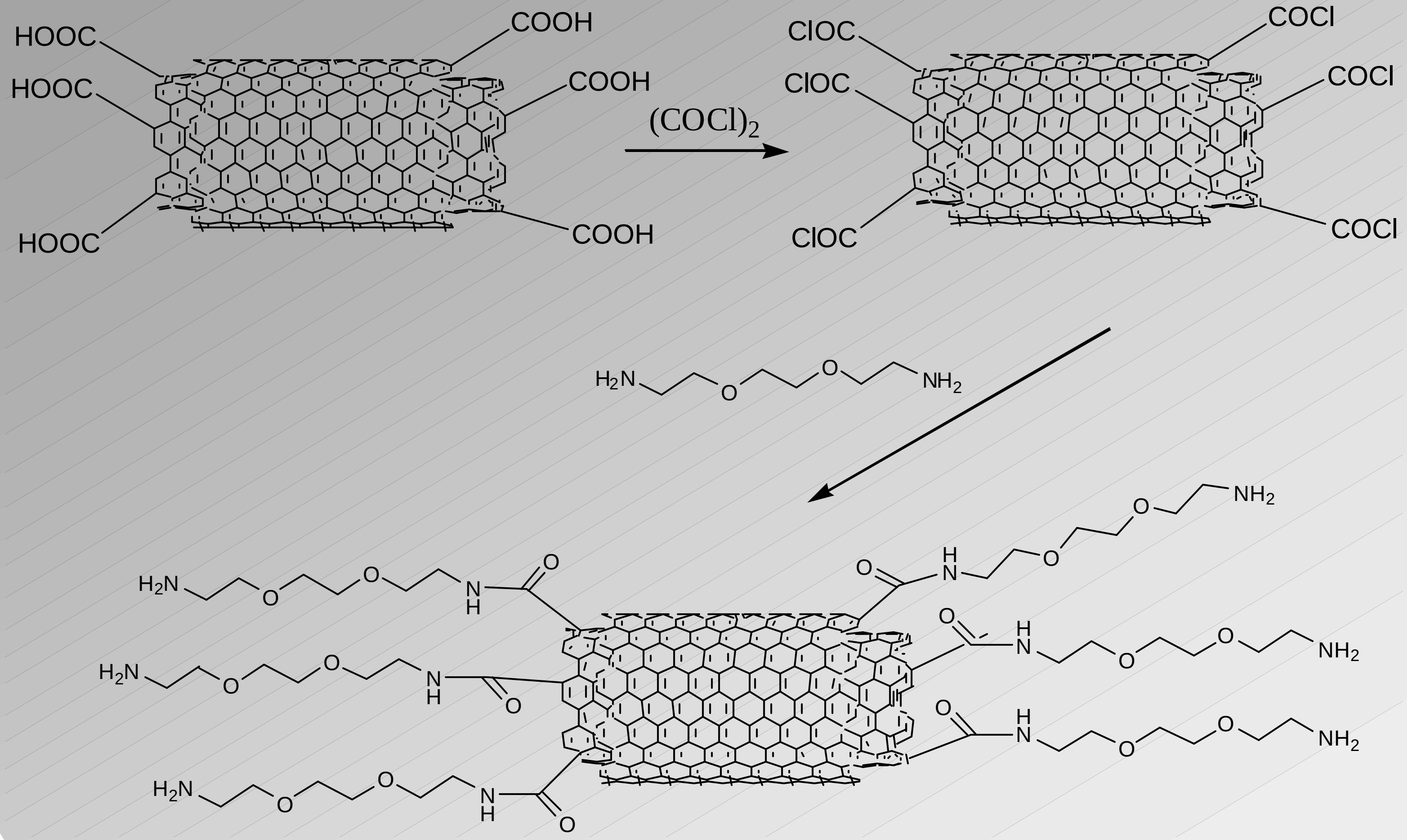
- The acid leaching can be reduced (and the residual conductivity increased) by a proper tailoring of the monomer repeat unit.
- The dispersion of functionalised silica strongly reduces the acid leaching.
- Residual conductivity 1000 higher than the pure PBI is observed, even in presence of small amounts of filler with imidazole units.

# Carbon nanotubes (CN) for drug delivery

## The problem: toxicity/solubility

### CN functionalization route: towards the "nano-oil"

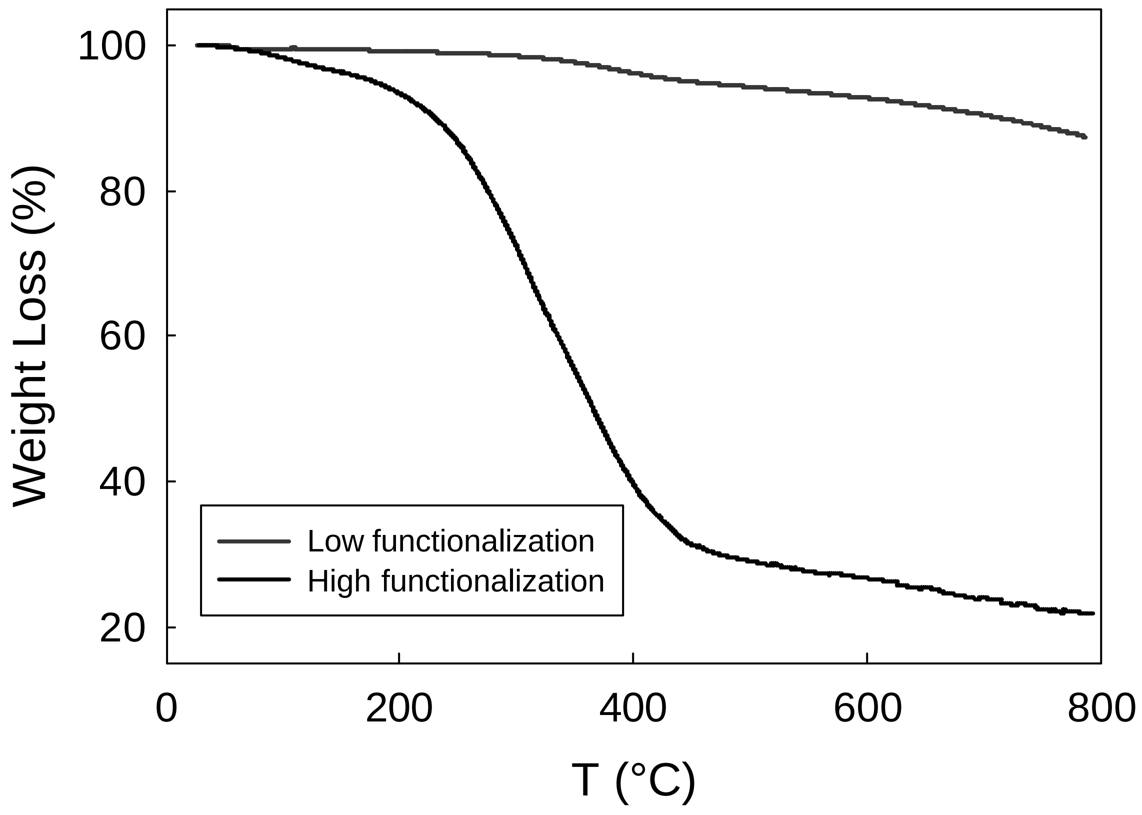




HOOC
HOOC
HOOC
COOH
COOH
COOH
(COCl)2
ClOC
ClOC
ClOC
COCl
COCl
COCl
H2N
O
O
NH2

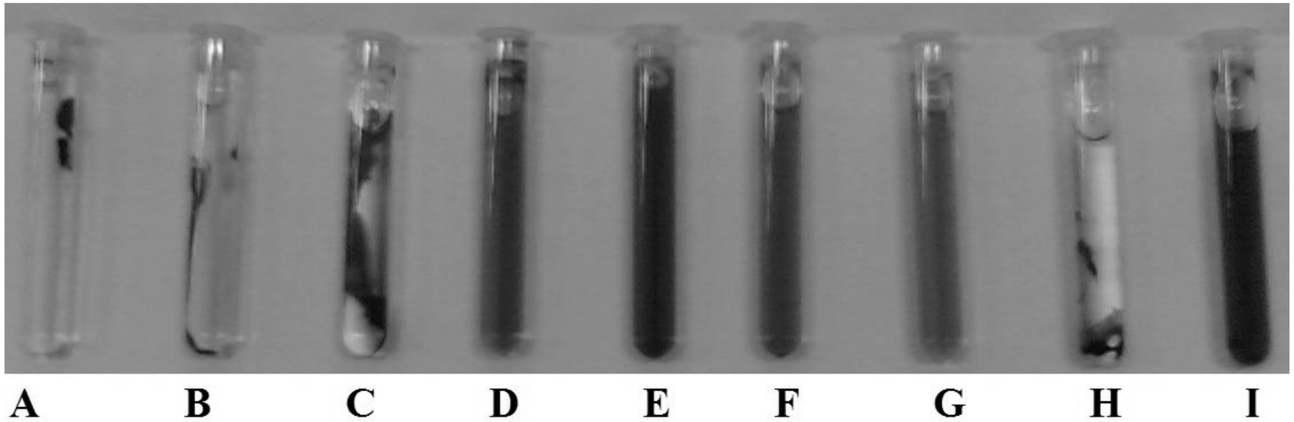
# Thermogravimetry

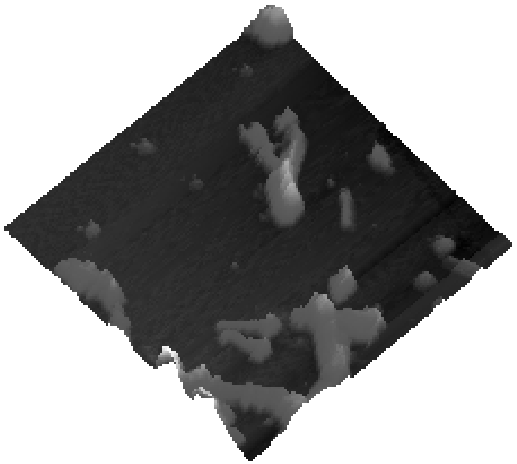
Our functionalized CNs: ~80 wt% is given by functional groups



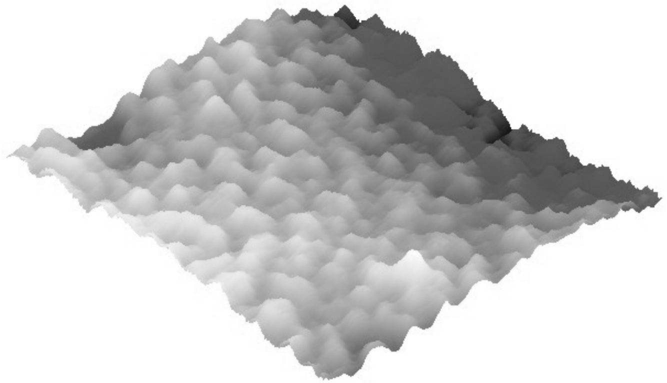
# Solubility properties and morphology

A: acetone
B: acetonitrile
C:benzene
D:chloroform
E:DMSO
F:DMF
G:ethanol
H:toluene
**<u>I:water</u>**



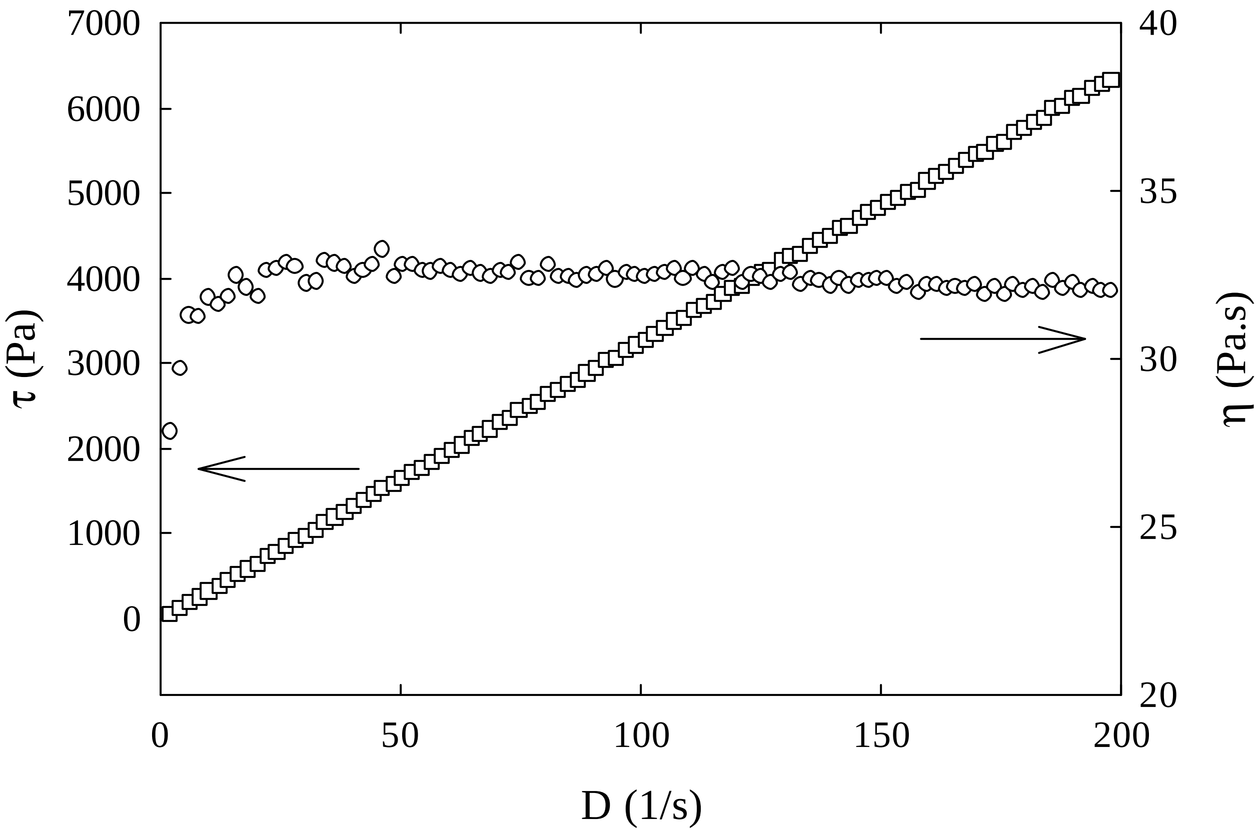
MWCNTs as purchased



MWCNTs highly functionalized

Nature Materials: to be submitted

# Viscosity



7000
6000
5000
4000
3000
2000
1000
0
τ (Pa)
40
35
30
25
20
η (Pa.s)
0
50
100
150
200
D (1/s)

# Thermal analysis and conductivity