# Effect of the molecular structure of oxetane additives on the enhancement of PEDOT:PSS films aqueous stability and conductivity

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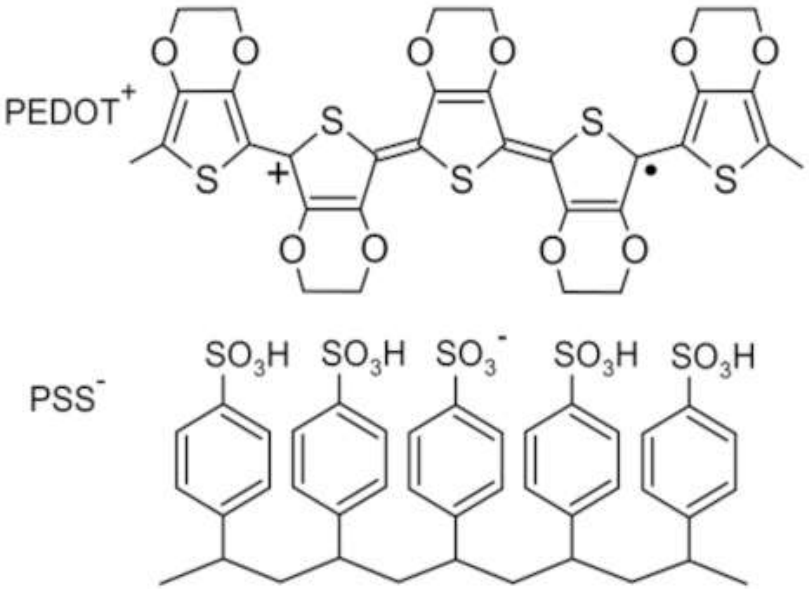
# Relevance

➢ **What is PEDOT:PSS ?**




➢ **Properties** (source: Heraeus (Clevios™))

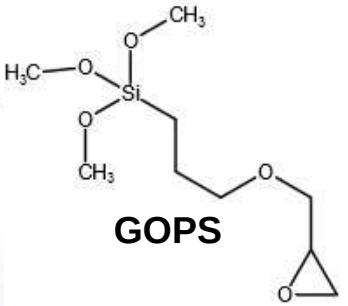
- Mixed (ionic/electronic) and tuneable conductivity

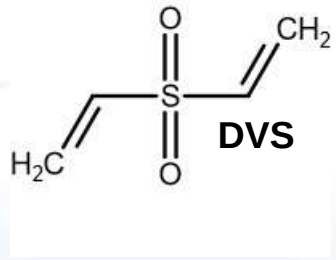
ca. $10^{-3}$ S/cm (AI4083 – 1:6, w/w)

ca. 0.1 S/cm (PH1000 – 1:2.5, w/w)

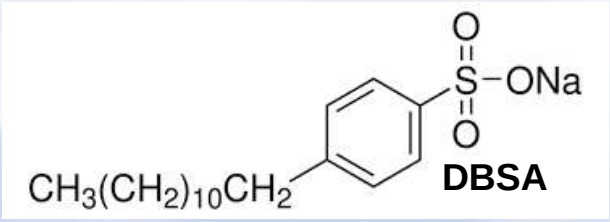
$\Longrightarrow$Increase up to ca. 4000 S/cm

- Stabilisation in aqueous media: cross-linking
  - GOPS+EG+DBSA ($\sigma$H 5-17 S/cm)
  - DVS+EG+DBSA ($\sigma$H13 S/cm)



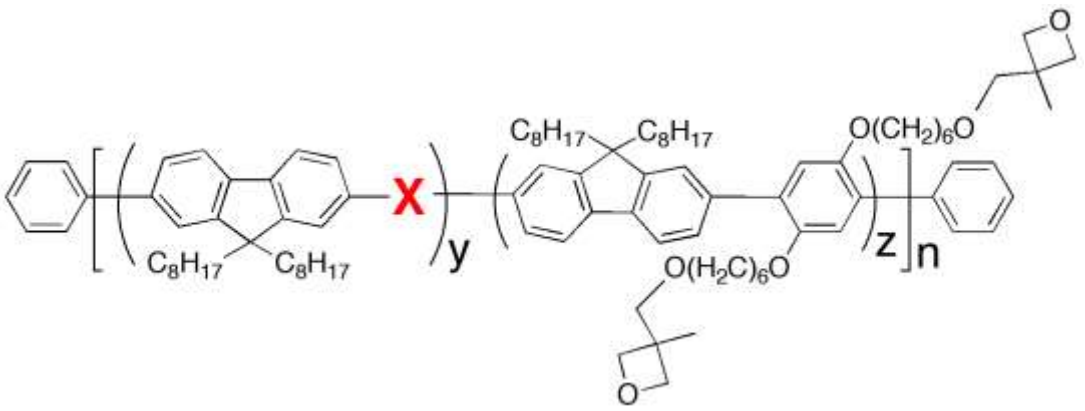



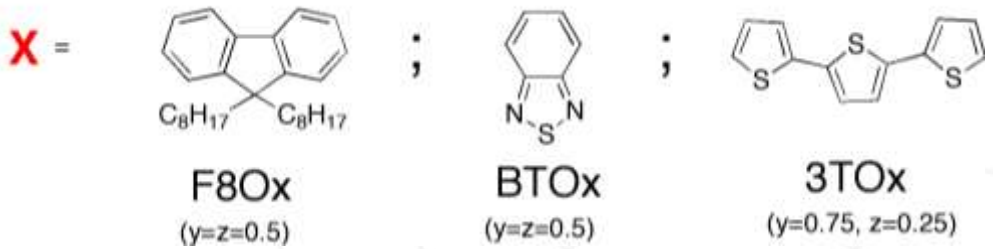

➢ **Applications**: (opto)electronics and biological



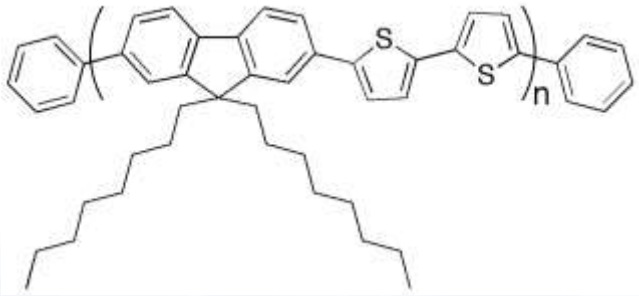
# Our previous work with oxetanes

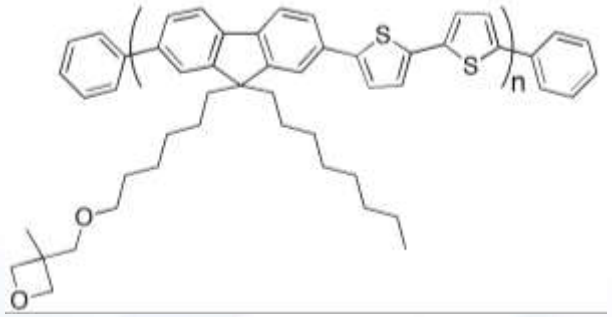
- **Oxetane-functionalised conjugated polymers – formation of insoluble networks**



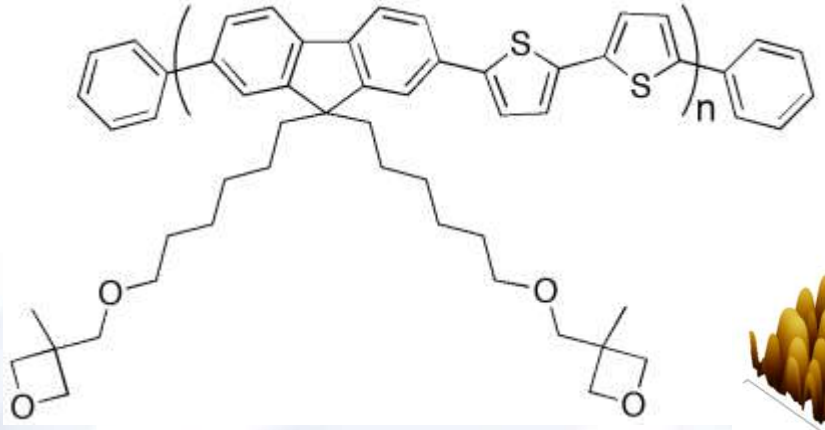



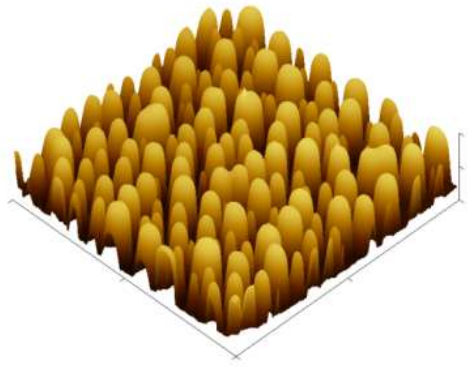

*Synth. Met.* **158**, 643 (2008)



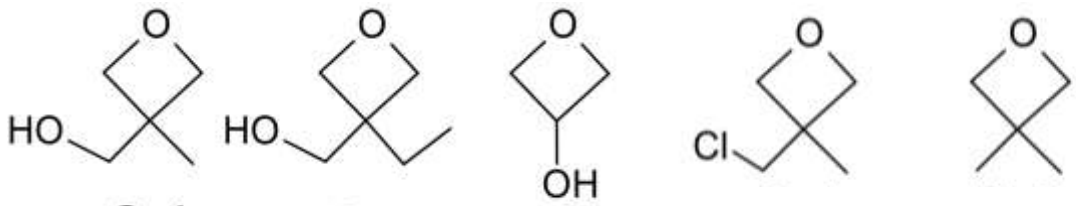




*APL* **91**, 063509(2007), *Chem. Phys. Lett.* **455**, 189 **(**2008), *JAP* **103**, 084510 (2008), *Macromolecules* **42**, 7903 (2009); *J.Mater Chem.* **21**, 12511 (2011)

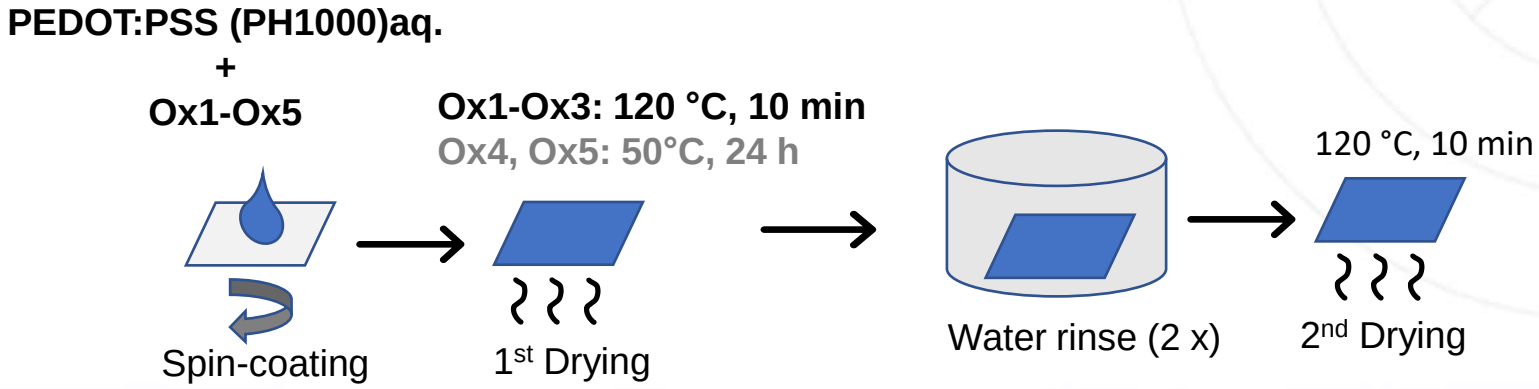


# Oxetanes as PEDOT:PSS additives

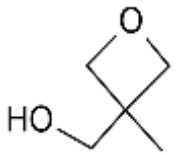



Ox1/HMO Ox2 Ox3 Ox4 Ox5

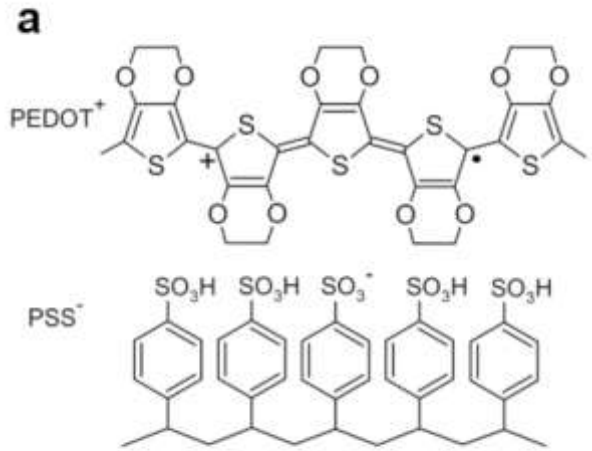


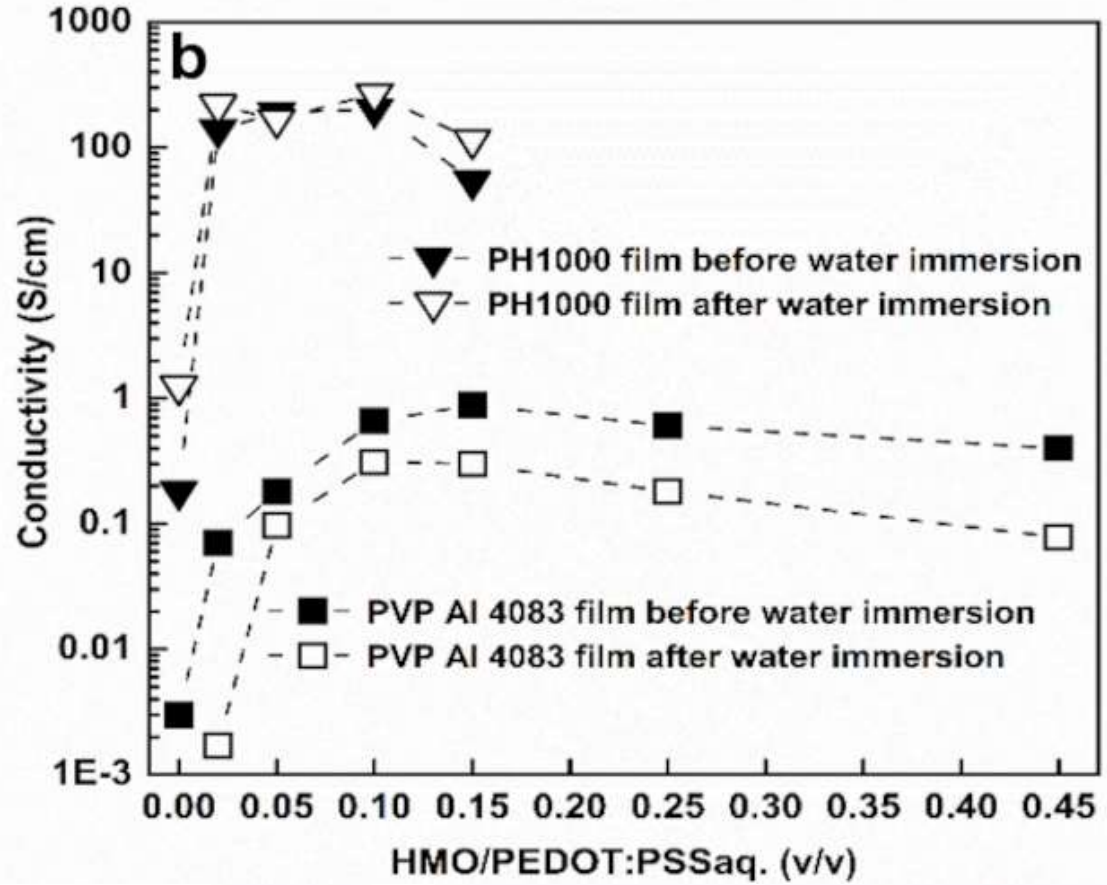

*Adv. Mater. Interfaces* 2100517 (2021); *Polymer* **282**,.126196 (2023); *Org. Elect.* **125**, 106987 (2024)

# HMO as PEDOT:PSS additive




Ox1/HMO




With respect to PEDOT:PSS:
- σ(PH1000) increases by ca. 3 orders of magnitude
- σ(AI4083) increases by 2 orders of magnitude

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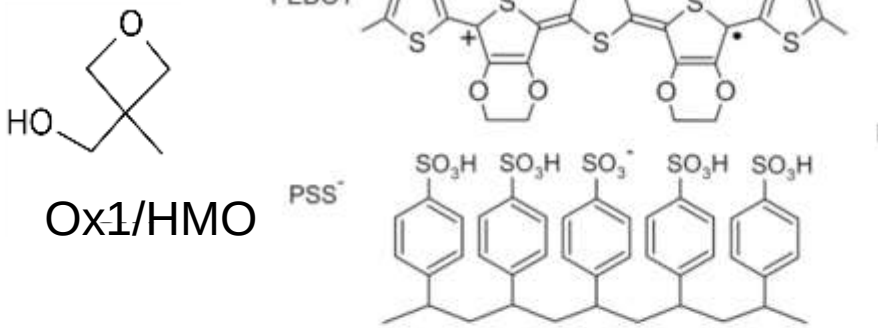
# HMO as PEDOT:PSS additive

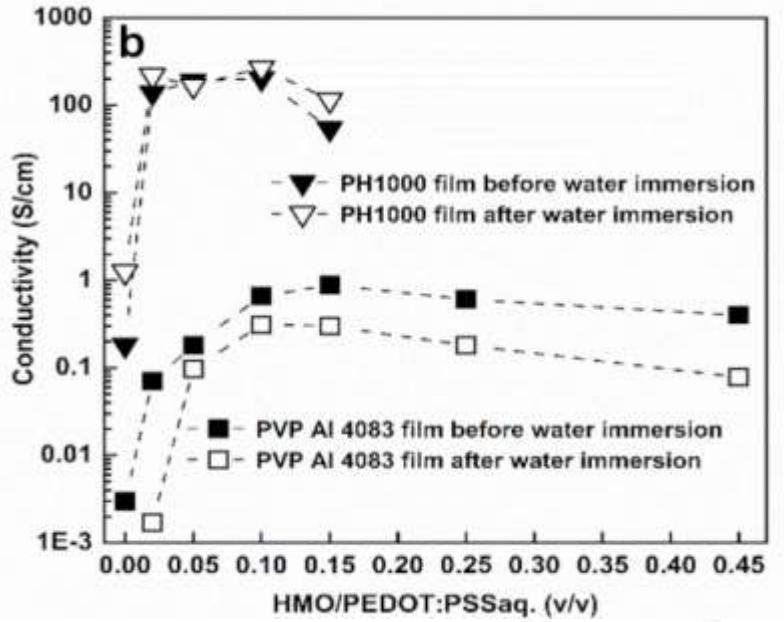
Need of the water immersion?

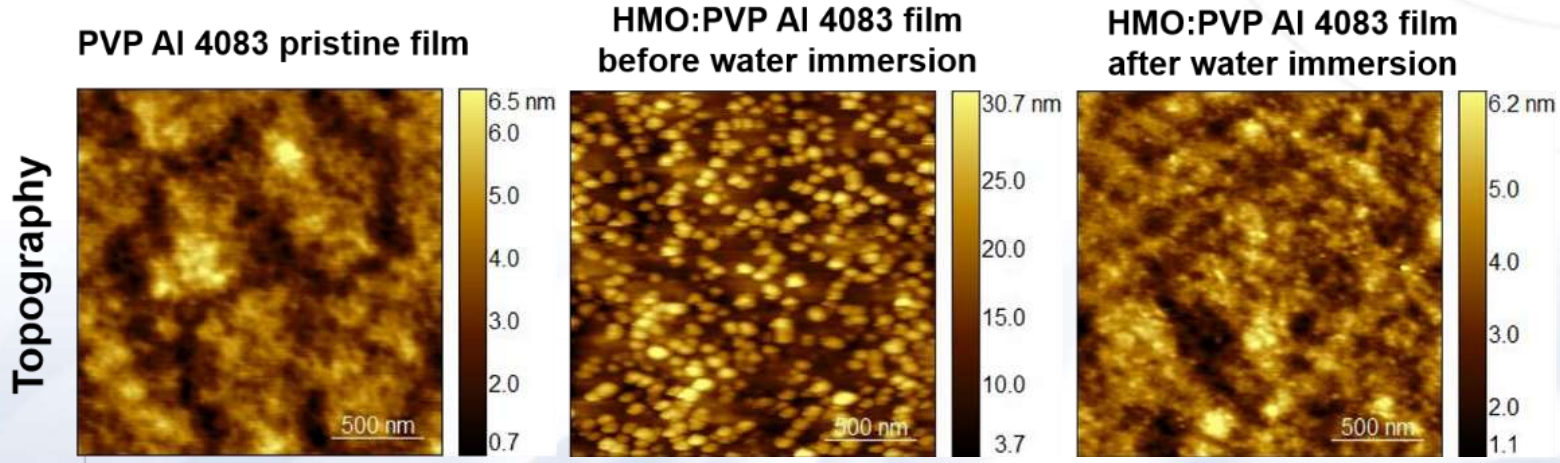






Ox1/HMO

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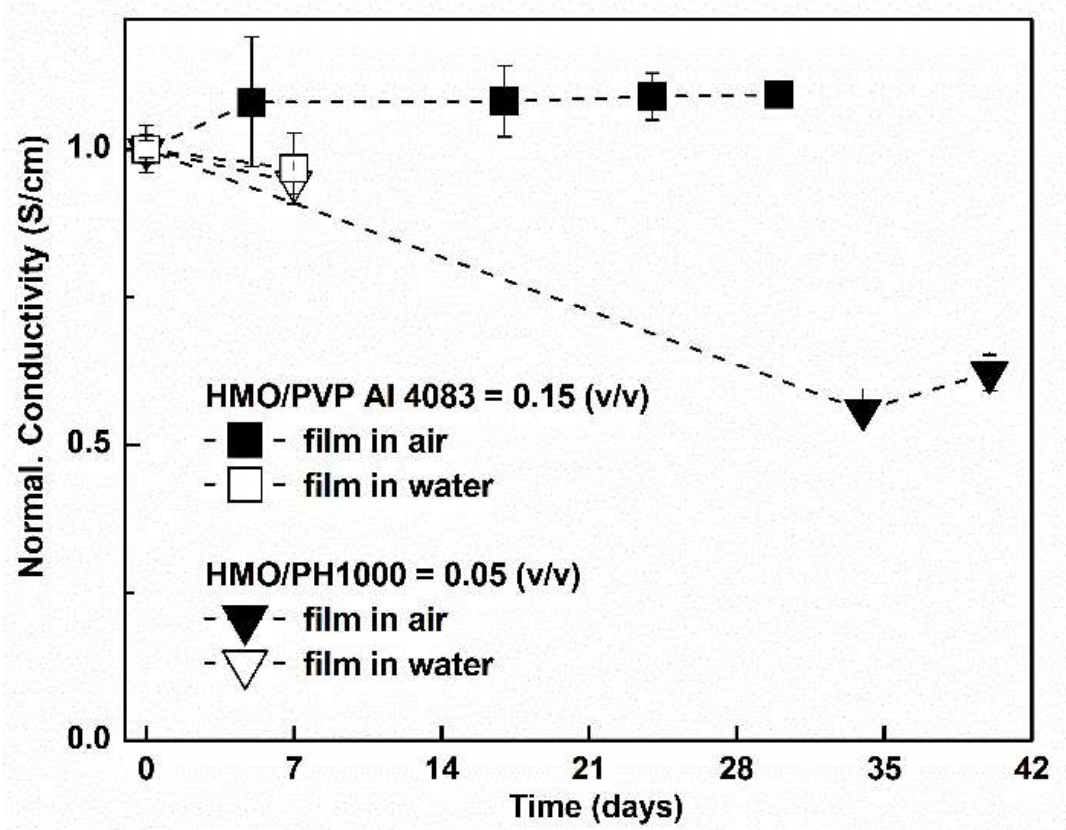
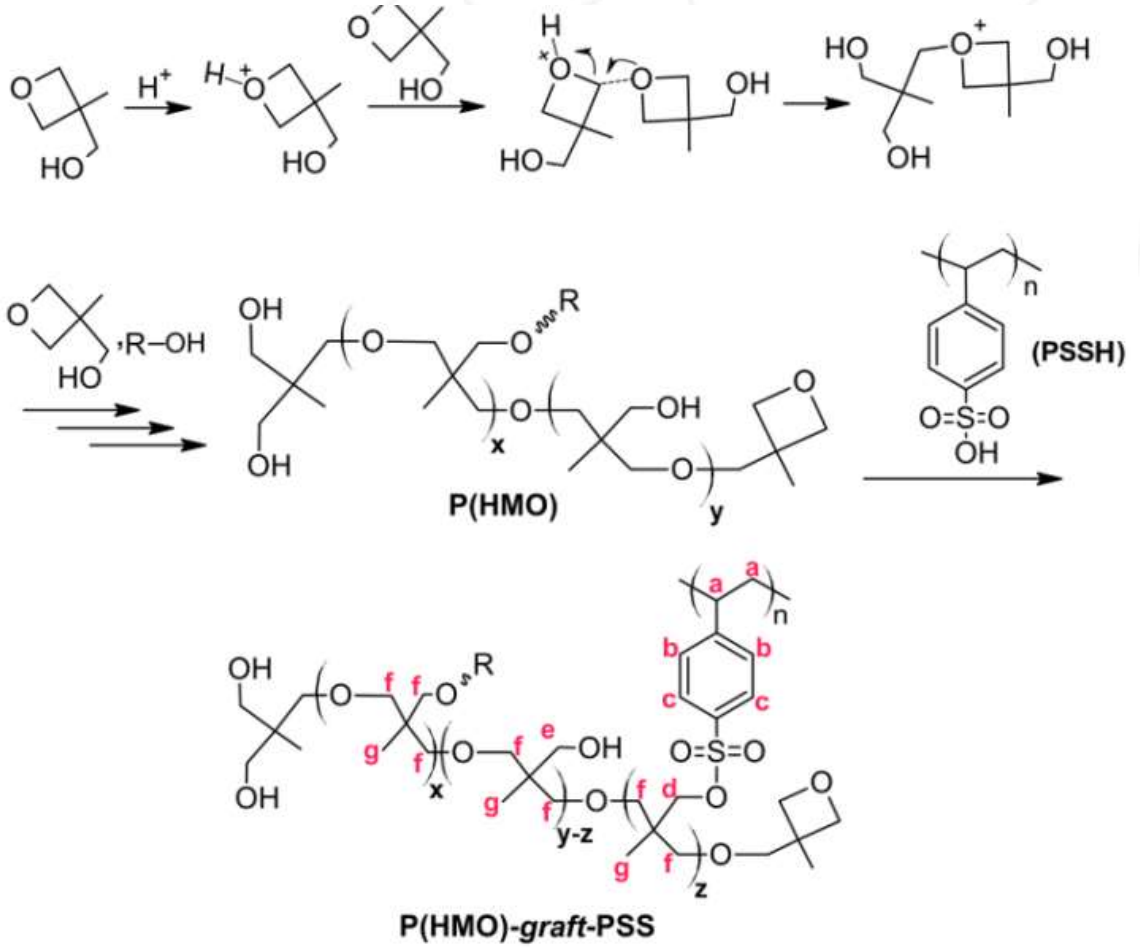
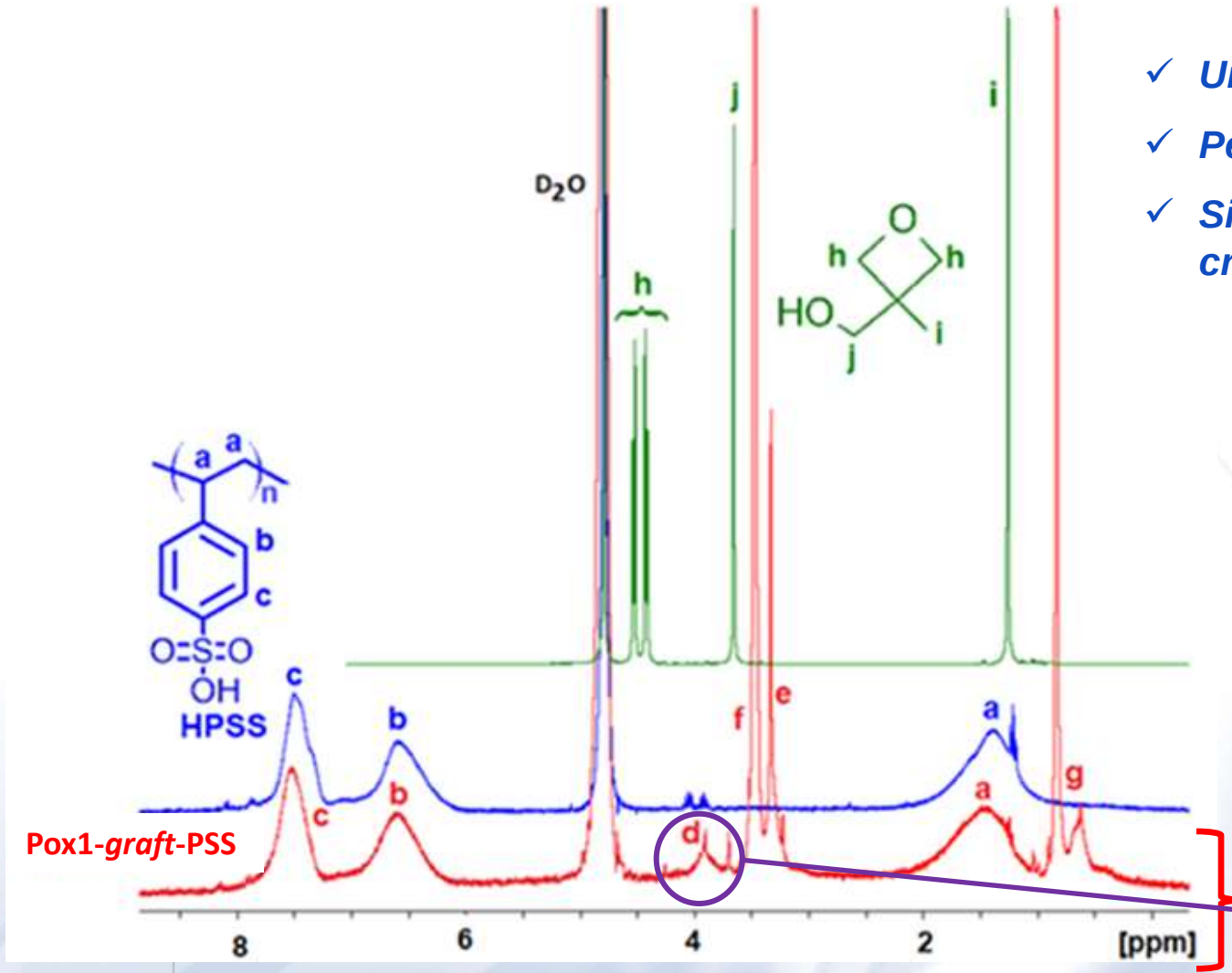
# HMO as PEDOT:PSS additive: stability in water



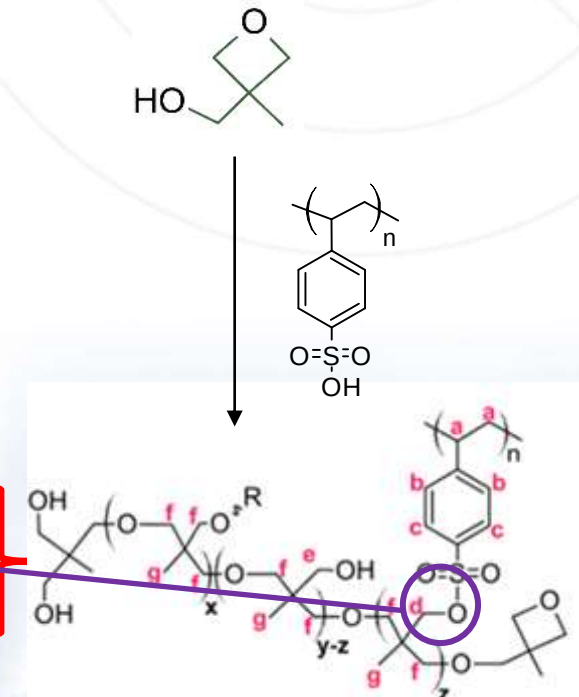



# HMO as PEDO:PSS additive: condensation with PSS

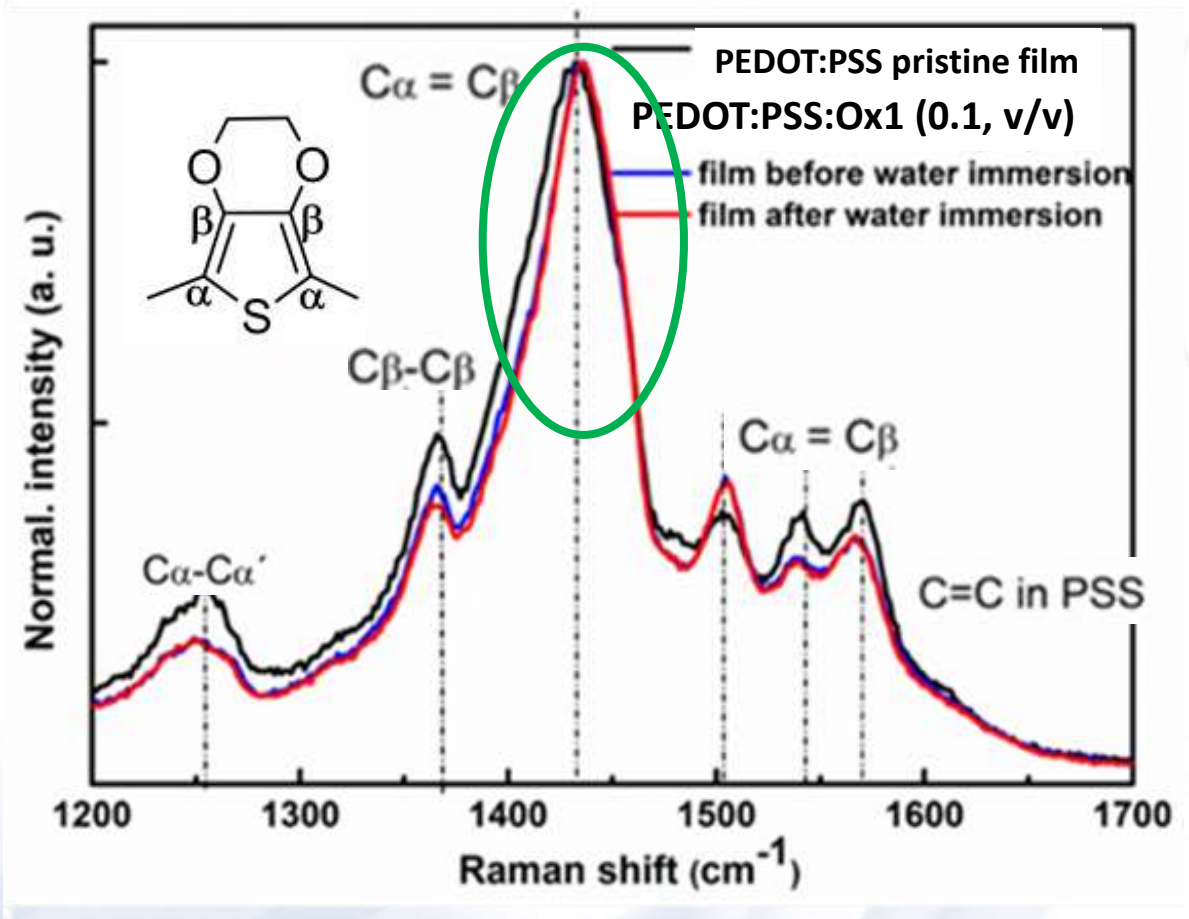
**$^1$H NMR of HPSS:Ox1 films ($D_2O$ soln.)**

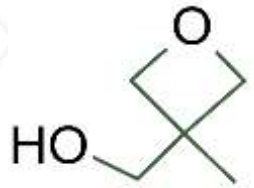



- ✓ *Unreacted oxetane is absent*
- ✓ *Peaks assigned to POx1*
- ✓ *Signal at 3.79 ppm assigned to PSS cross-linked with Pox1*



# Conformational changes of PEDOT:PSS network: Raman spectra



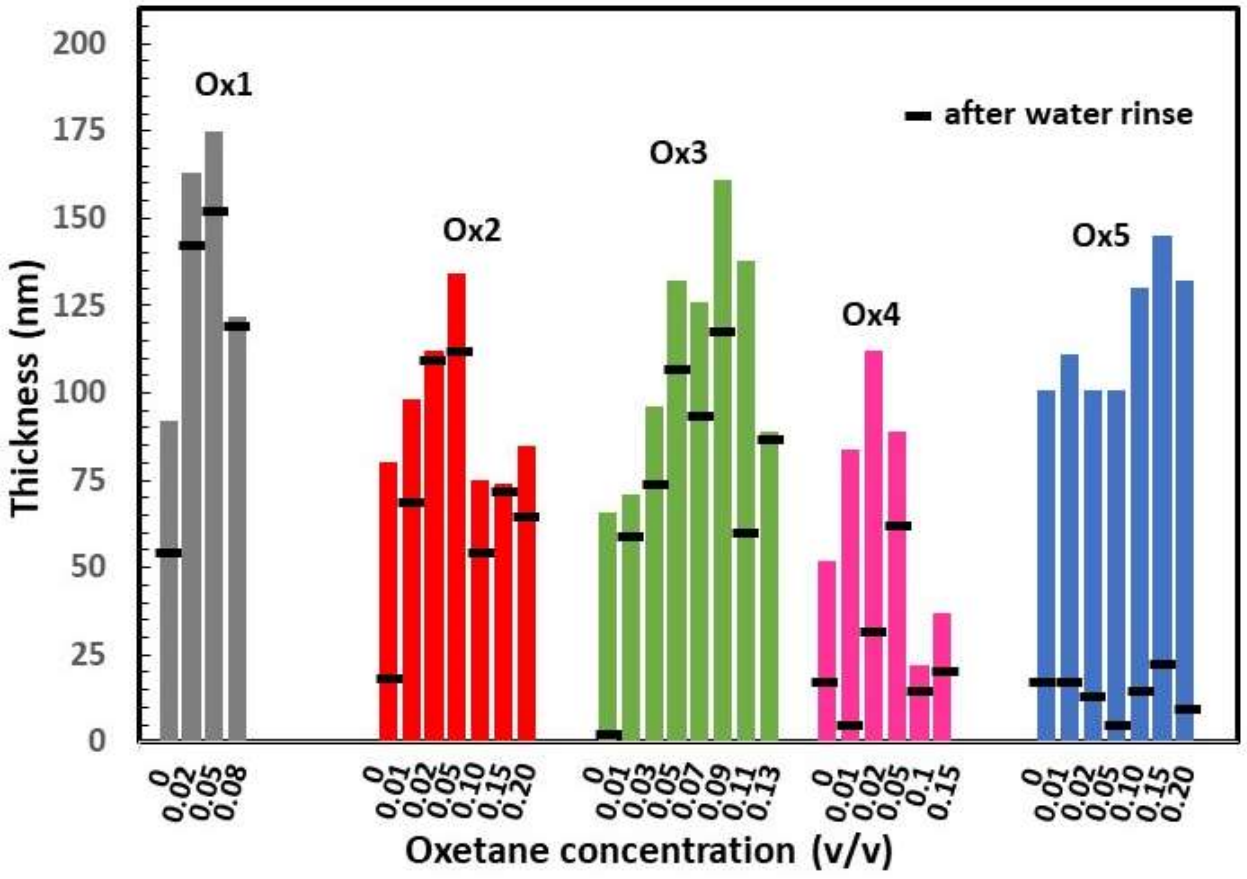




PEDOT:PSS:Ox1 films

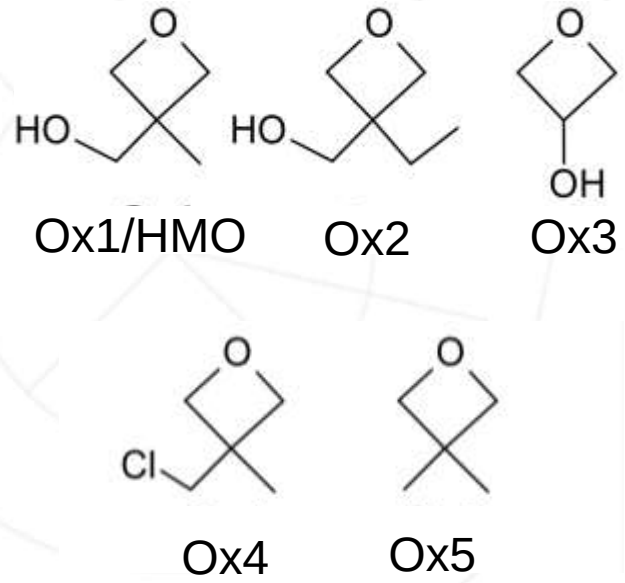
***Narrower C=C band***

**More crystalline PEDOT network**

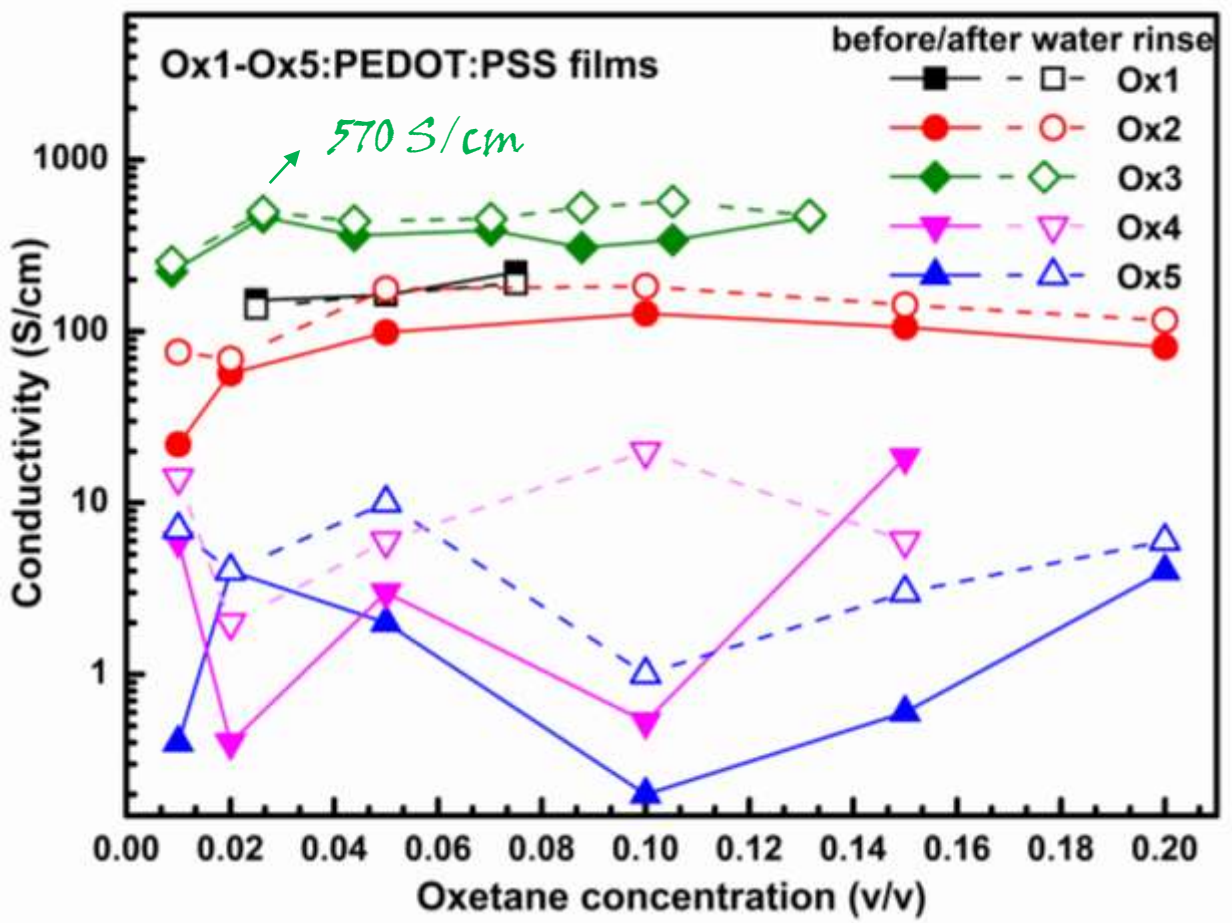
# Oxetanes as PEDOT:PSS additives: optimisation

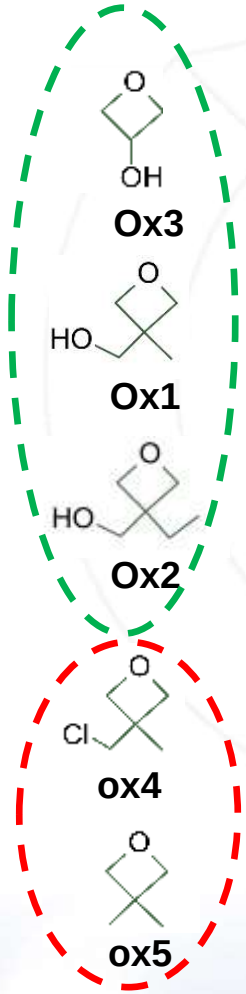


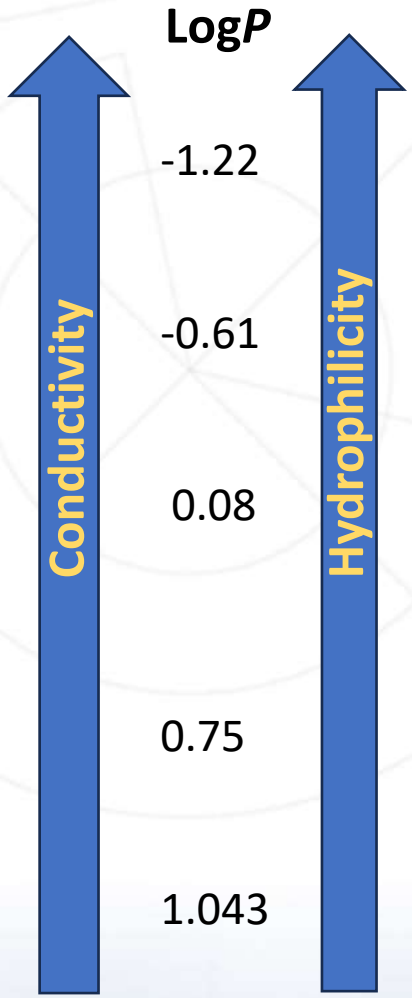

– ***thickness after water immersion***



# Oxetanes as PEDOT:PSS additives: optimisation

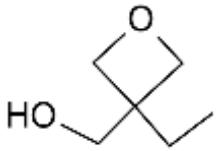


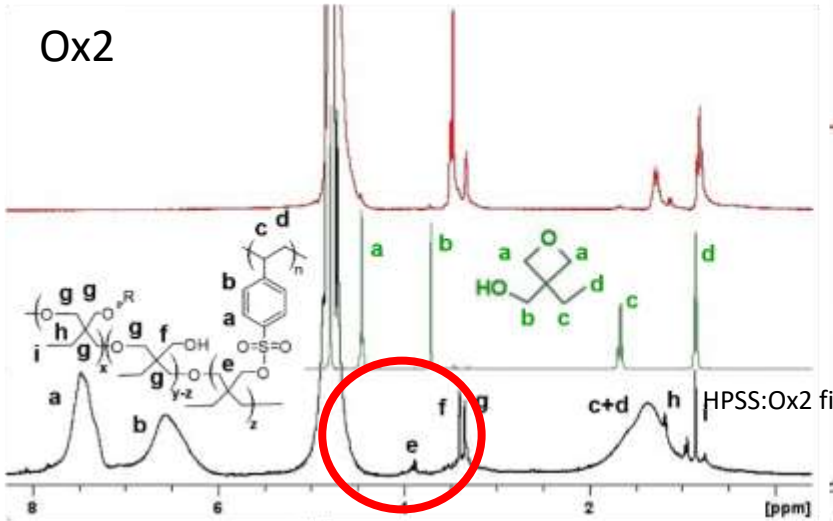




✓ **ca. three orders of magnitude increase in PEDOT:PSS (PH1000) films' conductivity upon addition of Ox1,Ox2,Ox3**

# Oxetanes as PEDO:PSS additives: condensation with PSS

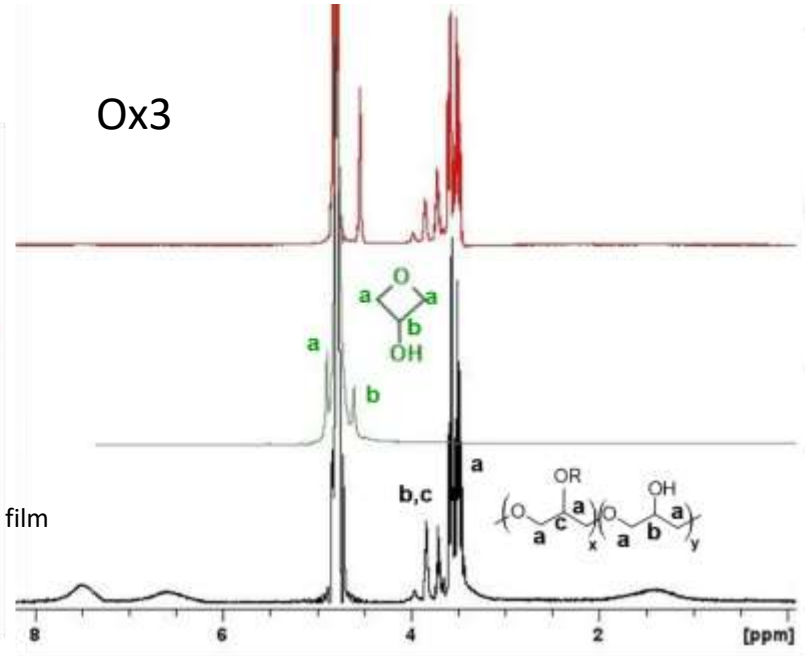


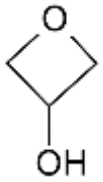

Ox2



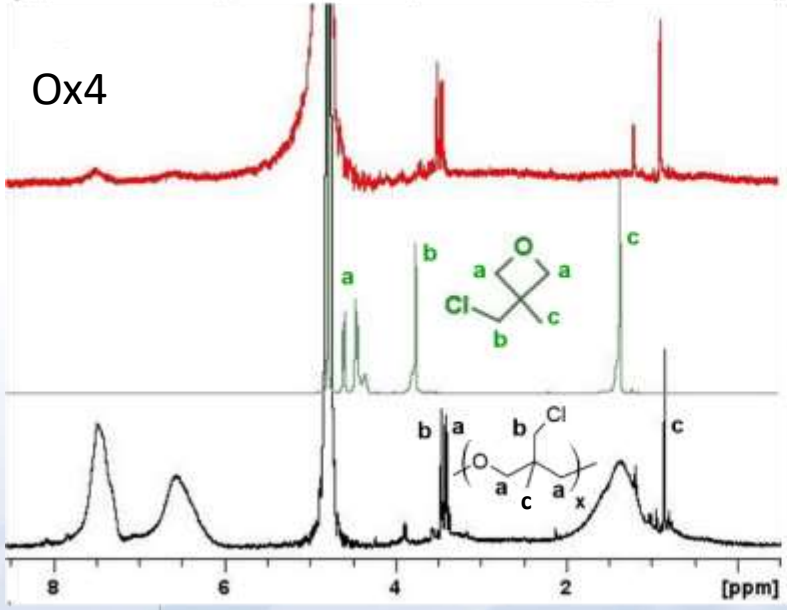

HPSS:Ox2 film

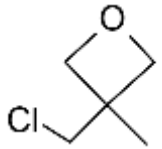
Ox3



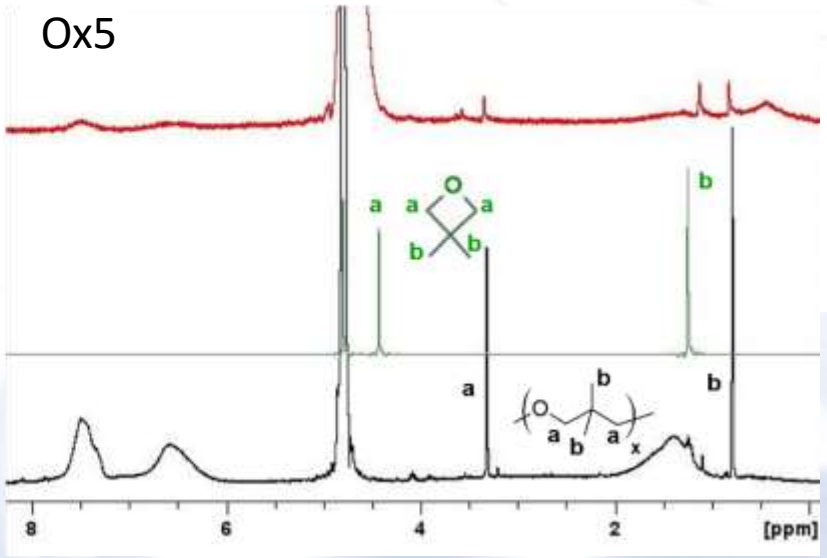




Ox4

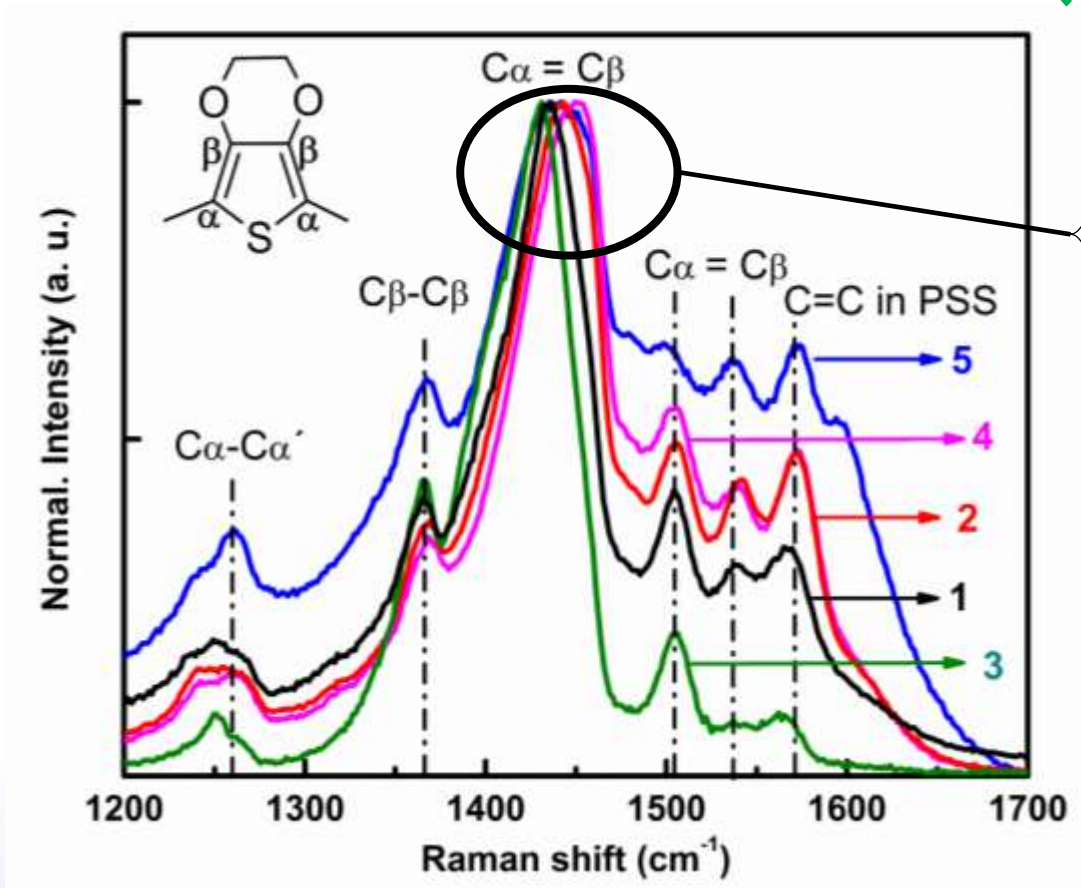


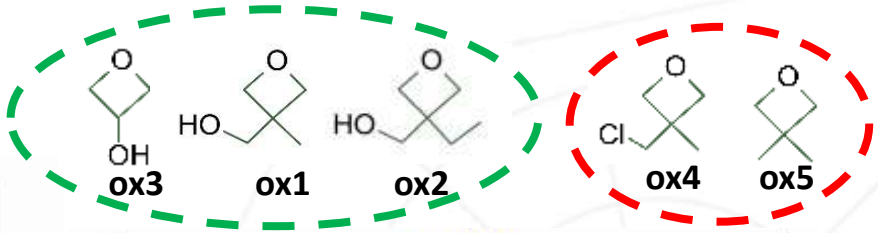



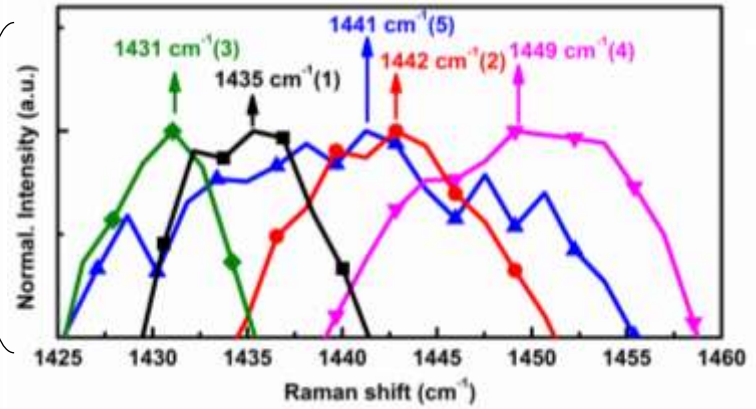

Ox5




# Conformational changes of PEDOT:PSS network: Raman spectra

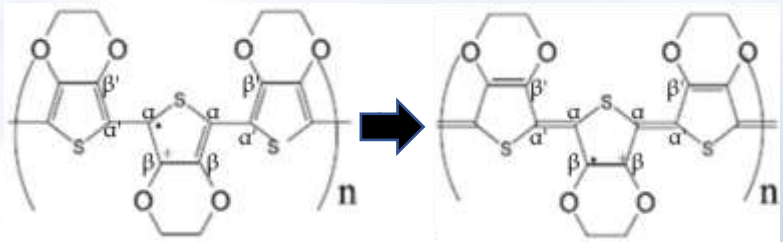



**Red shift of $C_\alpha$=$C_\beta$ peak**

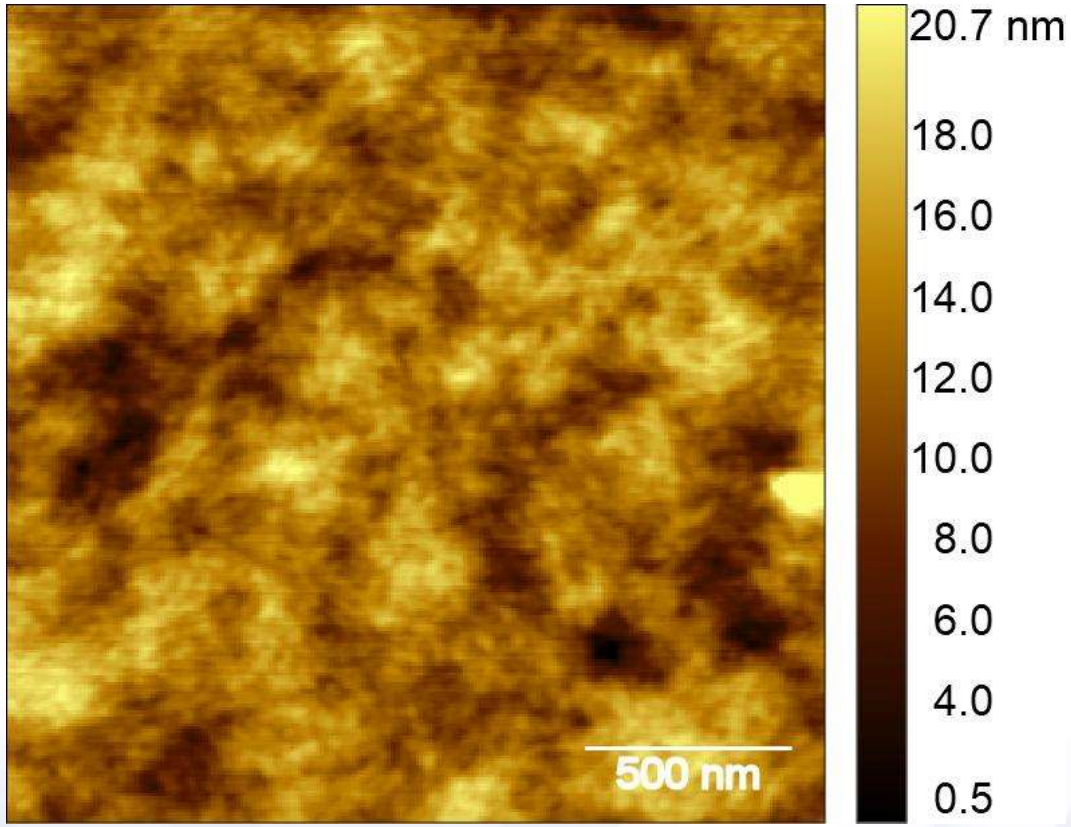
**Benzoid to Quinoid structure transition**



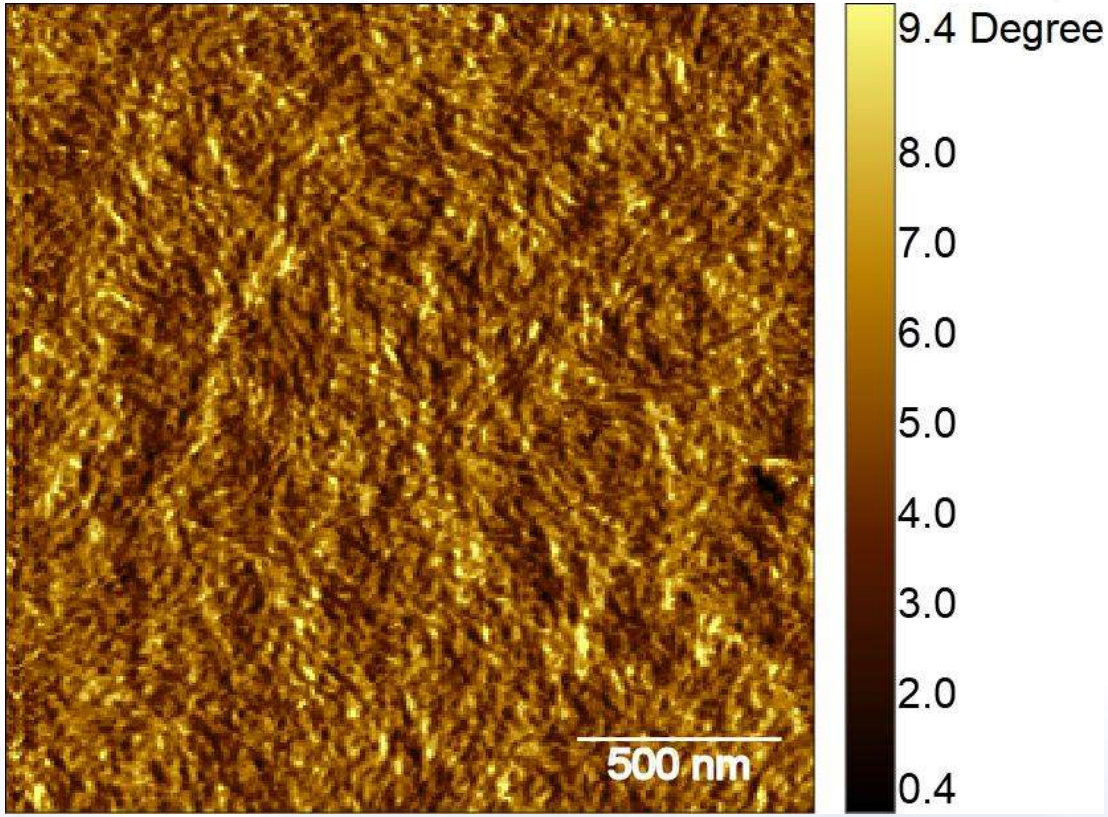
# AFM images of most conducting films

PEDOT:PSS:Ox3 (0.03 v/v) film/glass after water immersion

Topography




Phase



# Conclusions

1. The addition of oxetanes to the as-received PEDOT:PSS dispersion improves the films **structural stability** when in contact with water;

2. The use of Ox3, the most hydrophilic, improves the **conductivity** of PH1000 by more than **3 orders of magnitude** (from ca. 0.1 S/cm to 507 S/cm);

3. This improvement, involving mild conditions, **surpasses that obtained with GOPS** (+EG+DBSA), that reaches a conductivity of ca. 13 S/cm;

4. **Applications** where oxetane-crosslinked PEDOT:PSS films are in contact with aqueous solutions (OECTs and scaffolds for cells culture and electrical stimulation) are in progress.

# Acknowledgments

**Dr. *Ana Charas, Sara M. Jorge, António Ablú, Cátia Príncipe***
Instituto de Telecomunicações

***Dr. Fábio Garrudo***
Instituto de Telecomunicações and iBB - Institute for Bioengineering and Biosciences & Associate Laboratory i4HB - Institute for Health and Bioeconomy, Lisbon

**Prof. *Adelino Galvão, Prof. Luís F. Santos***
Centro de Química Estrutural, Institute of Molecular Sciences and Departamento de Engenharia Química, Instituto Superior Técnico, University of Lisbon

**Financial Support:**
FCT (Portuguese Foundation for Science and Technology) under the projects: PTDC/CTM-REF/28108/2017-POCI-01-0145-FEDER-028108), UIDB/04565/2020 and UIDB/50008/2020.