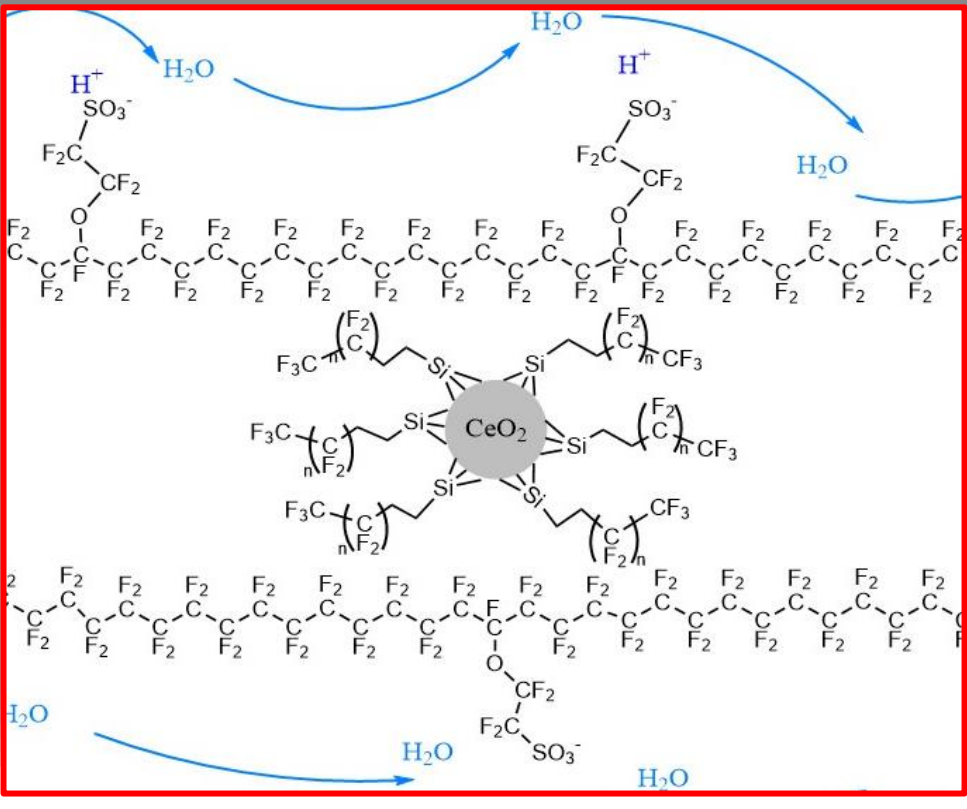


Fluorinated surface decoration of CeO₂ NPs as radical scavengers in nanocomposite Aquivion® PEMs



D. Stucchi¹, A. Di Tolla¹, A. R. Ferrari¹, G. Stucchi¹, T. Caielli¹, S. Saronni¹, M. R. S. Kebria¹, P. Mustarelli¹
¹Department of Material Science, Università degli Studi di Milano Bicocca, Via Cozzi 55, Milano 20125, Italy
d.stucchi7@campus.unimib.it

Graphical abstract

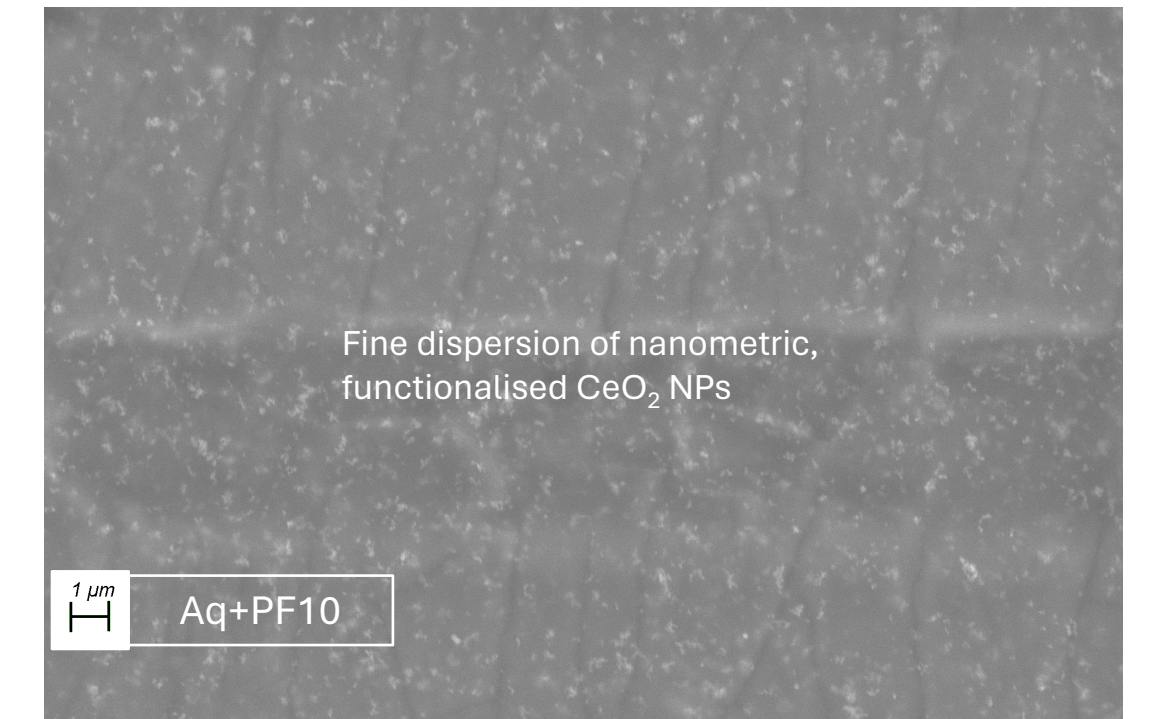
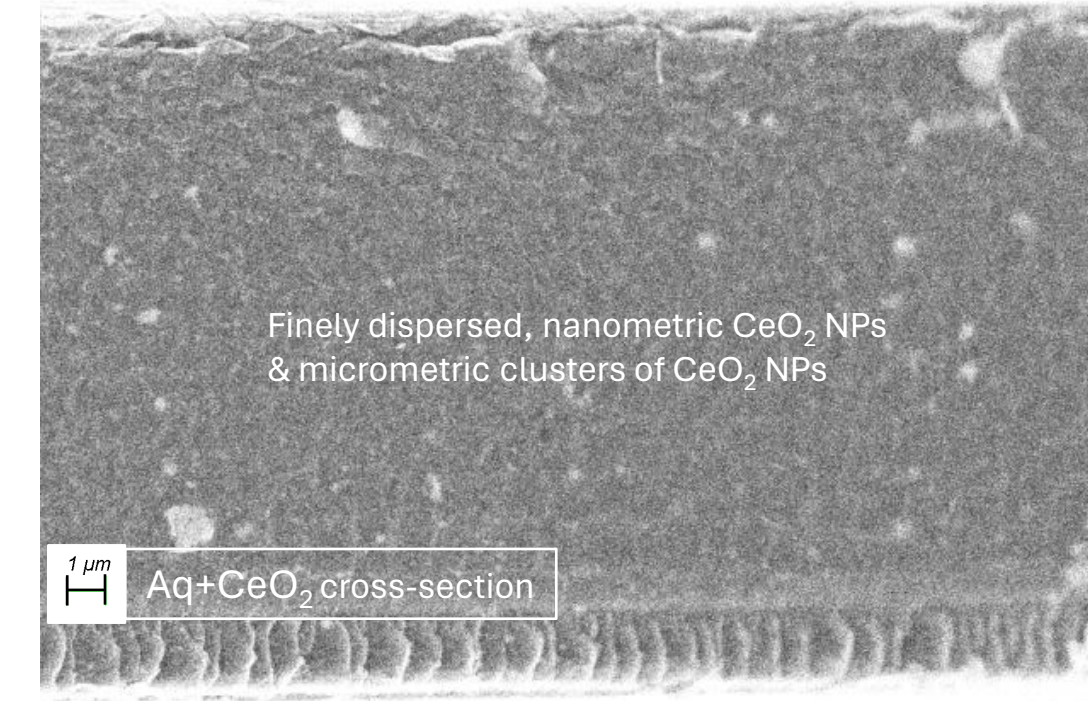
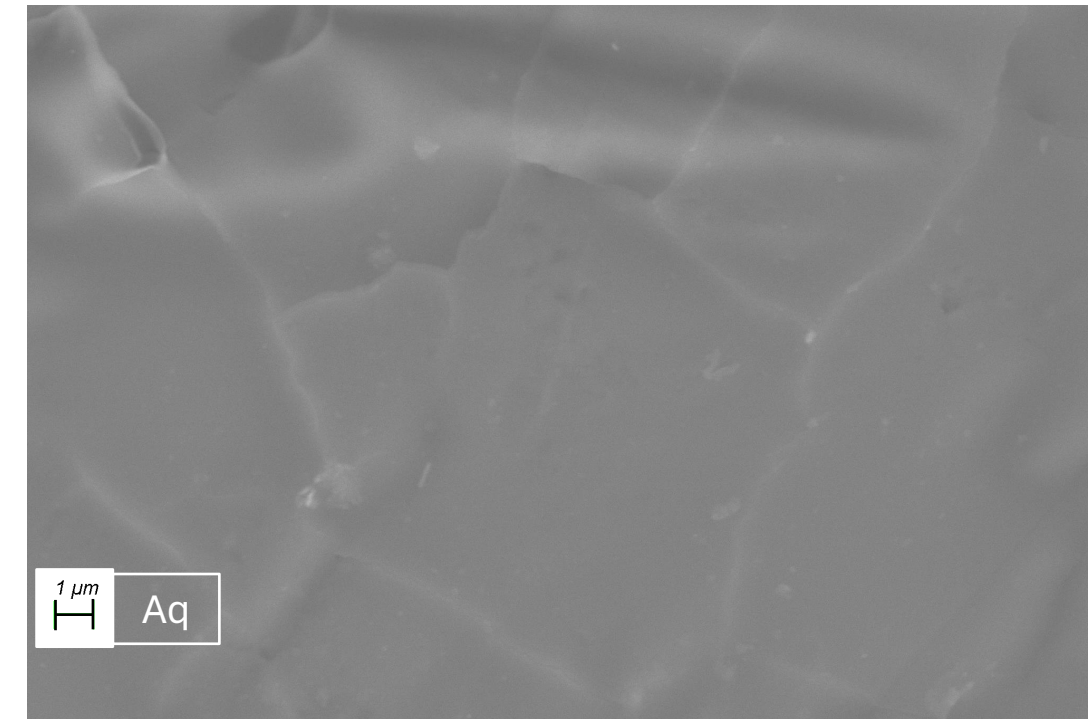
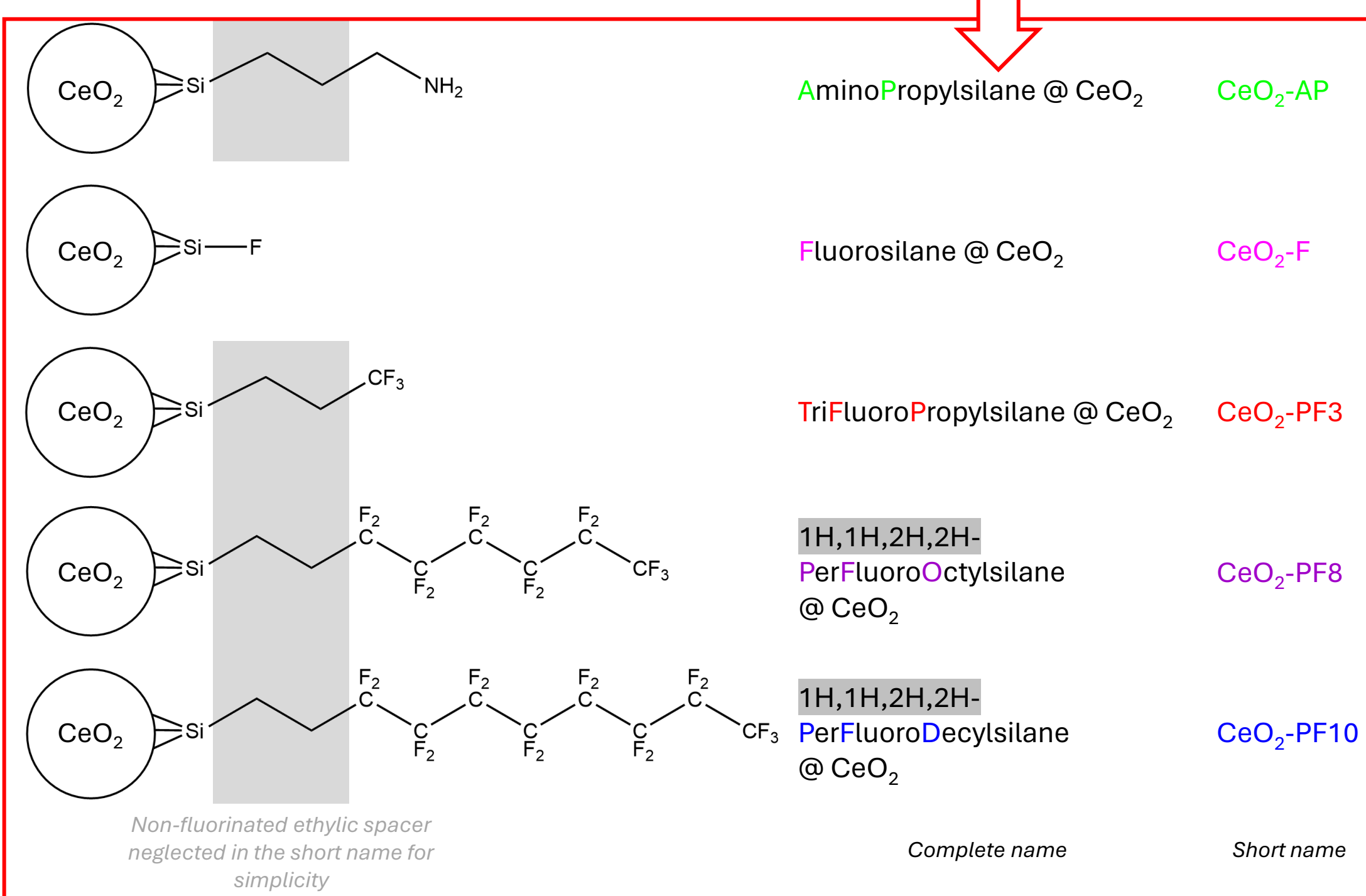
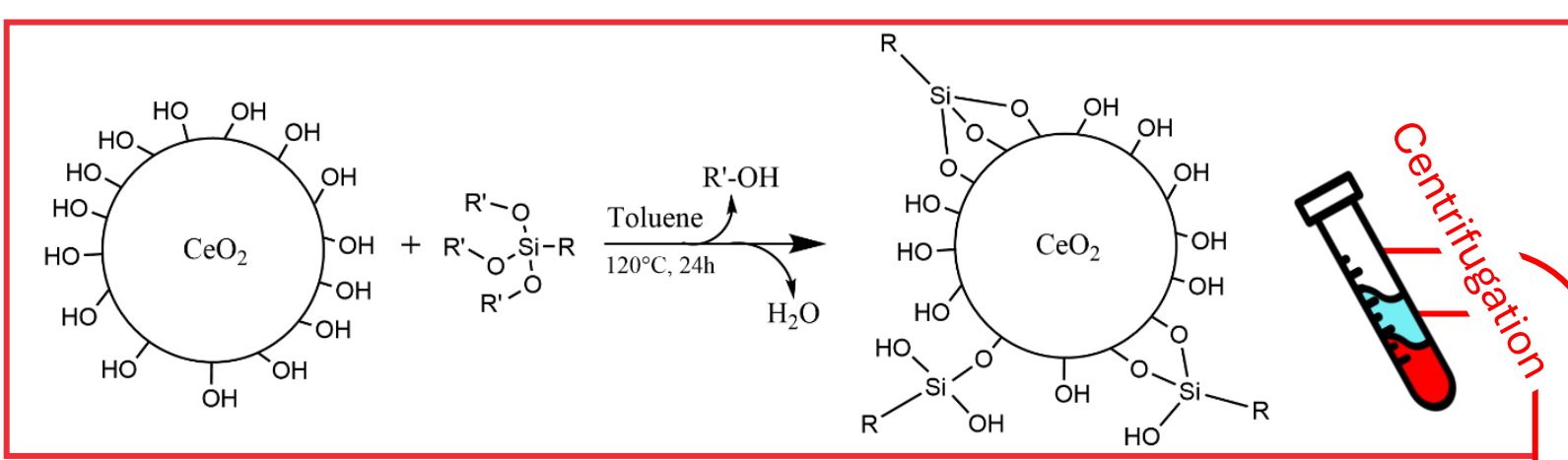


Introduction

The main limit of low temperature fuel cells is their relatively low lifetime caused by the degradation of the polymeric chains due to the attack by radical species ($\cdot\text{OH}$, $\cdot\text{OOH}$) generated at the cathode^[1]. The best strategy to improve the device's lifetime is the introduction of radical scavenger species in the membrane electrode assembly (MEA)^[2]. To enhance the compatibility between the inorganic filler and the organic polymeric matrix, we fabricated, through a grafting of the nanoparticles surface with organosilanes, CeO₂ NPs decorated with 4 different fluorinated moieties. This is expected to anchor them in the hydrophobic domain of the membrane; causing a lower disturbance on the delicate ionic channel network, while also possibly acting as a physical cross-linker and slowing down the oxide dissolution expected in the strongly acidic environment of the PEM. To do so, we dispersed both pristine and functionalized NPs in an Aquivion® matrix and characterized the nanocomposite membranes obtained this way both physicochemically as well as from a more functional point of view.

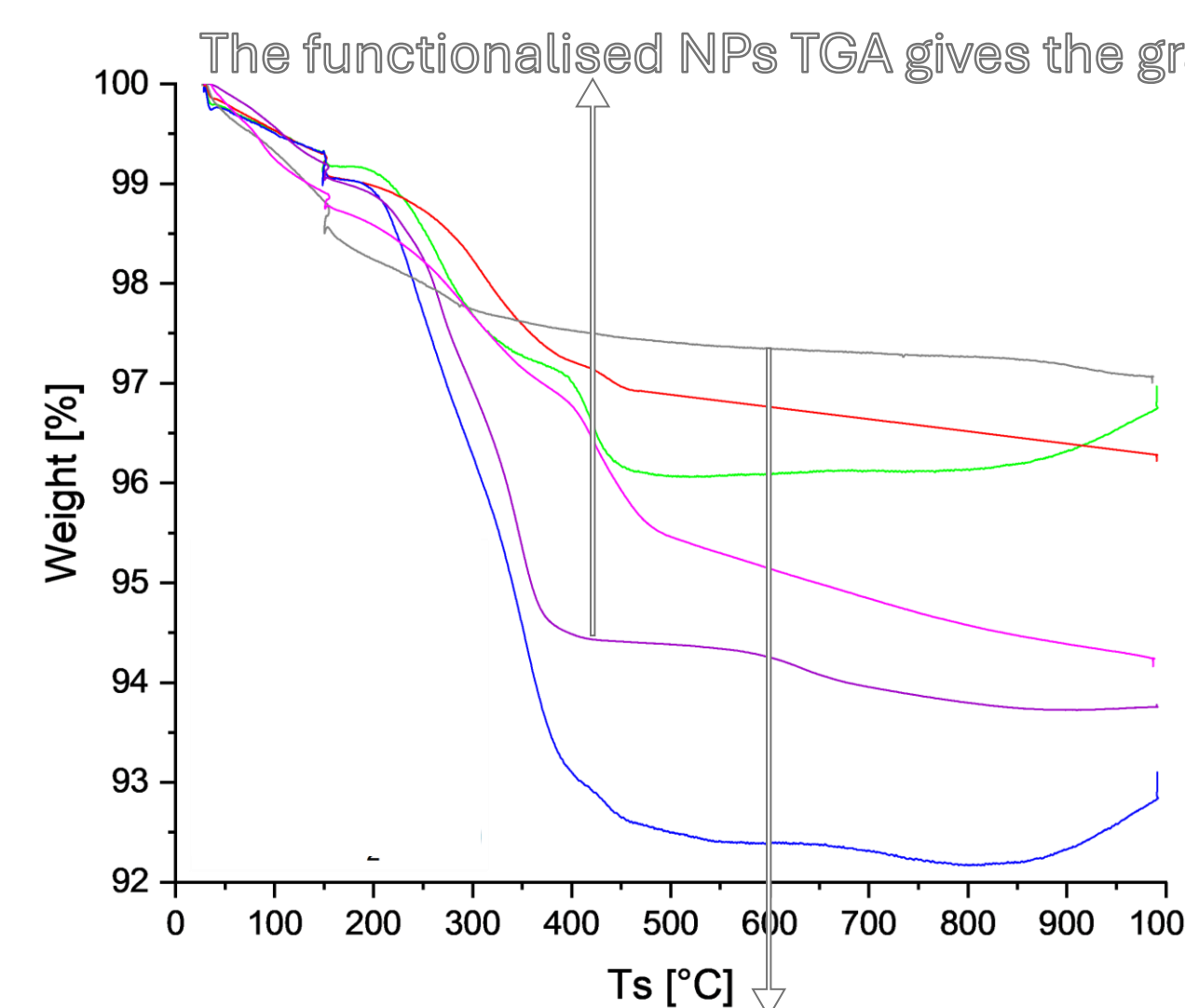
Nanoparticles functionalization

Commercial CeO₂ NPs (25nm diameter) were decorated with different organosilanes. Here are reported the reaction conditions.

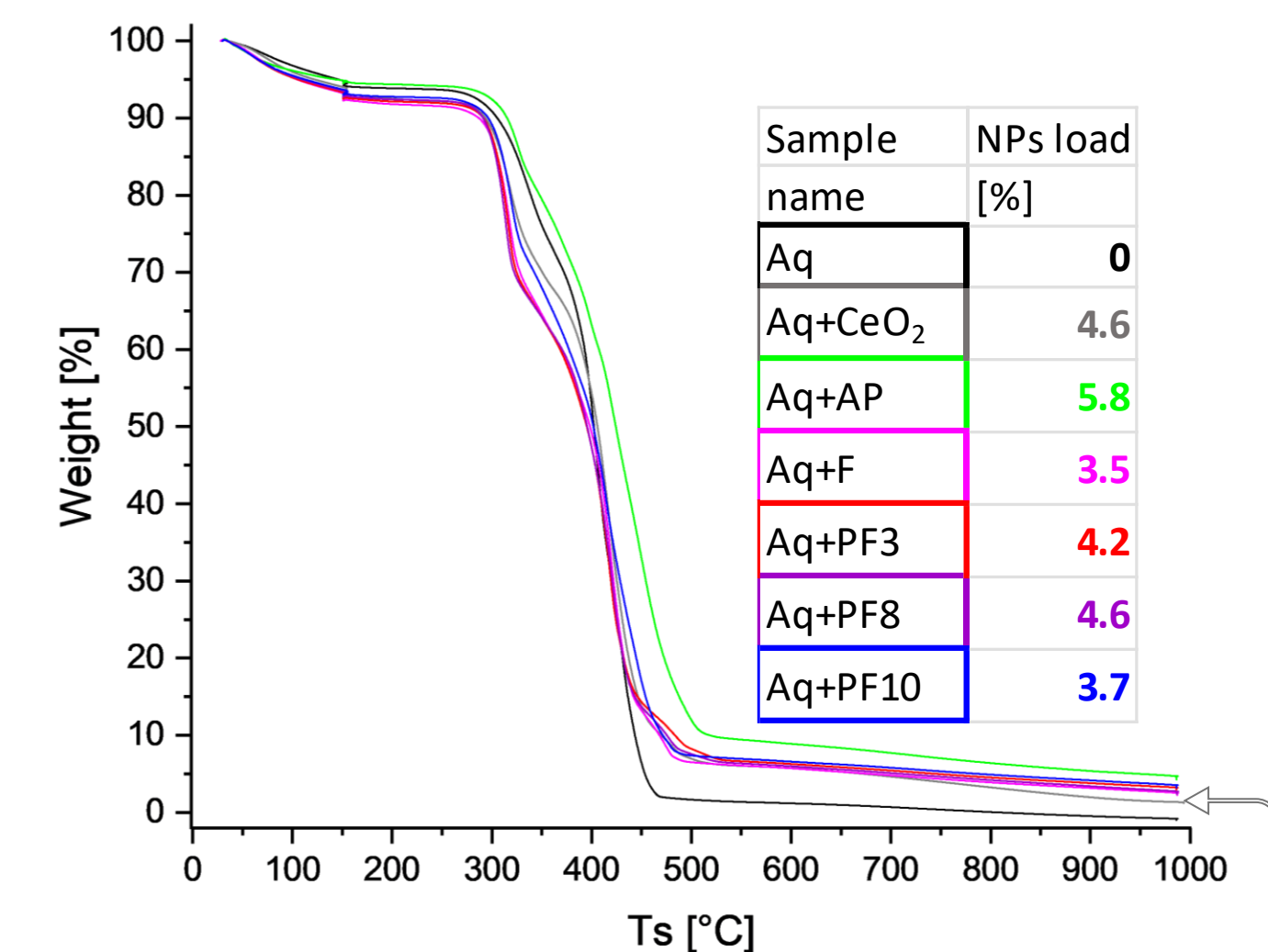


SEM images show a uniform distribution of CeO₂ NPs (as proven by EDX analysis), both in- and through-plane, within the polymeric matrix. Some bigger clusters of agglomerated nanofillers can be seen, however sub-micrometric particles are also visible, especially in Aq+PF10.

Physicochemical characterization



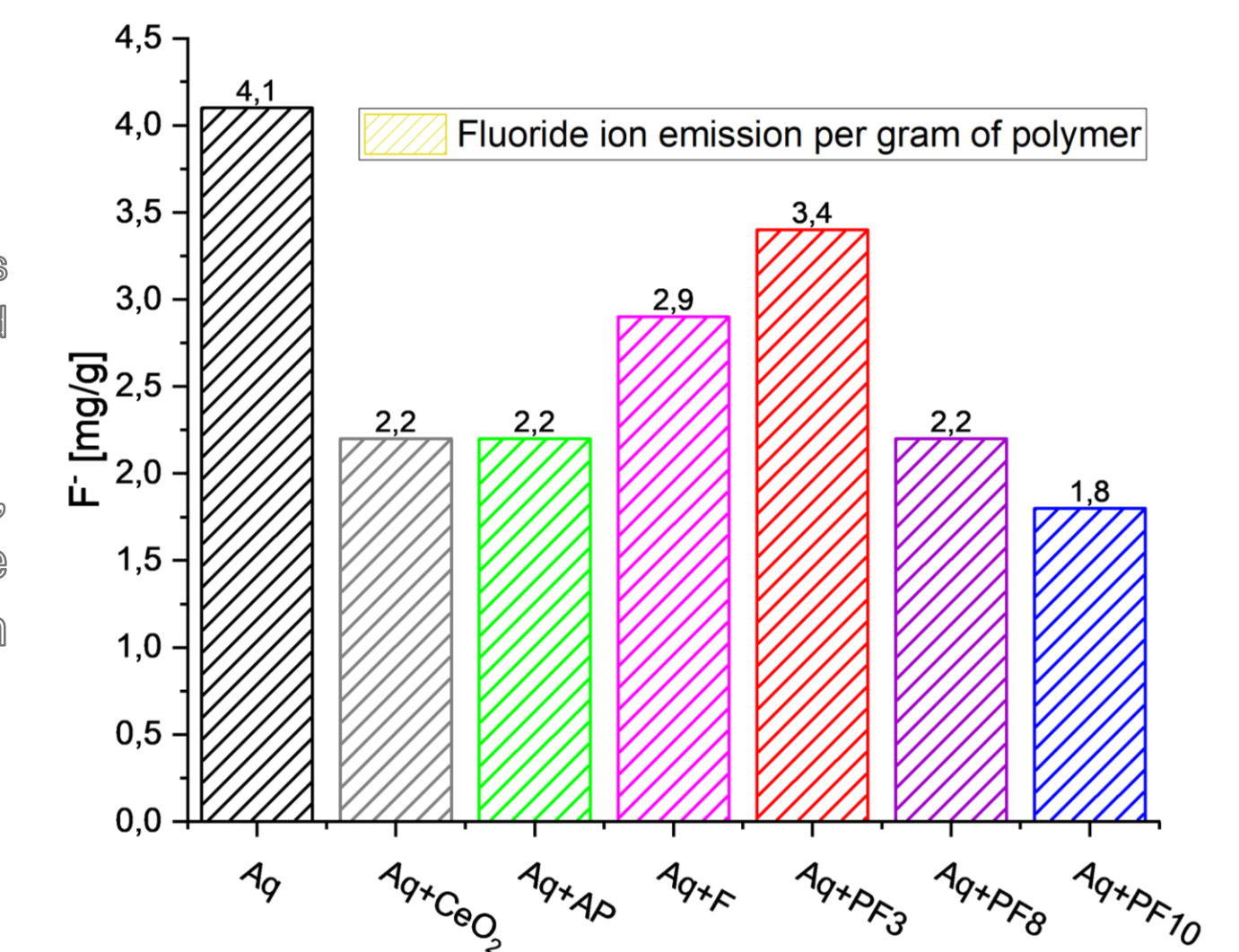
Pristine CeO₂ NPs TGA gives the amount of surface hydroxyl groups, needed to set the desired 1:3 stoichiometry of silane: -OH



The residual weight of nanocomposite membranes at 1000°C indicates the NPs loading; it was aimed at 5% wt/wt.

Fenton test was carried out by immersing the membranes in 20 mL of 1:1 vol/vol mixture of 30% wt/wt H₂O₂ and 400ppm Fe³⁺ in pH 4 H₂SO₄ (aq) solution for 4h at 80°C.

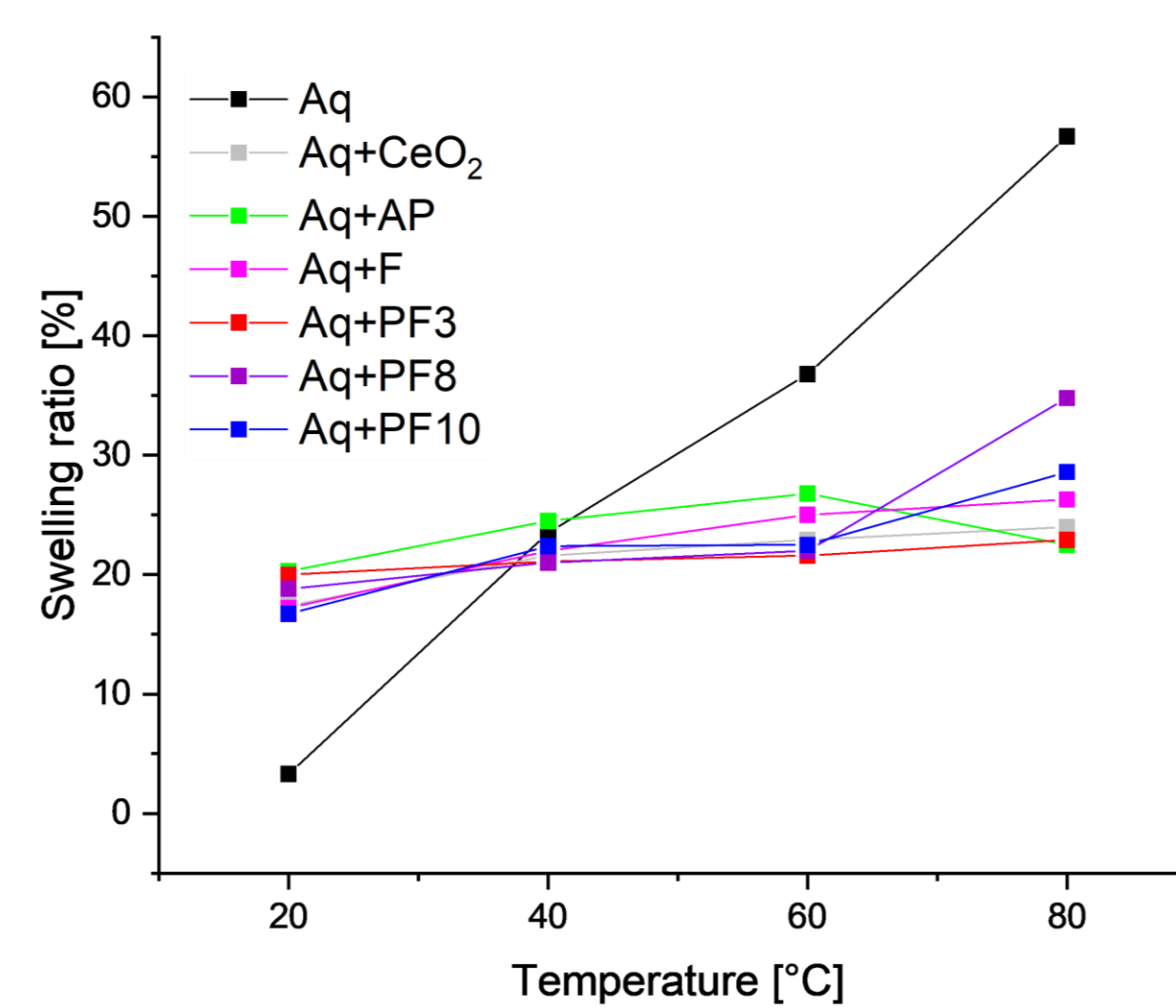
A reduction of roughly 50% in the amount of F₂ generated as a result of the attack on the polymeric matrix of radical species, can be seen for most nanocomposite membranes.



Membrane preparation

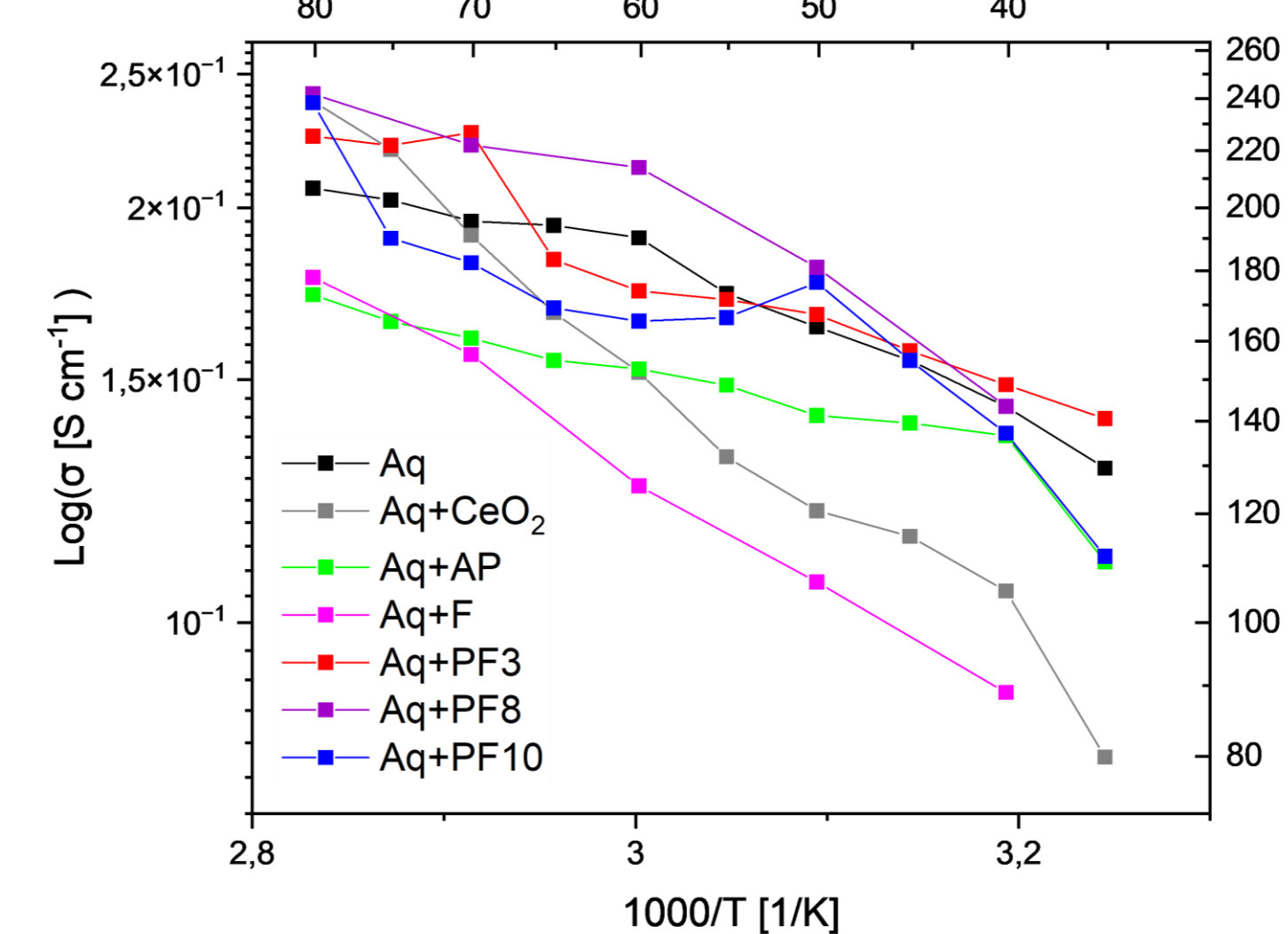
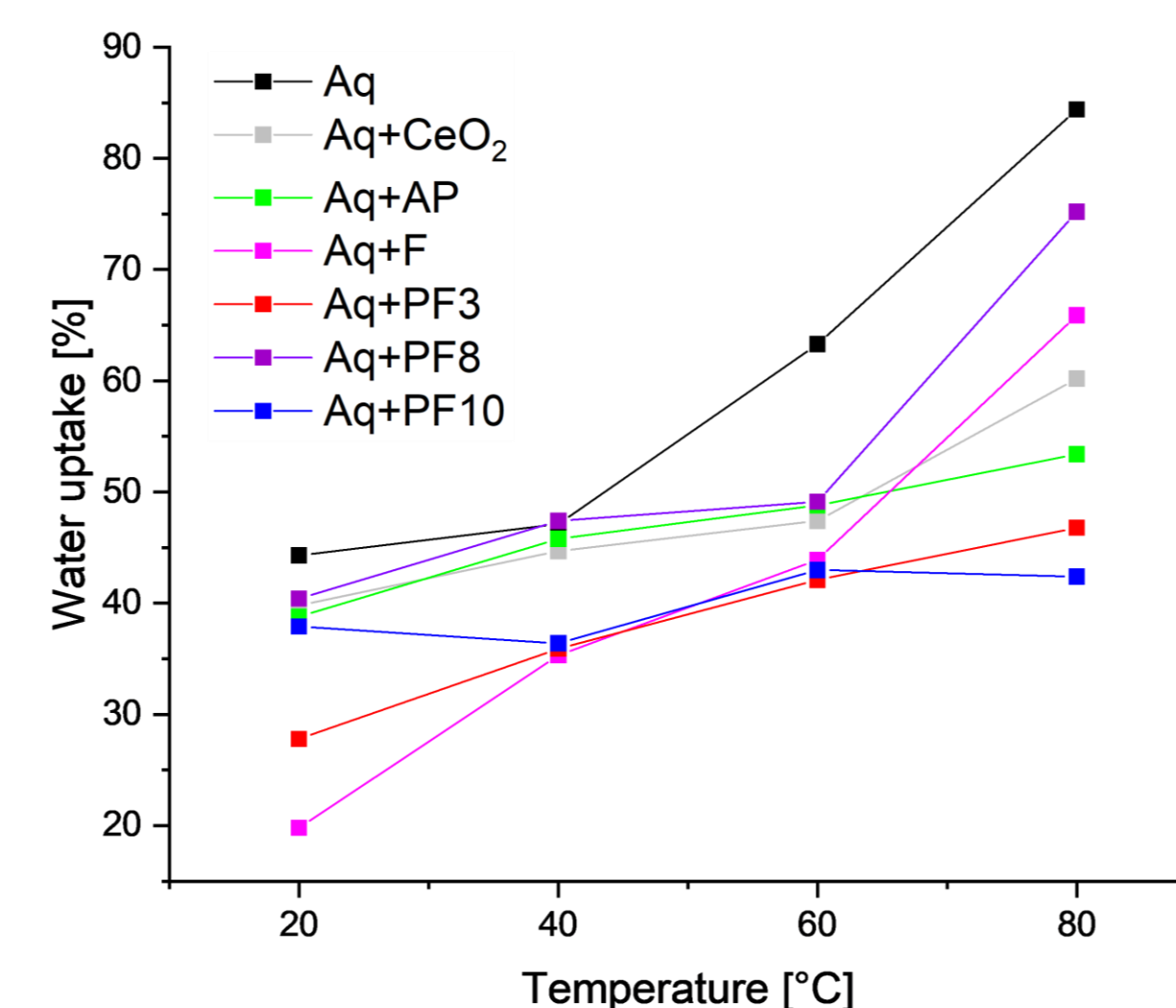
- Aquivion® → Aq
- Aquivion®+CeO₂ NPs → Aq+CeO₂
- Aquivion®+CeO₂-AP → Aq+AP
- Aquivion®+CeO₂-F → Aq+PF
- Aquivion®+CeO₂-PF3 → Aq+PF3
- Aquivion®+CeO₂-PF8 → Aq+PF8
- Aquivion®+CeO₂-PF10 → Aq+PF10

Substance	Amount [%]
Aquivion®	19.8
Water	50
1-propanol	24.8
DMSO ₂	4.5
NPs	1



Water management measurements show a lower S.R., as temperature increases, in nanocomposite membranes when compared to pure Aquivion®, despite comparable, albeit lower, values of W.U.

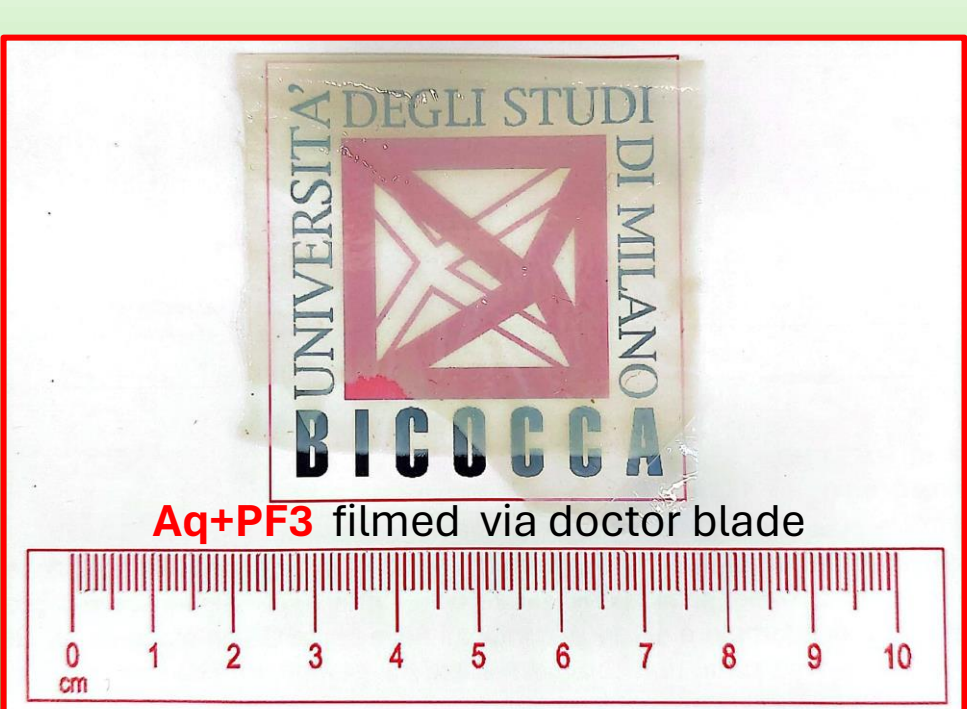
Functional characterization



In plane protonic conductivity is comparable to pure Aq, especially in samples with fluorinated NPs

Conclusion & further prospects

We have successfully decorated the surface of commercial nanoparticles of cerium oxide with different organosilanes, as proved by TGA analysis, four of which carry fluorinated moieties to improve the compatibility with the polymer. With those, we fabricated 7 Aquivion®-based membranes, six of which are nanocomposite, loaded with 4-5% radical scavenger. The dispersion of filler proved to be homogeneous, and the PEMs are more resilient to the attack of radical species, particularly the ones decorated with the longer perfluorinated chains. All nanocomposite samples also suffer from a lower S.R., especially at higher temperature, when compared to pure Aquivion® membranes, while absorbing a similar amount of water and achieving values of conductivity comparable to pure Aquivion®. Once again this is particularly true in the case of membranes with particles decorated with fluorinated NPs, thus proving our hypothesis of causing a lower disturbance on the ionic channels network. The preparation of a CCM and performing some tests in an actual Fuel cell setup are the next step of our research, paired with a more in depth-study on the fluoride emission in Fenton reagent overtime.



References

- [1] Ren et al. Prog. Energy Combust. Sci. 2020, 80, 100859
- [2] Akrouf et al. Membranes. 2020, 10, 208
- [3] Mezzomo et al. Electrochim. Acta. 2022, 411, 140060

Acknowledgments

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