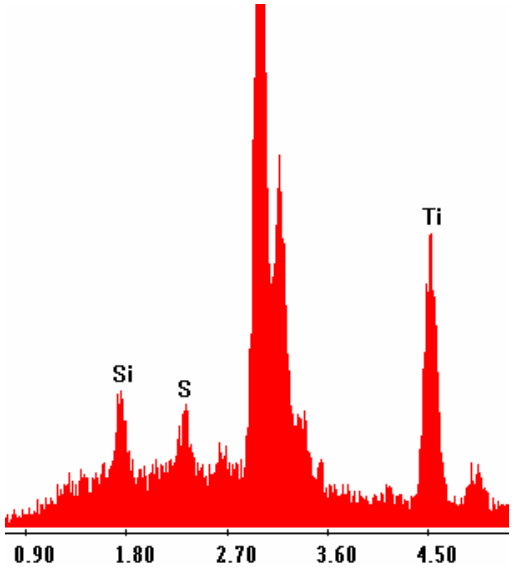
Electronic Supplementary Information

Ordered Mesoporous Hybrid Thin Films with Double Organic Functionality and Mixed Oxide Framework

P.C. Angelomé and G.J.A.A. Soler-Illia

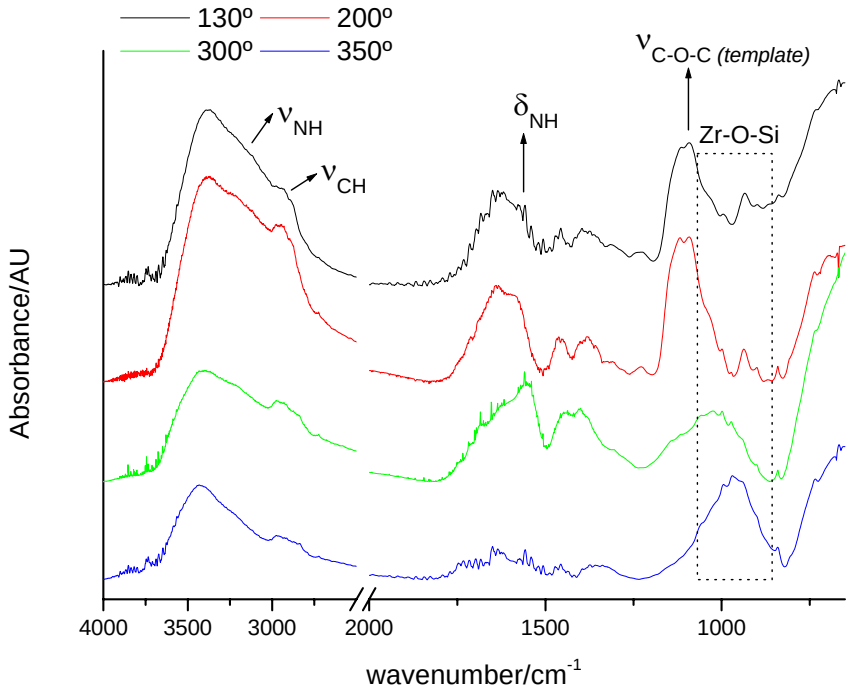
ESI 1: EDS spectra of TSS scratched films



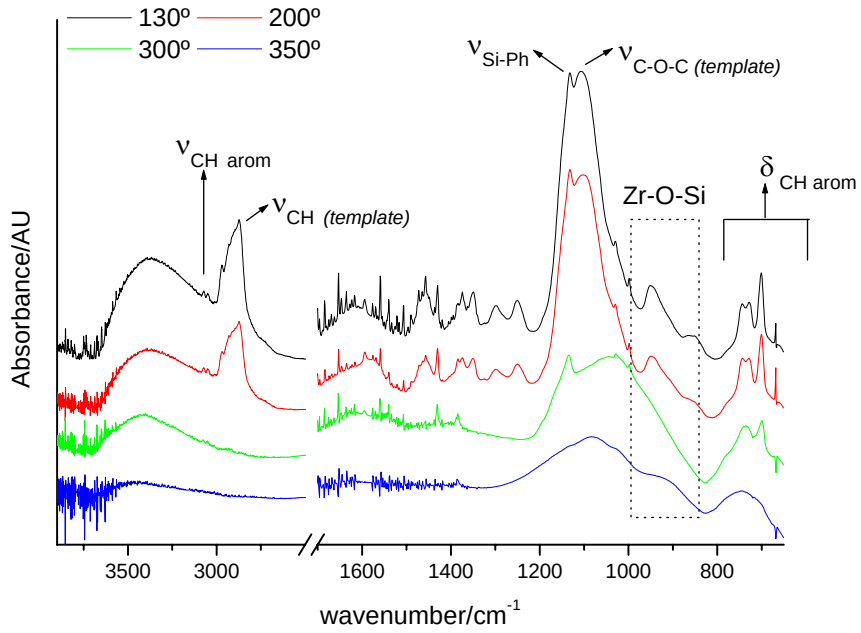
As FTIR measurements don't give information of the mercaptopropyl-substituted systems (visualization of bands is difficult, particularly ν_{SH}, which has a very low intrinsic intensity) EDS is a valid alternative in order to characterize the system.
EDS of TSS scratched film extracted overnight with ethanol shows the presence of S, Si and Ti. The S peak is present in the material even after the extraction process, showing that mercaptopropyl is incorporated to the material and remains in the film after the template elimination.

ESI 2: Characterisation of amino and phenyl substituted films

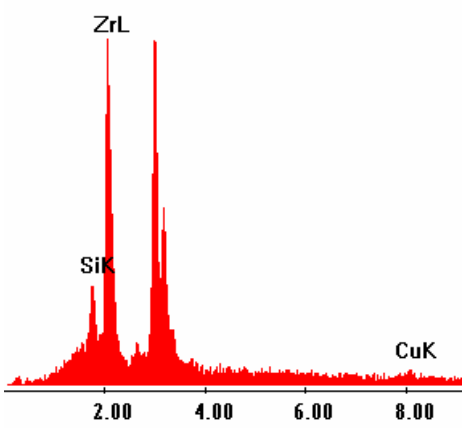
- *Detailed FTIR spectra of ZSA91 (dip coated on KBr pellets) with different thermal treatments*



Bands corresponding to the template (ν_{CH} at 2850-2920; $\nu_{C\text{-}O\text{-}C}$ at 1038 and 1118 cm^{-1}) are lost upon thermal treatment until 300ºC, while NH (ν_{NH} at 3200 cm^{-1}, δ_{NH} at 1570cm^{-1}; broad primary amine band at 650-895 cm^{-1}) and a fraction of the CH species (remaining CH bands at 2850-2920 cm^{-1}) are conserved until 350ºC indicating that the propylamino dangling groups are conserved. Si-O-Zr bands are observed at 960-1000 cm^{-1} and no Si-O-Si bands (1000-1200 cm^{-1}) are observed, ruling out phase segregation.



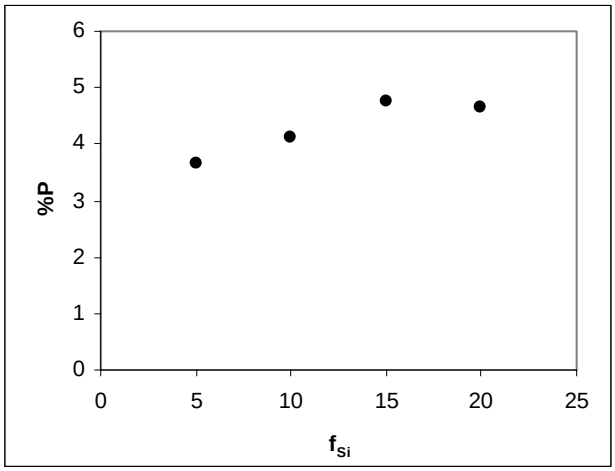
ESI 3:Cu(II) adsorption in ZSA82 as assessed by EDS



Si/(Zr+Si)	0.24
Cu/Si	0.24

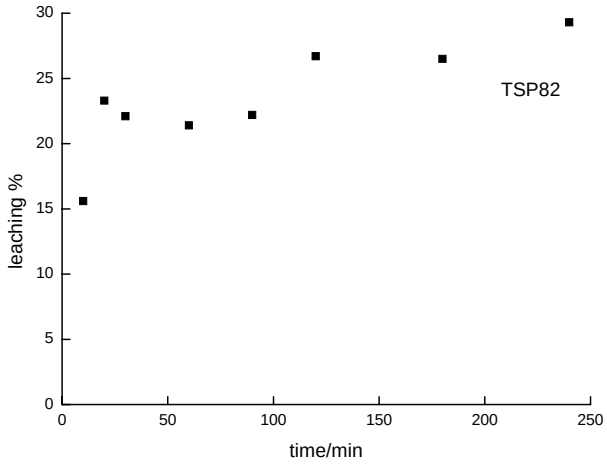
After 200min immersed in a Cu(II) solution (150ppm), ZSA82 film presents a Cu/Si relation of 0.24, indicating the pores and the functions attached to them are accessible to cations. Copper(II) does not adsorb on the surface of SiO_2 or ZrO_2 films in the same conditions, showing that the amino function is essential to cations adsorption.

ESI 4: DHDP adsorption on TSA systems as a function of f_{Si} followed by EDS



In TSA films, the trend in DHDP adsorption as a function of f_{Si} is opposite to the one found in phenyl-Si/Ti systems. EDS (and also FTIR) shows that in this system DHDP uptake increases with decreasing Ti content, indicating that the amino (ammonium) dangling groups play a fundamental role in the incorporation of the phosphate.

ESI 5: Leaching of DHDP in TSP films as assessed by FTIR



DHDP leaching in TSP82 system, showing the same kind of results as TSA systems.
About 20% of the DHDP weakly attached to the pore surface is lost quickly (within the first 30 minutes), but the rest of the function remains attached, indicating that the second function R' can be firmly attached to the pore surface through phosphate anchoring groups.