Supplementary Information (SI) for Nanoscale.

Pyrene Monomer-Excimer Dynamics to Reveal Molecular Organization in Mesoporous Hybrid Silica Films.

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Supporting Information

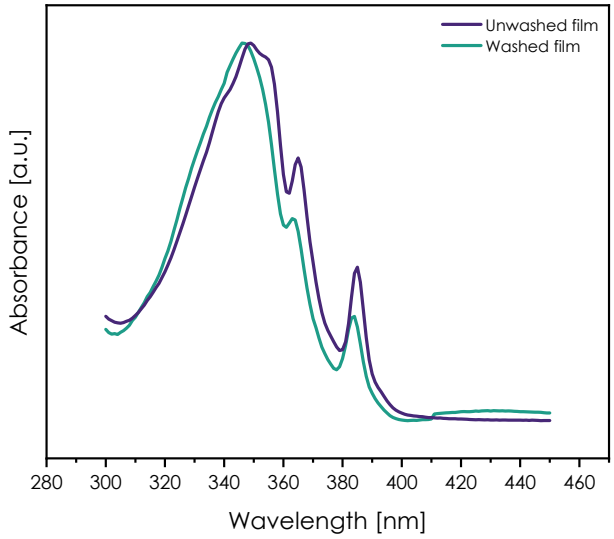


Figure S1: UV-Vis spectra for unwashed and washed film Py1.

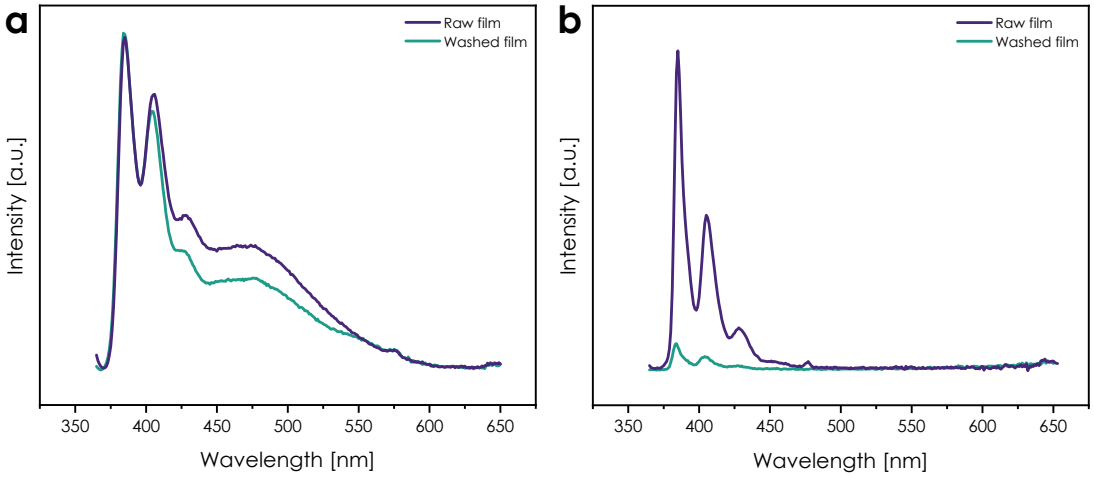


Figure S2: Fluorescence spectra of reference samples. **a**, Dense film prepared without the templating agent. Due to a weak signal baseline correction was done for these spectra. **b**, Mesostructured film doped with free pyrene molecules.

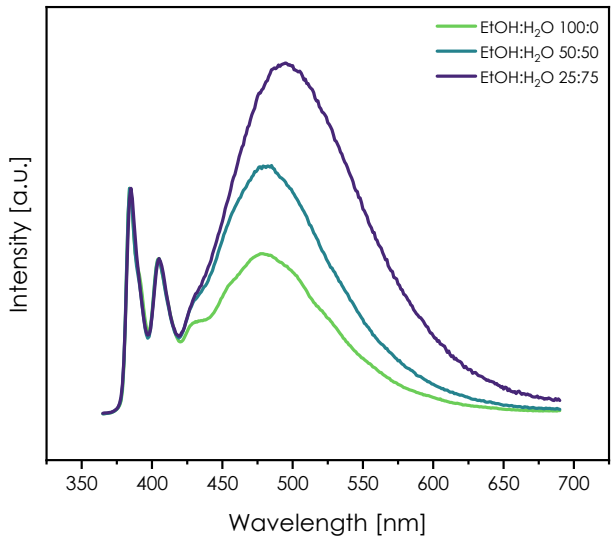


Figure S3: Influence of the polarity of the solvent on excimer formation. The film was immersed in water-ethanol mixtures of different volume ratios.

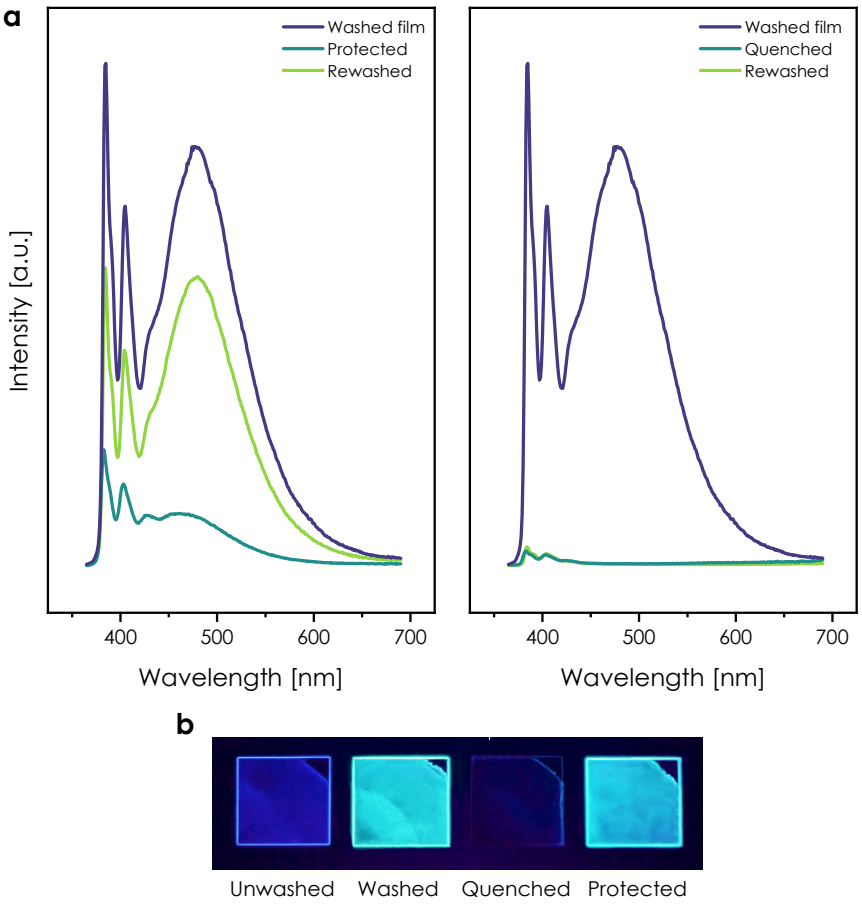


Figure S4: Quenching of the fluorescence emission for Py1 films. **a**, Spectra for protected (left) and unprotected (right) films exposed to photooxidation. **b**, Visual evolution of fluorescence after the photolysis.

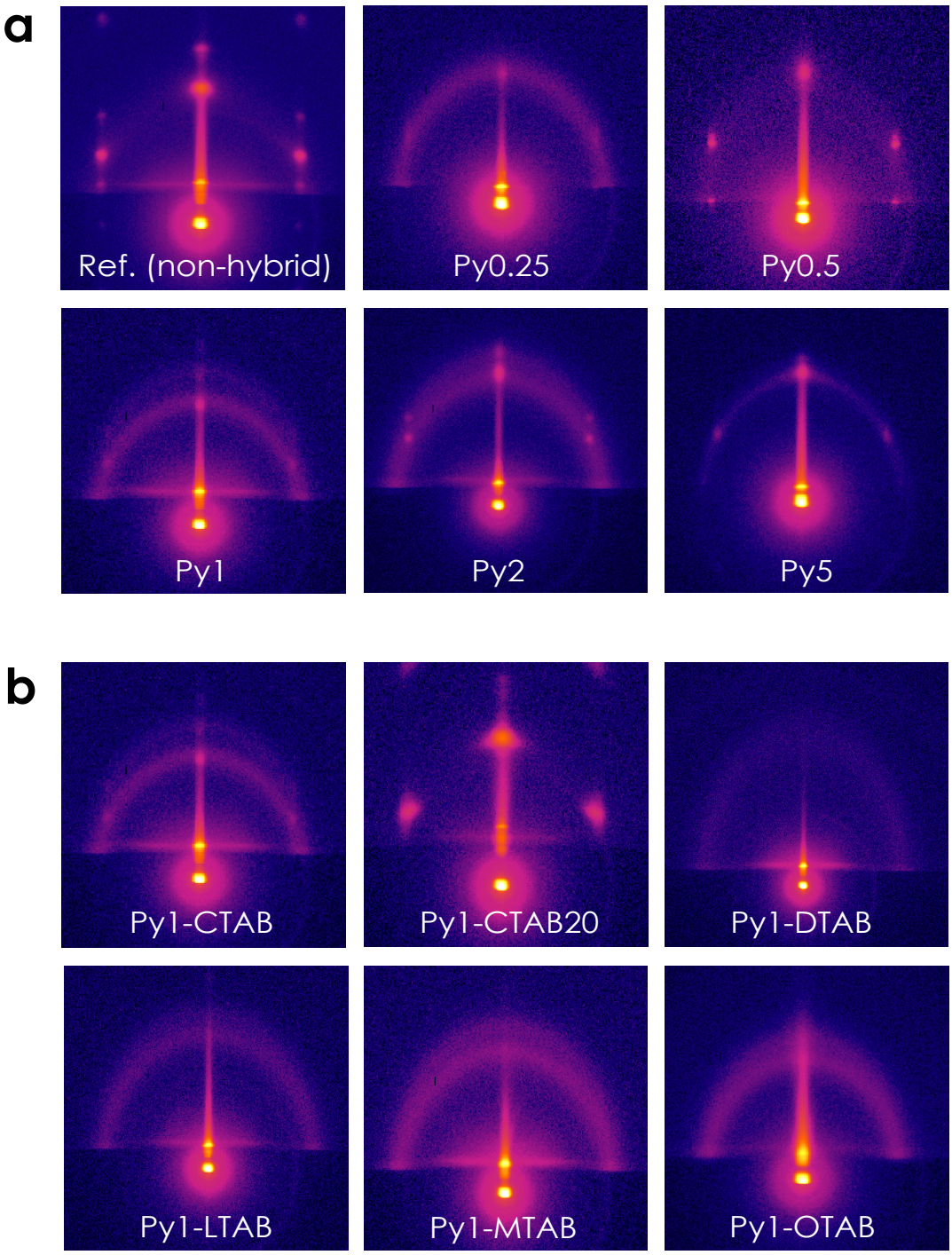


Figure S5: GI-SAXS patterns of hybrid thin films. **a** Samples with increasing PyTES concentration. **b** Samples containing 1 mol% of PyTES prepared with different templating agents.

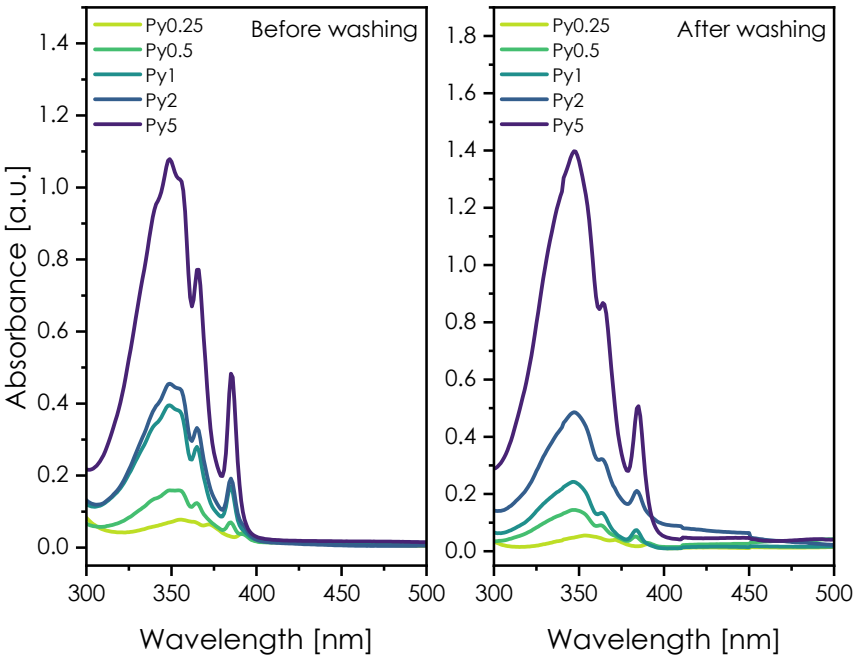


Figure S6: Full UV-Vis spectra of films with increasing concentration of PyTES, before (on the left), and after the template removal (on the right).

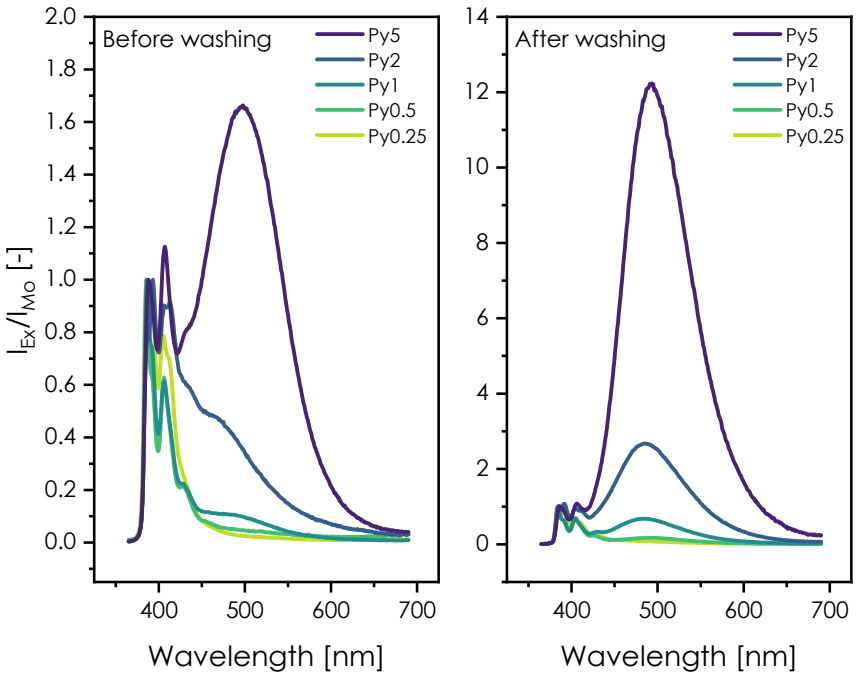


Figure S7: Full fluorescence spectra of films with increasing concentration of PyTES, before (on the left), and after the template removal (on the right)

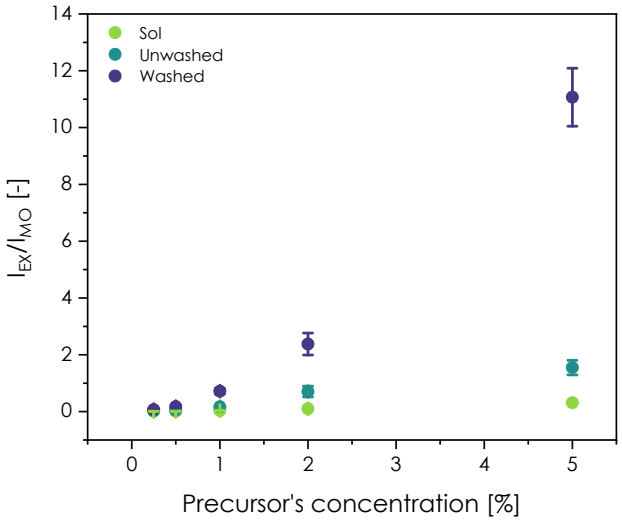


Figure S8: Evolution of I_{Ex}/I_{Mo} on linear scale.

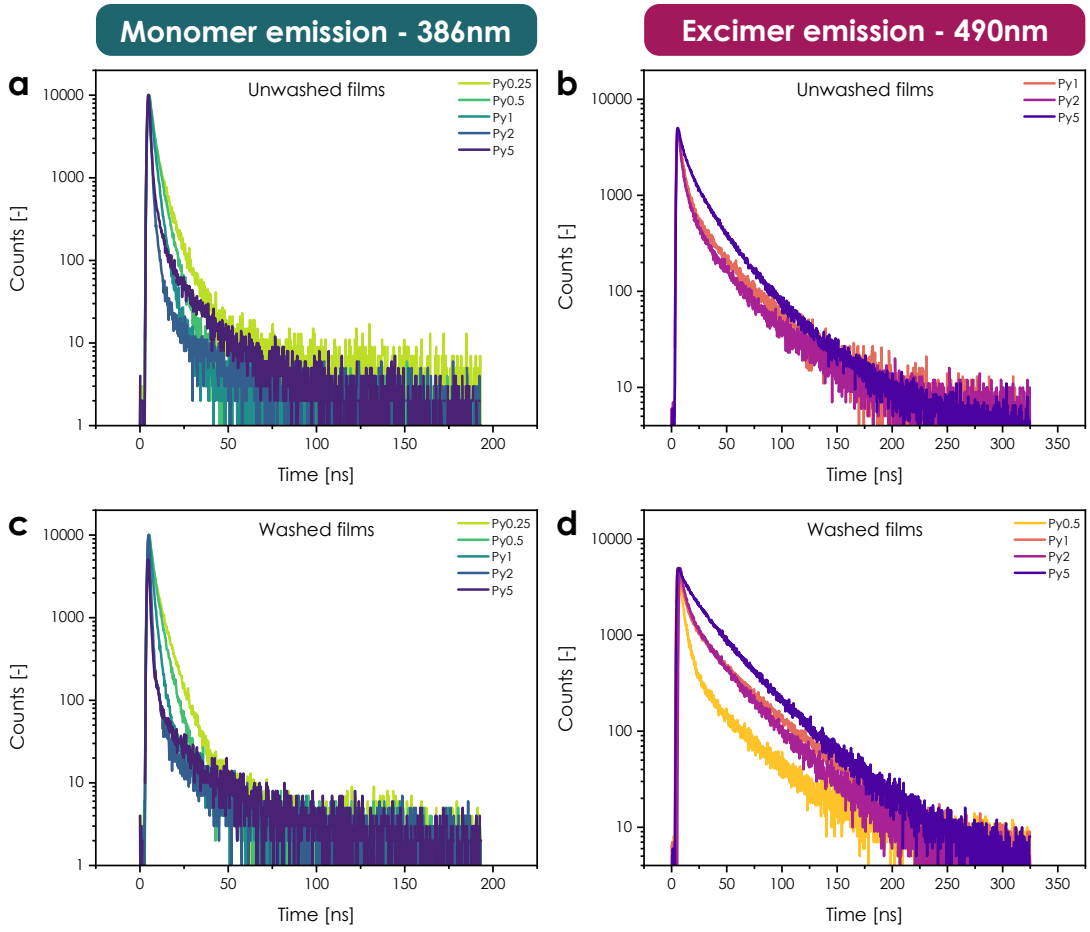
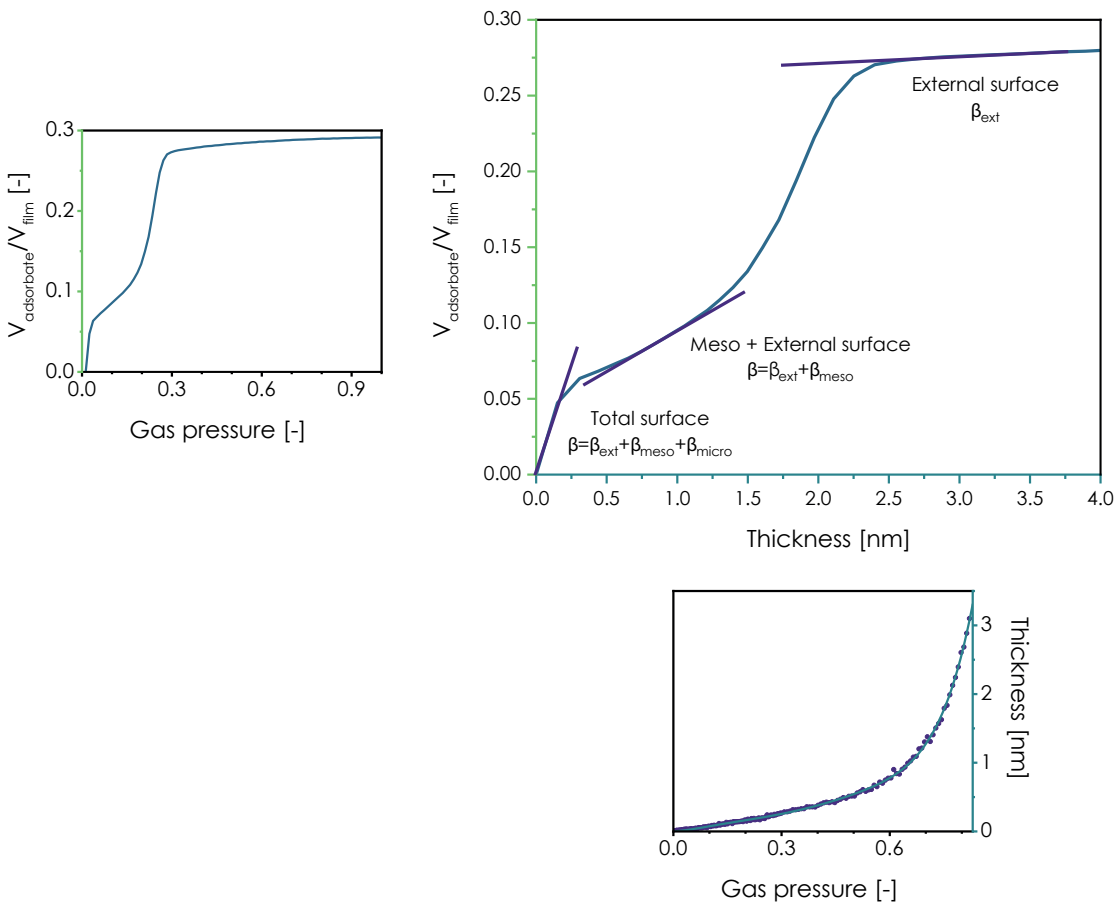


Figure S9: Emission decay recorded for monomer at 386 nm (**a**, **c**) and for excimer at 490 nm (**b**, **d**)). Decays of unwashed and washed films are presented in the top and bottom plots, respectively.

The t-plot method



Concept of the t-plot method used to calculate the mesoporous surface area from the EEP adsorption-desorption isotherm (left plot). The reference curve (bottom plot) was obtained by measuring the thickness of isopropanol adsorbed onto a dense silica layer of 26.8nm (thermal SiO_2 oxide grown from a silicon wafer). We determined the alcohol thickness from spectroscopic ellipsometry measurements by assuming that the adsorbed alcohol has the same optical properties as bulk alcohol. Then, the thickness t of alcohol was plotted as a function of the relative pressure of alcohol and a polynomial function $(126.82 \cdot\ x^6 - 233.02 \cdot\ x^5 + 164.88 \cdot\ x^4 - 53.416 \cdot\ x^3 + 8.2157 \cdot\ x^2 + 0.3221 \cdot\ x)$ was fitted to experimental points. The final t-plot combines these two graphs and shows the isotherm

as a function of the thickness of the layer at a given pressure. Linear regions of the t-plot correspond to the adsorption occurring in the same way as for the flat substrate, while capillary condensation results in a non-linear regime. The slope β of the fitted line is equal to the surface area at which the adsorption occurs. At low relative pressures, it includes micro- and mesopores, as well as at the external surface of the film. Micropores get filled as first, hence the second regime corresponds to adsorption in mesopores and external surfaces. Finally, after the capillary condensation in these pores, adsorption can occur only on the external surface. The specific surface area of mesopores can be obtained as the difference between the two last β coefficients.