Supporting Information File

Proton and calcium-gated ionic mesochannels: phosphate-bearing polymer brushes hosted in mesoporous thin films as biomimetic interfacial architectures

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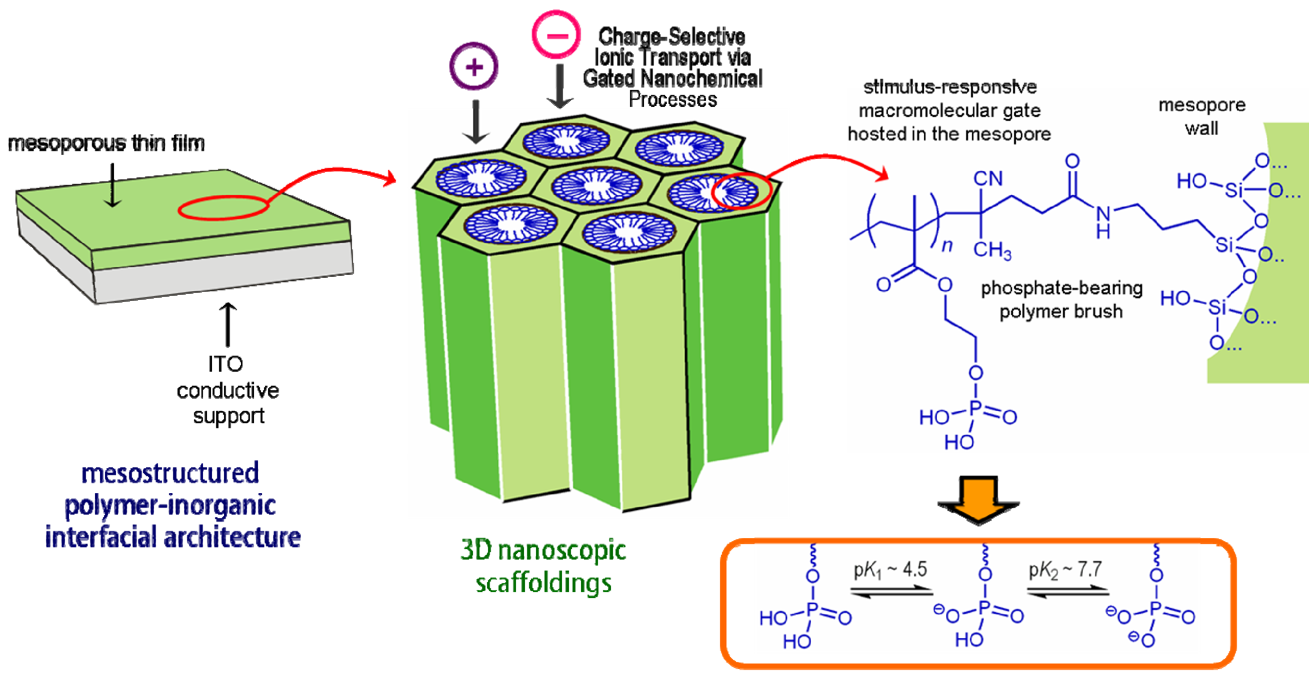

FIGURE S1. Simplified schematic depiction corresponding to the modification mesoporous thin films with poly(methacryloyl ethylene phosphate) brushes. The chemical structure of the polymer brush and the equilibrium associated to the pH-dependent behaviour of the polyprotic monomer units are also indicated. The pK values were taken from Zhang et al. *Anal. Chem.*, **2000**, *72*, 1973.

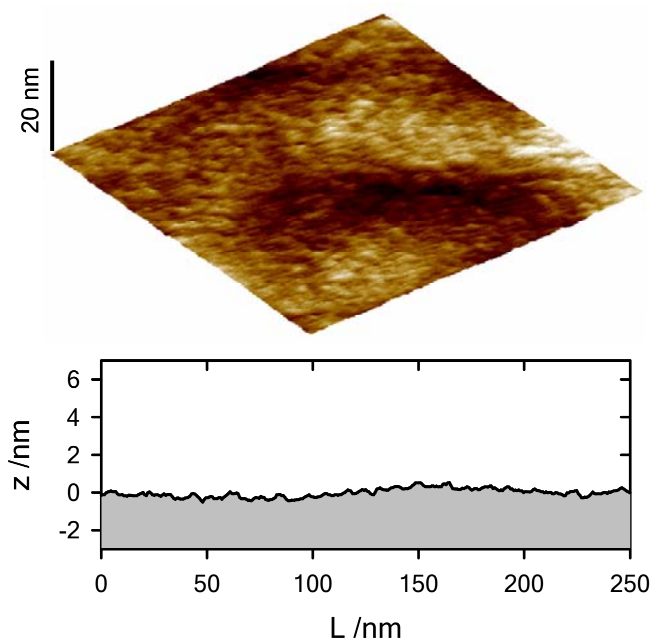

FIGURE S2. AFM three dimensional topography image and respective cross section of as-synthesized mesoporous thin film (tapping mode; maximum z-scale: 20 nm; scan size: 250 nm x 250 nm).

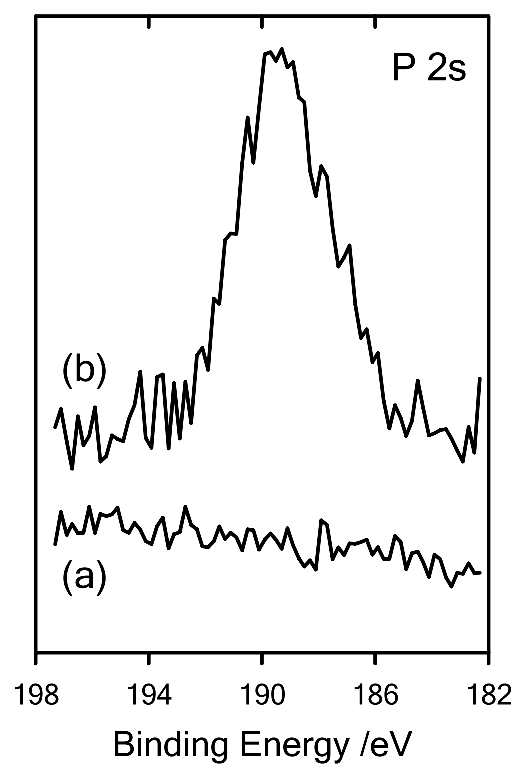

FIGURE S3. XPS spectra corresponding to the chemical characterization of mesoporous silica films prior to (a) and after (b) the surface-initiated polymerization of PMEP brushes.

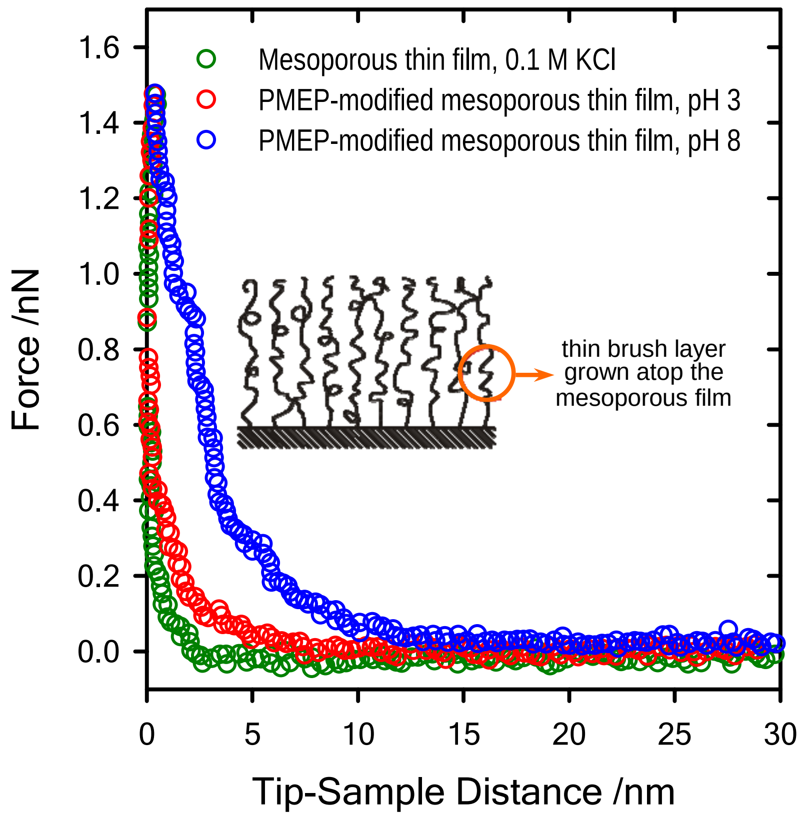

FIGURE S4. Representative force-distance approach curves obtained in 0.1 M KCl between a Si_3N_4 AFM tip and a mesoporous thin film (green), MEP-modified mesoporous film at pH 3 (red) and MEP-modified mesoporous thin film at pH 8 (blue). The force-distance plot of the mesoporous thin film shows the expected compressive curve of a hard surface (green dots). The blue curve in the figure shows the repulsive forces observed during the approach step obtained in 0.1 M KCl solution at pH 8. This repulsion is typical of an end-grafted polymer under compression in a good solvent (see Taunton *et al.*, *Nature*, **1998**, *332*, 712). The monotonically increasing repulsive forces, which are typical of a polymer brush under compression in a good solvent, are caused by the reduced configurationally entropy of the polymer chains which increases osmotic pressure upon approach of the surface. This is an indication that the polymer film behaves as a brush at pH 8. The force curve obtained at pH 3 shows a weak repulsion before the tip comes into hardwall repulsion with the underlying mesoporous silica substrate. Given the lack of repulsion on the AFM tip, this suggests that the polymer chains are no longer in a stretched state but forming more compact “collapsed” nanoaggregates.

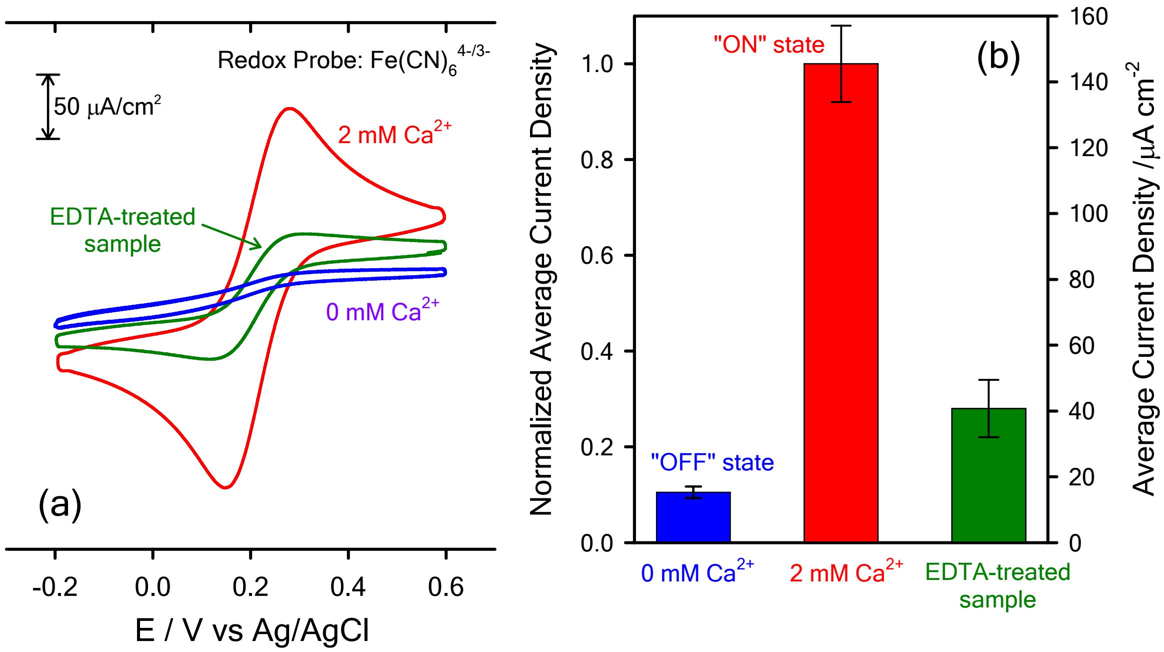

FIGURE S5. (a) Cyclic voltammetric studies of molecular transport through PMEP-modified mesoporous thin films in the presence of Ca^{2+} ions (2 mM $CaCl_2$ + supporting electrolyte) (red trace) and after treating the Ca^{2+}-complexed mesoporous substrate with EDTA. The voltammetric response in the absence of Ca^{2+} has been included as a comparative reference system. Scan rate: 200 mV/s. Supporting electrolyte: 1 mM $Fe(CN)_6^{3-}$ (redox probe) + 0.1 M KCl (pH 8). (b) Histograms showing (normalized and average) variations in electrochemical current densities arising from the influence of different chemical stimuli on the molecular transport of redox probes through the PMEP-modified mesopores.