**Supplementary Electronic Information**

**Facile molecular design of hybrid functional assemblies with controllable transport properties: Mesoporous films meet polyelectrolyte brushes**

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**Materials and methods.**

Sodium 4-vinylbenzenesulfonate (technical, ≥90%, Fluka), 2-bromoisobutyryl bromide 98%, 2,2’-bipyridine (BiPy) 99% were used as received. Copper(I) chloride, CuCl, ≥97% (Fluka) (Aldrich) were purified according to the procedure of Keller and Wycoff.\(^1\) Triethylamine was refluxed overnight with calcium hydride before distilling and stored under argon. Dry dichloromethane was obtained from Acros organics, Geel, Belgium.

**Synthesis of mesoporous amino-silica thin films.**

NH\(_2\)-functionalized mesoporous thin films were synthesized via the co-condensation route following the well-known sol gel method based on mixing the oxide precursor tetraethoxysilane (TEOS) and the amine precursor 3-aminopropiltrieoxysilane (APTES) in presence of the template (Pluronic F127, pore size 9 nm).\(^2\) The precursor solution was prepared using 0.8 TEOS: 0.2 APTES: 0.005 F127: 24 EtOH: 5.2 H\(_2\)O: 0.28 HCl. This solution was used to produce films by dip-coating on ITO under 40-50% relative humidity at 298 K (1-2 mm s\(^{-1}\) withdrawing speed). Freshly deposited films were submitted to 50% relative humidity chamber for 24 hours followed by a stabilizing thermal treatment of two successive 24 hours steps at 60 °C and 130 °C, and a final 2 hours step at 200 °C. The template was removed by extraction in 0.01 mol dm\(^{-3}\) HCl in ethanol for three days under stirring.

**Anchoring of ATRP initiator and subsequent SI-ATRP of PSSNa.**

A solution of 2-bromoisobutyryl bromide (BIBr) (0.185 mL, 3 mmol) and triethylamine (0.205 mL, 3 mmol) in dry dichloromethane (30 mL) was injected over the mesoporous amino-silica substrates under N\(_2\) at room temperature and left during 1 h. The substrate was then washed with dichloromethane followed by absolute ethanol, and dried under a stream of N\(_2\). Then, the synthesis of the PSS brushes was carried out by following an experimental procedure similar to that reported by Armes and co-workers.\(^3\) Briefly, 4 g of styrene sulfonate sodium salt and 0.15 g of bipyridine were first dissolved in 48 mL of water-methanol solvent mixture (1:1). The solution was stirred and degassed by N\(_2\)(g) bubbling for 1h before 38.4 mg of CuCl was added. The polymerization mixture was degassed with N\(_2\)(g) bubbling for
another 15 min. Initiator functionalized mesoporous substrate was sealed in a Schlenk tube and degassed by four high vacuum pump/N\(_2\)(g) refill cycles. The reaction mixture was syringed into this Schlenk tube, adding enough to cover the sample completely, and the mixture was left for 6 h under N\(_2\)(g). The sample was then removed and thoroughly rinsed with deionized water. After the polymerization, the mesoporous substrate with PSSNa brush was extensively rinsed with water.

_A chemical characterization by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)_

Figure 1 shows the DRIFT spectra for the mesoporous samples prior to (A) and after the surface-initiated polymerization (B). The signals described in the figure correspond to: N-H asymmetric bending of the amine groups at 1560-1590 cm\(^{-1}\); Si-OH and Si-O-Si stretching at \(~966\) cm\(^{-1}\) and \(~1080\) cm\(^{-1}\), respectively.\(^4\) After the polymerization, the symmetric and asymmetric stretching of \(-\text{SO}_3^−\) groups at 1200 and 1000 cm\(^{-1}\) can be observed. The three narrow peaks in the 1500-1450 cm\(^{-1}\) reveal the presence secondary amides which originated the covalent anchoring of the ATRP initiators.

![Fig. 1 DRIFT spectra of amino-silica mesoporous films prior to (A) and after the surface-initiated polymerization (B).](image)

_X-ray photoelectron spectroscopy (XPS) characterization._
XPS measurements were performed using a commercial XPS system (Specs SAGE 150) equipped with a dual anode Mg/Al X-Ray source and an hemispherical electron energy analyzer. Spectra were acquired using an un-monochromatic MgKα (1253.6 eV) source operated at 12.5 kV and 14 mAmp. Quoted binding energies (BEs) are referred to the adventitious C 1s emission at 285 eV. Measurements were also conducted onto powdered samples made by scratching a thin film using a conducting double stick carbon tape. Atomic ratios were calculated from the integrated intensities of core levels after instrumental and photoionization cross-section corrections. In all samples, the N:Si ratios evaluated by XPS reflected the global initial composition. Repeated measurements were performed along the samples, confirming reproducible XPS line positions and intensity profiles with up to 2 % accuracy.

**Estimation of the degree of polymerization of the PSS brushes from XPS measurements.**

In order to estimate the degree of polymerization of the brushes grown inside the mesoporous film, *i.e.*, the number of repeating units in a grafted polymer chain, we proceeded to a quantitative analysis of the XP spectra. The quantification was based on the XPS signal intensity comparison between the N1s and S2p signals (see figure 2), which correspond to the amide (grafting site) and the sulfonic groups, respectively. The XPS peak area is directly proportional to the concentration of an element, but the factor of proportionality depends on several factors such as photoionisation cross section (intrinsic of each element) and instrumental corrections. To simplify the analysis ammonium sulfate salt ((NH₄)₂SO₄) was used as a reference sample. This solid compound contains both elements, N and S, in a well-known stoichiometry, 2N:1S. From the reference XPS measurements of (NH₄)₂SO₄ (under exactly the same experimental conditions as those used in the brush-modified mesoporous films) it was possible to obtain the required calibration factor, \( \alpha \), for the analysis of both elements (N and S) in our experimental setup.

\[
\alpha = \frac{\text{Peak Area N1S (reference)}}{[2 \times \text{Peak Area S2p (reference)}]} = 0.77
\]

Then, considering that the amine groups were converted to amide bonds during the initiator anchoring step, the degree of polymerization or the average number of styrene sulfonate monomer units per grating site \( n \) was:

\[
n = \frac{\alpha \times \text{Peak Area S2p (sample)}}{\text{Peak Area N1S (sample)}} = 12 \pm 2
\]
In this case the term “peak area N1S” corresponds exclusively to the XPS signal originated from the surface amide bonds (blue trace in figure 2A).

References