## **Electronic Supplementary Information**

## A block copolymer-templated construction approach for the creation of nano-patterned polyelectrolyte multilayers and nanoscale objects

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**Figure S1.** XPS spectra of control samples, showing a comparison between neat polyelectrolyte films (green curves), PEs deposited over qP2VP homopolymer film (red curves), and PEs deposited over PS homopolymer films. The additional doublet observed in the sulfur spectrum of neat PSS film is attributed to a fraction of PSS that was protonated by the silicon substrate.



**Figure S2.** Control samples of LbL templates of stripes and dots patterns after 30 min dipping cycles with TsONa and EtACl electrolyte solutions, employing the same pH and ionic strength conditions used in the PEM assembly. No considerable change is observed in the template structures following this treatment.

**XPS analysis. Figure S3** shows XPS spectra of relevant elements at different stages of the deposition of the first PSS/PAH bilayer. Reacting the BCP pattern with DIB gives rise to two iodine doublets corresponding to the iodide counterions (at 618.4 and 629.9 eV, denoted as 'I<sup>-'</sup>) and partially reacted DIB molecules (at 620.4 and 631.9 eV, denoted as 'R-I'). Additionally, the intensity of the pyridine nitrogen signal at 399.3 eV (denoted as 'N') decreases, and a new peak corresponding to alkylated pyridine rings appears at 402.2 eV (denoted as 'N<sup>+</sup>'). The degree of pyridine quaternization is estimated from the nitrogen peaks to be ca. 20%; the fraction of cross-linked pyridine units out of the total number of pyridines in the volume sampled by the XPS is estimated to be ca. 16% (according to eq. 1). Deposition of PSS gives rise to the appearance of a sulfur peak and the disappearance of the iodine signals. This is attributed to the displacement of iodide counterions by the PSS. Subsequent deposition of PAH increases the intensity of the N<sup>+</sup> signal.



Figure S3. XPS spectra of the BCP patterns (black curves), LbL templates (blue curves), the first deposited PE layer (PSS; green curves) and the second deposited PE layer (PAH; red curves). Spectra were acquired at 90° take-off angle.