

Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

## **Surface Functionalized Nanostructures via Position Registered Supramolecular Polymer Assembly**

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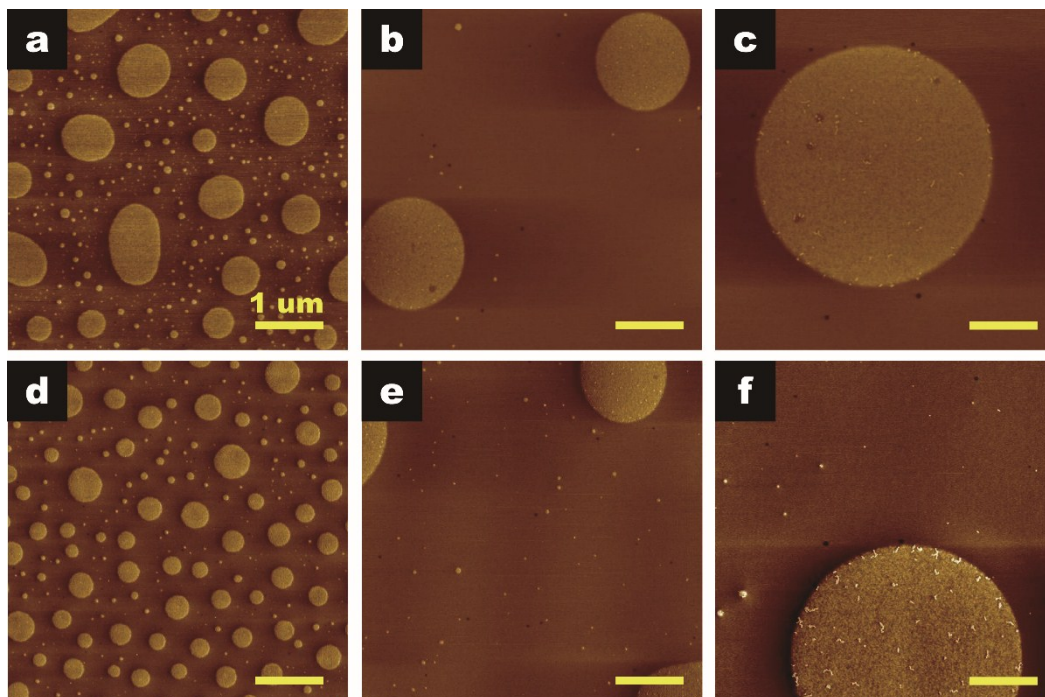


Fig. S1. Tapping-mode atomic force microscopy (TM-AFM) images in phase contrast of the morphologies of two polymer blends of PS/APBD and PS/SPBD film as-cast (a, d) and prepared at different solvent annealing time of 5 (b, e) and 30 min (c, f), respectively. All the polymer blends were prepared with the PS volume fraction( $\Phi_{PS}$ ) of 0.33.

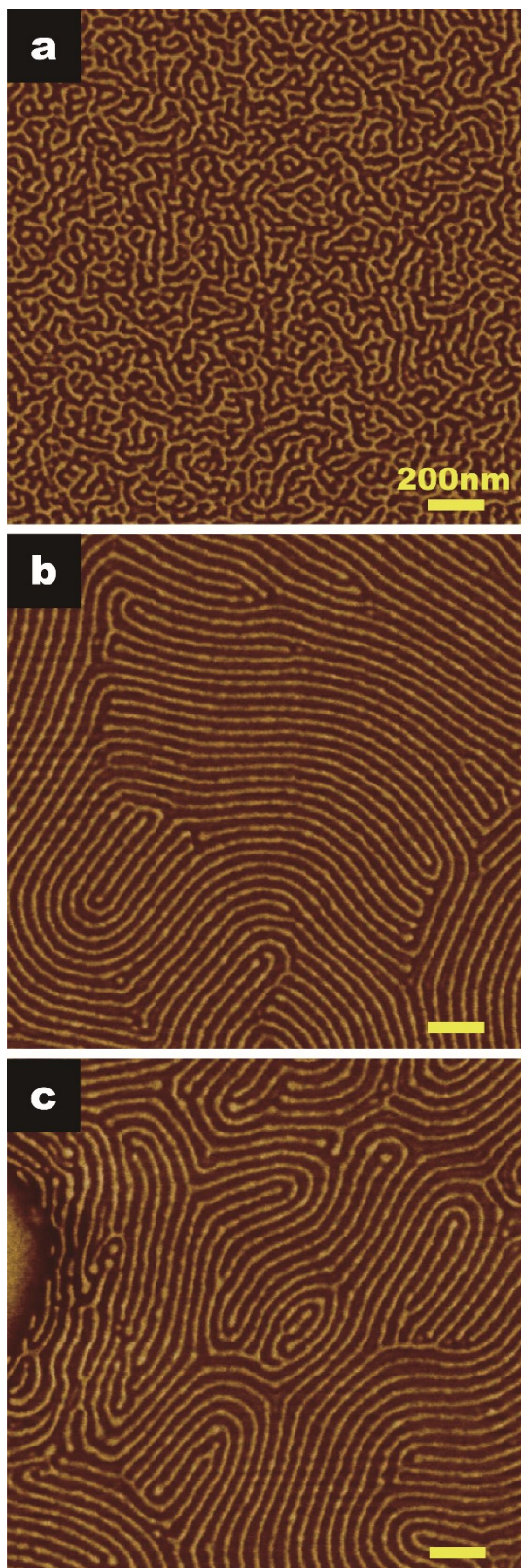


Fig. S2. Phase contrast TM-AFM images of supra 1 films prepared from a solution in pure benzene. (a) An as-cast film, (b) A film solvent-annealed with benzene, and (c) A film solvent-annealed with benzene/water mixture with benzene fraction of 0.8. (b, c) All the films were solvent-annealed for 5 minutes.



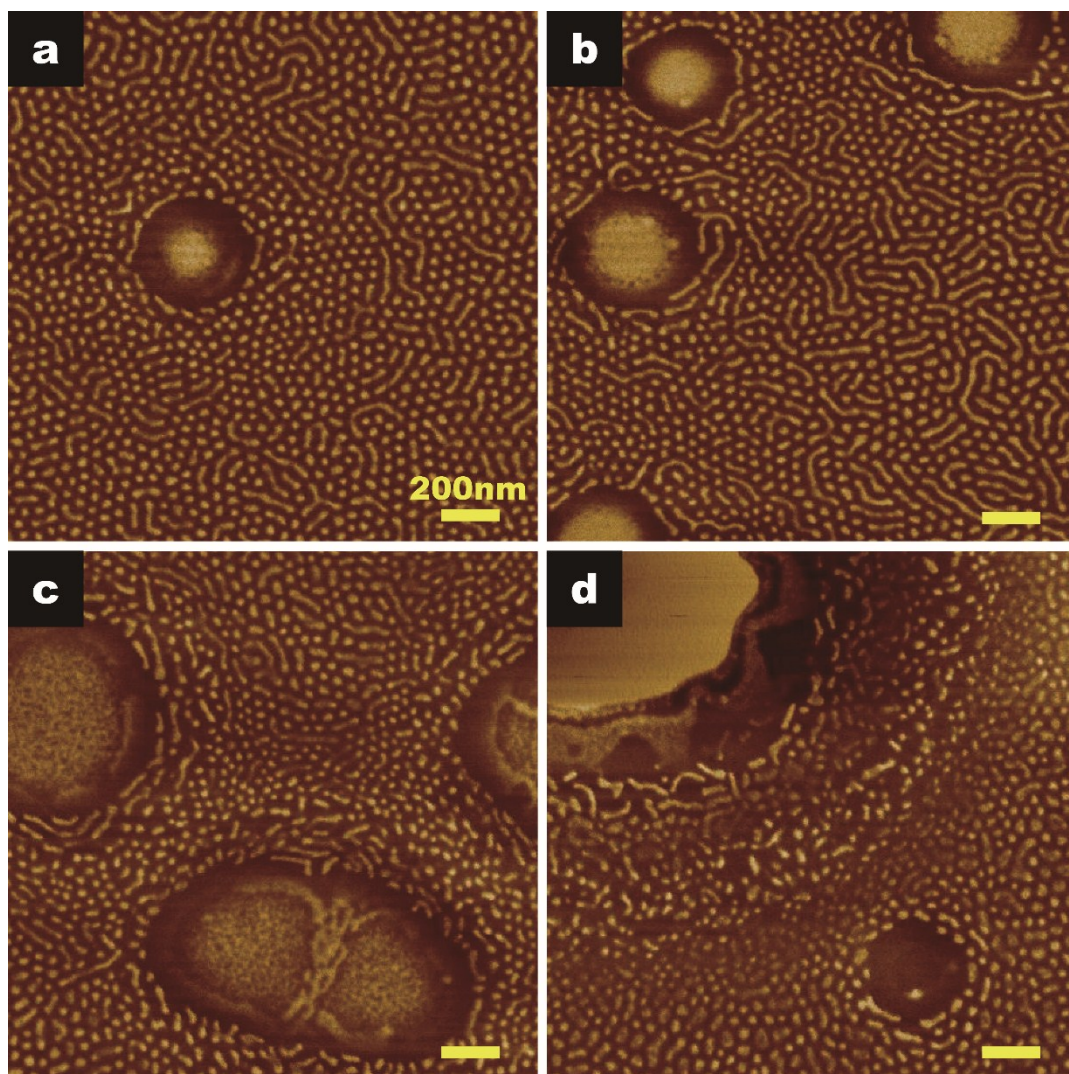


Fig. S3. Phase contrast TM-AFM images of supra 1 films solvent annealed with benzene/water mixture vapor containing benzene weight fraction of (a) 0.8, (b) 0.6, (c) 0.4, and (d) 0.2. All the films were solvent-annealed for 5 minutes.

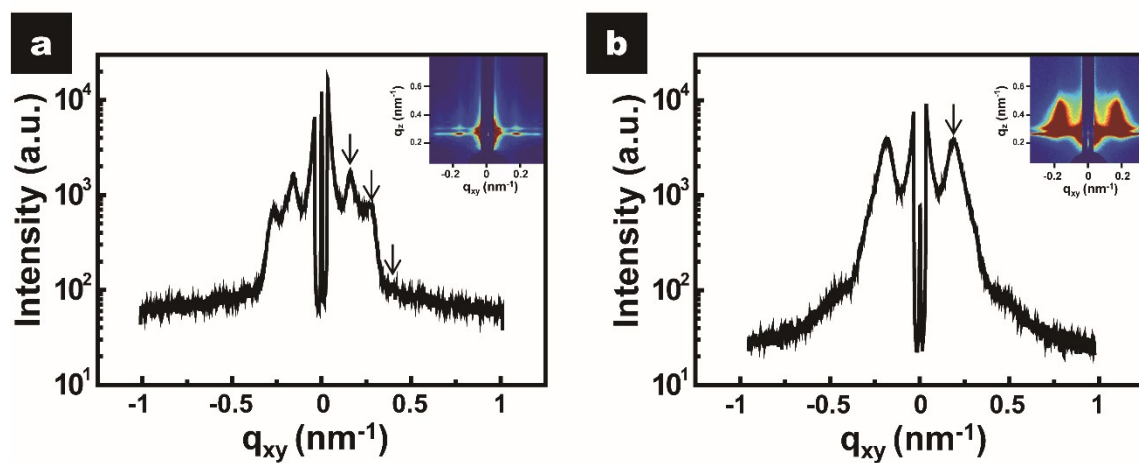


Fig. S4. One-dimensional grazing incidence small X-ray scattering (GISAXS) plots of supramolecularly assembled nanostructures with in-plane cylindrical domains after solvent annealing with benzene for 30 minutes: (a) supra 1 and (b) supra 2. The inset images show two-dimensional GISAXS patterns.

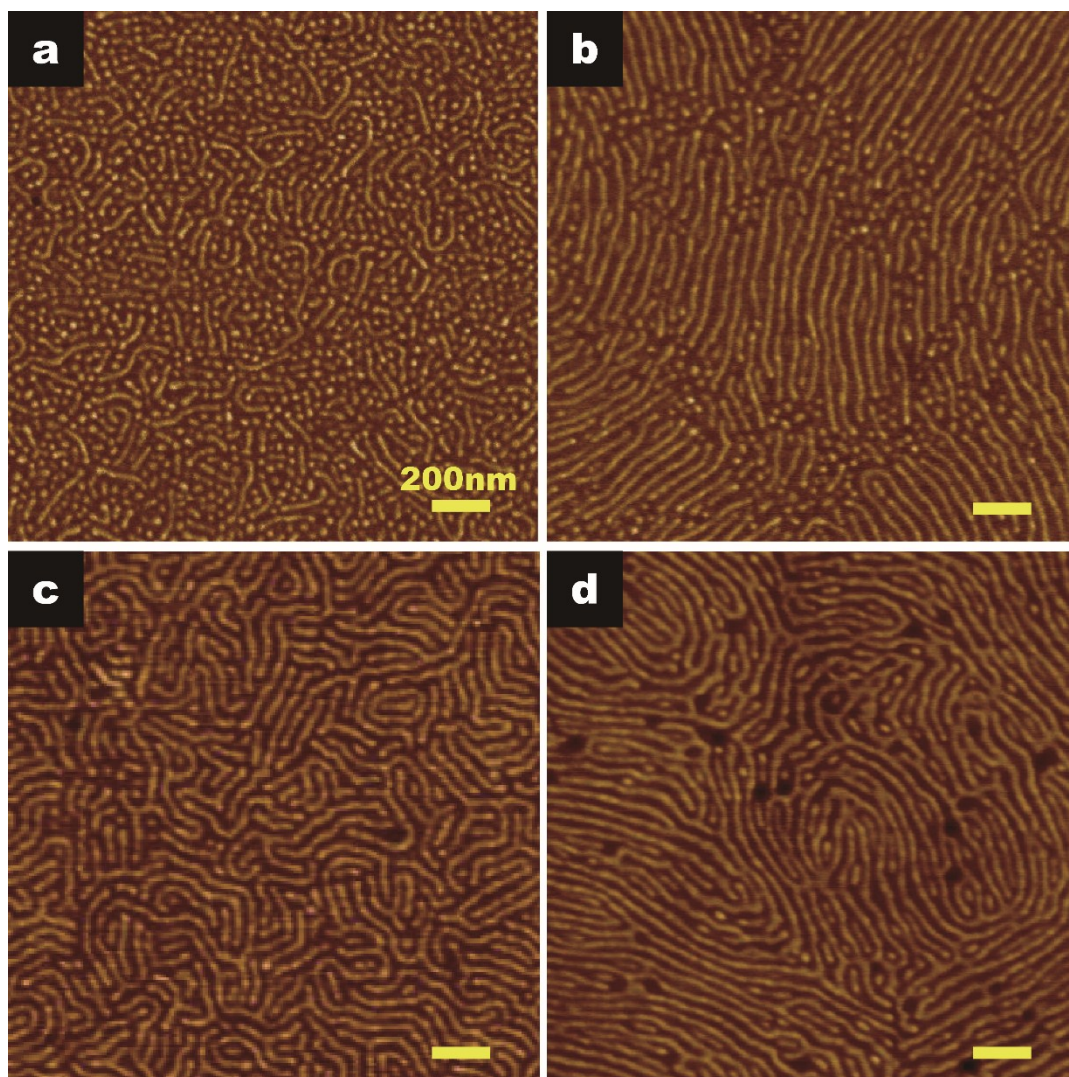


Fig. S5. Phase contrast tapping-mode atomic force microscopy (TM-AFM) images of thin supramolecularly assembled films after solvent annealing with benzene for 5 minutes of different concentration blends in supra 1 (a, b) and supra 2 (c, d). The concentration of the polymer solution is 2 wt% (a, c), and 3 wt% (b, d).



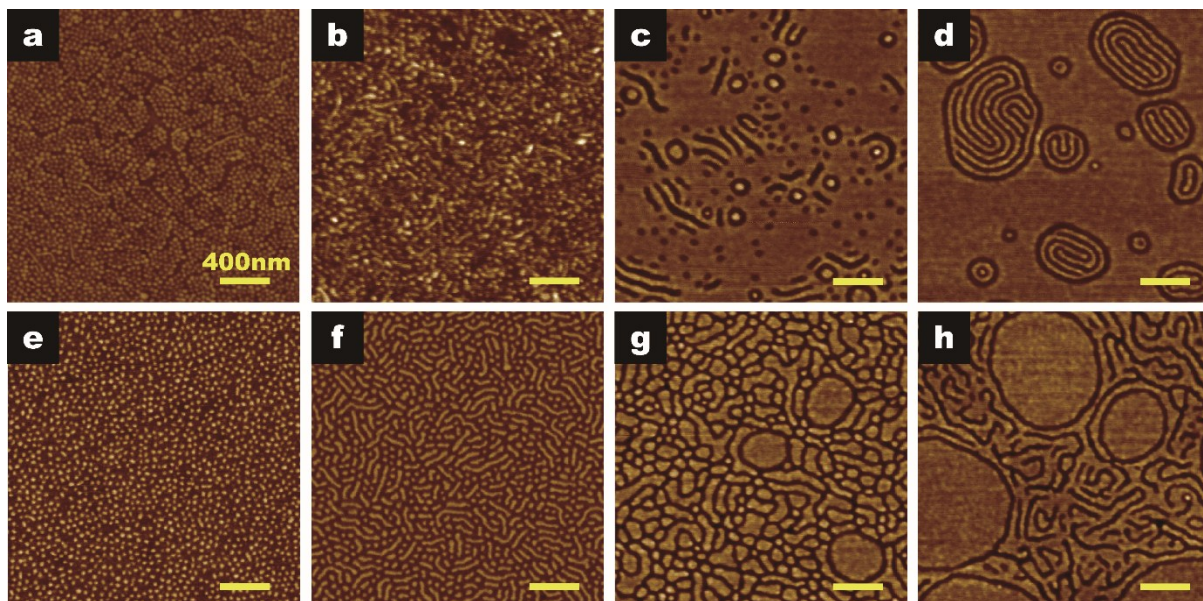


Fig. S6. Phase contrast TM-AFM images of nonstoichiometric supra 1 films with SPS weight fraction of (a) 0.19, (b) 0.30, (c) 0.50, and (d) 0.75. Phase contrast TM-AFM images showing the morphologies of nonstoichiometric supra 2 films with APS weight fractions of (e) 0.29, (f) 0.38, (g) 0.50, and (h) 0.67. All the films were solvent-annealed with benzene for 5 minutes.

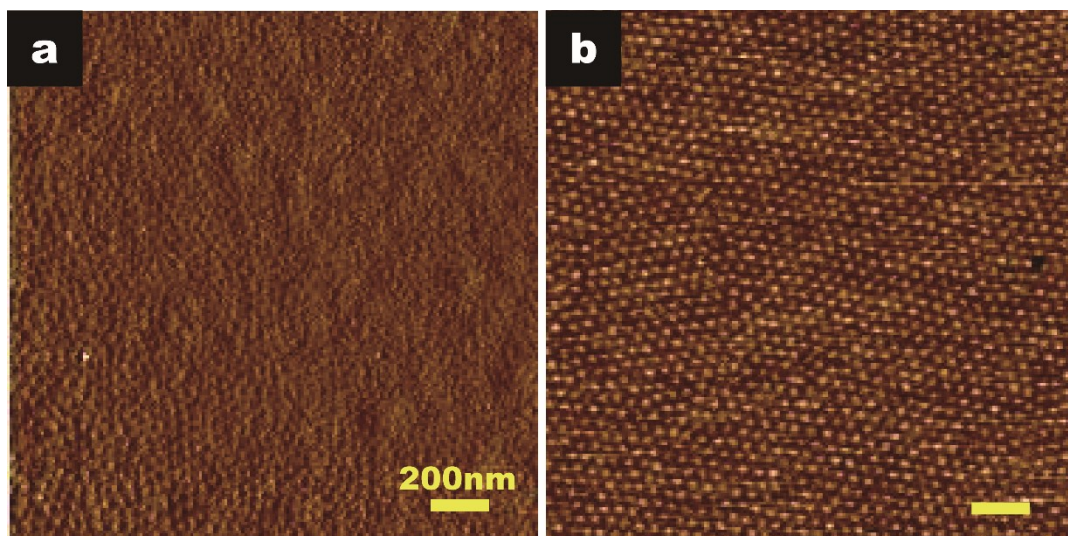


Fig. S7. Phase contrast TM-AFM images of (a) supra 1 and (b) supra 2 films solvent-annealed, followed by selective cross-linking of end-functionalized PBD.



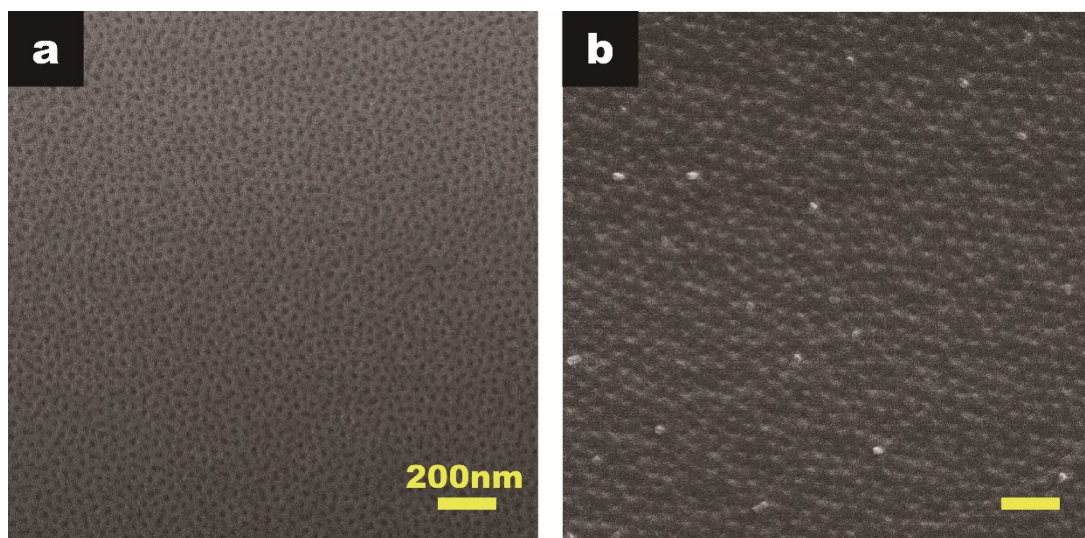


Fig. S8. Scanning electron microscopy (SEM) images of thin supramolecularly assembled films in which PS cylinders were selectively etched with a methyl ethyl ketone/HCl solvent mixture for (a) supra 1 and (b) supra 2.

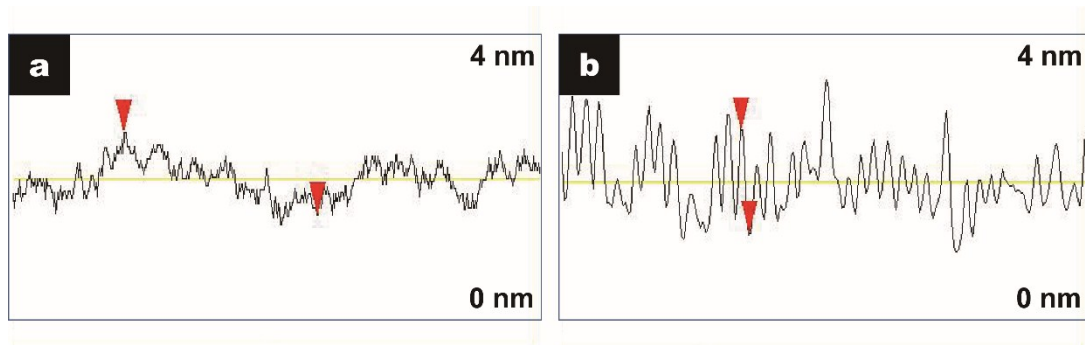


Fig. S9. Depth profiles of hexagonally ordered cylindrical nanostructures after solvent annealing of (a) supra 1 and (b) supra 2 with benzene for 5 minutes.

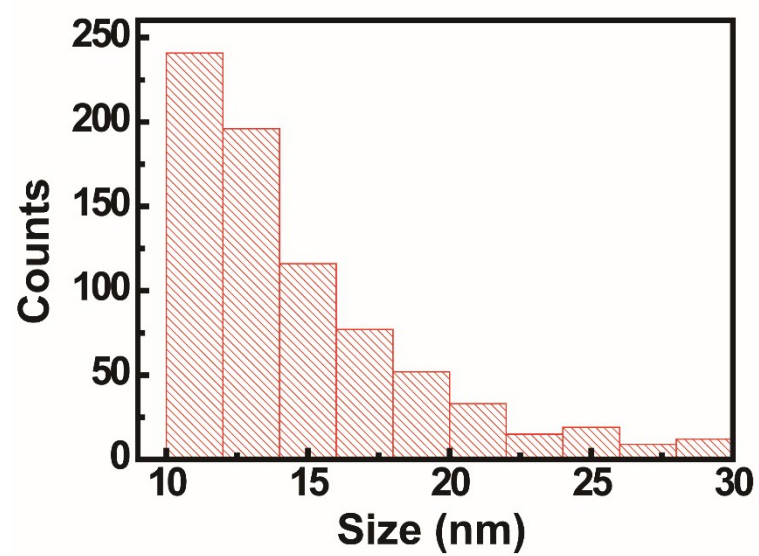


Fig. S10. Size distributions of templated Au nanoparticles calculated by particle analysis of figure 4b.



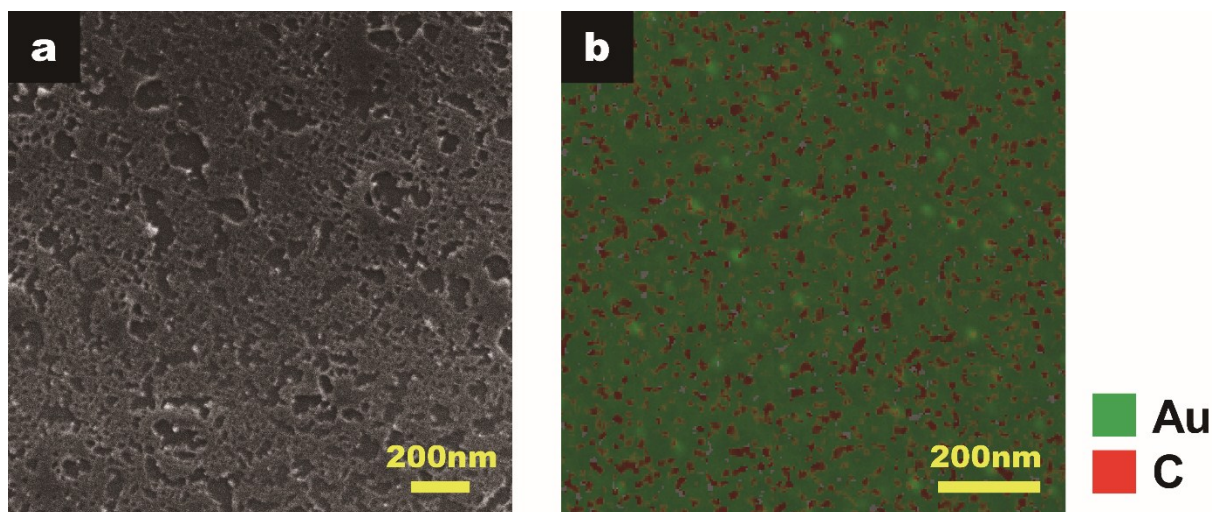


Fig. S11. (a) SEM image and (b) energy-dispersive X-ray (EDX) mapping of a gold film developed with P2VP film containing  $\text{HAuCl}_4$  deposited on supra 1 film, followed by the reduction of  $\text{Au}^{3+}$  by oxygen plasma.

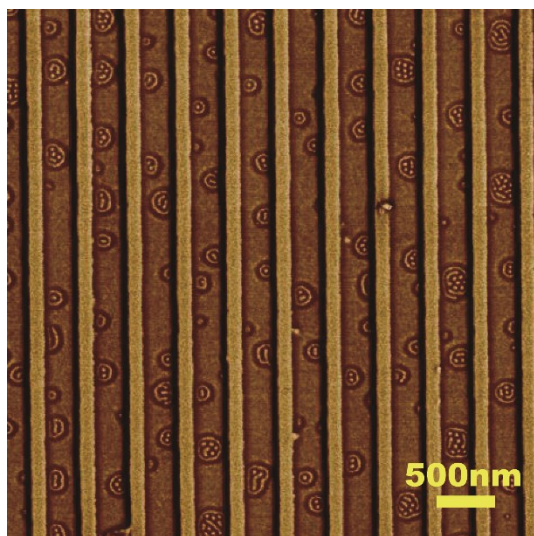


Fig. S12. A TM-AFM phase image of a nonstoichiometric supra 1 film morphology guided on a pre-patterned substrate with SPS weight fraction of 0.75.



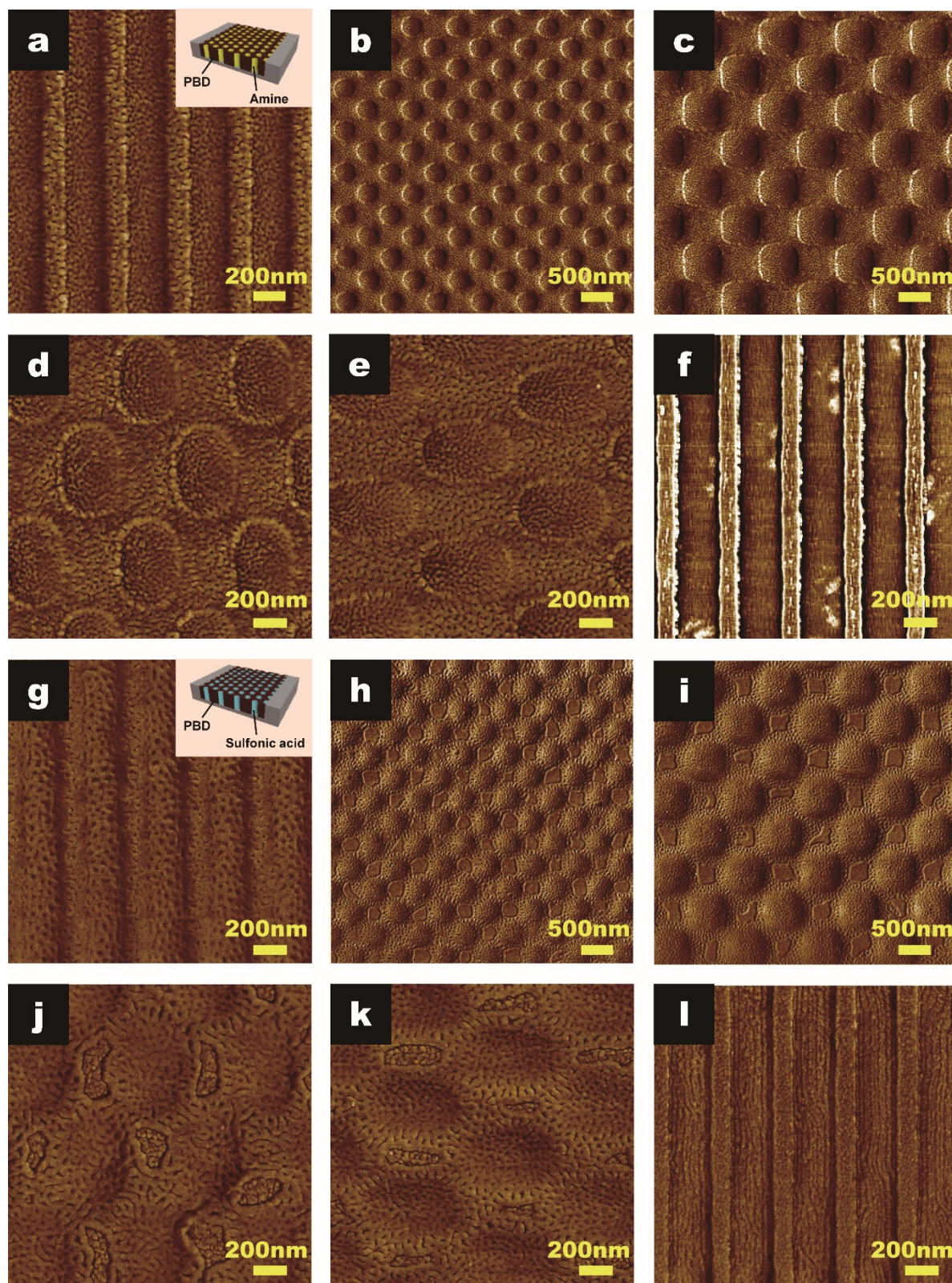


Fig. S13. Phase contrast TM-AFM images of hexagonally ordered cylindrical holes obtained by selective chemical etching of end-functionalized PS after cross-linking end-functionalized PBD of supra 1 (a–f) and supra 2 (g–l). The films were solvent annealed with benzene for 5 (a–e, g–k) and 30 minutes (f, l), respectively.



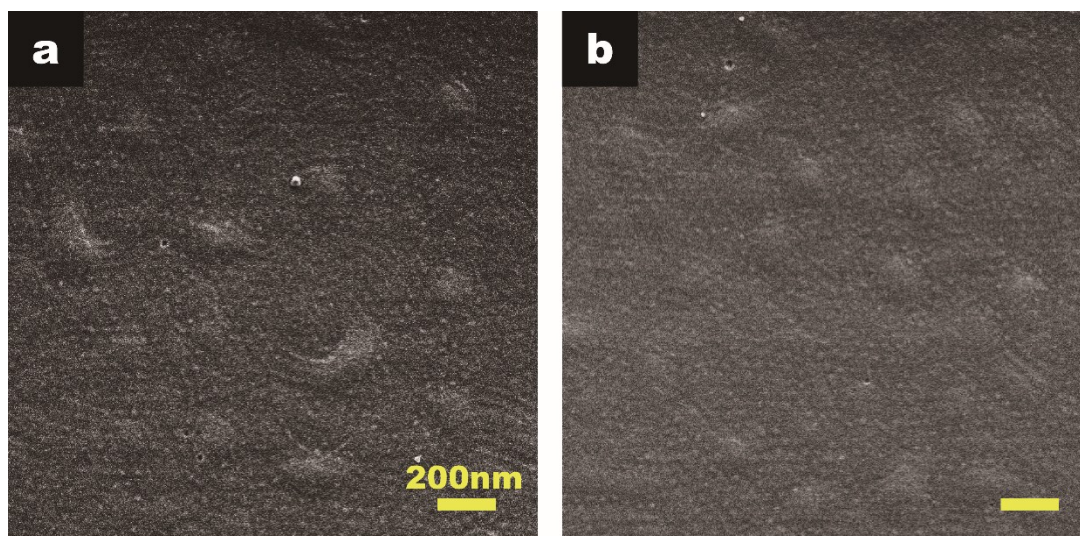


Fig. S14. SEM images of (a) PS nanoposts with a sulfonate surface developed from supra 1 film and (b) PS nanoposts with an amine surface from supra 2 film.