Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Optimising the Enzyme Response of Porous Silicon Photonic Crystal via the Modular Design of Enzyme Sensitive Polymers

Alexander H. Soeriyadi[+a,b], Bakul Gupta[+a,b], Peter J. Reece,[c] and J. Justin Gooding*[a,b]

[a]School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia

[b]Australian Centre of NanoMedicine, University of New South Wales, Sydney NSW 2052, Australia

[c]School of Physics, University of New South Wales, Sydney NSW 2052, Australia

[+] These authors contributed equally to this work

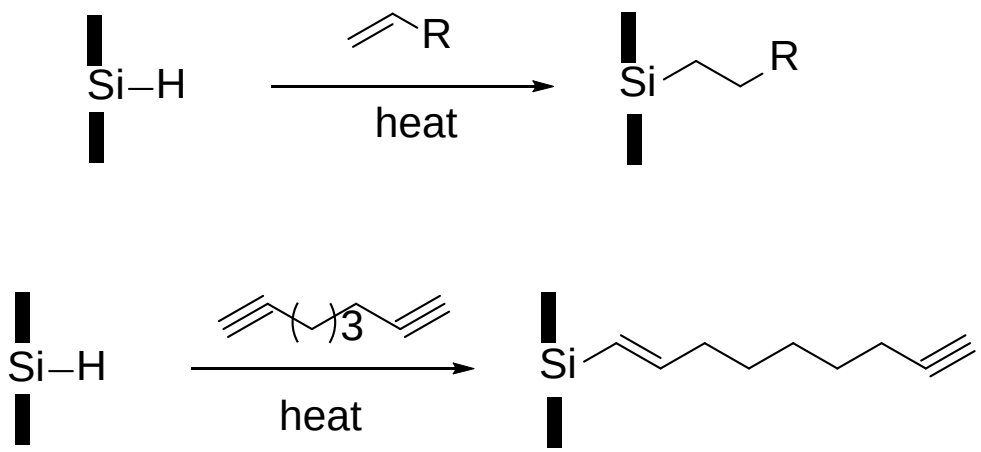
*Corresponding author: Prof. J. Justin Gooding email: justin.gooding@unsw.edu.au

Experimental Procedure

Fabrication of passivated PSi rugate filter

Modification of PSi Rugate Filters with 1,8-Nonadiyne. Assembly of the alkyne terminated PSi surface by covalent attachment of 1,8-nonadiyne followed a previously reported procedure.[1] Freshly etched filters were transferred, taking extra care to completely exclude air from the reaction vessel (a custom-made Schlenk flask), to a degassed (through a minimum of five freeze-pump-thaw cycles) sample of alkyne. The sample was kept under a stream of argon while the reaction vessel was immersed in an oil bath set to 170°C for 3 h. The flask was then opened to the atmosphere, and the functionalized surface sample rinsed consecutively with copious amounts of dichloromethane and ethanol and then blown dry under a gentle stream of argon, before being either analyzed or further reacted with substituted azido species.

Result and Discussion



Scheme S1. (Top) A general representation of hydrosilylation reaction to modify hydrogen terminated silicon surfaces with alkene or alkyne with heat. (Bottom) In this work, hydrosilylation was performed with 1,8-nonadiyne and formed alkyne terminated surfaces.

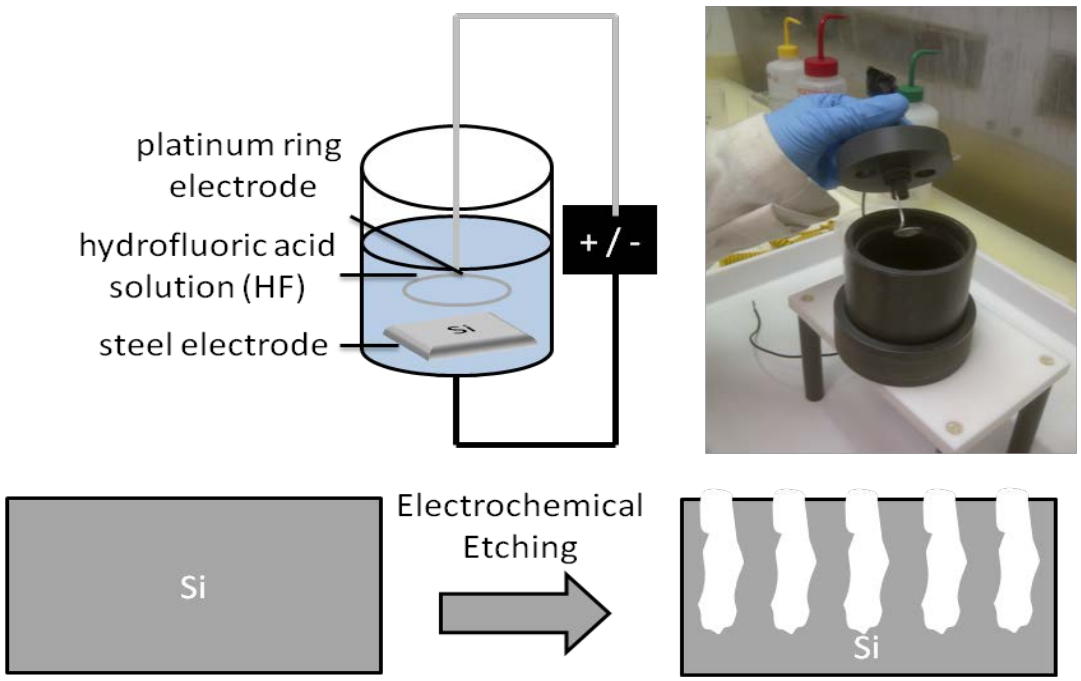


Figure S1. Schematic and photograph of the electrochemical etching cell used for anodization of silicon. The structure of the nanopores can be controlled by doping level, HF concentration, and current profile.

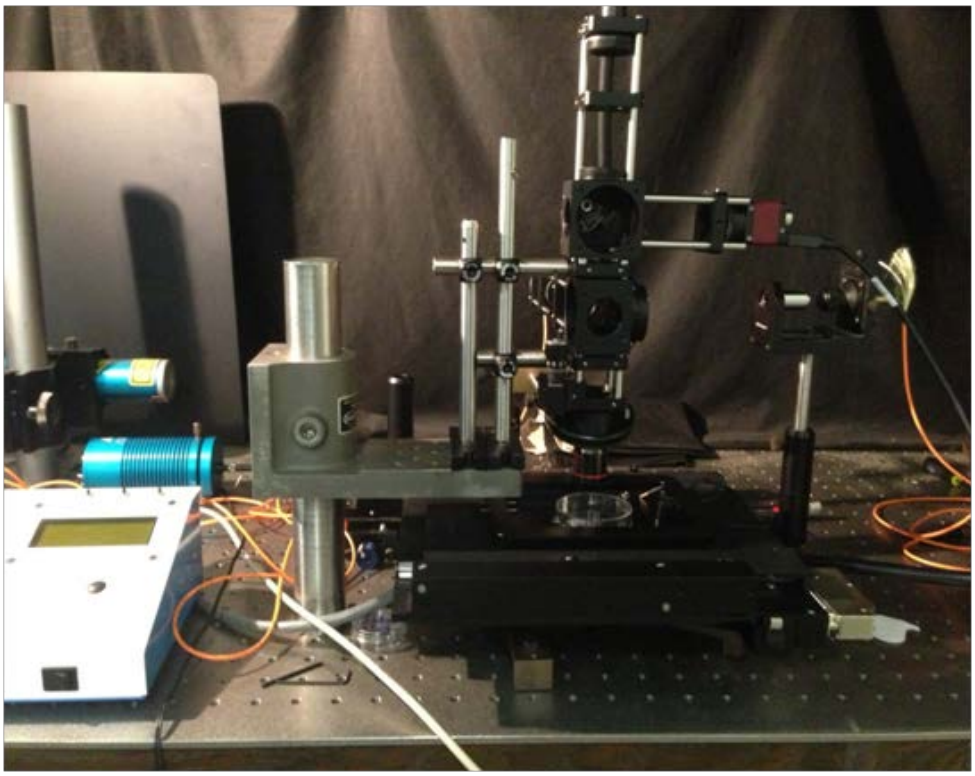


Figure S2. Optical reflectivity measurements set up to measure the reflectance of porous silicon.

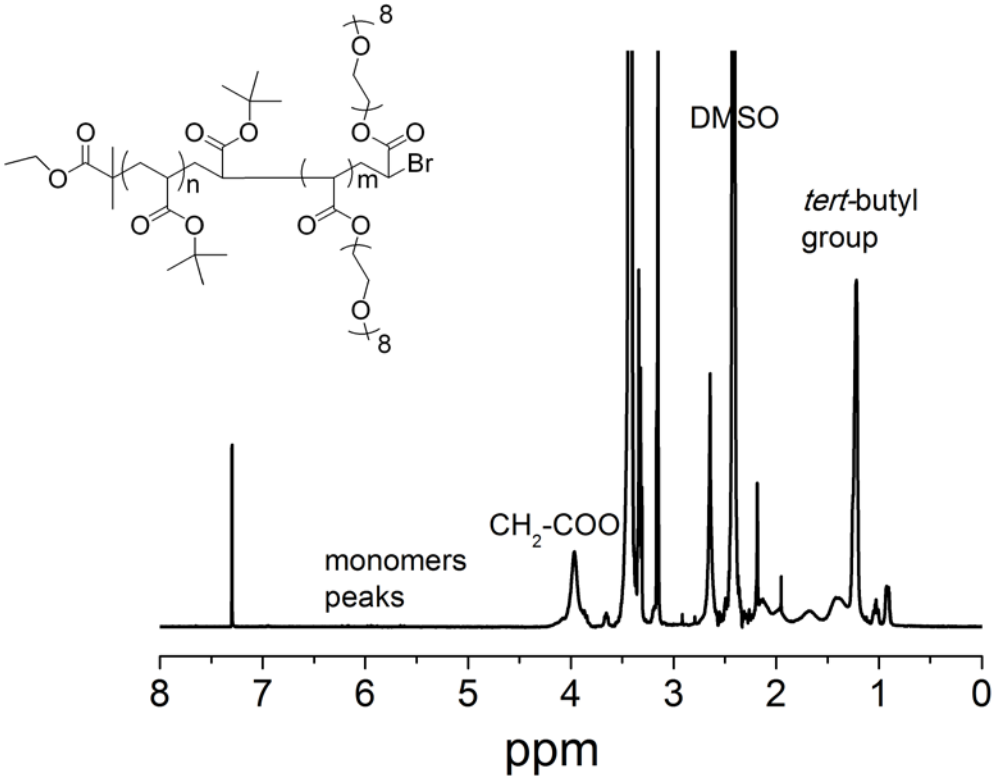


Figure S3. NMR characterization of antifouling polymer **P1** synthesis after polymerization showing >99% conversion. Successful polymerization is shown by the disappearance of monomer peaks at 5.5- 6.2 ppm Note : DMSO was used as solvent during reaction hence the DMSO peak in NMR spectrum at 2.4 ppm.

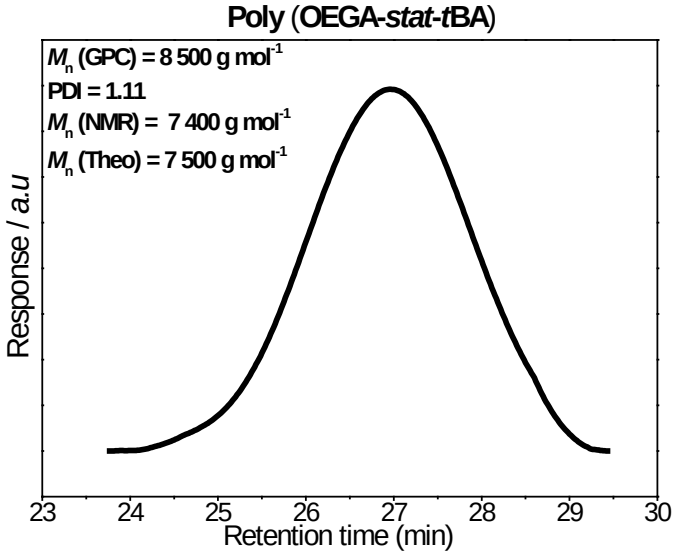


Figure S4. GPC of poly(OEGA-stat-*t*BA) synthesized via Cu(0)-mediated polymerization. The GPC results showing typical polymer synthesized via controlled radical polymerization with narrow PDI of 1.11.

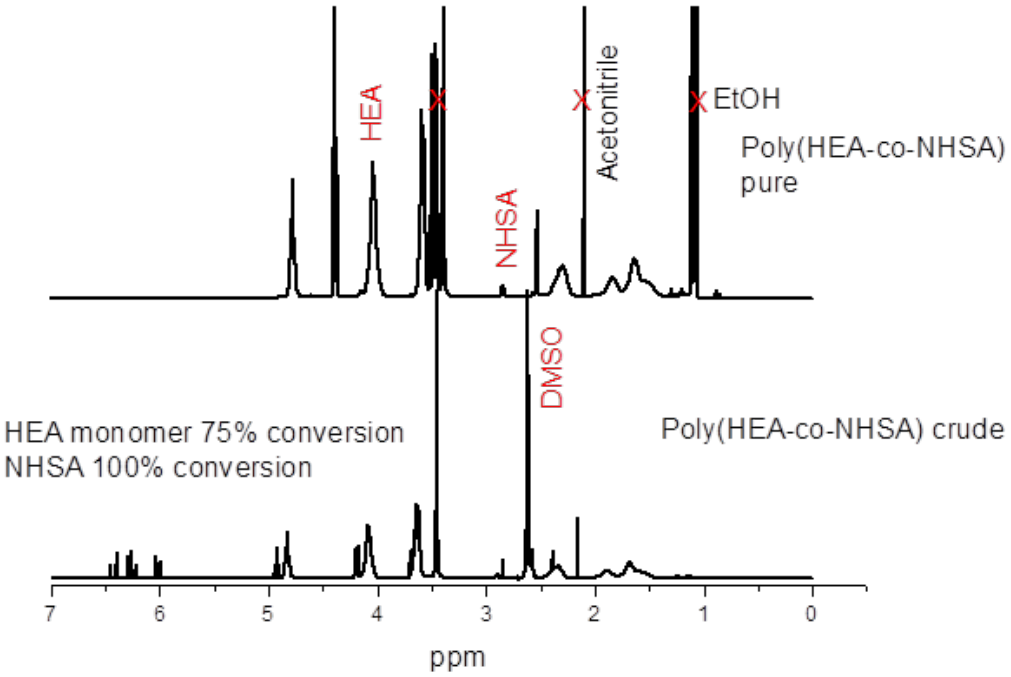


Figure S5. NMR characterization of sacrificial polymer **P2** synthesis after polymerization (bottom) and after purification (top). The expected peaks are presence from NMR characterization with peak corresponding of C**H**$_2$-C**H**$_2$ bond of *N*-hydroxysuccinimide (NHSA) at 2.82 and peak corresponding to C**H**$_2$-OH from HEA at 4.15. Note: X denotes presence of solvent from reaction or purification

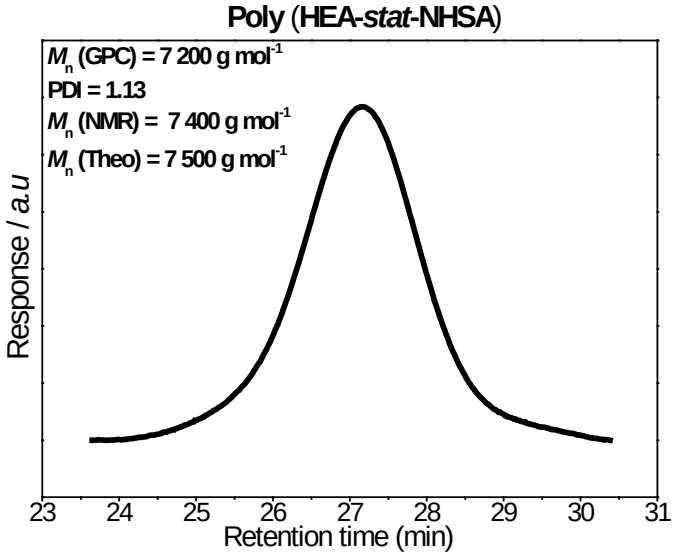


Figure S6. GPC characterization of sacrificial polymer **P2** poly(HEA-stat-NHSA) synthesized *via* Cu(0)-mediated polymerization. Molecular weight obtained for GPC is comparable to the theoretical and molecular weight obtained from NMR with a narrow PDI of 1.13

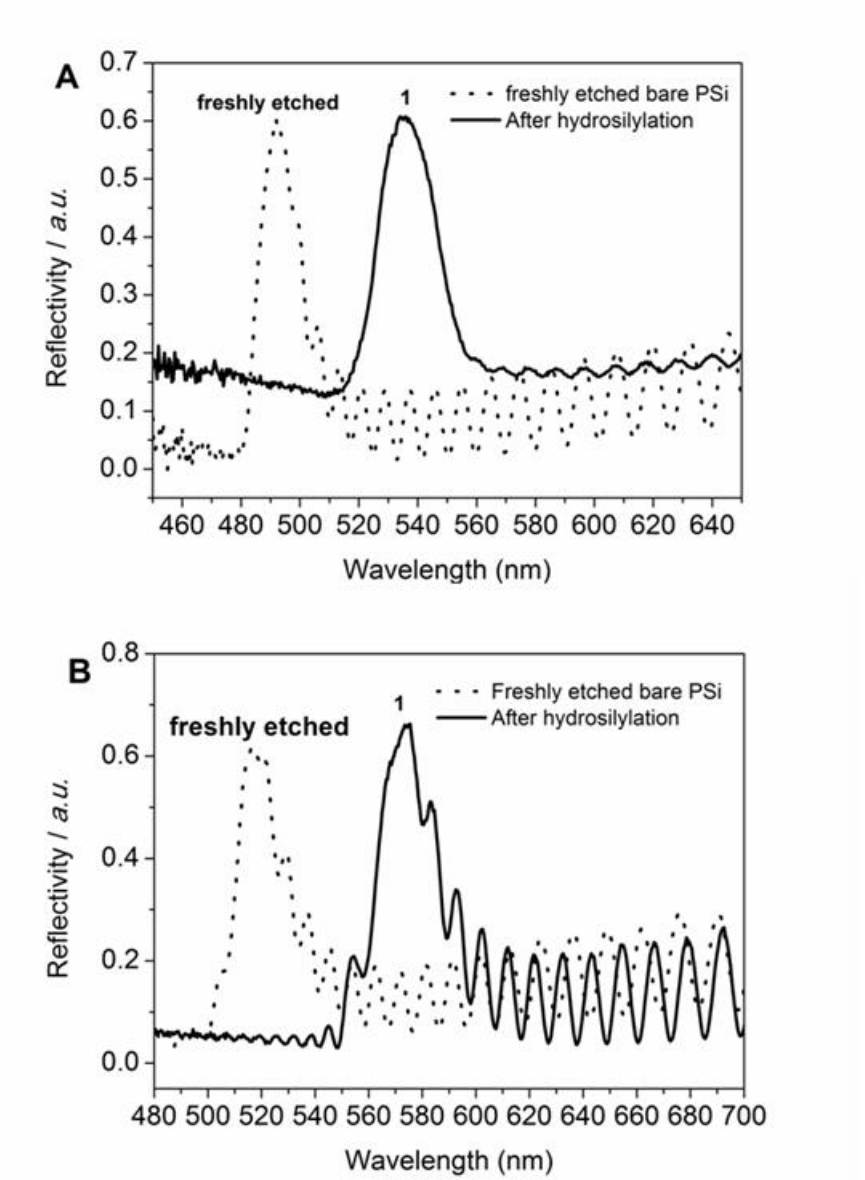


Figure S7. Typical reflectivity measurement of PSi after anodization process (surface **0**) and after hydrosilylation with 1,8-nonadiyne (surface **1**). PSi (A) was further prepared and modified for MMP-2 specific detection and PSi (B) for MMP-9 specific detection. Note: These reflectivity measurements were performed in air (that is, in dry conditions).

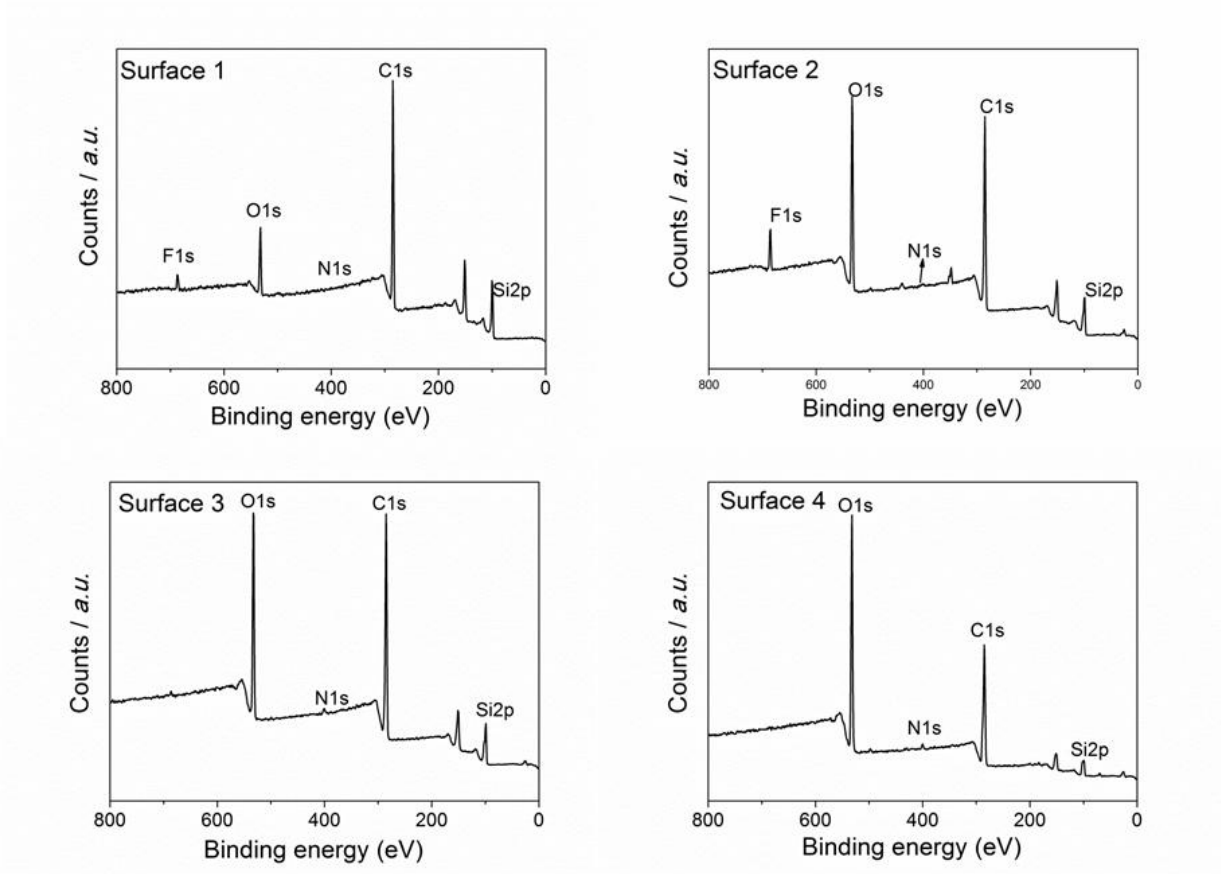


Figure S8. XPS Survey spectra of PSi during modification from surface **1** to surface **4.** Survey scan of surface 1 is showing the absence of N as expected while after modification steps (surface **2-4**), there is clearly peaks corresponding to N. Moreover the ratio of C/Si and O/Si is also increase through the modification with organic compounds.

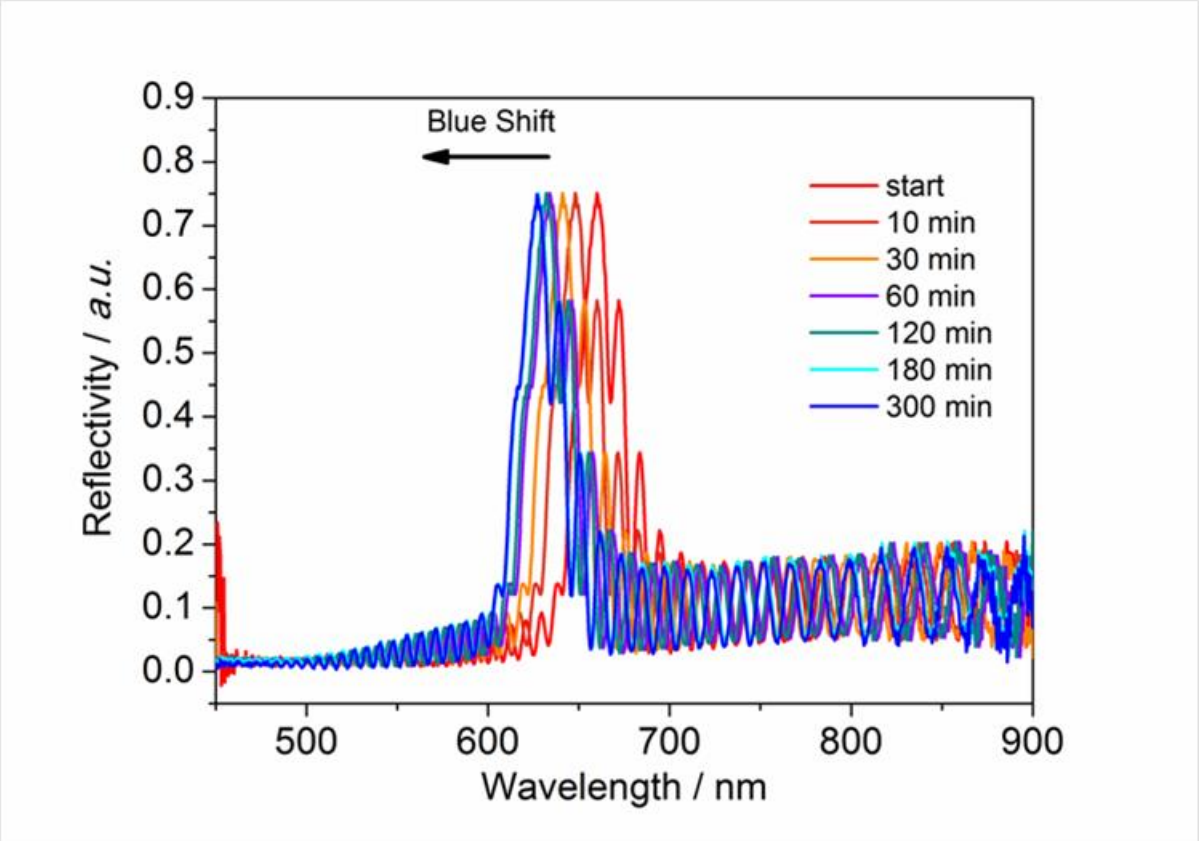


Figure S9. Reflectivity spectrum of PSi chip modified with SGKGPRQITAK cleavable polymer network after exposure to protease enzyme MMP-9 with reflectivity shift towards lower wavelength ("blue shift") indicating materials leaving the pores. The peaks is shifting because as protease digested the organic material over time, the space that is left by the organic material is filled with water which has lower refractive index than organic material. Note: protease assay experiment is stop at 5 hours at which the enzyme deemed inactive.

References

1. S. Ciampi, T. Böcking, K. A. Kilian, M. James, J. B. Harper and J. J. Gooding, *Langmuir*, 2007, **23**, 9320-9329.