## **Supporting Information**

## Dynamics of a nitroxide layer grafted onto porous silicon

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FIGURE S1: FT-IR spectrum of nitroxide 1.

FIGURE S2: ESR spectra of nitroxide 1 in toluene solution.

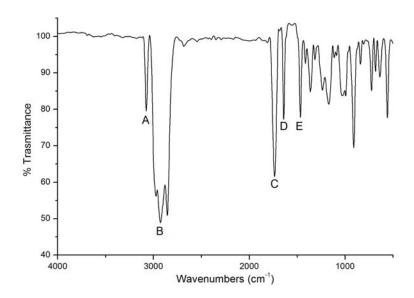
FIGURE S3: FT-IR spectrum of a freshly-etched porous silicon slab.

FIGURE S4: XPS survey scans and Si2p regions for a freshly-etched silicon substrate and for a nitroxide-grafted silicon slab.

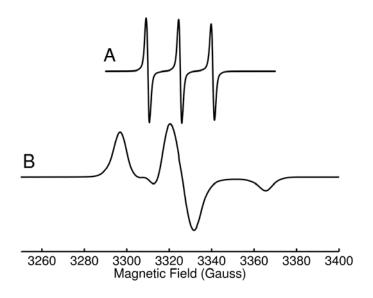
FIGURE S5: EPR spectra of 1-PS, PS and difference spectrum.

FIGURE S6: EPR spectrum of nitroxide 1 drop-casted on PS.

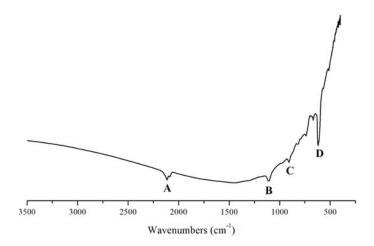
FIGURE S7: Experimental and calculated ESR spectra of 1-PS.



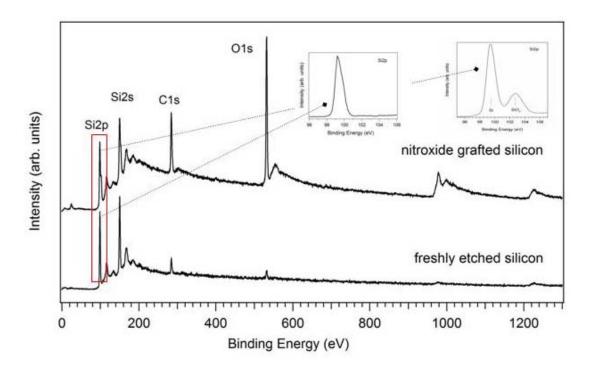
**Figure S1**. IR spectrum of **1**. A, 3075 cm<sup>-1</sup>,  $\nu$ (H-C=C); B, 2977, 2925, 2858 cm<sup>-1</sup>,  $\nu$ (Alkyl Chain); C, 1737 cm<sup>-1</sup>  $\nu$ (C=O); D, 1641cm<sup>-1</sup>  $\nu$ (C=C); E, 1467 cm<sup>-1</sup>  $\nu$ (N-O).



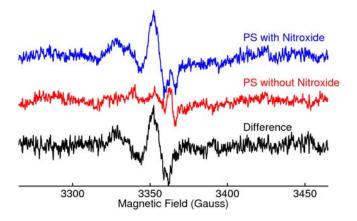
**Figure S2**. ESR spectra of **1** in toluene solution ( $c = 1 \times 10^{-4}$  M). (**A**) room temperature; (**B**) at 110 K.



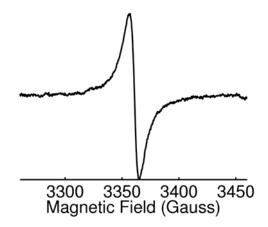
**Figure S3**. IR Spectrum for Porous Silicon (**PS**). A, 2110 cm<sup>-1</sup>,  $v(Si-H_x)$ ; B, 1100 cm<sup>-1</sup>, v(Si-O); C, 912 cm<sup>-1</sup>,  $v(Si-H_2)$ ; D, 617 cm<sup>-1</sup>, v(Si-Si). The broad band in the 2100 cm<sup>-1</sup> region (A) is associated to the stretching modes of Si-H, Si-H<sub>2</sub> and Si-H<sub>3</sub>. The band around 1100 cm<sup>-1</sup> (B) indicates the presence of silicon oxides (SiO<sub>x</sub>), most likely of interstitial nature. The peak at 912 cm<sup>-1</sup> (C) is associated to a  $v(Si-H_2)$  scissor mode absorption. The low energy part of the spectrum shows a strong adsorption at around 617 cm<sup>-1</sup> (D) with a smaller shoulder at 665 cm<sup>-1</sup>: the former is commonly assigned to the v(Si-Si) stretching mode and the latter to a v(Si-H) wagging mode.



**Figure S4**. XPS survey scans for a freshly etched silicon substrate and for a nitroxide-grafted silicon slide. Correspondingly, the Si2p regions are also shown.



**Figure S5.** EPR spectra recorded on samples of **1-PS** (blue), of **PS** (red) and the spectrum difference between the two (black). The spectra are shifted vertically to improve readability.



**Figure S6.** EPR spectrum recorded at T = 290K of nitroxide 1 drop-casted on **PS**.

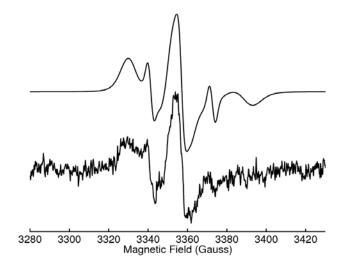


Figure S7. Calculated (upper) and experimental (lower) ESR spectra of 1-PS recorded at T = 300 K