Electronic supporting information

Surface enhanced DNP assisted solid-state NMR of functionalized SiO_2 coated Polycarbonate Membranes

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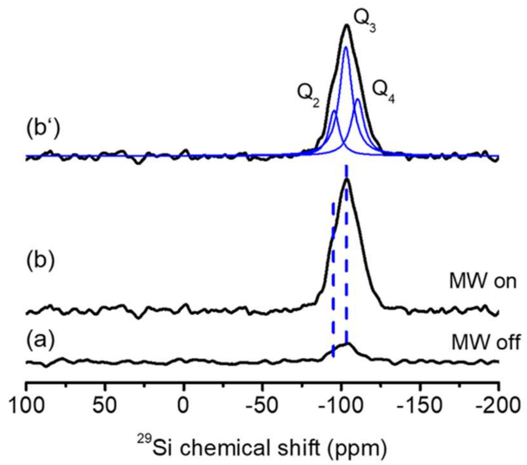

Figure S1. ^{29}Si CP-MAS spectra of the ALD coated polymer foils measured at 8 kHz spinning and nominally 110 K, measured with MW off (a) and MW on (b) to determine the signal enhancements. The deconvolution of spectrum (b) employing Lorentzian-Gaussian lines is shown in (b').

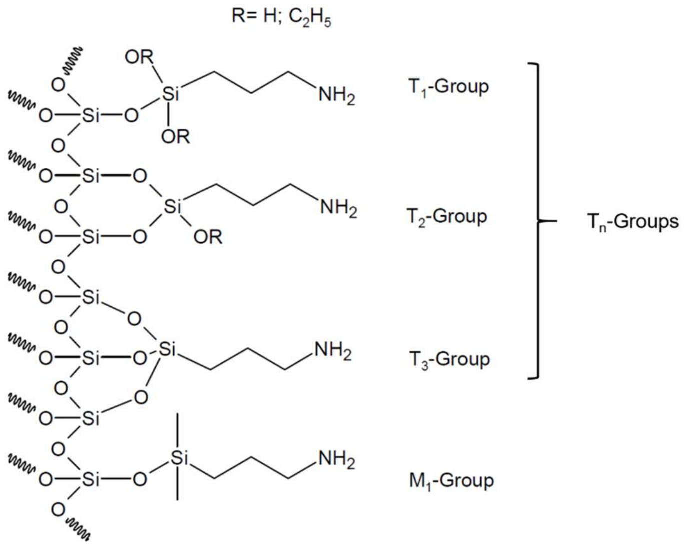

Figure S2. Structural assignment of M_1 and T_n groups to covalently grafted linker molecules.

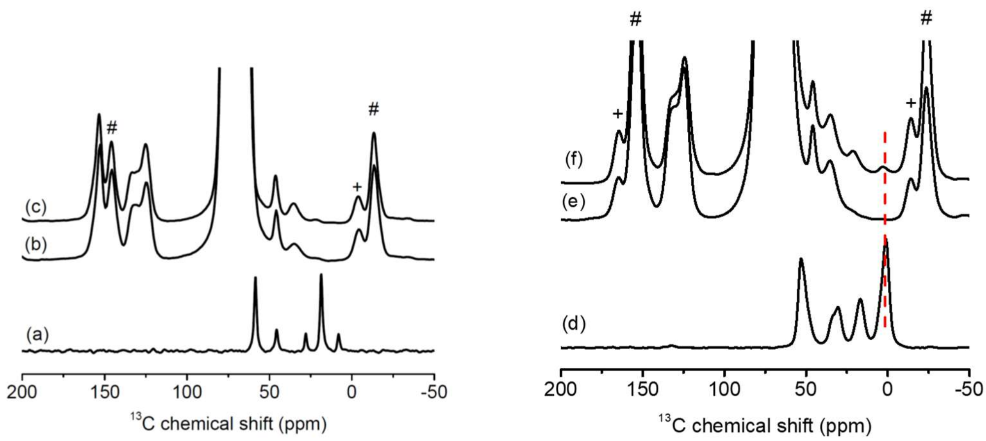

Figure S3. (a) Static ^{13}C NMR reference spectrum of the pure APTES linker, and comparison with the ^{13}C CP MAS spectra of (b) the silica coated membrane and (c) the APTES functionalized silica coated membrane. (d) ^{13}C CP MAS reference spectrum of the pure APDMS linker, and comparison of ^{13}C CP MAS spectra of (e) the silica coated membrane and (f) the APDMS functionalized silica coated membrane. *Note:* The reference spectrum (a) was recorded at room temperature. Spectra (b) and (c) were measured at 8 kHz spinning, nominally 110 K and MW on. The reference spectrum (d) was recorded at 110 K and 8 kHz spinning. Spectra (e) and (f) were measured at 9 kHz spinning, nominally 110 K and MW on. Signals marked with + or # are spinning sidebands of the glycerol.

Approximation of the ratio of the inner-pore surface to the foil surface and approximation of the surface area

To approximate the ratio of the inner-pore surface to the membrane surface excluding the inner-pore surface, a rough geometrical calculation can be performed assuming nominal values of thickness ($w = 2^{1/2} * 30$ µm because the PC foil was irraditated at an angle of 45°), number of channels ($N = 4x2x10^9$ cm^{-2}), and pore diameter (d = 95 nm).

$A_{pore\ surface}/A_{foil\ surface} = N*\pi*d*w = 4x2x10^{9}\ cm^{-2}*\ \pi*9500\ x10^{-9}cm*2^{1/2}*3000x10^{-6}cm=1013 \approx 1010$

After ALD coating with a 5 nm SiO_2 layer the inner channel diameter is reduced to ~85 nm, therefore:

$A_{pore\ surface}/A_{foil\ surface} = N*\pi*d*w = 4x2x10^{9}\ cm^{-2}*\ \pi*8500\ x10^{-9}cm*2^{1/2}*3000x10^{-6}cm=906 \approx 910$

Furthermore, the specific surface area for the SiO_2 coated membrane can be approximated as follows:

(1) The overall volume of a foil containing an area of 1 cm^2 and a thickness of 30 µm is 0.003 cm^3.
(2) In this volume, the surface that is given by the inner-pore surface is approximately 906 cm^2.
(3) 1 cm^3 of the SiO_2 coated membrane thus contains a surface that is given by 906 cm^2 /0.003 cm^3 $\approx$ 300000 cm^2/cm^3 = 30 m^2/cm^3
(4) Assuming a density of the polycarbonate of 1.20 g/cm^3 the specific surface area A_{spec} is 30 / 1.20 $m^2/g \approx 25\ m^2/g$.

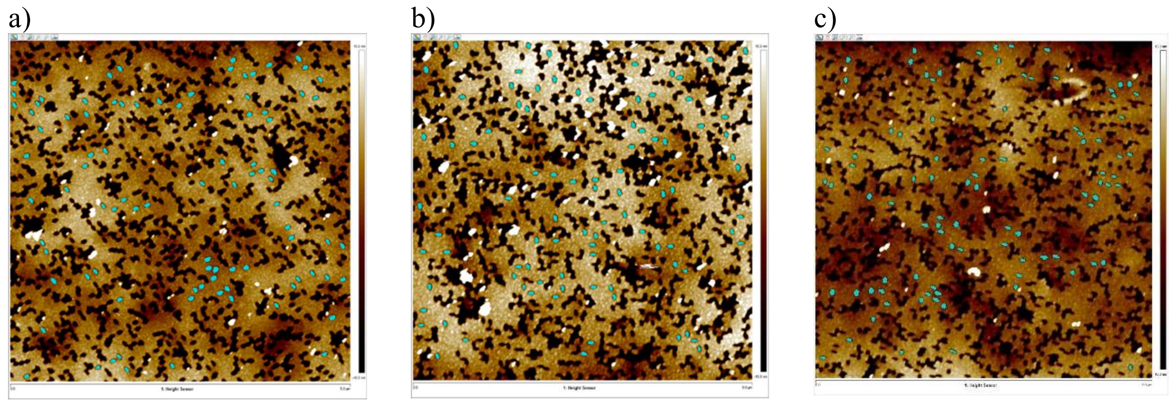

Figure S3. Selected single pores (blue) for the analysis of averaged pore diameter: Polymer foil after ion-etching (a), ALD layered polymer foil (b), and functionalized ALD layered polymer foil (c).

Sample (a)		**Sample (b)**		**Sample (c)**	
Area	Pore diameter	Area	Pore diameter	Area	Pore diameter
4123 nm^2	72 nm	4004 nm^2	71 nm	3629 nm^2	68 nm
		-2,9 %	-1.5 %	-9.4 %	-4.7 %

Table S1. Obtained pore diameters and pore areas from the analysis of the AFM images (Figure S3).