

Supporting Information

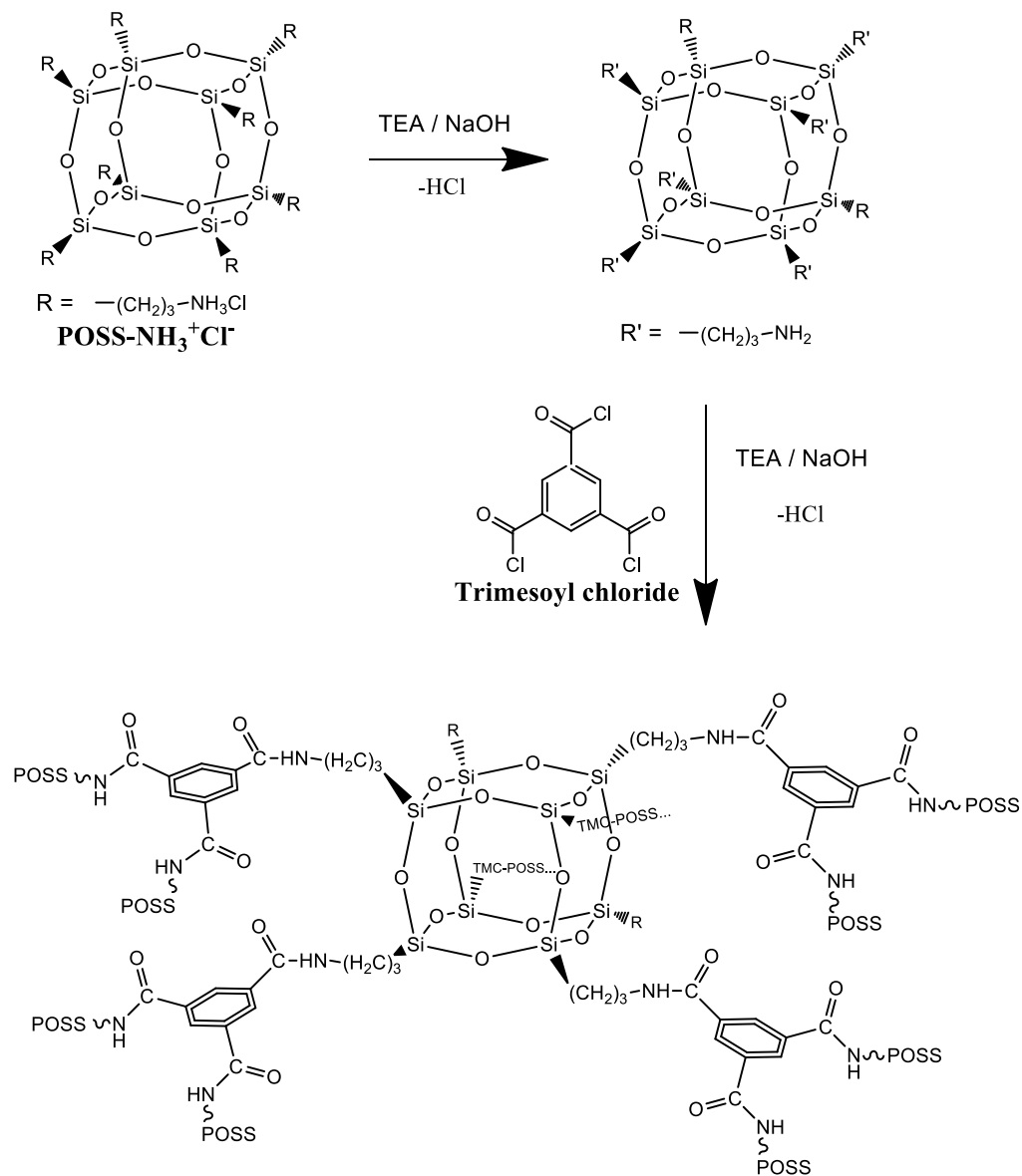
Experimental

Free-standing hybrid films were prepared by adjusting the pH of an aqueous solution of 0.9 wt% ammonium chloride salt functionalized POSS (OctaAmmonium POSS[®], Hybrid Plastics (USA)), by adding sodium hydroxide or triethylamine, and subsequently bringing the aqueous solution into contact with 0.2 wt% trimesoyl chloride in n-hexane. Supported films were prepared by impregnating a prewetted ultra-porous polyacrylonitrile membrane on a nonwoven, held fixed on a perforated plate by vacuum, with the aqueous POSS solution and subsequently submerging the membrane into 0.2 wt% trimesoyl chloride in n-hexane for 0.5 to 5 minutes. The supported films were cut (A5 size) from the perforated plate and dried overnight at room temperature in a nitrogen box.

Scanning electron microscopy (SEM) images were taken using LEO-1550 Schottky field emission scanning electron microscope (Carl-Zeiss, Germany). X-ray photoelectron spectroscopy measurements, on supported films, were performed on Quanterra SXM (scanning XPS microprobe) from Physical Electronics. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR FT-IR), on supported films, was done using an ALPHA FT-IR Spectrometer (Bruker Optics Inc, Germany) which is equipped with an ATR diamond crystal. Positron annihilation lifetime spectroscopy (PALS) measurements were performed in vacuum at 20 °C using an EG&G Ortec fast-fast coincidence system (Ortec, USA).

Permeation experiments were performed at room temperature in a dead-end filtration setup. The trans-membrane pressure was 10 bar. The effective membrane surface area was 13.86 cm². The molecular weight cut-off (MWCO) of the membranes was evaluated with an aqueous mixture of polyethylene glycols (PEGs) with mean molar masses 200 g mol⁻¹, 600 g mol⁻¹ and 1500 g mol⁻¹. The MWCO of the membrane was also determined with a toluene solution containing a mixture of polystyrene with molar masses of 300 g mol⁻¹, 400 g mol⁻¹, 1500 g mol⁻¹, 3000 g mol⁻¹ and 10000 g mol⁻¹. Compositions of feed, permeate and retentate were analyzed by gel permeation chromatography (GPC).

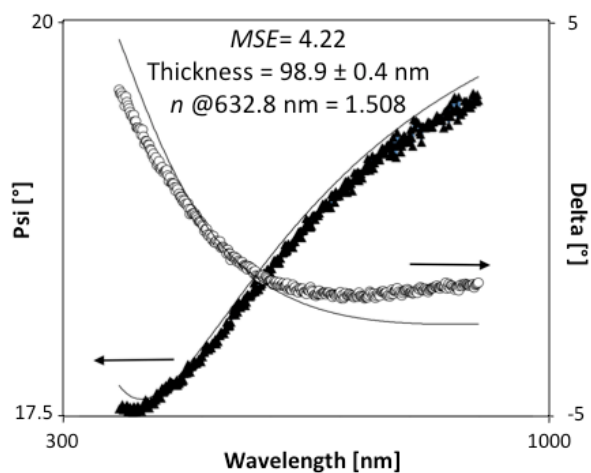
Reaction Scheme



Formation of the POSS-polyamide macromolecular network. Water soluble ammonium chloride salt functionalized POSS is first dissolved in an alkaline aqueous solution, allowing the conversion of ammonium to primary amine. The alkaline aqueous POSS solution is brought into contact with a trimesoyl chloride/n-hexane solution; the POSS and acid chloride react at the water/n-hexane interface forming the thin film hybrid POSS-polyamide network.

Spectroscopic ellipsometry

Spectroscopic ellipsometry measurements were performed with a rotating compensator ellipsometer (M-2000X, J.A. Woolam Co., Inc.) at a 70° angle of incidence. The sample was prepared by transferring a freestanding film onto a glass substrate. The results indicate that the surface is homogeneous (low degree of depolarization, <2%) and the film thickness is approximately 100 nm.



Mean square error = 4.22

Film thickness = 98.93 ± 0.390 nm

Film refractive index (Cauchy): $A = 1.552 \pm 0.00030156$, $B = 0.01062 \pm 0.00020849$

n of Cauchy Substrate @ 632.8 nm = 1.508

Movies

001 - Free standing film formation.avi

The movie shows the facile formation of a thin freestanding POSS-polyamide film. A solution of acyl chloride in hexane is poured onto an alkaline aqueous solution of ammonium chloride salt functionalized POSS.

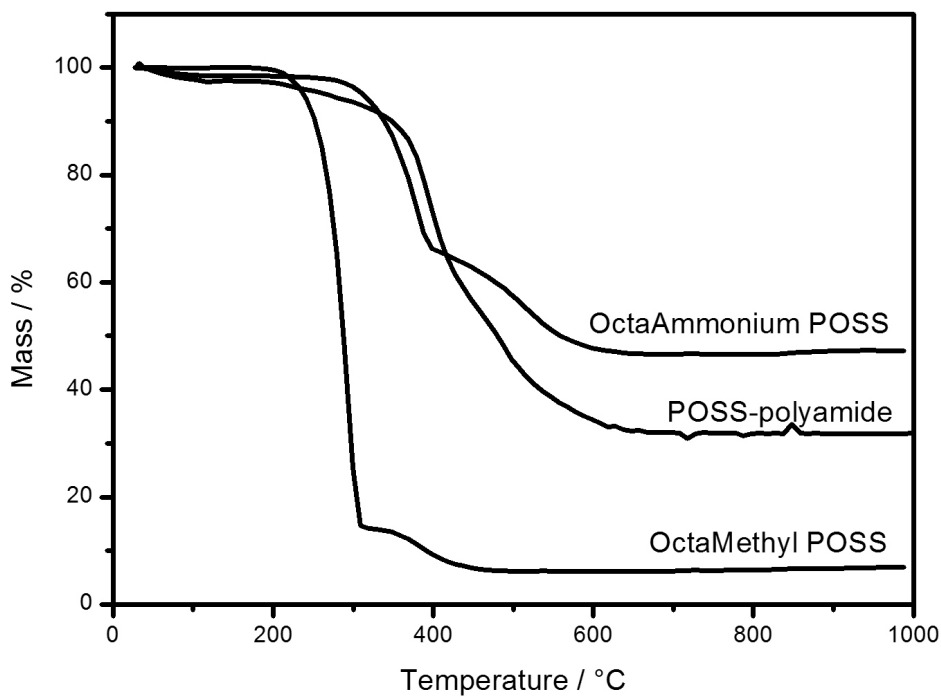
002 - Free standing film folding-unfolding.avi

The movie shows unfolding and folding of a freestanding POSS-polyamide film. No apparent damage to the film occurs after several times of repeated folding unfolding.

003 - Free standing film - Suction through orifice.avi

The movie shows suction and the subsequent release of a freestanding POSS-polyamide film through an orifice, without apparent damage to the film.

Thermal gravimetric analysis



Thermal gravimetric analysis (TGA) was performed with NETZSCH STA 449 (Germany). Measurements were done on 5 mg samples in alumina pans, under a nitrogen atmosphere (50 ml/min), with a heating rate of 10 °C. The thermal gravimetric evolution of unreacted OctaAmonium POSS and freestanding POSS-polyamide is comparable up to 400 °C. The asymptotic value observed at higher temperatures indicates a higher degree of degradation for the POSS-polyamide. For comparison, TGA data are shown for OtcaMethyl POSS. This material shows appreciable sublimation above 200 °C, which is in accordance with the observations reported for alkyl functionalized POSS by Mantz et al.¹

XPS

X-ray photoelectron spectroscopy measurements were performed on a Quantera SXM scanning XPS microprobe (Physical Electronics). The results indicate that the element concentrations and element ratios of OctaAmmonium POSS are in reasonable agreement with its molecular formula (Table 1). The element concentration and element ratio of a supported POSS-polyamide (Table 1) are ascribed to the conversion of ammonium groups to primary amine groups in the alkaline solution, and the subsequent reaction of these groups with TMC.

Table 1. Element concentration and element ratio of OctaAmmonium POSS and POSS-polyamide

	Element concentration (%)					Element ratio			
	C	N	O	Si	Cl	C/N	O/Si	O/N	Cl/N
OctaAmmonium POSS (exp.)	43.4	12.95	20.18	12.29	11.18	3.35	1.64	1.56	0.91
*OctaAmmonium POSS (theor.)	40	13.33	20	13.33	13.33	3.00	1.50	1.50	1.00
POSS-polyamide (exp.)	57.40	7.78	24.84	8.07	1.91	7.38	3.08	3.19	0.25

*The molecular formula of OctaAmmonium is $C_{24}H_{72}C_{18}N_8O_{12}Si_8$.

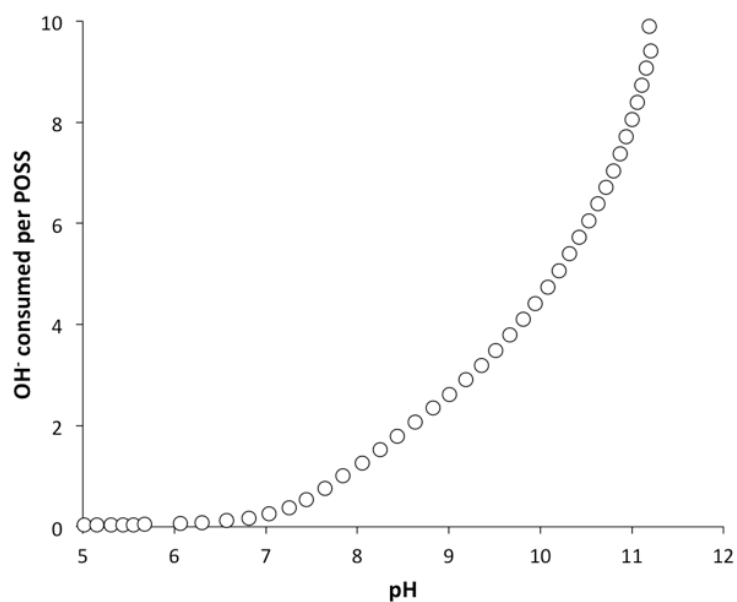
Analysis of the binding energy shift and peak area of C, N and O (Table 2) indicates that 5 to 6 of the 8 functional groups of POSS are involved in the crosslinking reaction.

Table 2. Binding energy, peak area concentration and peak assignment for elements C, N, O, Si and Cl.

		C			N		O		Si	Cl
		^a BE								
OctaAmmonium POSS	^a BE	284.8	286			401.0	532.1		102.3	197.2
	^b %	70 %	30 %			100 %	100 %		100 %	100 %
	^c id	C*-C	C*-N			N*-Cl	O*-Si		Si*-O	Cl*-N
POSS polyamide	^a BE	284.7	286.0	287.9	399.6	401.3	532.1	531.3	102.2	198.1
	^b %	80.1 %	8.2 %	11.7 %	80.3 %	19.7 %	63.3 %	36.7 %	100 %	100 %
	^c id	C*-C	C*-N	N-C*=O	N*-C=O	N*-Cl	O*-Si	O*=C	Si*-O	Cl*-N

^a BE = binding energy; ^b % = concentration of peak area at identified BE; ^c peak identification.

Titration of OctaAmmonium POSS[®]



The titration of 100 ml aqueous POSS solution (1.92 μM) with NaOH solution (0.1005 M) was performed using a 716 DMS Titrino (Metrohm, Germany). The method used for the titration was the dynamic equivalence-point titration (DET). The consumed amount of OH^- per POSS was calculated from the difference between the OH^- added and the measured OH^- , divided by the amount of POSS present in the solution. The data indicate that below $\text{pH}=7$ no significant conversion of ammonium groups to primary amines has occurred. At increasing pH the consumption of OH^- per POSS molecule increases, indicating conversion of ammonium to amine. In the pH range 9-10 about 4 to 5 amine groups have been formed per POSS molecule. At strongly alkaline conditions consumption of OH^- is also due to hydrolysis of the Si-O-Si bonds in the POSS molecule.

PALS

Positron annihilation lifetime spectroscopy (PALS) was used to investigate the pore size and relative pore concentration within the POSS and POSS-polyamide hybrid networks. The size of the nanoscale porosity within the polymers can then be related to the transport properties of the membranes. Long lifetimes were collected by setting the range of the time-to-amplitude converter to 200 ns and removing the coincident unit to increase count rates. Each file consisted of 4.5×10^6 integrated counts and a minimum of 5 files were collected for each sample. The full width at half maximum (FWHM) resolution of the instrument was determined to be 240 ps when measured with ^{60}Co . The positron source was prepared with 30 μCi of ^{22}Na which was dried between 2.54 μm thick Mylar films which required a background subtraction (1.664 ns and 3.13%). The hybrid materials were packed to 2 mm thickness and placed on each side of the positron source. The sample and source were then placed in the vacuum cell and brought to 5×10^{-4} Pa. The samples were measured at room temperature (20 °C) under vacuum. The PALS data were deconvoluted using a four component fit with LTv9 software by fixing the first lifetime (τ_1) to 0.125 ns due to annihilation of paraPositronium (pPs) and freeing the second lifetime (τ_2) ~ 0.4 ns due to free positron annihilation. Two orthoPositronium (oPs) components (τ_3 and τ_4) are associated with the bimodal porosity of the samples. The lifetimes were converted to pore sizes using the Rectangular Tao-Eldrup (RTE) model² adapted from the Tao-Eldrup semi-empirical formula.^{3,4}

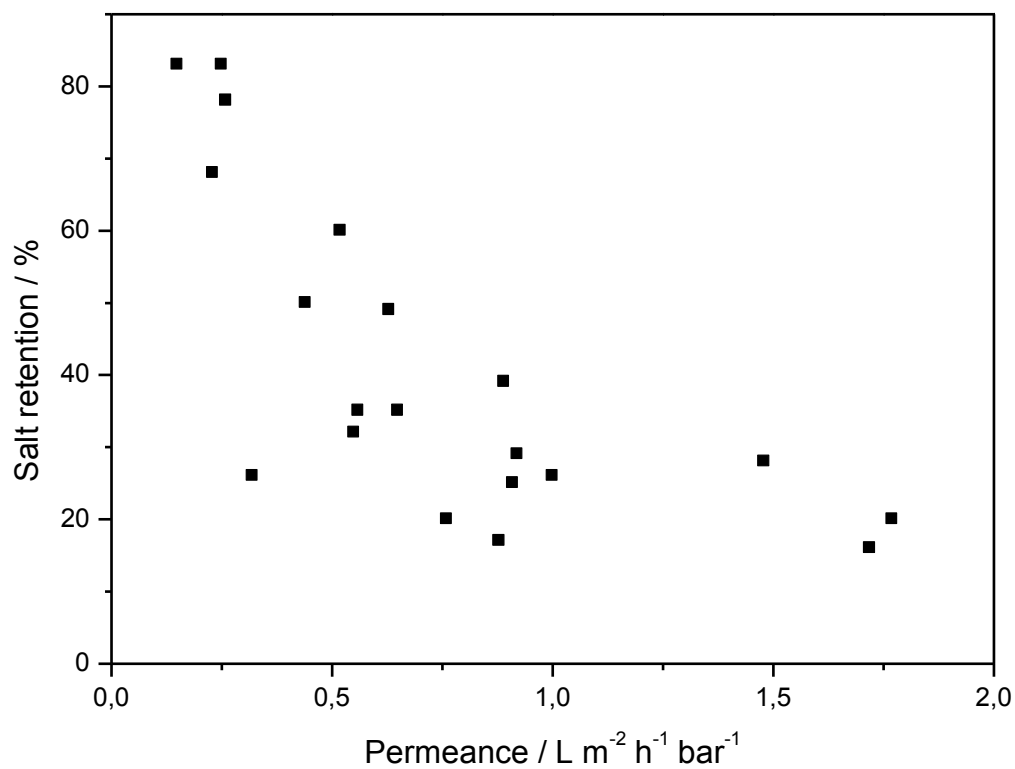
$$\tau_3^{-1} = 2 \left[1 - \frac{r_3}{r_3 + \Delta r} + \frac{1}{2\pi} \sin \left(\frac{2\pi(r_3)}{r_3 + \Delta r} \right) \right]$$

Table 3. PALS results for POSS samples prepared under different pH conditions.

	τ_3			τ_4		
	Lifetime (ns)	Pore Diameter (nm)	Intensity (%)	Lifetime (ns)	Pore Diameter (nm)	Intensity (%)
OctaAmmonium POSS	0.99±0.07	0.39±0.03	8.3±1.2	2.05±0.02	0.65±0.01	9.9±0.3
OctaAmmonium POSS pH 9.46	0.60±0.05	0.21±0.06	17.4±6.2	2.22±0.08	0.68±0.02	2.6±0.2
OctaAmmonium POSS pH 10.90	1.56±0.12	0.55±0.03	5.5±0.2	3.40±0.62	0.86±0.06	1.6±0.3

Salt retention

Salt retention measurements were performed in a lab-made dead-end filtration setup, with a feed solution of 2 g L⁻¹ NaCl in water, and a feed pressure of 10 bar. The permeance was calculated as the ratio of the flux over the applied trans-membrane pressure difference. Retention was calculated based on the conductivity of the feed, permeate, and retentate solutions. The significant salt retention indicates nanofiltration properties of the supported thin hybrid films



References

1. R. Mantz, P. Jones, K. Chaffee, J. Lichtenhan, J. Gilman, I. Ismail, and M. Burmeister, *Chem Mater*, 1996, **8**, 1250–1259.
2. T. Dull, W. Frieze, D. Gidley, J. Sun, and A. Yee, *J Phys Chem B*, 2001, **105**, 4657–4662.
3. S. Tao, *The Journal of Chemical Physics*, 1972, **56**, 5499.
4. M. Eldrup, D. Lightbody, and J. Sherwood, *Chemical Physics*, 1981, **63**, 51–58.