

Sieving of hot gases by hypercrosslinked nanoscale-hybrid membranes

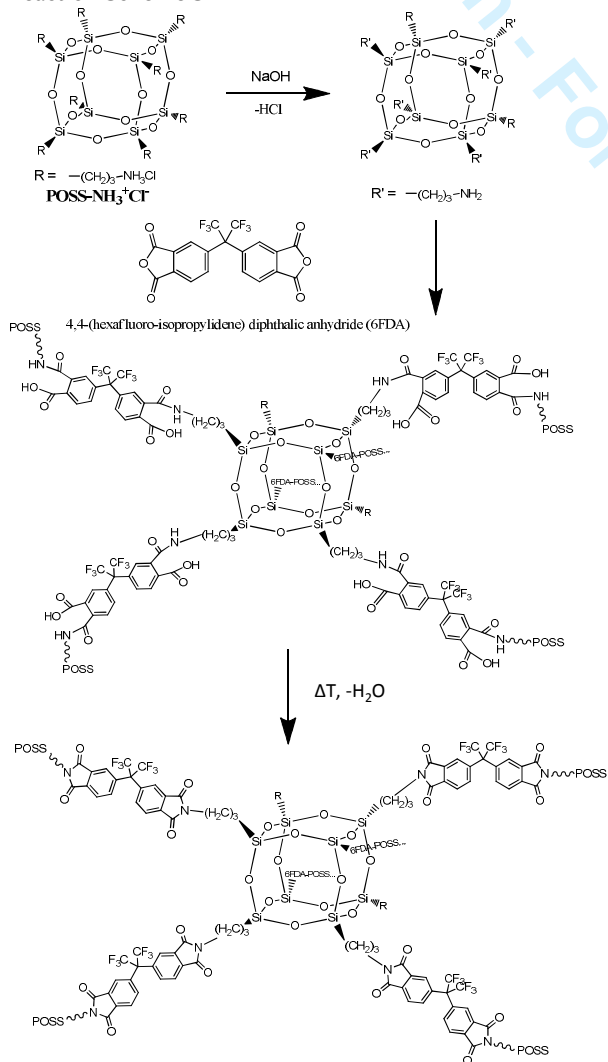
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Supporting Information

Reaction Scheme S1



Reaction scheme S1 shows the formation of polyPOSS-(amic acid) and polyPOSS-imide 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 6FDA solution in toluene; the POSS and anhydride react at the water/toluene interface forming the thin film hybrid polyPOSS-(amic acid) network. Next, formation of polyPOSS-imide is achieved by heat treatment at temperatures up to 300 °C, converting the amic acid into cyclic imide bonds. Any unreacted POSS and 6-FDA on the sample surface was removed by acetone and water washes. Samples were dried for 24 hours in dry nitrogen atmosphere to remove any toluene and unbound water.

Supported thin films were produced on α -alumina discs coated with 3 μm thick γ -alumina (porosity of 60 % and a pore size of 2-3 nm). Pre-wetted discs, held fixed on a perforated plate by vacuum, were impregnated with the POSS solution. Following, the discs were left to dry in a nitrogen atmosphere for 30 minutes and subsequently submerged in the 6-FDA in toluene solution (0.075 wt%).

Material characterization

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 8000. Free standing polyPOSS-imide was placed in an aluminum sample pan and cycled from 50 to 300 °C with a heating rate of 20 °C/min. Four subsequent heating and cooling cycles were used to prevent influence from sorbed water on the measurement. The heat flow as function of temperature shown in figure S1 displays a steady increase of the heat flow with temperature. The absence of any peaks in the heat flow as a function of temperature evidences that there is no glass transition for temperatures up to 300 °C.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy measurements were performed on a Quantera SXM scanning XPS microprobe (Physical Electronics), using a monochromatic Al K α source (1486.6 eV). The ratio of silica and fluor elements indicates the presence of 1.9 dianhydride bridging molecules per POSS cage. Assuming complete conversion of the anhydride groups to cyclic imides, each POSS cage is connected with an average of 3.8 bridges. This assumption follows from the absence of anhydride and carboxylic acid peaks in the FTIR-ATR spectra and is in agreement with the nitrogen and carbon elemental fits.

The nitrogen, carbon, oxygen and silica elemental fits of octa-ammonium POSS powder and polyPOSS-imide on α -alumina discs coated with 3 μ m thick γ -alumina are shown in Figure S3. The nitrogen elemental fit of octa-ammonium POSS shows two distinct peaks, attributed to the partially deprotonated ammonia groups. The binding energies of the amine and

ammonia groups were fixed in the polyPOSS-imide nitrogen peak fit, to determine the number of imide bonds per POSS molecule. The resulting fit indicates that 4 out of 8 groups per POSS molecule have been converted to imide groups. The imide binding energy is in agreement with values found for other polyimides.² The remaining unreacted groups mainly consist of amine groups, indicating that most ammonia groups are deprotonated upon interfacial polymerization.

The binding energies of the octa-ammonium POSS were fixed in the carbon elemental fit of the polyPOSS-imide. The polyPOSS-imide carbon elemental peak fit shows two additional peaks with respect to octa-ammonium POSS. These peaks are attributed to the imide bond (288.6 eV) and trifluoromethyl groups (292.5 eV), in accordance to typical binding energies found for these bonds. The ratio of the imide:trifluoromethyl peak fit area (approximately 2:1) is in good agreement with the supposition that both anhydride groups of the 6-FDA are converted to cyclic imide bonds.

The silicon elemental fit of octa-ammonium POSS shows a single peak, attributed to the SiO₃C groups of the POSS cage. The silicon elemental fit of the polyPOSS-imide shows two additional peaks at a lower and higher binding energy. These peaks are associated with silanol and SiO- formed by partial hydrolysis of the POSS cage.³ The formation of SiOH is known to both shift the binding energy, and broaden the XPS spectrum.⁴

The oxygen elemental spectrum of octa-ammonium shows a single peak associated with siloxane bonds in the POSS cages. The polyPOSS-imide oxygen elemental spectrum shows an additional peak at a binding energy of 530.7 eV, and is associated with the C=O of the imide group. The binding energy peak that emerged at 532.6 eV is considered to be from silanol bonds, in agreement with the peak fit of silicon for the polyPOSS-imide sample. In summary, the XPS spectra suggests a high degree of crosslinking between the POSS cages, with approximately 4 out of 8 functional groups that have reacted with a dianhydride. Also, the data shows that the POSS cage is partially hydrolysed during the interfacial polymerization reaction.

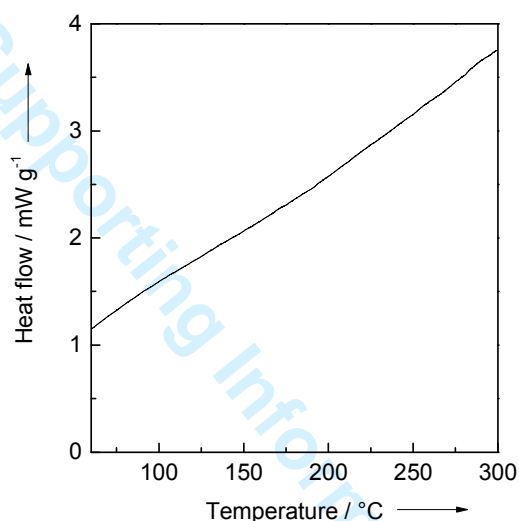


Figure S1: DSC analysis of a polyPOSS-imide powder sample.

Thermal gravimetric analysis

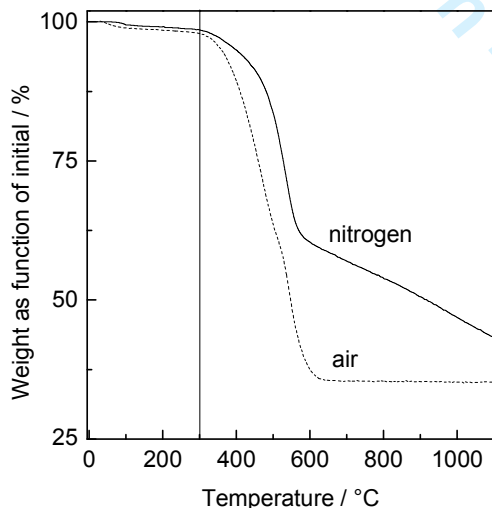


Figure S2: TGA analysis in air and nitrogen of a polyPOSS-imide powder sample

Thermal gravimetric analysis (TGA) was performed with NETZSCH STA 449 (Germany). Measurements were done on 1.5 mg samples in alumina pans, under an air and nitrogen atmosphere (50 ml/min) respectively, with a heating rate of 10 °C. The thermal gravimetric evolution of freestanding polyPOSS-imide shown in Figure S2 demonstrates that both under air and nitrogen the onset of weight loss is located above 300 °C. In air the sample reaches a constant mass at around 600 °C while for nitrogen weight loss persists even at 1000 °C, indicating two distinct degradation mechanisms. Both samples reach a final mass of 35% of the initial mass, having the appearance of a white powder in air atmosphere, and black powder in nitrogen atmosphere.

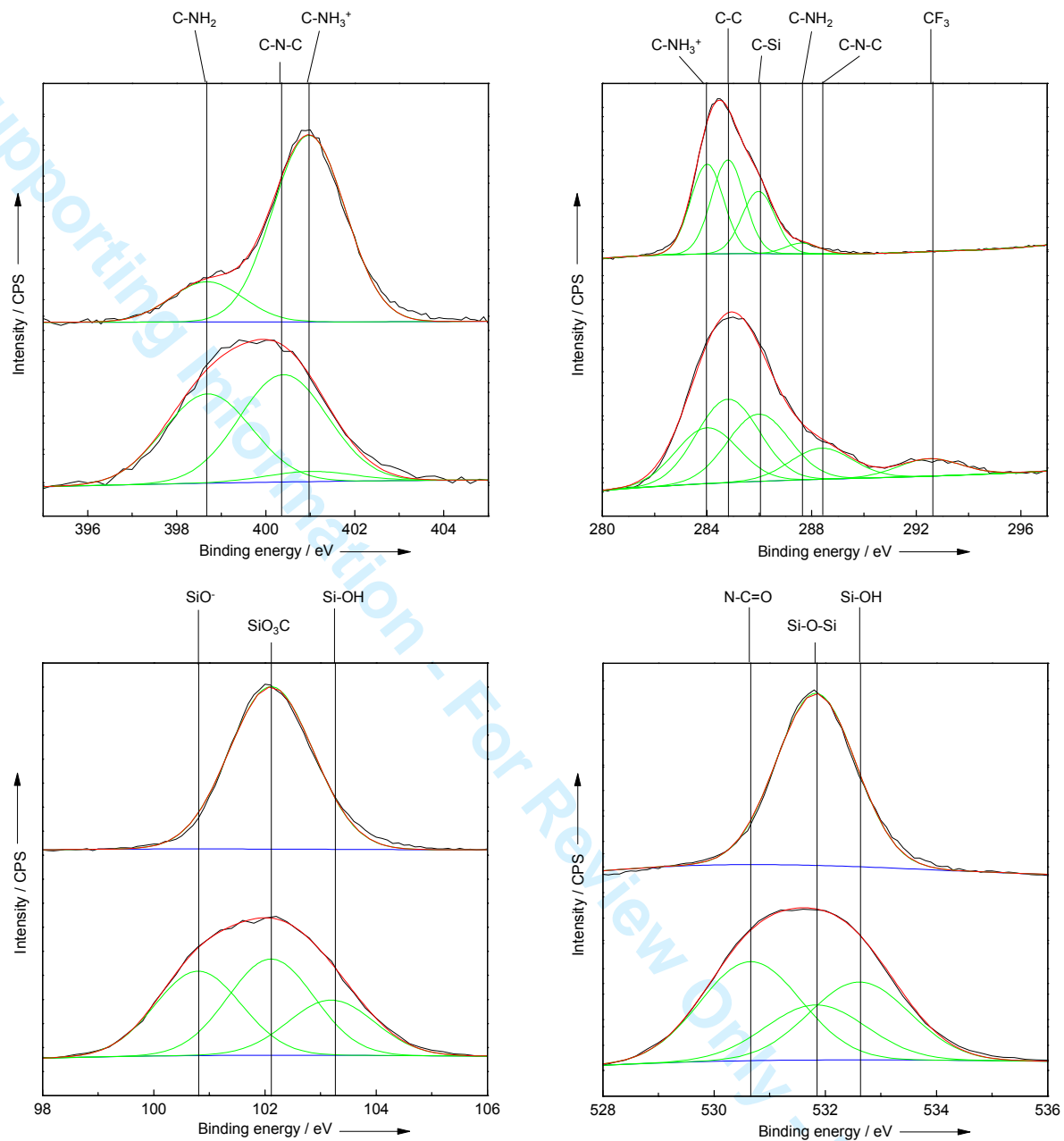


Figure S3: XPS elemental spectra for the N1s, C1s, Si2p and O1s signal. The data fitting has been performed using the peak analyzer function of Origin software. The peaks were fitted using Gaussians with similar FWHM values.

Table S1: XPS elemental composition table for Octa-ammonium POSS and polyPOSS-imide samples.

	Octa-ammonium POSS (theoretical)	Octa-ammonium POSS		polyPOSS-imide	
	Element concentration (%)	Element concentration (%)	Standard deviation (%)	Element concentration (%)	Standard deviation (%)
C	40	47.8	3.7	54.7	1.0
N	13.33	9.8	1.1	5.0	0.4
O	20	22.0	2.4	22.5	0.6
Si	13.33	11.5	1.1	6.9	0.1
F	-	-	-	9.8	0.1
Cl	13.33	9.0	1.5	-	-
Na	-	0.8	0.9	0.5	0.3
C/N	3	3.4		10.9	
F/Si	-	-		1.4	
O/N	1.5	1.6		4.5	
Cl/N	1	0.9		-	

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

The chemical structures of the polyPOSS-(amic acid) and polyPOSS-imide were analyzed with Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) on free standing films using an ALPHA FT-IR Spectrometer (Bruker Optics Inc, Germany) equipped with a ZnSe crystal. All spectra were recorded at room temperature. Thermal imidization was done by heat treatment in air for two hours at temperatures ranging from 0-300 °C. A detailed analysis of the polyPOSS-(amic acid) and polyPOSS-imide infrared absorption spectra is given in table S2. The infrared data confirms the presence of the partially hydrolyzed POSS cage, in accordance with the XPS data. Presence of aliphatic carbon originating from octa-ammonium POSS, trifluoromethyl groups and phenyl groups of the 6-FDA bridging molecule is confirmed by the infrared data. The differences between the spectra of the polyPOSS-(amic acid) and polyPOSS-imide originate solely from the conversion of the amic acid groups to cyclic imide.

Table S2: gas permeance activation energy for polyimide membranes

E_p (kJ/mol)			Ref
CO ₂	N ₂	CH ₄	
3.7	31.7	33.3	Current study
-3.3	3.5		¹
-1.3			²
0.2	4.45	7.25	³
10.5	24.1		⁴
14.3	27.3		
21.0	31.2		

Membrane single gas permeation experiments

Membrane single gas permeation experiments were performed in a dead-end mode at a trans-membrane pressure of 2 bar, and atmospheric pressure at the permeate side. Single gas permeation of N₂, CH₄, H₂, and CO₂ were measured at temperatures between 50-300 °C. The activation energy was determined using a linear fit using OriginPro 9 software. The activation energies for gas permeation were compared with the activation energies of conventional and 6FDA based polyimides, as given in table S2.

Table S2: FTIR-ATR peak analysis data for a polyPOSS-(amic acid) and polyPOSS-imide sample

Wavenumber	polyPOSS-(amic acid)	polyPOSS-imide		
cm ⁻¹	Intensity	Intensity	Bond	Vibrational mode
691	high	shoulder	CF ₃	def vib
706	high	high	NH ₂	def vib of primary amine
725	shoulder	high	CF ₃	def vib
750	medium	medium	CH	out of plane 1,2,4, trisubstituted benzene
769	shoulder	-	NH	def vib amide
793	shoulder	medium	NH ₂	out of plane bend of primary amine
846	medium	medium	NH ₂	out of plane bend of primary amine
910	medium	shoulder	C-C	rocking
965	medium	medium	C-C	rocking
1000	shoulder	shoulder	C-C	rocking
1040	high	high	Si-O cage	str
1093	high	high	Si-O ladder	str
1122	shoulder	high	CF ₃	str
1185	medium	medium	CF ₃	str
1212	medium	medium	CF ₃	str
1245	medium	medium	CF ₃	str
1255	medium	medium	CF ₃	str
1364	-	low	C=O or C-N	str
1393	-	medium	C=O or C-N	str
1374	high	-	C-N	str
1445	low	medium	CH ₂	scissoring
1475	low	low	CH ₂	def vib
1560	high	-	N-H	bend amide
1627	high	low	C=O	str amide
1670	-	shoulder	C=O	str carboxylic acid
1710	-	high	C=O	asym str imide
1780	-	low	C=O	sym str imide
2886	shoulder	-	CH ₂	sym str
2939	low	-	CH ₂	asym str
3068	broad	-	H ₂ O/COOH	bend
3235	broad	-	H ₂ O/COOH	OH str
3380	broad	broad	NH ₂	asym str

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