SUPPORTING INFORMATION

The Stability of Amino-functionalized Polyhedral Oligomeric Silsesquioxanes (POSS) in Water

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A) FTIR SPECTROSCOPY

The three functionalized POSS structures, POSS-amine1, POSS-amine2 and POSS-amide were experimentally characterized using FTIR. The spectra recorded on a Perkin-Elmer Spectrum One FTIR spectrophotometer are provided below in Figure S1 along with Table S1, which identifies the functional chemical groups associated to the main bands according to Refs. 1,2.

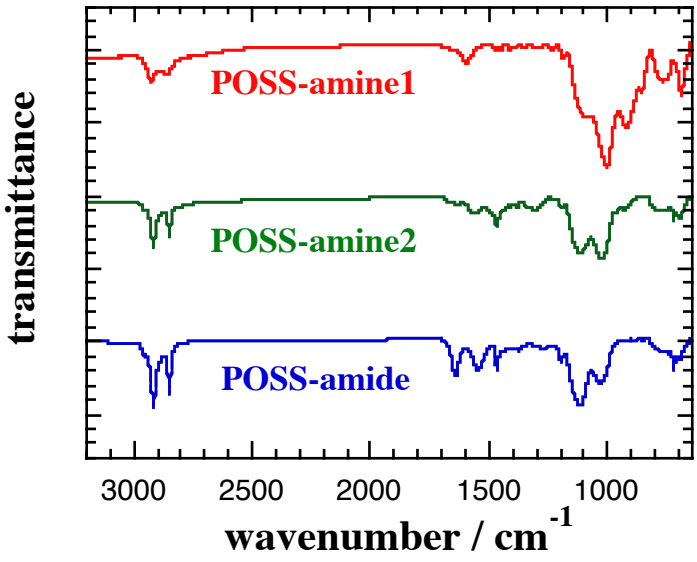

Figure S1. FTIR spectra for all three POSS under study

	Band / cm^{-1}	Chemical group
POSS-amine1	2928	CH_2
	2861	CH_2
	1597	R-NH_2
	1115	Si-O-Si
	1002	R-Si-O
	919	R-NH_2
	858	R-CH_2-NH_2
	766	R-CH_2-NH_2
	689	NH_2
POSS-amine2	2916	CH_2
	2849	CH_2
	1561	R-CH_2-NH-CH_2-R'
	1468	CH_3
	1115	Si-O-Si
	1024	R-Si-O
	719	$(CH_2)_n$
	693	NH
POSS-amide	2912	CH_2
	2849	CH_2
	1641	R-CO-NH-R'
	1548	R-CO-NH-R'
	1468	CH_3
	1195	R-CO-NH-R'
	1115	Si-O-Si
	1032	R-Si-O
	719	$(CH_2)_n$
	693	NH

Table S1. Functional groups associated to the main bands in Fig. S1

B) MOLECULAR MODELLING

The classical force-field used for the MD simulations is given by equation A:

$$U_{pot} = \sum_{\theta} U_{bend}(\theta) + \sum_{\tau} U_{tors}(\tau) + \sum_{i-planar} U_{oop}(i) + \sum_{(i,j)nb} U_{vdw}(r) + \sum_{(i,j)nb} U_{coul}(r) \qquad \text{(A)}$$

The different terms in Eq. A are given in detail below and all parameters can be found in the associated Table S2. The atom-types used are defined in Figure S2.

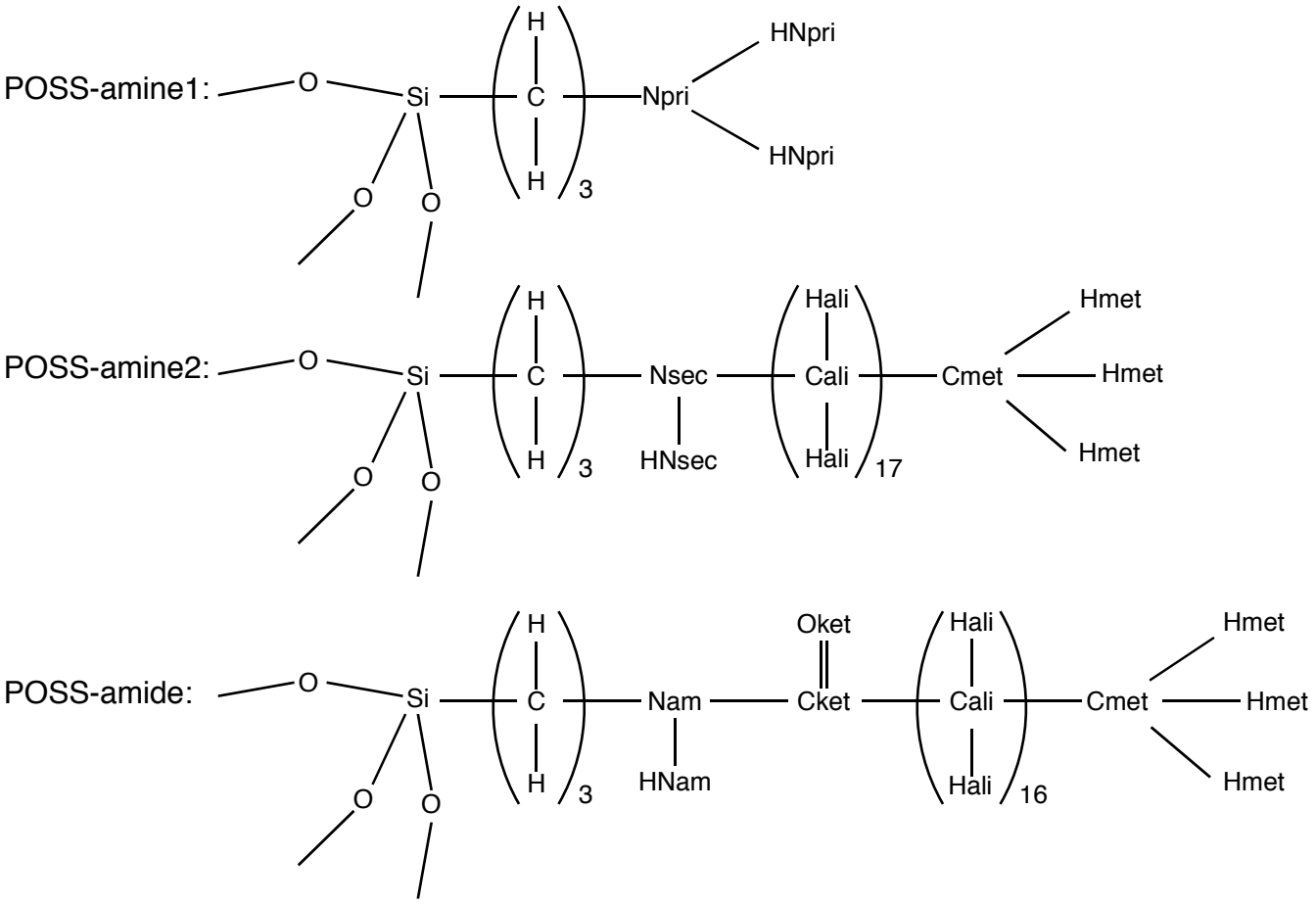

Figure S2. The different atom-types defined for the three POSS under study. The water atom-types are Owat and Hwat.

In the force-field, the angle-bending deformations are described by a harmonic function in the cosine of the bond angles θ:

$$U_{bend}(\theta) = \frac{k_\theta}{2} \left(\cos\theta - \cos\theta_0\right)^2 \qquad \text{(B)}$$

where k_θ is a constant determining the flexibility of the angle and θ_0 is the equilibrium bond angle. No specific angle-bending potentials were used to restrict the Si-O-Si and O-Si-O angles, since the combination of the rigid Si-O bonds and the non-bonded U_{vdw} and U_{coul} terms were sufficient to maintain the geometry of the cage. On the other hand, high-frequency motions of the hydrogens in all CH_2 and CH_3 groups were removed using special constraints.[3]

The torsional motions around the dihedral angles τ are represented by a third-order polynomial in $cos\ \tau$:

$$U_{tors}(\tau) = \sum_{n=0}^{3} a_n \cos^n \tau \qquad \text{(C)}$$

with the dihedral angle τ varying from -180° to +180°, $\tau = 0°$ being the *trans* conformation and a_n being the torsional coefficients. The wild card denotes any atom-type, except when the coefficients for a specific dihedral are defined elsewhere.

The out-of-plane term, keeps sp^2 structures planar by using a harmonic function in the perpendicular distance *d* from the central atom *i* to the plane defined by its three attached atoms with k_{oop} being the force constant:

$$U_{oop}(i) = \frac{k_{oop}}{2} d^2 \tag{D}$$

The "non-bonded" van der Waals interactions are described in Eq. (A) by the 12-6 Lennard-Jones form:

$$U_{vdw}(r) = U_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \tag{E}$$

where ε is the well-depth of the potential, σ is the distance at which the potential is zero and *r* is the distance between the interacting sites. The cross-terms for unlike-atom pairs are obtained from the standard combination rules given by:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \qquad \varepsilon_{ij} = \sqrt{\left(\varepsilon_{ii} \times \varepsilon_{jj}\right)} \tag{F}$$

The last term of Eq. (A) accounts for the Coulombic interactions with q_i and q_j being the partial charges on atoms *i* and *j* respectively, and ε_0 being the vacuum permittivity:

$$U_{coul}(r) = \frac{q_i\, q_j}{4\, \pi\, \varepsilon_0\, r} \tag{G}$$

These partial charges were obtained by performing Density Functional Theory calculations on representative fragments of the amino-functionalized POSS. They were carried out using the Gaussian09 code[4] at the B3LYP/6-31G** level and the Merz-Singh-Kollman (MK) procedure,[5,6] which derives the net atomic charges using a least squares fit of the quantum mechanically calculated electrostatic potential to that of the partial charge model. The partial charges were then symmetrized with respect to the nature and the position of the atoms.

Bond types	b_0 / Å	**Bond-angle type**	θ_0 / deg	k_θ / kJ mol^{-1}	**Out-of-plane atom**	k_{oop} / kg s^{-2}
Si-O	1.65	O-Si-O	109.1	-	Nam	167
Si-C	1.86	Si-O-Si	149.2	-	Cket	667
C-C	1.54	O-Si-C	109.9	477.8		
C-Npri	1.47	Si-C-C	117.2	618.3		
C-Nsec	1.46	Si-C-H	106.9	494.6		
C-Nam	"	C-C-C	114.0	742.0		
Npri-HNpri	1.02	C-C-Npri	110.4	742.0		
Nsec-HNsec	"	C-C-Nsec	110.8	742.0		
Nam-HNam	1.01	C-C-Nam	113.1	556.5		
Nsec-Cali	1.46	C-C-H	109.3	494.6		
Nam-Cket	1.37	Npri-C-H	110.8	494.6		
Cket-Oket	1.23	Nsec-C-H	110.3	494.6		
Cket-Cali	1.53	Nam-C-H	107.7	622.2		
Cali-Cali	"	H-C-H	106.1	-		
Cali-Cmet	"	C-Npri-HNpri	110.0	1236.6		
C-H	1.10	HNpri-Npri-HNpri	106.4	1236.6		
Cali-Hali	"	C-Nsec-Cali	113.5	556.5		
Cmet-Hmet	"	C-Nsec-HNsec	108.7	1236.6		
Owat-Hwat	1.00	Cali-Nsec-HNsec	108.6	1236.6		
Hwat-Hwat	1.63	C-Nam-Cket	122.6	1550.4		
		C-Nam-HNam	118.4	692.0		
		Cket-Nam-HNam	118.4	574.6		
		Nam-Cket-Oket	121.9	1171.7		
		Nam-Cket-Cali	115.3	692.0		
		Oket-Cket-Cali	121.9	952.3		
		Nsec-Cali-Cali	111.4	742.0		
		Nsec-Cali-Hali	110.2	494.6		
		Cket-Cali-Cali	112.5	556.5		
		Cket-Cali-Hali	108.9	497.8		
		Cali-Cali-Cali	113.6	742.0		
		Cali-Cali-Cmet	113.3	742.0		

		Cali-Cali-Hali		109.3	494.6		
		Cmet-Cali-Hali		109.5	494.6		
		Hali-Cali-Hali		106.0	-		
		Cali-Cmet-Hmet		111.3	-		
		Hmet-Cmet-Hmet		107.6	-		
Dihedral type	a_0 / kJ mol^{-1}	a_1 / kJ mol^{-1}	a_2 / kJ mol^{-1}	a_3 / kJ mol^{-1}	**Like-atom pair i···i**	σ_{ii} / Å	ε_{ii}/k_B / K
-Si-C-	0.349	1.046	0	-1.395	Si···Si	3.385	294.38
*-C-C-H	1.339	4.017	0	-5.356	O···O	2.955	102.15
*-C-C-C	0.837	2.510	0	-3.347	C···C	3.029	53.84
-C-Npri-	0.837	2.510	0	-3.347	Cket···Cket	"	"
-C-Nsec-	0.837	2.510	0	-3.347	Cali···Cali	"	"
-C-Nam-	0.837	2.510	0	-3.347	Cmet···Cmet	"	"
-Nsec-Cali	0.837	2.510	0	-3.347	Oket···Oket	2.708	58.37
-Nam-Cket-	54.057	0	-54.057	0	Npri···Npri	2.762	47.81
Nam-Cket-Cali-Cali	0.527	1.582	0	-2.109	Nsec···Nsec	"	"
Oket-Cket-Cali-Cali	2.929	-8.786	0	11.715	Nam···Nam	"	"
*-Cket-Cali-Hali	1.146	3.439	0	-4.586	H···H	2.673	21.14
Nsec-Cali-Cali-Cali	0.837	2.510	0	-3.347	HNpri···HNpri	"	"
*-Cali-Cali-Hali	1.339	4.017	0	-5.356	HNsec···HNsec	"	"
Cket-Cali-Cali-Cali	0.527	1.582	0	-2.109	HNam···HNam	"	"
*-Cali-Cali-Cali	2.092	6.276	0	-8.368	Hali···Hali	"	"
*-Cali-Cmet-Hmet	1.339	4.017	0	-5.356	Hmet···Hmet	"	"
					Owat···Owat	3.167	78.00

Atom type	q_i/e **in POSS-amine1**	q_i/e **in POSS-amine2**	q_i/e **in POSS-amide**
cage Si	1.656	1.792	1.710
cage O	-0.952	-1.068	-0.976
C1	-0.627	-0.657	-0.561
C2	0.139	0.179	-0.019
C3	0.285	0.261	0.242
Npri	-0.989	-	-
Nsec	-	-0.876	-
Nam	-	-	-0.787
Cket	-	-	0.855
Oket	-	-	-0.601

Cali1	-	0.403	-0.519
Cali2	-	-0.034	0.194
Cali3	-	-0.153	0.032
Cali4	-	0.191	-0.144
Cali5	-	-0.029	0.085
Cali6	-	-0.037	0.028
Cali7	-	0.037	-0.028
Cali8	-	0.018	0.008
Cali9	-	-0.026	0.038
Cali10	-	0.027	-0.007
Cali11	-	0.029	-0.005
Cali12	-	-0.032	0.011
Cali13	-	0.013	0.065
Cali14	-	0.070	-0.067
Cali15	-	-0.071	0.000
Cali16	-	-0.010	0.151
Cali17	-	0.157	-
Cmet	-	-0.290	-0.299
H on C1	0.127	0.128	0.128
H on C2	0.005	-0.003	0.039
H on C3	-0.006	-0.007	0.034
HNpri	0.356	-	-
HNsec	-	0.334	-
HNam	-	-	0.365
Hali on Cali1	-	-0.039	0.114
Hali on Cali2	-	0.020	-0.016
Hali on Cali3	-	0.019	0.002
Hali on Cali4	-	-0.038	0.025
Hali on Cali5	-	0.005	-0.018
Hali on Cali6	-	0.004	-0.006
Hali on Cali7	-	-0.007	0.001
Hali on Cali8	-	-0.004	-0.005
Hali on Cali9	-	0.003	-0.009
Hali on Cali10	-	-0.006	-0.002
Hali on Cali11	-	-0.006	-0.003
Hali on Cali12	-	0.004	-0.003
Hali on Cali13	-	-0.003	-0.015
Hali on Cali14	-	-0.014	0.007

Hali on Cali15	-	0.010	0.002
Hali on Cali16	-	0.005	-0.020
Hali on Cali17	-	-0.020	-
Hmet on Cmet	-	0.068	0.069
Owat	-0.848		
Hwat	0.424		

Table S2. Force-field parameters. The atom-types are those defined in the Figure above. The symbols * denote a wild card, the ditto symbols " mean that the parameters are the same as those above and the symbols - show that there are no parameters explicitly defined for these interactions. For the charges, the organic chain atom closest to the siloxane cage is C1, the next one is C2, then C3, etc... up to the end of the chain.

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