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Supplementary Information for:

Stability and behaviour in aqueous solutions of the anionic cubic silsesquioxane substituted with tetramethylammonium

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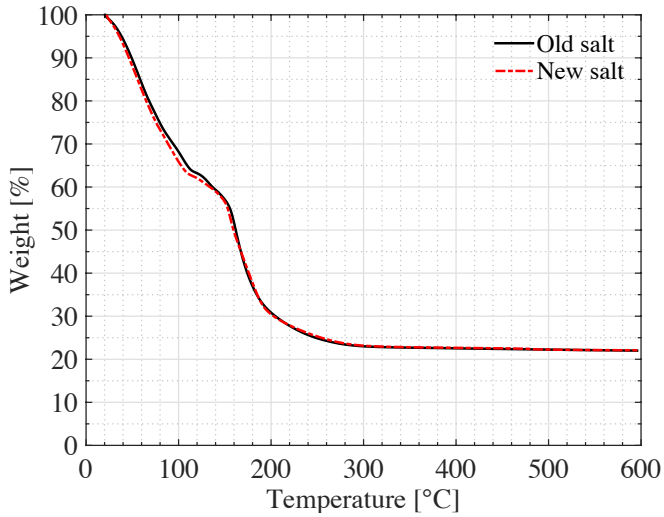

Figure S1: *TGA graphs of the silica salt, one from a bottled opened just before the measurements, one that was opened 2 years before. The TGA data shows that 22.3% of the salt (assumed to be $SiO_{2.5}$) remains at 600°C. The remaining part, the silica, corresponds to 47.9% of the salt's molar weight. This reveals that 53.2% of the weight is water; giving $[N(CH_3)_4]_8[Si_8O_{20}] \bullet 72\ H_2O$.*

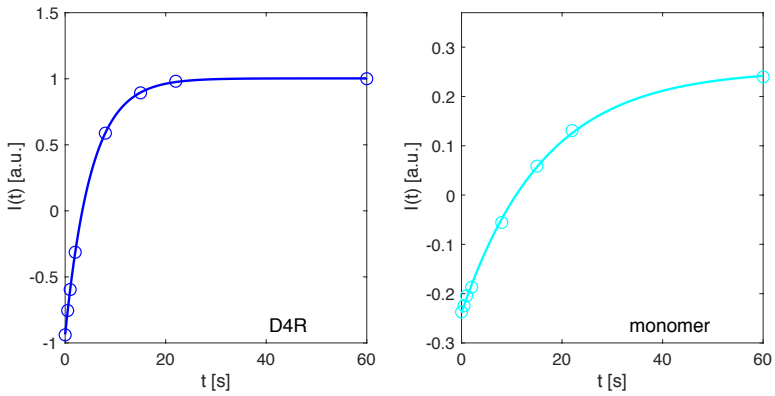

Figure S2: *Example of non-linear fitting of the data from the inversion recovery experiment to a single exponential function. The obtained longitudinal relaxation times (T1) are shown in Table 1 of the main text. The figure shows the D4R, with the shortest value (5.2 sec), and the monomer with the longest value (16.4 sec).*

Table S1: *EPSR model parameters.*

Silica Species	Atom	Label	Lennard-Jones parameters		Atomic mass	Coulomb parameter	Bond Lengths	
			ε [kJ/mol]	σ [Å]	u [amu]	q [e]	atoms	[Å]
monomer	Si	Si_1	0.8280	4.405	28.086	0.885	Si-O(-H)	1.65
	O	O_{11}	0.3350	3.300	15.999	-1.000	$Si\text{-}O^-$	1.65
	O	O_{21}	0.3350	3.300	15.999	-0.315	O-H	0.97
	H	H_{Si}	0.0962	2.878	2.000	0.0200		
dimer	Si	Si_2	0.8280	4.405	28.086	0.9975	Si-O(-Si)	1.65
	O	O_{12}	0.3350	3.300	15.999	-1.000	Si-O(-H)	1.65
	O	O_{22}	0.3350	3.300	15.999	-0.415	$Si\text{-}O^-$	1.65
	O	O_{32}	0.3350	3.300	15.999	-0.415	O-H	0.97
	H	H_{Si}	0.0962	2.878	2.000	0.0200		
double-4-ring, D4R, cubic octamer	Si	Si_8	0.8280	4.405	28.086	0.6225	Si-O(-Si)	1.63
	O	O_{18}	0.3350	3.300	15.999	-1.000	$Si\text{-}O^-$	1.63
	O	O_{28}	0.3350	3.300	15.999	-0.415		1.63

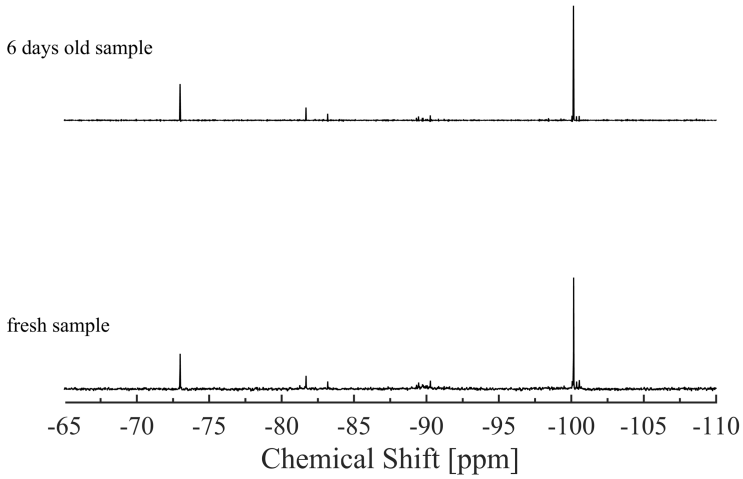

Figure S3: *^{29}Si-NMR spectroscopy of a 22 wt% salt sample, measured right after preparation (bottom) and after 6 days (top).*

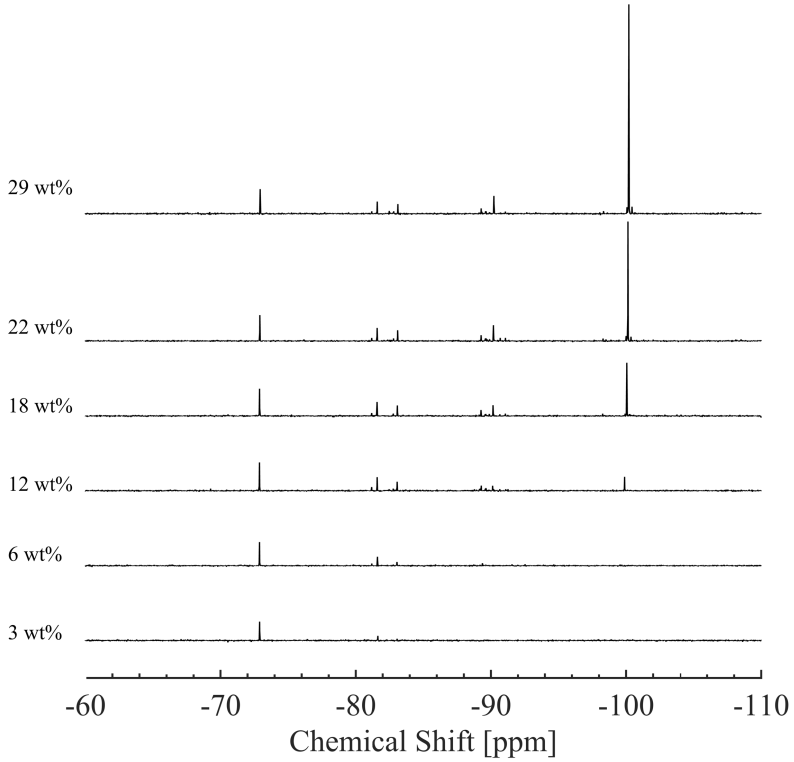

Figure S4: *^{29}Si-NMR spectra of concentration series.*

Table S2: *Relative concentration of Si-species for all investigated samples.*

sample	monomer	dimer	S3R	S4R	D3R	D4R	other
3 wt%	89.5 %	10.5 %	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %
6 wt%	65.1 %	24.7 %	6.2 %	3.5 %	0.0 %	0.6 %	0.0 %
12 wt%	40.7 %	20.0 %	11.6 %	4.0 %	3.3 %	17.5 %	2.9 %
18 wt%	22.5 %	11.6 %	7.9 %	4.5 %	7.0 %	40.8 %	0.9 %
22 wt%	13.6 %	7.0 %	5.3 %	1.4 %	7.0 %	58.0 %	7.7 %
29 wt%	9.4 %	3.8 %	2.8 %	0.7 %	5.4 %	74.7 %	3.2 %
6 wt% + 0.1 M TMAOH	57.0 %	24.9 %	12.1 %	3.4 %	1.8 %	0.9 %	0.0 %
6 wt% + 0.1 M TMACl	80.6 %	12.3 %	2.4 %	0.0 %	0.0 %	4.7 %	0.0 %
6 wt% + 0.1 M TMABr	76.1 %	17.3 %	1.5 %	2.0 %	0.0 %	3.0 %	0.0 %
6 wt% + 0.1 M TEABr	80.6 %	14.5 %	1.5 %	0.8 %	0.0 %	2.5 %	0.0 %
6 wt% + 0.1 M TPABr	71.8 %	20.6 %	2.6 %	2.6 %	0.0 %	2.4 %	0.0 %
6 wt% + 0.1 M NaCl	84.9 %	10.5 %	1.8 %	2.8 %	0.0 %	0.0 %	0.0 %
6 wt% + 0.1 M NaBr	80.2 %	11.7 %	4.6 %	2.8 %	0.8 %	0.0 %	0.0 %
6 wt% + 0.1 M NaI	78.9 %	21.1 %	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %
6 wt% + 0.2 M NaCl	72.0 %	19.2 %	5.9 %	2.9 %	0.0 %	0.0 %	0.0 %
6 wt% + 0.2 M NaI	66.1 %	19.0 %	6.1 %	5.3 %	3.6 %	0.0 %	0.0 %
6 wt% + MeOH	63.7 %	25.1 %	5.4 %	2.4 %	0.0 %	3.5 %	0.0 %
6 wt% + EtOH	55.5 %	22.1 %	5.2 %	4.1 %	0.0 %	13.1 %	0.0 %
22 wt% + MeOH	3.2 %	0.2 %	0.3 %	0.5 %	1.5 %	85.5 %	8.7 %
22 wt% + EtOH	0.1 %	0.0 %	0.0 %	0.0 %	0.1 %	91.9 %	7.8 %

Table S3: *Variation in pH with the silica-salt, i.e. initial concentration cubic octamers, D4R, and additives.*

Weight % silica salt	Si atom concentration [M]	Additive	pH
3 wt%	0.096	-	11.53
6 wt%	0.195	-	11.85
12 wt%	0.390	-	12.11
18 wt%	0.585	-	12.26
22 wt%	0.736	-	12.32
29 wt%	0.928	-	12.34
6 wt%	0.195	0.1M TMACl	11.90
6 wt%	0.195	0.1M TMABr	11.80
6 wt%	0.195	0.1M TEABr	11.80
6 wt%	0.195	0.1M TPABr	11.80
6 wt%	0.195	0.1M TMAOH	12.90
6 wt%	0.195	0.1M NaCl	11.75
6 wt%	0.195	0.1M NaBr	11.78
6 wt%	0.195	0.1M NaI	11.80
6 wt%	0.195	0.2M NaCl	11.70
6 wt%	24.4	0.2M NaI	11.71

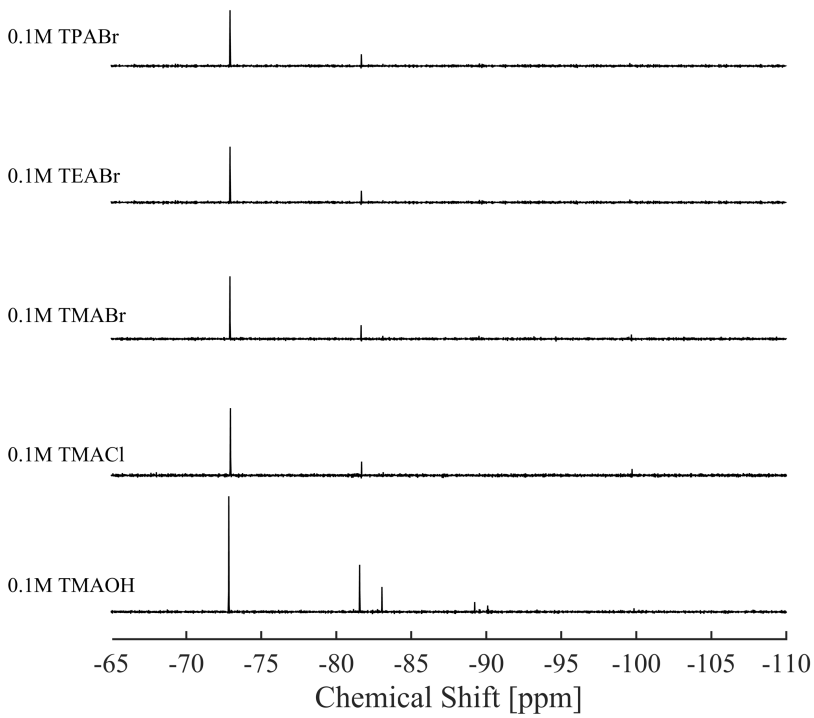

Figure S5: *^{29}Si-NMR spectra of TAA-salt addition to 6 wt% salt samples.*

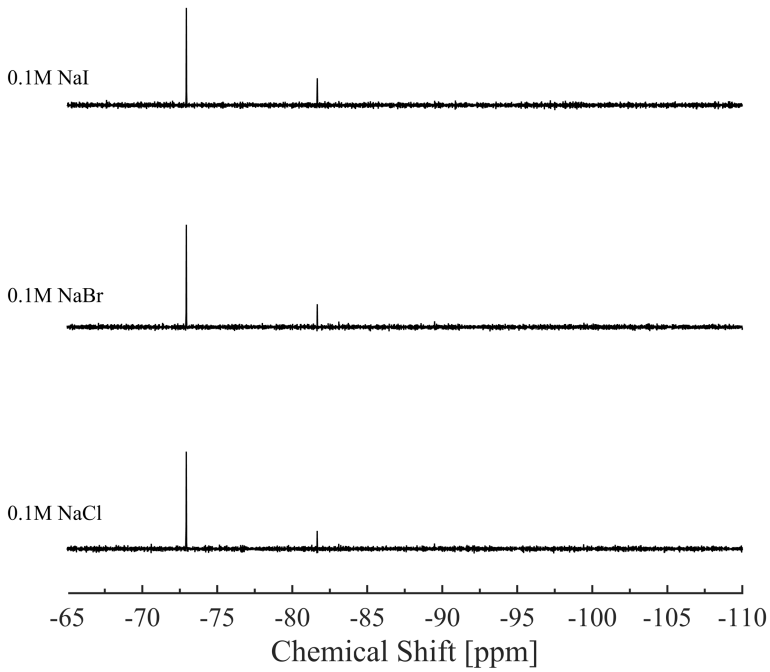

Figure S6: *^{29}Si-NMR spectra of samples containing 6 wt% silica salt and 0.1M Na-salts.*

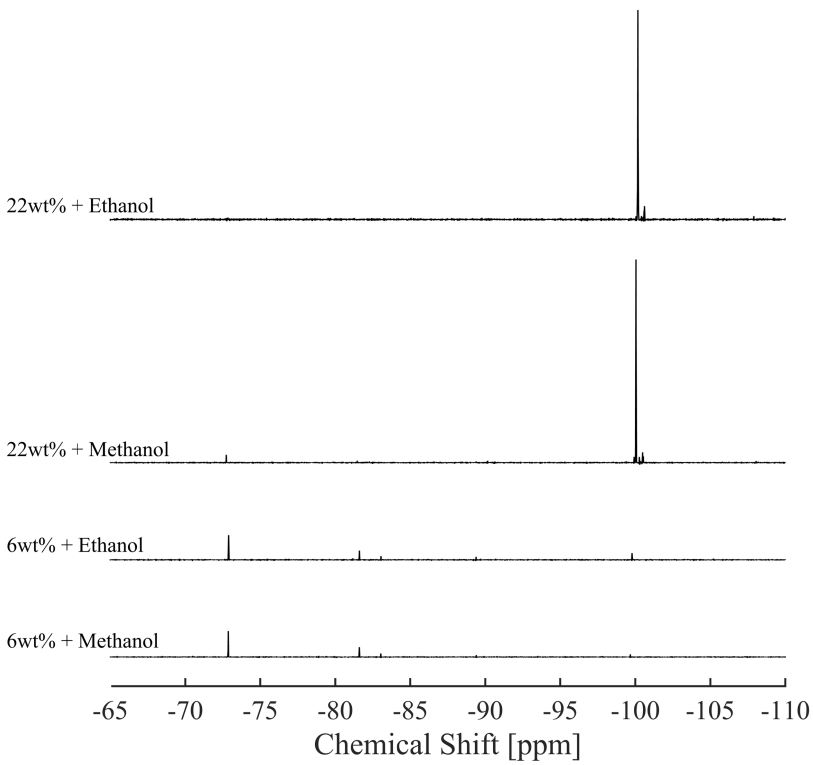

Figure S7: *^{29}Si-NMR spectra of samples with 6 or 22 wt% silica salt and methanol or ethanol at a Si:alcohol ratio of 1:8.6.*

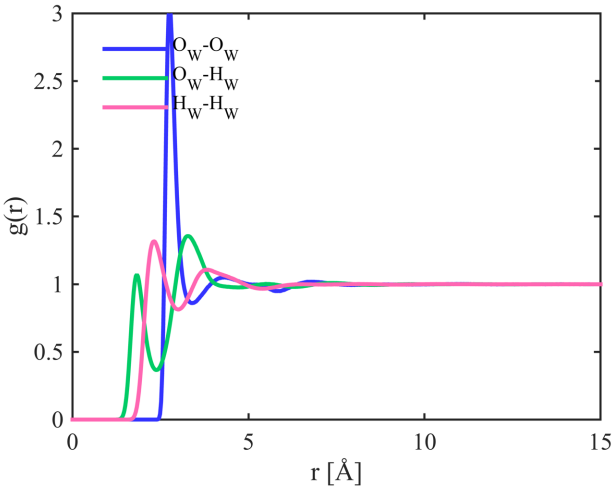

Figure S8: *Site-site radial distribution functions for the oxygen (O_W) and hydrogen (H_W) of the water.*

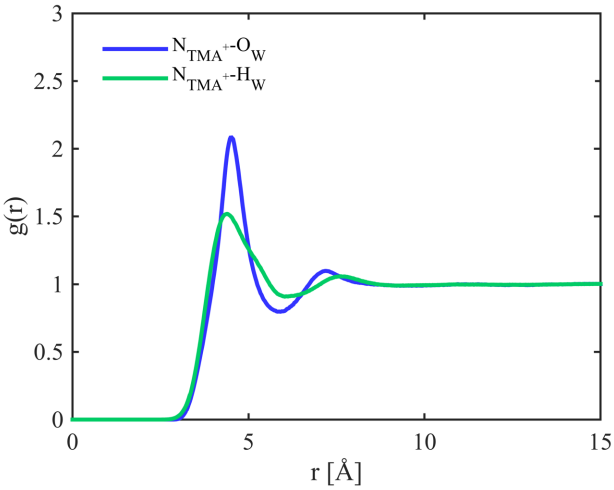

Figure S9: *Site-site radial distribution functions for the central nitrogen in TMA+ to the oxygen (O_W) and hydrogen (H_W) of water.*

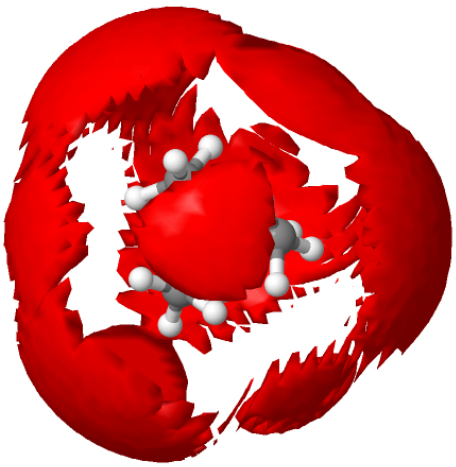

Figure S10: *Spatial density function for the central nitrogen in TMA+ to oxygen of water (OW), showing the top 15% of the positions between 3 to 6Å.*

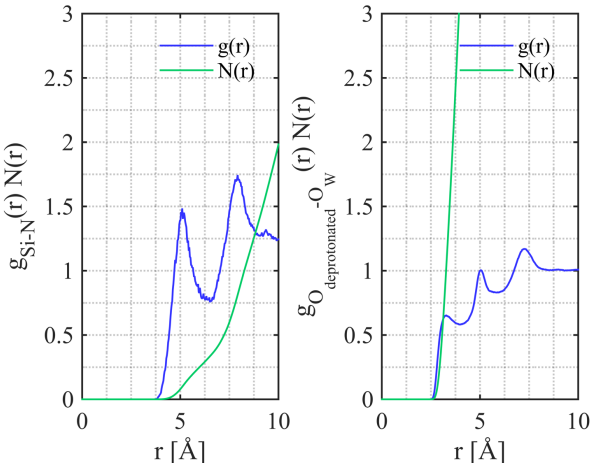

Figure S11: *Site-site radial distribution together with the corresponding coordination numbers for (left) Si_{cube}-N_{TMA} and (right) $O_{deprotonated}$-O_W in the cubic octamer.*

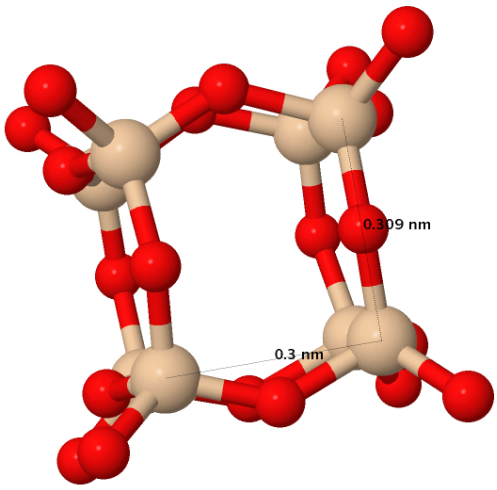

Figure S12: *Conformation of a cubic octamer, which displays a slight deformation of the cubic, giving it a more rectangular shape; one side being 3.09 Å and the other 3.00Å.*