

# The Role Of Water In Silica Oligerization.

## SUPPORTING INFORMATION

### Computational Details:

Calculations were performed with the CPMD package, version 3.11. (<http://www.cpmd.org>).

Electronic states are expanded in plane waves with a wavenumber of up to 70 Ry. The mass associated with the fictitious electronic degree-of-freedom is 700 a.u. The time-step in the numerically integrated equations-of-motion is 0.145 fs. In these simulations, the hydrogen atom mass was set to 2.014102 amu.

### Initial geometry of dimerization reaction (xyz format)

H	0.311481	0.585451	-1.042149	H	2.227763	-4.564827	4.432310	H	0.685059	-9.203787	3.052693
H	-1.678220	0.122518	1.961928	H	-5.659183	0.199226	0.176036	H	6.142979	5.899603	2.181011
H	1.468546	-2.075391	1.315842	H	-4.191079	0.321307	-0.582318	H	6.934358	4.546375	2.001285
H	1.511598	1.484792	2.544985	H	-0.489265	-5.769066	-1.211646	H	6.089192	3.009110	5.563368
H	-1.129898	-2.413114	-2.300284	H	-1.706540	-4.678224	-1.332153	H	5.907396	2.806014	4.043834
H	0.971692	-0.549148	-5.316777	H	3.284561	-4.158305	6.713814	H	-6.765122	-3.188806	1.985861
H	-1.838260	0.320839	-5.317337	H	2.616823	-5.588573	6.603053	H	-7.535677	-4.420735	2.418565
H	4.008167	1.691280	-3.487276	H	-1.056033	-6.658243	7.186507	H	-4.304327	7.733551	3.492980
H	4.898250	1.845568	-2.391243	H	-0.177402	-5.853806	6.458090	H	-4.680736	7.274236	4.931990
H	-4.395242	6.343857	-0.986587	H	3.056870	3.400155	-2.091826	H	-0.609078	5.133978	4.775023
H	-2.822484	6.168455	-0.759732	H	2.942903	4.762559	-1.321479	H	-0.498679	5.830651	3.481661
H	0.099511	3.064411	-5.247952	H	4.346148	3.886362	4.526238	H	2.943430	5.243745	5.872906
H	0.623344	4.137452	-4.210106	H	2.935630	3.970901	3.698525	H	1.891939	5.448329	7.265686
H	0.620732	3.539446	-2.216036	H	3.518044	-5.627026	-1.177928	H	5.224991	-4.225537	-4.955053
H	-0.259304	2.228079	-2.212958	H	3.999741	-6.318091	0.104464	H	4.048560	-3.669247	-4.103629
H	4.072895	-1.773621	-0.220231	H	1.097203	6.847082	-3.740698	H	0.331418	0.351562	3.753343
H	3.755980	-1.109261	-1.678619	H	1.721974	5.494836	-3.176589	H	-0.943016	0.007300	4.781491
H	-0.730194	-4.772048	2.614479	H	4.235525	-0.356705	-3.896168	H	5.311519	-7.052307	-1.520373
H	-0.129785	-5.887153	1.531432	H	2.678329	-0.228295	-3.725287	H	6.341243	-7.288850	-0.450643
H	1.491826	-6.556715	0.017603	H	-5.316268	-3.348691	4.097202	H	3.720691	5.419662	8.195059
H	0.367966	-7.712436	0.540857	H	-6.060705	-1.920336	4.554896	H	4.509910	4.623863	9.194676
H	2.526058	2.519682	-5.549343	H	7.730068	-1.418338	-0.952223	H	-2.255067	2.749260	7.515970
H	3.246119	2.641642	-6.977498	H	6.194874	-1.984515	-1.469330	H	-1.675145	2.622506	6.071453
H	0.356930	-3.468155	-3.660958	H	-7.080480	1.954071	-5.429914	H	2.507870	-2.678864	3.867160
H	1.322307	-3.999523	-4.824861	H	-5.838699	1.499856	-6.252939	H	2.581898	-1.511356	4.835707
H	6.705669	2.706566	-0.584244	H	-3.639204	6.749456	1.461988	H	-1.348137	-4.806134	5.468876
H	5.340610	2.067128	-0.087404	H	-2.342054	7.271134	2.308326	H	-2.743383	-4.409158	4.769606
H	-1.721860	-1.542541	6.611140	H	-4.940892	-4.495357	-3.891951	H	-4.309664	-0.404912	-5.784124
H	-1.586728	-2.516736	5.391533	H	-4.247908	-3.518329	-4.853183	H	-3.543570	0.336332	-6.939449
H	3.356986	-1.698080	2.228406	H	-5.922369	-5.395169	-2.042480	H	-2.331654	0.653600	-1.856691
H	3.590014	-2.942255	1.324418	H	-5.389168	-3.835237	-1.770738	H	-3.826353	0.645782	-2.377506
H	-4.344659	-1.980608	-3.591819	H	9.613668	2.568814	-0.825013	H	-4.282668	2.550613	1.484869
H	-3.037049	-1.614507	-4.168691	H	9.367027	4.206423	-0.652007	H	-3.925083	2.912663	2.861608
H	-5.335550	4.746389	5.163414	H	2.117348	0.559616	6.259282	H	-2.798531	4.950575	-4.988537
H	-3.855950	4.365651	4.730160	H	0.654407	0.178941	5.655877	H	-4.040431	4.485602	-5.816264
H	6.518206	-1.006407	-5.189830	H	-3.863817	-0.983644	1.439417	H	-0.507695	3.823303	-0.799542
H	5.247731	-2.047554	-5.040681	H	-4.394870	-1.580136	2.755064	H	-1.415288	3.643313	0.542677
H	-3.519077	-3.370657	-0.937054	H	-2.804039	-5.511164	-4.393591	H	4.098426	7.180540	4.079589
H	-2.354540	-3.239484	0.134349	H	-1.563986	-5.957266	-3.469869	H	5.753513	7.259647	4.389863
H	-4.166767	2.987918	-3.784634	H	-7.393189	-0.670944	5.910068	H	-6.043739	7.600211	8.045584
H	-5.408188	2.081326	-3.373397	H	-8.410787	-0.863943	4.818535	H	-7.452615	6.803610	8.544691
H	1.133491	-5.261270	3.514055	H	0.952017	-9.545027	1.637137	H	4.037795	1.632486	2.068662

H	3.163557	1.585811	0.663512	O	3.207806	-1.975819	1.297946	O	6.486048	5.268768	1.482458
H	-6.164087	1.299135	-10.442195	O	-3.975259	-1.660914	-4.416618	O	5.885426	3.548710	4.711505
H	-6.896712	0.582800	-9.164450	O	-4.375276	4.973634	5.381258	O	-7.369827	-3.886468	1.610555
H	2.437482	-3.974426	-2.653726	O	5.523031	-0.985614	-4.998339	O	-4.709742	8.100287	4.370495
H	3.714760	-3.052719	-2.024464	O	-2.576085	-3.267968	-0.867557	O	-0.347391	4.921609	3.843576
H	-2.707283	-2.788333	1.930078	O	-4.459958	2.259134	-3.176293	O	2.680292	5.800954	6.703904
H	-1.166997	-2.581627	1.586167	O	1.960799	-4.743809	3.530947	O	4.585409	-3.359210	-4.944353
H	-2.103982	2.045526	3.901804	O	-4.761286	-0.292506	0.038980	O	-0.486327	0.765217	4.271029
H	-1.615648	3.540304	3.609052	O	-1.439493	-5.592890	-1.486096	O	6.247015	-7.164701	-1.428262
O	1.116262	0.578864	-0.347387	O	2.422139	-4.526742	6.490561	O	4.197570	5.518961	9.041772
O	-0.669956	0.455441	-2.266692	O	-0.511976	-6.755670	6.350646	O	-1.695839	2.163907	6.939283
O	-1.602399	-0.547360	-4.850018	O	2.389808	4.150891	-1.895906	O	3.124842	-1.968354	4.203100
O	-0.939358	0.578355	1.479560	O	3.291881	3.975914	4.573943	O	-1.727014	-4.198562	4.771134
O	0.527608	-1.825870	1.250239	O	3.309330	-6.449920	-0.631933	O	-4.430322	0.108148	-6.594584
O	-0.619276	-2.291106	-3.145035	O	0.955222	5.839006	-3.708919	O	-3.251998	0.798977	-1.553082
O	1.095792	-0.455962	-4.349987	O	3.535097	0.044697	-3.272591	O	-4.768703	2.844952	2.326634
O	1.602515	0.486075	2.467771	O	-5.415748	-2.374969	3.950357	O	-3.526759	4.219877	-5.043714
O	4.367051	2.451988	-3.003448	O	7.232057	-1.996622	-1.654987	O	-0.490072	3.872669	0.285569
O	-3.751881	5.881436	-0.336871	O	-6.392853	2.300093	-6.060558	O	5.027291	7.330755	3.692160
O	0.970928	3.447363	-4.880686	O	-3.379389	7.347224	2.209953	O	-7.061332	7.509347	7.860305
O	-0.380126	3.261375	-2.232635	O	-4.406322	-4.492403	-4.807735	O	3.978188	1.900615	1.054508
O	4.344322	-1.775249	-1.214475	O	-5.214020	-4.702283	-2.277145	O	-7.005093	1.201139	-9.943003
O	-0.195159	-5.600511	2.494526	O	9.640420	3.329417	-0.202740	O	3.341600	-3.969150	-2.253081
O	0.557598	-6.757156	0.367874	O	1.505224	-0.213154	6.016401	O	-1.884354	-3.288880	1.589005
O	3.174410	2.084171	-6.163025	O	-3.540800	-1.184266	2.368407	O	-2.288504	2.978120	4.051944
O	1.097668	-4.150287	-3.793283	O	-1.979924	-6.104908	-4.358822	Si	0.599099	-0.020656	1.124434
O	6.178765	1.818138	-0.588292	O	-7.468477	-0.599602	4.984157	Si	-0.418996	-0.592497	-3.518236
O	-1.596594	-1.554204	5.583405	O	1.165877	-9.916145	2.591649				

Snapshots of representative configurations of ab initio molecular dynamics simulations of anionic mechanism of silica dimerization. White, red, and yellow indicate hydrogen, oxygen, and silicon atoms, respectively. Numbers indicate bond lengths [ $\text{\AA}$ ].

Figure S1. *Snapshot of dimer formation*

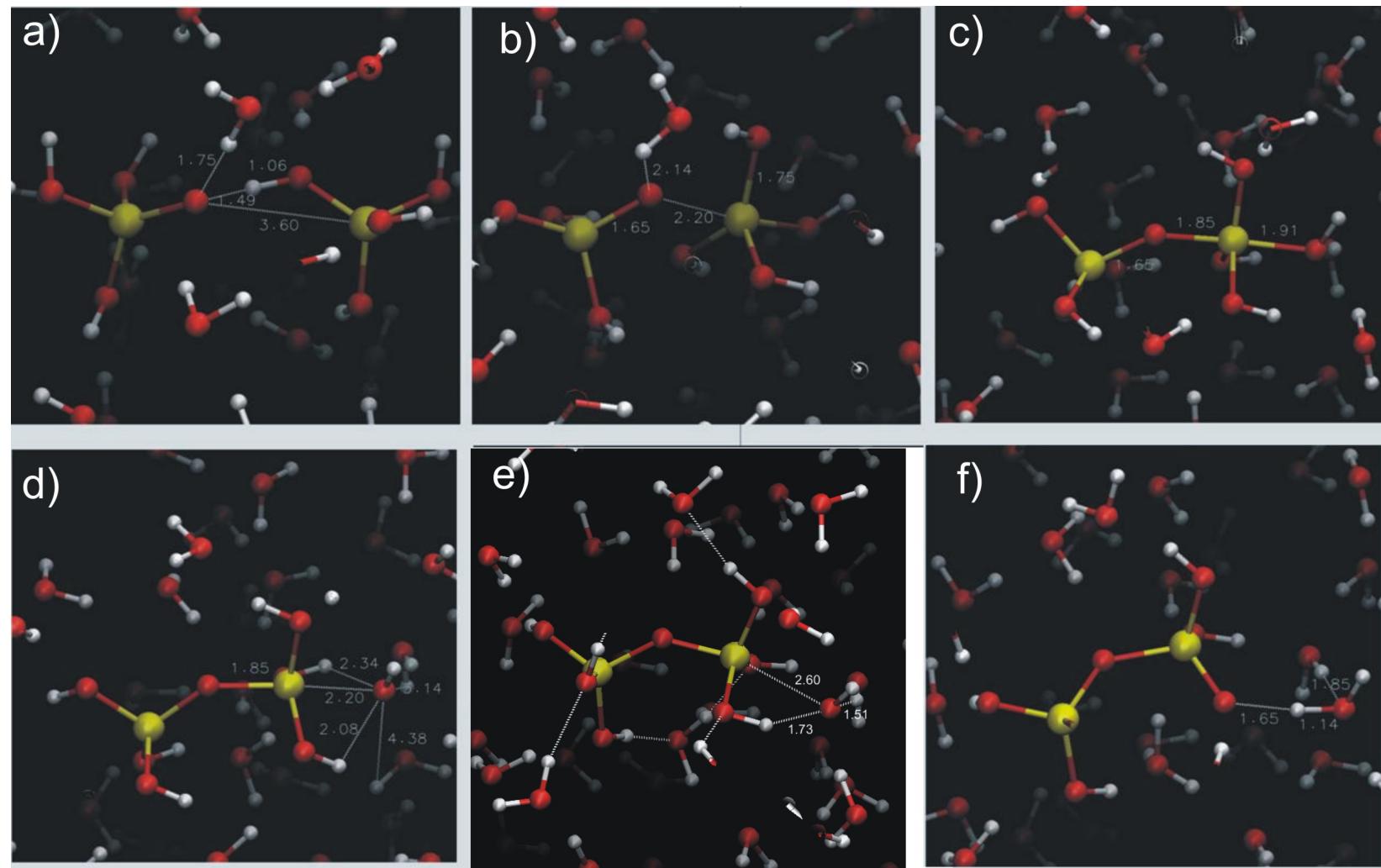


Figure S2. Snapshot of linear trimer formation.

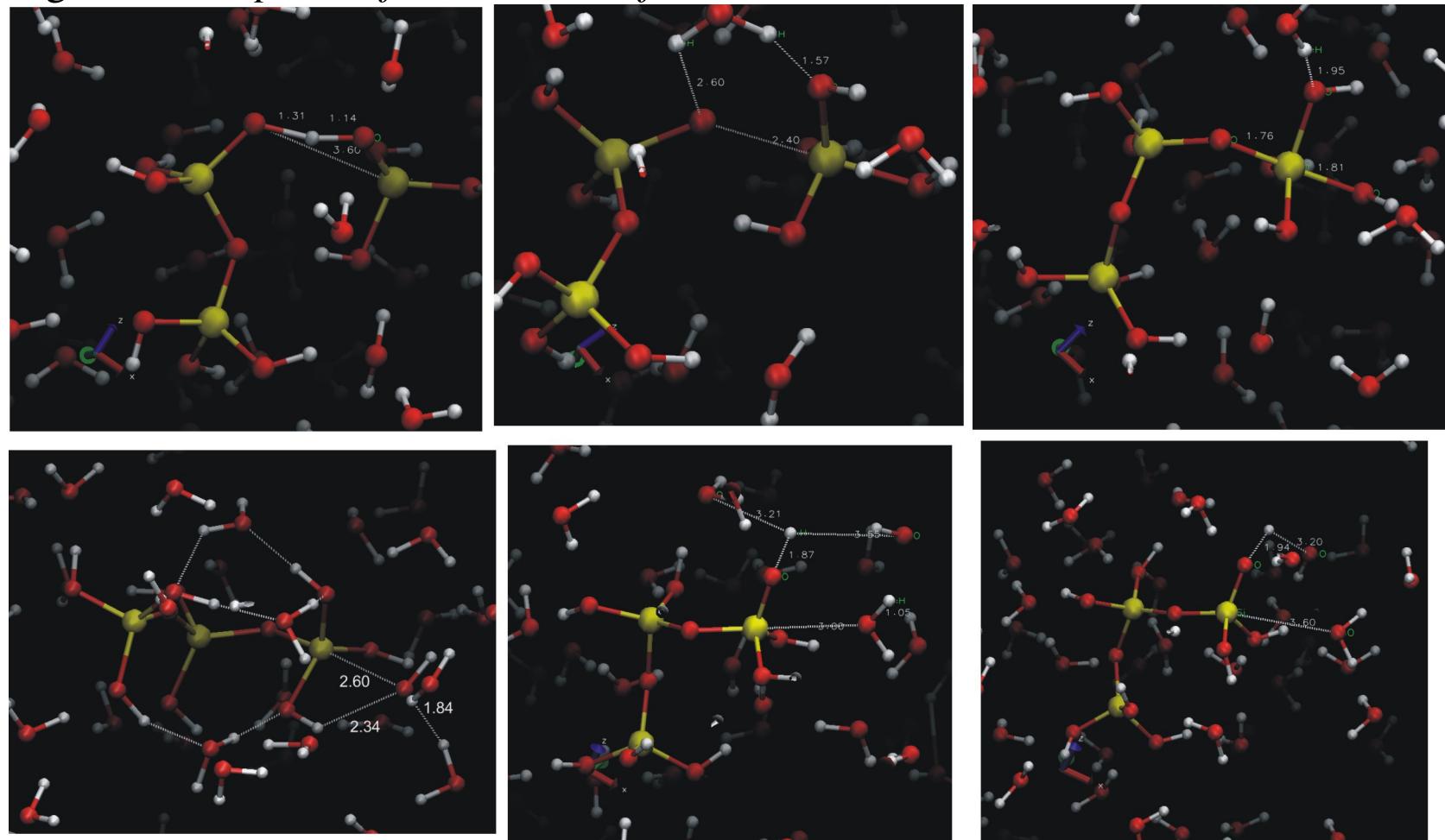
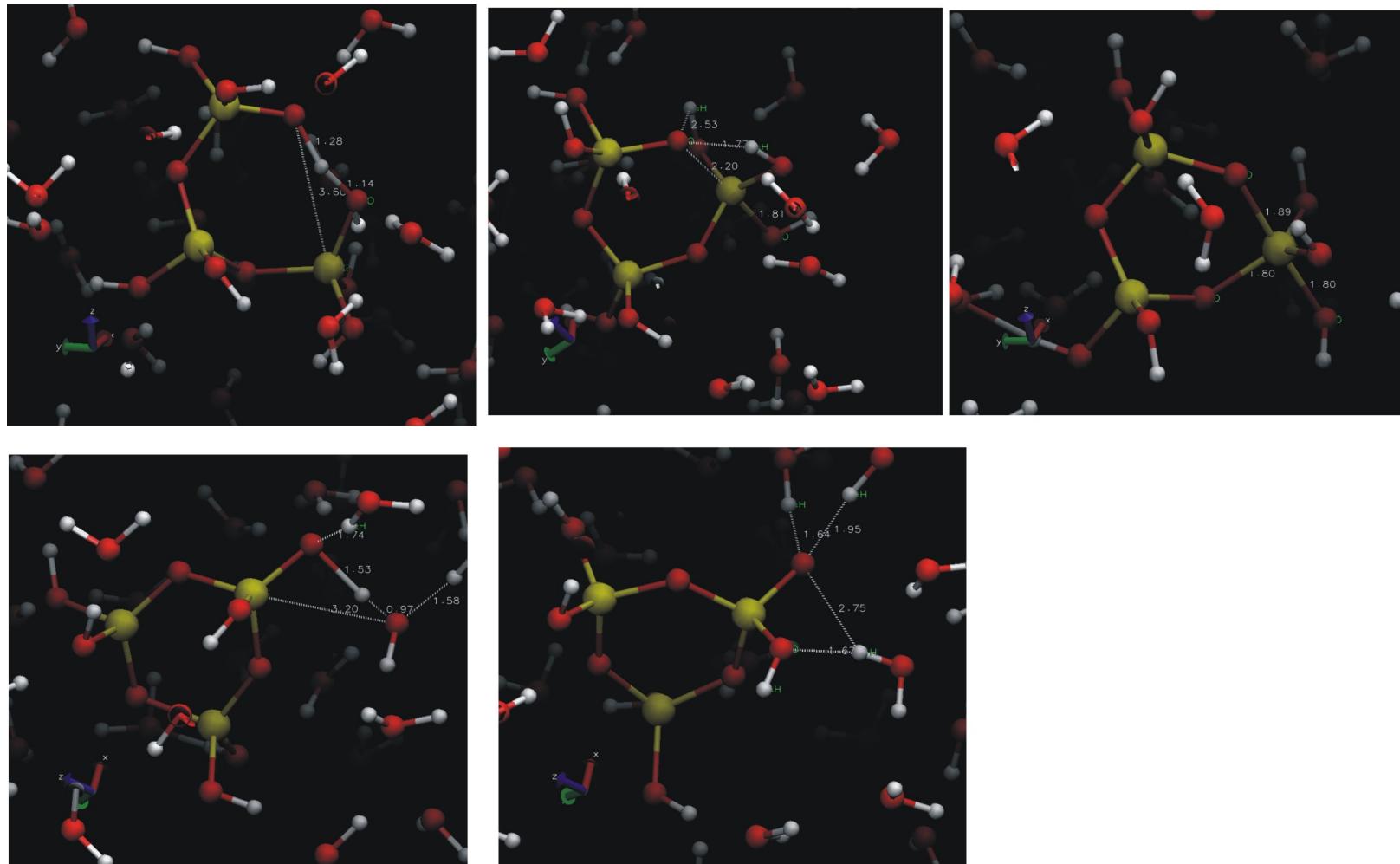


Figure S3. Snapshot of 3-ring formation



## Captions

Figure S1. Formation of a silica dimer. Snapshots of subsequent stages in the formation as observed in an ab initio molecular dynamics simulation. Panels a, b, and c show the formation of a Si-O bond. Panels d, e, and f show how a water molecule detaches from the silica dimer.

Figure S2. Formation of a linear silica trimer. Snapshots of subsequent stages in the formation as observed in an ab initio molecular dynamics simulation. Panels a, b, and c show the formation of a Si-O bond. Panels d, e, and f show how a water molecule detaches from the linear silica trimer.

Figure S3. Formation of a three-ring silica trimer. Snapshots of subsequent stages in the formation as observed in an ab initio molecular dynamics simulation. Panels a, b, and c show the formation of a Si-O bond that converts the linear trimer in to a three-ring. Panels d, e, and f show how a water molecule detaches from the three-ring trimer.