The Role Of Water In Silicate Oligomerization Reaction

SUPPORTING INFORMATION

Computational Details:

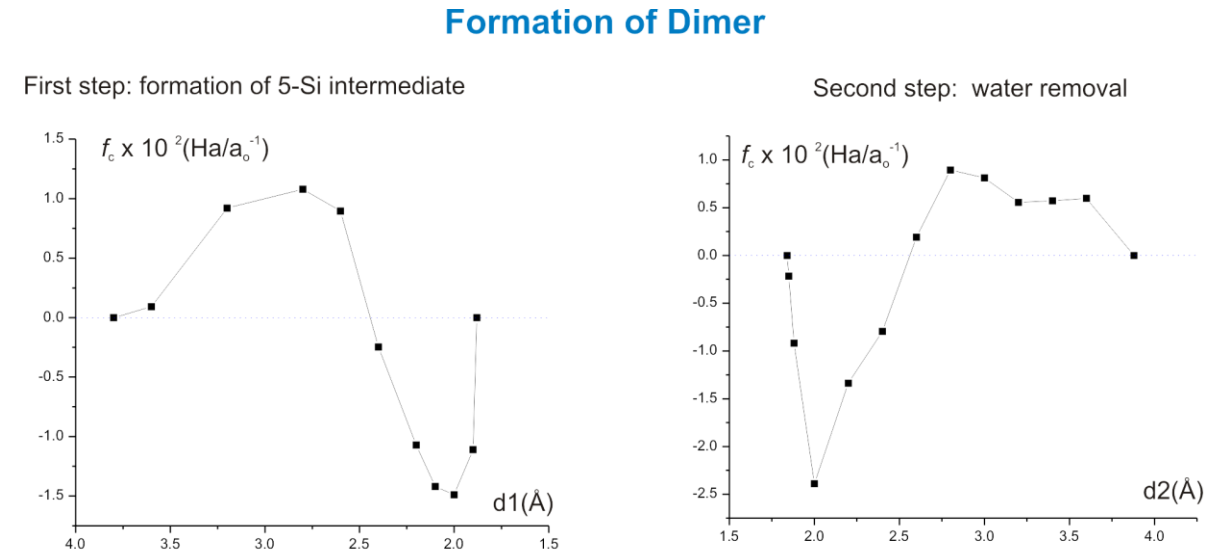
Calculations were performed with the CPMD package, version 3.11.(http://www.cpmd.org). Electronic states are expanded in plane waves with a wavenumber of up to 70 Ry. The mass associated with the fictitious electronic degree-of-freedom is 700 a.u. The time-step in the numerically integrated equations-of-motion 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	3.590014	-2.942255	1.324418	H	2.678329	-0.228295	-3.725287
H	-1.678220	0.122518	1.961928	H	-4.344659	-1.980608	-3.591819	H	-5.316268	-3.348691	4.097202
H	1.468546	-2.075391	1.315842	H	-3.037049	-1.614507	-4.168691	H	-6.060705	-1.920336	4.554896
H	1.511598	1.484792	2.544985	H	-5.335550	4.746389	5.163414	H	7.730068	-1.418338	-0.952223
H	-1.129898	-2.413114	-2.300284	H	-3.855950	4.365651	4.730160	H	6.194874	-1.984515	-1.469330
H	0.971692	-0.549148	-5.316777	H	6.518206	-1.006407	-5.189830	H	-7.080480	1.954071	-5.429914
H	-1.838260	0.320839	-5.317337	H	5.247731	-2.047554	-5.040681	H	-5.838699	1.499856	-6.252939
H	4.008167	1.691280	-3.487276	H	-3.519077	-3.370657	-0.937054	H	-3.639204	6.749456	1.461988
H	4.898250	1.845568	-2.391243	H	-2.354540	-3.239484	0.134349	H	-2.342054	7.271134	2.308326
H	-4.395242	6.343857	-0.986587	H	-4.166767	2.987918	-3.784634	H	-4.940892	-4.495357	-3.891951
H	-2.822484	6.168455	-0.759732	H	-5.408188	2.081326	-3.373397	H	-4.247908	-3.518329	-4.853183
H	0.099511	3.064411	-5.247952	H	1.133491	-5.261270	3.514055	H	-5.922369	-5.395169	-2.042480
H	0.623344	4.137452	-4.210106	H	2.227763	-4.564827	4.432310	H	-5.389168	-3.835237	-1.770738
H	0.620732	3.539446	-2.216036	H	-5.659183	0.199226	0.176036	H	9.613668	2.568814	-0.825013
H	-0.259304	2.228079	-2.212958	H	-4.191079	0.321307	-0.582318	H	9.367027	4.206423	-0.652007
H	4.072895	-1.773621	-0.220231	H	-0.489265	-5.769066	-1.211646	H	2.117348	0.559616	6.259282
H	3.755980	-1.109261	-1.678619	H	-1.706540	-4.678224	-1.332153	H	0.654407	0.178941	5.655877
H	-0.730194	-4.772048	2.614479	H	3.284561	-4.158305	6.713814	H	-3.863817	-0.983644	1.439417
H	-0.129785	-5.887153	1.531432	H	2.616823	-5.588573	6.603053	H	-4.394870	-1.580136	2.755064
H	1.491826	-6.556715	0.017603	H	-1.056033	-6.658243	7.186507	H	-2.804039	-5.511164	-4.393591
H	0.367966	-7.712436	0.540857	H	-0.177402	-5.853806	6.458090	H	-1.563986	-5.957266	-3.469869
H	2.526058	2.519682	-5.549343	H	3.056870	3.400155	-2.091826	H	-7.393189	-0.670944	5.910068
H	3.246119	2.641642	-6.977498	H	2.942903	4.762559	-1.321479	H	-8.410787	-0.863943	4.818535
H	0.356930	-3.468155	-3.660958	H	4.346148	3.886362	4.526238	H	0.952017	-9.545027	1.637137
H	1.322307	-3.999523	-4.824861	H	2.935630	3.970901	3.698525	H	0.685059	-9.203787	3.052693
H	6.705669	2.706566	-0.584244	H	3.518044	-5.627026	-1.177928	H	6.142979	5.899603	2.181011
H	5.340610	2.067128	-0.087404	H	3.999741	-6.318091	0.104464	H	6.934358	4.546375	2.001285
H	-1.721860	-1.542541	6.611140	H	1.097203	6.847082	-3.740698	H	6.089192	3.009110	5.563368
H	-1.586728	-2.516736	5.391533	H	1.721974	5.494836	-3.176589	H	5.907396	2.806014	4.043834
H	3.356986	-1.698080	2.228406	H	4.235525	-0.356705	-3.896168	H	-6.765122	-3.188806	1.985861

H	-7.535677	-4.420735	2.418565	H	6.341243	-7.288850	-0.450643	H	-3.826353	0.645782	-2.377506	
H	-4.304327	7.733551	3.492980	H	3.720691	5.419662	8.195059	H	-4.282668	2.550613	1.484869	
H	-4.680736	7.274236	4.931990	H	4.509910	4.623863	9.194676	H	-3.925083	2.912663	2.861608	
H	-0.609078	5.133978	4.775023	H	-2.255067	2.749260	7.515970	H	-2.798531	4.950575	-4.988537	
H	-0.498679	5.830651	3.481661	H	-1.675145	2.622506	6.071453	H	-4.040431	4.485602	-5.816264	
H	2.943430	5.243745	5.872906	H	2.507870	-2.678864	3.867160	H	-0.507695	3.823303	-0.799542	
H	1.891939	5.448329	7.265686	H	2.581898	-1.511356	4.835707	H	-1.415288	3.643313	0.542677	
H	5.224991	-4.225537	-4.955053	H	-1.348137	-4.806134	5.468876	H	4.098426	7.180540	4.079589	
H	4.048560	-3.669247	-4.103629	H	-2.743383	-4.409158	4.769606	H	5.753513	7.259647	4.389863	
H	0.331418	0.351562	3.753343	H	-4.309664	-0.404912	-5.784124	H	-6.043739	7.600211	8.045584	
H	-0.943016	0.007300	4.781491	H	-3.543570	0.336332	-6.939449	H	-7.452615	6.803610	8.544691	
H	5.311519	-7.052307	-1.520373	H	-2.331654	0.653600	-1.856691	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					

Constrained force profile of oligomerization reaction



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 [Å].

Figure S1.*Snapshot of dimer formation (first step)*

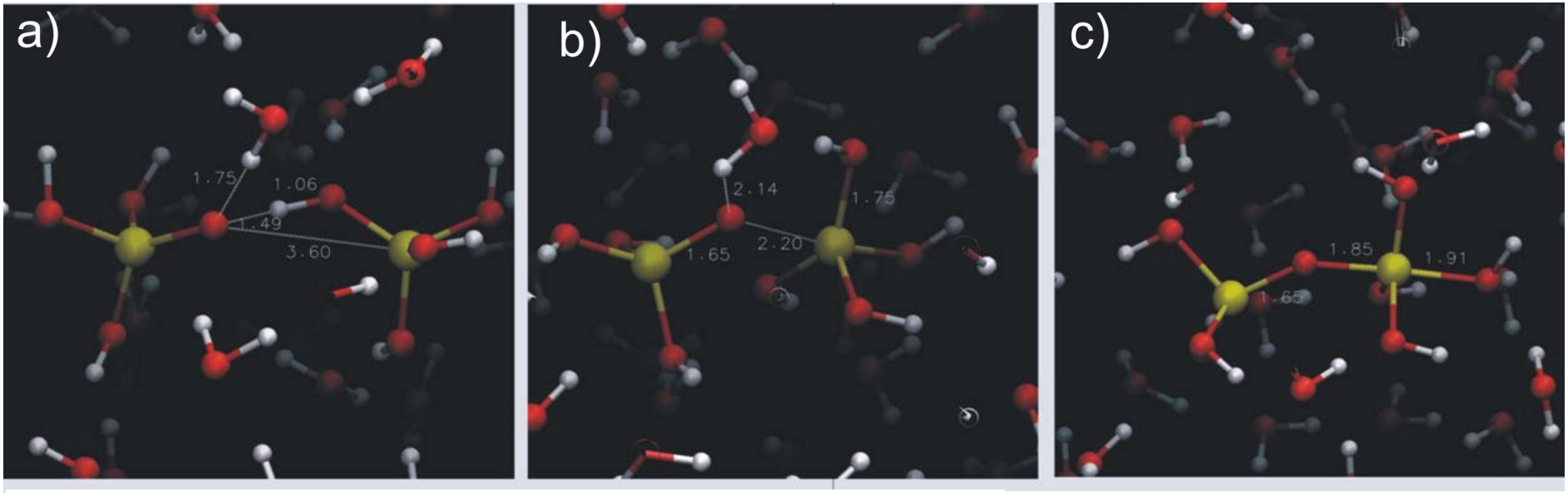


Figure S2.*Snapshot of linear trimer formation (first step).*

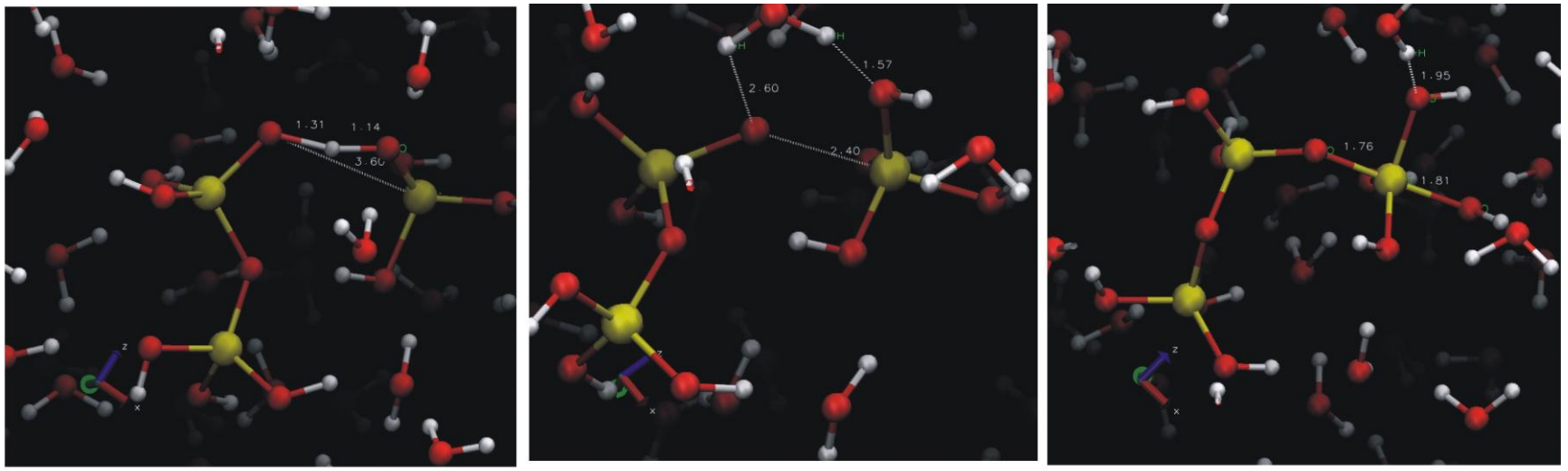
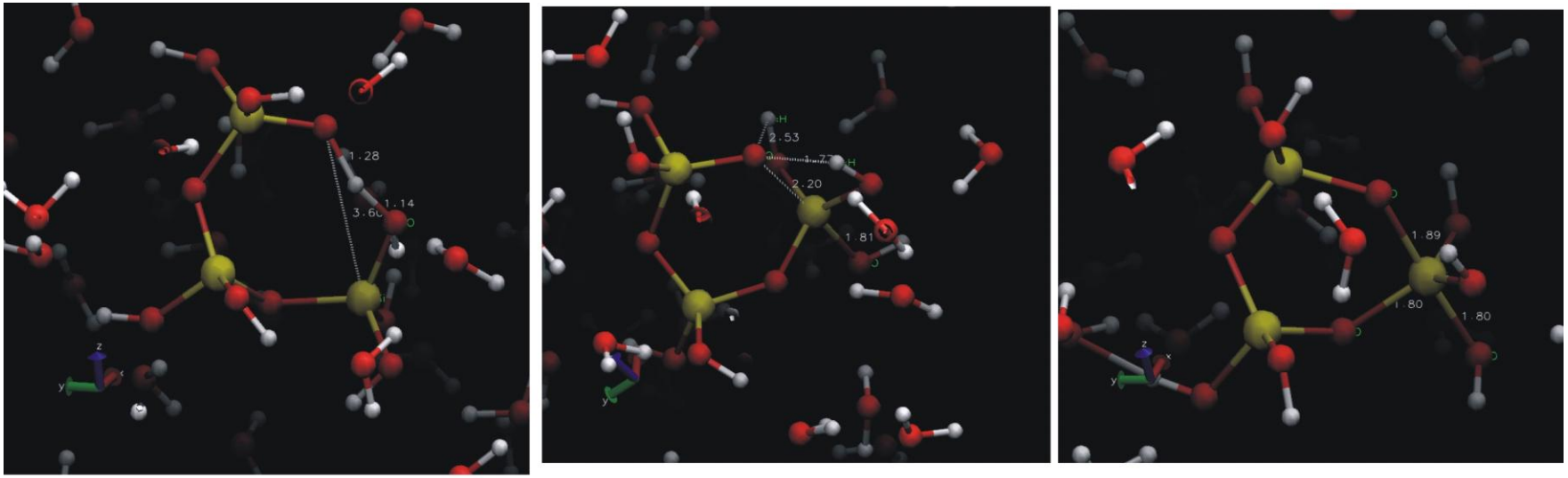


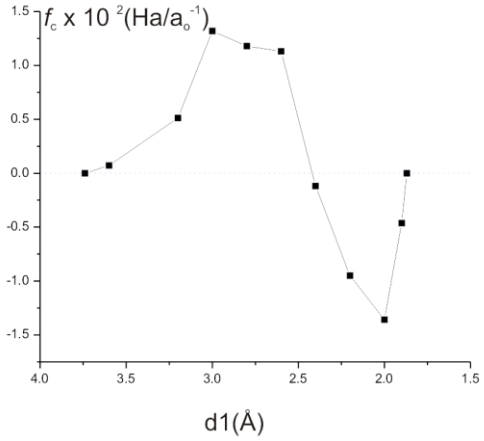
Figure S3. *Snapshot of 3-ring formation* (first step)



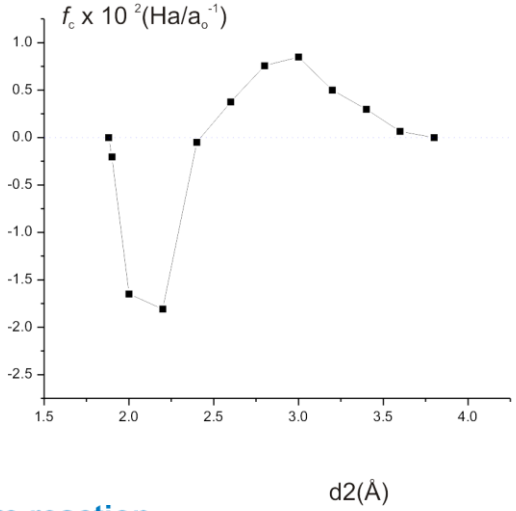
Constrained force profile of oligomerization reaction

Formation of Linear trimer

First step: formation of 5-Si intermediate

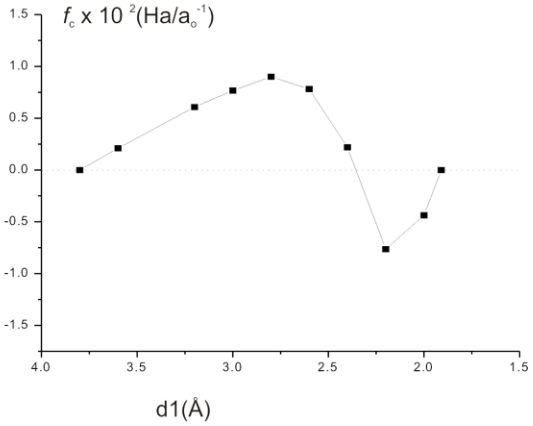


Second step: water removal

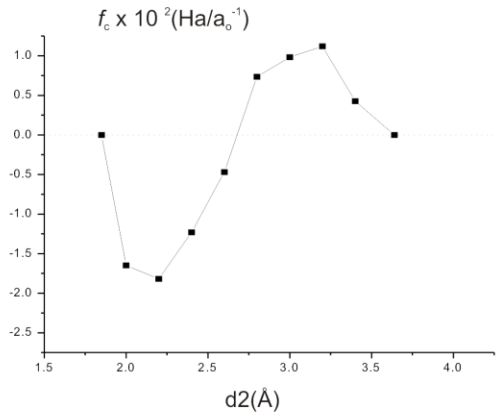


3-ring closure reaction

First step: formation of 5-Si intermediate

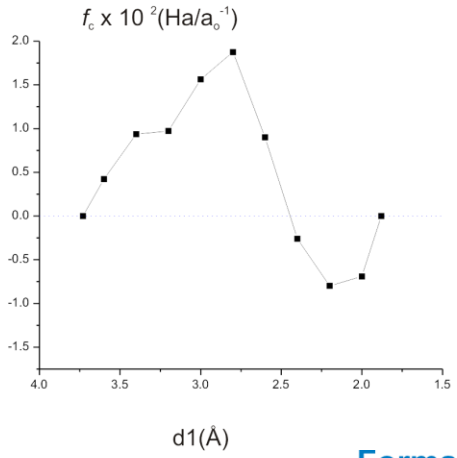


Second step: water removal

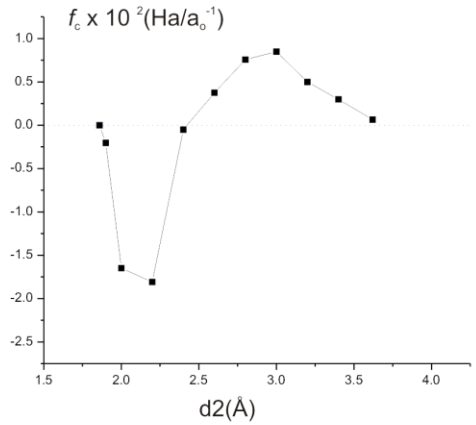


4-ring closure reaction

First step: formation of 5-Si intermediate

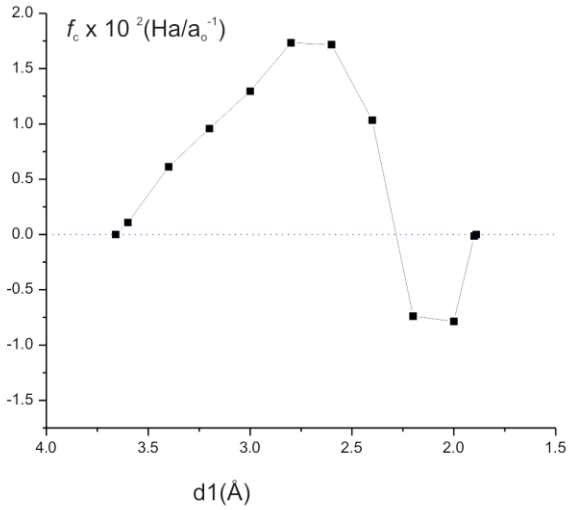


Second step: water removal



Formation of branched tetramer

First step: formation of 5-Si intermediate



Second step: water removal