Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Structure Analysis and DFT Benchmarking of Rydberg-type Alkali-Metal-Crown Ether, -Cryptand, and -Adamanzane Complexes

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Electronic Supporting Information

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Table S1. Optimized geometries of M(9-Crown-3) and $[M(9\text{-Crown-3})_2]^{0/+}$ (M = Li, Na) at CAM-B3LYP (Li/Na,C,O: cc-pVTZ and H: aug-cc-pVTZ) level of theory.

Li(9-Crown-3) (C_3)				Na(9-Crown-3) (C_3)				$Li(9\text{-Crown-3})_2$ (S_6)				$[Li(9\text{-Crown-3})_2]^+$ (S_6)				$Na(9\text{-Crown-3})_2$ (S_6)				$[Na(9\text{-Crown-3})_2]^+$ (S_6)			
O	1.530882	0.289007	0.451158	O	-0.000000	1.604810	0.185816	O	-1.540830	0.289797	1.363390	O	-1.540373	0.290917	1.377190	O	-1.578292	0.299190	1.737670	O	-1.574958	0.299855	1.753515
O	-1.015729	1.181279	0.451158	O	-1.389806	-0.802405	0.185816	O	1.021387	1.189499	1.363390	O	1.022128	1.188543	1.377190	O	1.048252	1.217246	1.737670	O	1.047161	1.214026	1.753515
O	-0.515154	-1.470287	0.451158	O	1.389806	-0.802405	0.185816	O	0.519443	-1.479297	1.363390	O	0.518245	-1.479461	1.377190	O	0.530040	-1.516436	1.737670	O	0.527796	-1.513881	1.753515
C	1.209171	1.273776	-0.521730	C	-1.016677	1.418315	-0.780516	C	-1.207736	1.272602	2.339567	C	-1.205936	1.271393	2.355530	C	-1.206732	1.271598	2.705484	C	-1.204614	1.269525	2.725480
C	0.498537	-1.684060	-0.521730	C	1.736635	0.171311	-0.780516	C	-0.498238	-1.682231	2.339567	C	-0.498091	-1.680068	2.355530	C	-0.497870	-1.680859	2.705484	C	-0.497134	-1.677989	2.725480
C	0.000000	2.050750	-0.029859	C	-2.009015	0.382273	-0.279226	C	0.000000	2.052153	1.851073	C	0.000000	2.053204	1.863160	C	0.000000	2.050734	2.211766	C	0.000000	2.051470	2.227713
C	-1.707708	0.410285	-0.521730	C	-0.719958	-1.589626	-0.780516	C	1.705973	0.409629	2.339567	C	1.704027	0.408675	2.355530	C	1.704602	0.409261	2.705484	C	1.701748	0.408464	2.725480
C	-1.776002	-1.025375	-0.029859	C	0.673449	-1.930995	-0.279226	C	1.777217	-1.026076	1.851073	C	1.778127	-1.026602	1.863160	C	1.775988	-1.025367	2.211766	C	1.776625	-1.025735	2.227713
C	1.776002	-1.025375	-0.029859	C	1.335566	1.548722	-0.279226	C	-1.777217	1.026076	1.851073	C	-1.778127	1.026602	1.863160	C	-1.775988	1.025367	2.211766	C	-1.776625	1.025735	2.227713
H	1.015005	0.805487	-1.487731	H	-0.587253	1.121600	-1.738526	H	-1.013579	0.798632	3.301778	H	-1.005524	0.793082	3.313722	H	-1.006182	0.794549	3.664254	H	-0.996408	0.787502	3.680028
H	2.055580	1.952455	-0.647014	H	-1.545129	2.361524	-0.942395	H	-2.050695	1.953865	2.477352	H	-2.048312	1.950008	2.499421	H	-2.035906	1.967218	2.859072	H	-2.034178	1.960614	2.886938
H	0.190070	-1.281764	-1.487731	H	1.264960	-0.052224	-1.738526	H	-0.184846	-1.277101	3.301778	H	-0.184067	-1.267351	3.313722	H	-0.185008	-1.268654	3.664254	H	-0.183793	-1.256665	3.680028
H	0.663086	-2.756412	-0.647014	H	2.817704	0.157359	-0.942395	H	-0.666750	-2.752887	2.477352	H	-0.664600	-2.748894	2.499421	H	-0.685707	-2.746755	2.859072	H	-0.680852	-2.741957	2.886938
H	0.275263	2.661210	0.828098	H	-2.545560	0.777051	0.582069	H	-0.275034	2.672358	1.001451	H	-0.278103	2.667498	1.010619	H	-0.279466	2.667363	1.358574	H	-0.282922	2.663146	1.372556
H	-0.382081	2.706580	-0.815895	H	-2.740254	0.164437	-1.064128	H	0.377424	2.699825	2.645645	H	0.378216	2.705410	2.652813	H	0.354140	2.716831	3.003257	H	0.357102	2.720063	3.014733
H	-1.205075	0.476276	-1.487731	H	-0.677707	-1.069376	-1.738526	H	1.198425	0.478469	3.301778	H	1.189592	0.474268	3.313722	H	1.191191	0.474105	3.664254	H	1.180201	0.469163	3.680028
H	-2.718665	0.803957	-0.647014	H	-1.272575	-2.518883	-0.942395	H	2.717445	0.799021	2.477352	H	2.712912	0.798886	2.499421	H	2.721614	0.779538	2.859072	H	2.715030	0.781343	2.886938
H	-2.442307	-1.092220	0.828098	H	0.599834	-2.593045	0.582069	H	2.451847	-1.097993	1.001451	H	2.449173	-1.092904	1.010619	H	2.449738	-1.091657	1.358574	H	2.447813	-1.086556	1.372556
H	-2.152926	-1.684182	-0.815895	H	1.227720	-2.455348	-1.064128	H	2.149405	-1.676772	2.645645	H	2.153846	-1.680249	2.652813	H	2.175775	-1.665109	3.003257	H	2.177093	-1.669291	3.014733
H	2.535007	-1.022398	-0.815895	H	1.512534	2.290911	-1.064128	H	-2.526829	-1.023053	2.645645	H	-2.532062	-1.025160	2.652813	H	-2.529915	-1.051722	3.003257	H	-2.534194	-1.050772	3.014733
H	2.167044	-1.568990	0.828098	H	1.945725	1.815994	0.582069	H	-2.176813	-1.574366	1.001451	H	-2.171069	-1.574594	1.010619	H	-2.170271	-1.575707	1.358574	H	-2.164892	-1.576590	1.372556
Li	0.000000	0.000000	1.822820	Na	0.000000	0.000000	2.191337	Li	0.000000	0.000000	0.000000	Li	0.000000	0.000000	0.000000	Na	0.000000	0.000000	0.000000	Na	0.000000	0.000000	0.000000
								O	-1.021387	-1.189499	-1.363390	O	-1.022128	-1.188543	-1.377190	O	-1.048252	-1.217246	-1.737670	O	-1.047161	-1.214026	-1.753515
								C	-1.705973	-0.409629	-2.339567	C	-1.704027	-0.408675	-2.355530	C	-1.704602	-0.409261	-2.705484	C	-1.701748	-0.408464	-2.725480
								H	-2.717445	-0.799021	-2.477352	H	-2.712912	-0.798886	-2.499421	H	-2.721614	-0.779538	-2.859072	H	-2.715030	-0.781343	-2.886938
								H	-1.198425	-0.478469	-3.301778	H	-1.189592	-0.474268	-3.313722	H	-1.191191	-0.474105	-3.664254	H	-1.180201	-0.469163	-3.680028
								H	-2.451847	1.097993	-1.001451	H	-2.449173	1.092904	-1.010619	H	-2.449738	1.091657	-1.358574	H	-2.447813	1.086556	-1.372556
								H	-2.149405	1.676772	-2.645645	H	-2.153846	1.680249	-2.652813	H	-2.175775	1.665109	-3.003257	H	-2.177093	1.669291	-3.014733
								C	-1.777217	1.026076	-1.851073	C	-1.778127	1.026602	-1.863160	C	-1.775988	1.025367	-2.211766	C	-1.776625	1.025735	-2.227713
								O	-0.519443	1.479297	-1.363390	O	-0.518245	1.479461	-1.377190	O	-0.530040	1.516436	-1.737670	O	-0.527796	1.513881	-1.753515
								H	0.666750	2.752887	-2.477352	H	0.664600	2.748894	-2.499421	H	0.685707	2.746755	-2.859072	H	0.680852	2.741957	-2.886938
								C	0.498238	1.682231	-2.339567	C	0.498091	1.680068	-2.355530	C	0.497870	1.680859	-2.705484	C	0.497134	1.677989	-2.725480
								H	0.184846	1.277101	-3.301778	H	0.184067	1.267351	-3.313722	H	0.185008	1.268654	-3.664254	H	0.183793	1.256665	-3.680028
								C	1.777217	1.026076	-1.851073	C	1.778127	1.026602	-1.863160	C	1.775988	1.025367	-2.211766	C	1.776625	1.025735	-2.227713
								H	2.526829	1.023053	-2.645645	H	2.532062	1.025160	-2.652813	H	2.529915	1.051722	-3.003257	H	2.534194	1.050772	-3.014733
								H	2.176813	1.574366	-1.001451	H	2.171069	1.574594	-1.010619	H	2.170271	1.575707	-1.358574	H	2.164892	1.576590	-1.372556
								O	1.540830	-0.289797	-1.363390	O	1.540373	-0.290917	-1.377190	O	1.578292	-0.299190	-1.737670	O	1.574958	-0.299855	-1.753515
								C	1.207736	-1.272602	-2.339567	C	1.205936	-1.271393	-2.355530	C	1.206732	-1.271598	-2.705484	C	1.204614	-1.269525	-2.725480
								H	1.013579	-0.798632	-3.301778	H	1.005524	-0.793082	-3.313722	H	1.006182	-0.794549	-3.664254	H	0.996408	-0.787502	-3.680028
								H	2.050695	-1.953865	-2.477352	H	2.048312	-1.950008	-2.499421	H	2.035906	-1.967218	-2.859072	H	2.034178	-1.960614	-2.886938
								C	-0.000000	-2.052153	-1.851073	C	-0.000000	-2.053204	-1.863160	C	-0.000000	-2.050734	-2.211766	C	-0.000000	-2.051470	-2.227713
								H	0.275034	-2.672358	-1.001451	H	0.278103	-2.667498	-1.010619	H	0.279466	-2.667363	-1.358574	H	0.282922	-2.663146	-1.372556
								H	-0.377424	-2.699825	-2.645645	H	-0.378216	-2.705410	-2.652813	H	-0.354140	-2.716831	-3.003257	H	-0.357102	-2.720063	-3.014733

Table S2. Optimized geometries of $[M[2.1.1]Cryptand]^{0/+}$ (M = Li, Na) at CAM-B3LYP (Li/Na,C,O,N: cc-pVTZ and H: aug-cc-pVTZ) level of theory.

Li[2.1.1]Cryptand (C_1)				Li[2.1.1]Cryptand (C_2)				$[Li[2.1.1]Cryptand]^+$ (C_2)				Na[2.1.1]Cryptand (C_2)				$[Na[2.1.1]Cryptand]^+$ (C_2)			
Li	-0.074571	0.117611	-0.122346	Li	0.000000	0.000000	0.202607	Li	0.000000	-0.000000	0.270400	Na	0.000000	0.000000	0.255981	Na	0.000000	0.000000	0.332046
O	-0.242827	-1.090752	-1.728554	O	1.848429	-0.022943	-0.775563	O	1.827856	-0.019070	-0.787316	O	1.982319	-0.016410	-0.865775	O	1.942612	0.137146	-0.872695
O	1.869290	1.714615	-0.844278	O	0.519270	-1.189294	1.914542	O	0.471951	-1.194349	1.901698	O	0.573095	-1.250073	2.034597	O	-0.167651	-1.390668	2.100916
O	-0.278388	-0.389685	1.887955	O	-1.848429	0.022943	-0.775563	O	-1.827856	0.019070	-0.787316	O	-1.982319	0.016410	-0.865775	O	-1.942612	-0.137146	-0.872695
N	1.839864	-0.996252	0.127647	N	0.000000	-2.095701	-0.640842	N	-0.000000	-2.117311	-0.646786	N	0.000000	-2.122491	-0.664134	N	0.175239	-2.139461	-0.695787
N	-2.261411	-0.162851	-0.036070	N	0.000000	2.095701	-0.640842	N	0.000000	2.117311	-0.646786	N	0.000000	2.122491	-0.664134	N	-0.175239	2.139461	-0.695787
C	-1.478634	-1.135128	2.081772	C	-1.846849	0.986712	-1.824507	C	-1.824656	0.975679	-1.835163	C	-1.885238	1.026800	-1.865853	C	-1.932165	0.843506	-1.896950
H	-1.703575	-1.211378	3.148931	H	-2.863566	1.132617	-2.199204	H	-2.837354	1.110968	-2.222701	H	-2.874655	1.231234	-2.284559	H	-2.931227	0.944517	-2.329050
H	-1.360791	-2.155853	1.702182	H	-1.239620	0.640652	-2.667669	H	-1.195193	0.633431	-2.662169	H	-1.252998	0.692385	-2.694624	H	-1.253283	0.549759	-2.702589
C	-2.589534	-0.401453	1.369339	C	-1.317007	2.279880	-1.252659	C	-1.316078	2.279248	-1.259527	C	-1.341602	2.293540	-1.227378	C	-1.515644	2.169549	-1.283113
H	-3.523292	-0.965144	1.482799	H	-1.298977	3.042007	-2.040684	H	-1.318112	3.049538	-2.039719	H	-1.366780	3.093593	-1.977942	H	-1.610666	2.955037	-2.043408
H	-2.733811	0.559828	1.858218	H	-2.012361	2.623181	-0.490390	H	-2.019467	2.599636	-0.494907	H	-2.020291	2.583776	-0.428081	H	-2.229298	2.405124	-0.495527
C	-1.595672	-1.316433	-2.107455	C	2.264901	1.278723	-1.162865	C	2.260147	1.284387	-1.150857	C	2.284031	1.298169	-1.314500	C	2.166923	1.484098	-1.268419
H	-1.692752	-2.261836	-2.644522	H	3.010657	1.224396	-1.959257	H	3.026132	1.234335	-1.927051	H	2.948771	1.266400	-2.181434	H	2.897364	1.528812	-2.079530
H	-1.853948	-0.516188	-2.799876	H	2.750333	1.712662	-0.289419	H	2.725868	1.704891	-0.261611	H	2.837623	1.764393	-0.499679	H	2.612659	1.969203	-0.401947
C	-2.505226	-1.322449	-0.891546	C	1.085564	2.115903	-1.620658	C	1.091546	2.137131	-1.616025	C	1.050172	2.115065	-1.685382	C	0.891024	2.202729	-1.695695
H	-3.552147	-1.389481	-1.216618	H	1.423286	3.137011	-1.842976	H	1.443248	3.155564	-1.825110	H	1.379628	3.132266	-1.940696	H	1.150264	3.237831	-1.954051
H	-2.309366	-2.224668	-0.310412	H	0.709998	1.711918	-2.560970	H	0.718136	1.741561	-2.559036	H	0.626744	1.704562	-2.602217	H	0.520840	1.747532	-2.612406
C	-2.060983	2.292080	-0.051580	C	-0.589879	2.592075	1.703931	C	-0.578994	2.597178	1.707166	C	-0.516528	2.643044	1.745963	C	-0.540613	2.568577	1.742901
C	-2.818385	1.076878	-0.556977	C	0.241510	2.977903	0.491128	C	0.230518	3.006208	0.487186	C	0.304067	2.956820	0.490702	C	0.000000	3.078913	0.415584
H	-3.884538	1.191538	-0.319871	H	0.051653	4.033260	0.248191	H	0.013927	4.055384	0.245669	H	0.176534	4.029513	0.278994	H	-0.464645	4.049069	0.201992
H	-2.734683	1.056254	-1.641246	H	1.294655	2.901678	0.756829	H	1.287143	2.953212	0.743374	H	1.358485	2.814128	0.725634	H	1.064858	3.263364	0.543504
C	0.547854	-2.262726	-1.555885	C	1.846849	-0.986712	-1.824507	C	1.824656	-0.975679	-1.835163	C	1.885238	-1.026800	-1.865853	C	1.932165	-0.843506	-1.896950
H	0.643091	-2.792860	-2.507065	H	2.863566	-1.132617	-2.199204	H	2.837354	-1.110968	-2.222701	H	2.874655	-1.231234	-2.284559	H	2.931227	-0.944517	-2.329050
H	0.068342	-2.948850	-0.849850	H	1.239620	-0.640652	-2.667669	H	1.195193	-0.633431	-2.662169	H	1.252998	-0.692385	-2.694624	H	1.253283	-0.549759	-2.702589
C	1.912991	-1.821712	-1.082163	C	1.317007	-2.279880	-1.252659	C	1.316078	-2.279248	-1.259527	C	1.341602	-2.293540	-1.227378	C	1.515644	-2.169549	-1.283113
H	2.542092	-2.707718	-0.929855	H	1.298977	-3.042007	-2.040684	H	1.318112	-3.049538	-2.039719	H	1.366780	-3.093593	-1.977942	H	1.610666	-2.955037	-2.043408
H	2.367325	-1.231764	-1.874211	H	2.012361	-2.623181	-0.490390	H	2.019467	-2.599636	-0.494907	H	2.020291	-2.583776	-0.428081	H	2.229298	-2.405124	-0.495527
C	0.894110	-1.006203	2.405793	C	-2.264901	-1.278723	-1.162865	C	-2.260147	-1.284387	-1.150857	C	-2.284031	-1.298169	-1.314500	C	-2.166923	-1.484098	-1.268419
H	0.649104	-1.657857	3.246957	H	-3.010657	-1.224396	-1.959257	H	-3.026132	-1.234335	-1.927051	H	-2.948771	-1.266400	-2.181434	H	-2.897364	-1.528812	-2.079530
H	1.522220	-0.202082	2.788722	H	-2.750333	-1.712662	-0.289419	H	-2.725868	-1.704891	-0.261611	H	-2.837623	-1.764393	-0.499679	H	-2.612659	-1.969203	-0.401947
C	1.597298	-1.804989	1.327764	C	-1.085564	-2.115903	-1.620658	C	-1.091546	-2.137131	-1.616025	C	-1.050172	-2.115065	-1.685382	C	-0.891024	-2.202729	-1.695695
H	2.526936	-2.231053	1.727408	H	-1.423286	-3.137011	-1.842976	H	-1.443248	-3.155564	-1.825110	H	-1.379628	-3.132266	-1.940696	H	-1.150264	-3.237831	-1.954051
H	0.968652	-2.654261	1.060276	H	-0.709998	-1.711918	-2.560970	H	-0.718136	-1.741561	-2.559036	H	-0.626744	-1.704562	-2.602217	H	-0.520840	-1.747532	-2.612406
C	3.080783	0.999884	-0.718376	C	0.589879	-2.592075	1.703931	C	0.578994	-2.597178	1.707166	C	0.516528	-2.643044	1.745963	C	0.540613	-2.568577	1.742901
H	3.899055	1.671196	-0.437313	H	0.229234	-3.133242	2.580299	H	0.215780	-3.139598	2.580739	H	0.087338	-3.192351	2.586150	H	0.405096	-3.340781	2.504652
H	3.297307	0.628605	-1.717100	H	1.640163	-2.849422	1.569565	H	1.635903	-2.837444	1.590710	H	1.546834	-2.977714	1.631296	H	1.610879	-2.346834	1.679586
C	3.011603	-0.140304	0.289116	C	-0.241510	-2.977903	0.491128	C	-0.230518	-3.006208	0.487186	C	-0.304067	-2.956820	0.490702	C	-0.000000	-3.078913	0.415584
H	3.946385	-0.714673	0.217680	H	-0.051653	-4.033260	0.248191	H	-0.013927	-4.055384	0.245669	H	-0.176534	-4.029513	0.278994	H	0.464645	-4.049069	0.201992
H	2.987990	0.271449	1.296160	H	-1.294655	-2.901678	0.756829	H	-1.287143	-2.953212	0.743374	H	-1.358485	-2.814128	0.725634	H	-1.064858	-3.263364	0.543504
O	-0.678336	2.026247	-0.192951	O	-0.519270	1.189294	1.914542	O	-0.471951	1.194349	1.901698	O	-0.573095	1.250073	2.034597	O	0.167651	1.390668	2.100916
H	-2.280960	2.509002	0.997642	H	-1.640163	2.849422	1.569565	H	-1.635903	2.837444	1.590710	H	-1.546834	2.977714	1.631296	H	-1.610879	2.346834	1.679586
H	-2.343570	3.168401	-0.641442	H	-0.229234	3.133242	2.580299	H	-0.215780	3.139598	2.580739	H	-0.087338	3.192351	2.586150	H	-0.405096	3.340781	2.504652
C	1.568094	2.609622	0.199190	C	-0.048862	-0.751622	3.129773	C	-0.056899	-0.751610	3.139012	C	-0.075372	-0.753842	3.189741	C	0.307088	-0.690745	3.242675
C	0.181034	3.139722	-0.057820	C	0.048862	0.751622	3.129773	C	0.056899	0.751610	3.139012	C	0.075372	0.753842	3.189741	C	-0.307088	0.690745	3.242675
H	0.157606	3.734152	-0.975206	H	1.096856	1.060611	3.192946	H	1.103638	1.055229	3.229541	H	1.137522	1.016945	3.181313	H	1.397642	0.611734	3.206490
H	-0.130533	3.769412	0.780544	H	-0.491829	1.160263	3.988032	H	-0.504878	1.167160	3.978373	H	-0.380346	1.161881	4.096564	H	-0.027760	1.216700	4.158883
H	1.586487	2.105910	1.170726	H	-1.096856	-1.060611	3.192946	H	-1.103638	-1.055229	3.229541	H	-1.137522	-1.016945	3.181313	H	-1.397642	0.611734	3.206490
H	2.286014	3.436681	0.227930	H	0.491829	-1.160263	3.988032	H	0.504878	-1.167160	3.978373	H	0.380346	-1.161881	4.096564	H	0.027760	-1.216700	4.158883

Table S3. Optimized geometries of [M(*o*-Me$_2$-1.1.1)]$^{0/+}$ (M = Li, Na) at CAM-B3LYP (Li/Na,C,O: cc-pVDZ and H: aug-cc-pVDZ) level of theory.

Li(*o*-Me$_2$-1.1.1) (C_1)				[Li(*o*-Me$_2$-1.1.1)]$^+$ (C_1)				Li(*o*-Me$_2$-1.1.1) (C_{3h})				[Li(*o*-Me$_2$-1.1.1)]$^+$ (C_{3h})				Na(*o*-Me$_2$-1.1.1) (C_{3h})				[Na(*o*-Me$_2$-1.1.1)]$^+$ (C_{3h})			
C	2.726643	0.073443	-0.025054	C	2.688229	0.042174	0.004064	C	0.000000	0.000000	2.642273	C	0.000000	0.000000	2.647306	C	0.000000	0.000000	2.795914	C	0.000000	0.000000	2.790951
C	4.238034	-0.036315	-0.134599	C	4.202831	-0.013190	-0.027481	C	0.000000	0.000000	4.157156	C	0.000000	0.000000	4.161902	C	0.000000	0.000000	4.310861	C	0.000000	0.000000	4.305068
C	-2.726675	0.072908	-0.025002	C	-2.688250	0.042199	0.003895	C	0.000000	0.000000	-2.642273	C	0.000000	0.000000	-2.647306	C	0.000000	0.000000	-2.795914	C	0.000000	0.000000	-2.790951
C	-4.238047	-0.037322	-0.134354	C	-4.202854	-0.013078	-0.027810	C	0.000000	0.000000	-4.157156	C	0.000000	0.000000	-4.161902	C	0.000000	0.000000	-4.310861	C	0.000000	0.000000	-4.305068
O	-2.208034	1.117285	-0.791941	O	-2.156346	1.137347	-0.669674	O	0.903747	-0.905155	-2.072390	O	0.907100	-0.902846	-2.078058	O	0.922903	0.895541	-2.237334	O	0.919071	0.899896	-2.230770
O	-2.051007	-1.080692	-0.469236	O	-2.073158	-1.080440	-0.603541	O	-1.235761	-0.330090	-2.072390	O	-1.235438	-0.334149	-2.078058	O	0.314110	-1.247028	-2.237334	O	0.319798	-1.245887	-2.230770
O	-2.299813	0.260064	1.288384	O	-2.156690	0.067602	1.292732	O	0.332014	1.235245	-2.072390	O	0.328337	1.236995	-2.078058	O	-1.237013	0.351487	-2.237334	O	-1.238869	0.345991	-2.230770
O	0.000203	-1.806784	-1.838567	O	0.000100	-1.498417	-2.123083	O	-1.907993	-1.918293	0.000000	O	-1.913317	-1.925614	0.000000	O	1.763081	-1.862777	0.000000	O	1.786959	-1.868983	0.000000
O	-0.000360	2.804128	-0.271327	O	0.000066	2.763771	-0.038328	O	2.615287	-0.693224	0.000000	O	2.624289	-0.694174	0.000000	O	0.731672	2.458262	0.000000	O	0.725107	2.482044	0.000000
O	0.000204	-0.979704	2.214827	O	-0.000128	-1.323062	2.253411	O	-0.707294	2.611517	0.000000	O	-0.710972	2.619788	0.000000	O	-2.494753	-0.595484	0.000000	O	-2.512067	-0.613060	0.000000
O	2.051389	-1.080492	-0.469005	O	2.073165	-1.080449	-0.603407	O	-1.235761	-0.330090	2.072390	O	-1.235438	-0.334149	2.078058	O	0.314110	-1.247028	2.237334	O	0.319798	-1.245887	2.230770
O	2.299959	0.260364	1.288414	O	2.156500	0.067582	1.292839	O	0.332014	1.235245	2.072390	O	0.328337	1.236995	2.078058	O	-1.237013	0.351487	2.237334	O	-1.238869	0.345991	2.230770
O	2.207464	1.117610	-0.791966	O	2.156449	1.137307	-0.669639	O	0.903747	-0.905155	2.072390	O	0.907100	-0.902846	2.078058	O	0.922903	0.895541	2.237334	O	0.919071	0.899896	2.230770
Li	0.000078	-0.973375	0.052538	Li	0.000050	-0.590275	-0.149777	Li	0.000000	0.000000	0.000000	Li	0.000000	0.000000	0.000000	Na	0.000000	0.000000	0.000000	Na	0.000000	0.000000	0.000000
C	2.401550	-0.854187	2.176147	C	2.365294	-1.074788	2.124084	C	-0.530926	2.344988	2.331848	C	-0.540464	2.345834	2.331285	C	-2.333563	-0.555254	2.367550	C	-2.335548	-0.561681	2.366363
C	1.163417	-0.868167	3.028487	C	1.172866	-1.159401	3.037632	C	-0.349631	3.297872	1.181455	C	-0.347882	3.301596	1.183763	C	-3.230794	-0.322532	1.179674	C	-3.239259	-0.324718	1.182716
C	2.315965	-1.557383	-1.792770	C	2.328817	-1.313211	-1.991513	C	-1.765356	-1.632289	2.331848	C	-1.761320	-1.640973	2.331285	C	1.647646	-1.743298	2.367550	C	1.654204	-1.741804	2.366363
C	1.198613	-2.515920	-2.113299	C	1.193990	-2.180793	-2.471286	C	-2.681226	-1.951725	1.181455	C	-2.685325	-1.952072	1.183763	C	1.894718	-2.636684	1.179674	C	1.900844	-2.642922	1.182716
C	2.338527	2.455549	-0.322986	C	2.334699	2.441824	-0.108242	C	2.296282	-0.712699	2.331848	C	2.301784	-0.704862	2.331285	C	0.685917	2.298552	2.367550	C	0.681345	2.303485	2.366363
C	1.183780	3.242970	-0.892699	C	1.184901	3.287904	-0.593021	C	3.030856	-1.346147	1.181455	C	3.033207	-1.349524	1.183763	C	1.336076	2.959216	1.179674	C	1.338415	2.967640	1.182716
C	-2.339206	2.455064	-0.322587	C	-2.334574	2.441825	-0.108186	C	2.296282	-0.712699	-2.331848	C	2.301784	-0.704862	-2.331285	C	0.685917	2.298552	-2.367550	C	0.681345	2.303485	-2.366363
C	-1.184725	3.242831	-0.892377	C	-1.184788	3.287924	-0.592962	C	3.030856	-1.346147	-1.181455	C	3.033207	-1.349524	-1.183763	C	1.336076	2.959216	-1.179674	C	1.338415	2.967640	-1.182716
C	-1.198104	-2.515972	-2.113579	C	-1.193789	-2.180760	-2.471362	C	-2.681226	-1.951725	-1.181455	C	-2.685325	-1.952072	-1.183763	C	1.894718	-2.636684	-1.179674	C	1.900844	-2.642922	-1.182716
C	-2.315598	-1.557599	-1.792989	C	-2.328622	-1.313134	-1.991696	C	-1.765356	-1.632289	-2.331848	C	-1.761320	-1.640973	-2.331285	C	1.647646	-1.743298	-2.367550	C	1.654204	-1.741804	-2.366363
C	-1.162992	-0.868064	3.028531	C	-1.173185	-1.159454	3.037551	C	-0.349631	3.297872	-1.181455	C	-0.347882	3.301596	-1.183763	C	-3.230794	-0.322532	-1.179674	C	-3.239259	-0.324718	-1.182716
C	-2.401218	-0.854340	2.176347	C	-2.365547	-1.074797	2.123917	C	-0.530926	2.344988	-2.331848	C	-0.540464	2.345834	-2.331285	C	-2.333563	-0.555254	-2.367550	C	-2.335548	-0.561681	-2.366363
H	4.603681	-0.914417	0.412901	H	4.570652	-0.927616	0.453427	H	-0.787068	0.663077	4.538765	H	-0.775858	0.674687	4.542732	H	-0.710469	-0.745477	4.690415	H	-0.712291	-0.742348	4.684889
H	4.693970	0.863186	0.297920	H	4.612425	0.851802	0.508084	H	0.967776	0.350082	4.538765	H	0.972226	0.334569	4.542732	H	-0.290367	0.988023	4.690415	H	-0.286747	0.988036	4.684889
H	4.549001	-0.115503	-1.182624	H	4.568185	0.015739	-1.060569	H	-0.180708	-1.013159	4.538765	H	-0.196367	-1.009257	4.542732	H	1.000836	-0.242546	4.690415	H	0.999038	-0.245688	4.684889
H	-4.549152	-0.116454	-1.182343	H	-4.568102	0.015891	-1.060934	H	-0.180708	-1.013159	-4.538765	H	-0.196367	-1.009257	-4.542732	H	1.000836	-0.242546	-4.690415	H	0.999038	-0.245688	-4.684889
H	-4.694198	0.861982	0.298356	H	-4.612467	0.851919	0.507734	H	0.967776	0.350082	-4.538765	H	0.972226	0.334569	-4.542732	H	-0.290367	0.988023	-4.690415	H	-0.286747	0.988036	-4.684889
H	-4.603333	-0.915614	0.413078	H	-4.570765	-0.927499	0.453041	H	-0.787068	0.663077	-4.538765	H	-0.775858	0.674687	-4.542732	H	-0.710469	-0.745477	-4.690415	H	-0.712291	-0.742348	-4.684889
H	3.286162	-0.740562	2.823352	H	3.283826	-0.954305	2.718749	H	-0.252637	2.832515	3.280006	H	-0.273763	2.830833	3.282373	H	-2.886381	-0.354604	3.299649	H	-2.881691	-0.363976	3.301469
H	2.487652	-1.795444	1.616522	H	2.444811	-1.981921	1.510009	H	-1.573840	2.002711	2.384104	H	-1.582464	2.000134	2.368364	H	-1.967703	-1.590784	2.373403	H	-1.967798	-1.596216	2.365037
H	3.285578	-2.077781	-1.827365	H	3.292403	-1.825569	-2.128178	H	-2.326711	-1.635048	3.280006	H	-2.314692	-1.652502	3.282373	H	1.750286	-2.322377	3.299649	H	1.756058	-2.313629	3.301469
H	2.313741	-0.707258	-2.489336	H	2.333900	-0.355072	-2.528744	H	-0.947478	-2.364341	2.384104	H	-0.940935	-2.370521	2.368364	H	2.361511	-0.908689	2.373403	H	2.366263	-0.906055	2.365037
H	3.293586	2.887639	-0.665954	H	3.291378	2.870447	-0.444827	H	2.579349	-1.197467	3.280006	H	2.588454	-1.178331	3.282373	H	1.136095	2.676981	3.299649	H	1.125633	2.677606	3.301469
H	2.296420	2.477423	0.773687	H	2.318043	2.379928	0.987677	H	2.521318	0.361630	2.384104	H	2.523399	0.370387	2.368364	H	-0.393808	2.499473	2.373403	H	-0.398465	2.502271	2.365037
H	-2.296872	2.476668	0.774090	H	-2.317889	2.379862	0.987731	H	2.521318	0.361630	-2.384104	H	2.523399	0.370387	-2.368364	H	-0.393808	2.499473	-2.373403	H	-0.398465	2.502271	-2.365037
H	-3.285113	-2.078180	-1.827520	H	-3.292219	-1.825429	-2.128522	H	-2.326711	-1.635048	-3.280006	H	-2.314692	-1.652502	-3.282373	H	1.750286	-2.322377	-3.299649	H	1.756058	-2.313629	-3.301469
H	-2.313581	-0.707470	-2.489553	H	-2.333572	-0.354977	-2.528892	H	-0.947478	-2.364341	-2.384104	H	-0.940935	-2.370521	-2.368364	H	2.361511	-0.908689	-2.373403	H	2.366263	-0.906055	-2.365037
H	-3.285788	-0.740727	2.823616	H	-3.284123	-0.954333	2.718519	H	-0.252637	2.832515	-3.280006	H	-0.273763	2.830833	-3.282373	H	-2.886381	-0.354604	-3.299649	H	-2.881691	-0.363976	-3.301469
H	-2.487247	-1.795710	1.616918	H	-2.445025	-1.981904	1.509801	H	-1.573840	2.002711	-2.384104	H	-1.582464	2.000134	-2.368364	H	-1.967703	-1.590784	-2.373403	H	-1.967798	-1.596216	-2.365037
H	1.252930	-3.424677	-1.486399	H	1.216407	-3.169932	-1.981103	H	-3.492984	-1.204583	1.122728	H	-3.488257	-1.195692	1.127459	H	1.165998	-3.467344	1.165621	H	1.160625	-3.462504	1.166071
H	1.241720	-2.814712	-3.175835	H	1.258172	-2.326760	-3.562097	H	-3.136208	-2.948425	1.329611	H	-3.149931	-2.942412	1.332496	H	2.910379	-3.067927	1.248312	H	2.908350	-3.087511	1.259982
H	-1.252414	-3.424855	-1.486865	H	-1.216274	-3.169889	-1.981162	H	-3.492984	-1.204583	-1.122728	H	-3.488257	-1.195692	-1.127459	H	1.165998	-3.467344	-1.165621	H	1.160625	-3.462504	-1.166071
H	-1.241056	-2.814553	-3.176183	H	-1.257893	-2.326746	-3.562175	H	-3.136208	-2.948425	-1.329611	H	-3.149931	-2.942412	-1.332496	H	2.910379	-3.067927	-1.248312	H	2.908350	-3.087511	-1.259982
H	1.095523	0.064881	3.613953	H	1.091056	-0.230866	3.628246	H	0.703292	3.627304	1.122728	H	0.708628	3.618765	1.127459	H	-3.585807	0.723888	1.165621	H	-3.578929	0.726121	1.166071
H	1.212641	-1.722210	3.727213	H	1.292635	-2.006231	3.735283	H	-0.985307	4.190248	1.329611	H	-0.973238	4.199126	1.332496	H	-4.112093	-0.986499	1.248312	H	-4.128038	-0.974950	1.259982
H	-1.095108	0.065122	3.613777	H	-1.091428	-0.230953	3.628225	H	0.703292	3.627304	-1.122728	H	0.708628	3.618765	-1.127459	H	-3.585807	0.723888	-1.165621	H	-3.578929	0.726121	-1.166071
H	-1.212124	-1.721944	3.727458	H	-1.292998	-2.006327	3.735142	H	-0.985307	4.190248	-1.329611	H	-0.973238	4.199126	-1.332496	H	-4.112093	-0.986499	-1.248312	H	-4.128038	-0.974950	-1.259982
H	1.127265	3.079784	-1.984676	H	1.136647	3.260224	-1.696871	H	2.789692	-2.422721	1.122728	H	2.779628	-2.423073	1.127459	H	2.419809	2.743456	1.165621	H	2.418304	2.736383	1.166071
H	1.348197	4.322791	-0.713354	H	1.341527	4.336590	-0.281403	H	4.121515	-1.241823	1.329611	H	4.123169	-1.256714	1.332496	H	1.201713	4.054426	1.248312	H	1.219688	4.062461	1.259982
H	-1.128399	3.079886	-1.984399	H	-1.136567	3.260289	-1.696815	H	2.789692	-2.422721	-1.122728	H	2.779628	-2.423073	-1.127459	H	2.419809	2.743456	-1.165621	H	2.418304	2.736383	-1.166071
H	-1.349319	4.322581	-0.712772	H	-1.341402	4.336599	-0.281298	H	4.121515	-1.241823	-1.329611	H	4.123169	-1.256714	-1.332496	H	1.201713	4.054426	-1.248312	H	1.219688	4.062461	-1.259982
H	-3.294421	2.887051	-0.665243	H	-3.291260	2.870472	-0.444719	H	2.579349	-1.197467	-3.280006	H	2.588454	-1.178331	-3.282373	H	1.136095	2.676981	-3.299649	H	1.125633	2.677606	-3.301469

Table S4. Optimized geometries of $[M(24\text{-Crown-}8)]^{0/+}$ (M = Li, Na) at CAM-B3LYP (Na/K,C,O: cc-pVDZ and H: aug-cc-pVDZ) level of theory.

Na(24-Crown-8) (S_4)				$[Na(24\text{-Crown-}8)]^+$ (S_4)				K(24-Crown-8) (S_4)				$[K(24\text{-Crown-}8)]^+$ (S_4)			
Na	0.000000	0.000000	0.000000	Na	0.000000	0.000000	0.000000	K	0.000000	0.000000	0.000000	K	0.000000	0.000000	0.000000
O	-1.416934	0.592792	1.979135	O	-1.360296	0.735270	1.961848	O	-1.746962	1.078416	1.853436	O	-1.731895	1.138241	1.884172
O	0.000000	2.461218	0.468663	O	0.242636	2.484727	0.480463	O	0.000000	2.839159	0.451957	O	0.000000	2.843578	0.393599
O	0.592792	1.416934	-1.979135	O	0.735270	1.360296	-1.961848	O	1.078416	1.746962	-1.853436	O	1.138241	1.731895	-1.884172
O	2.461218	-0.000000	-0.468663	O	2.484727	-0.242636	-0.480463	O	2.839159	-0.000000	-0.451957	O	2.843578	-0.000000	-0.393599
C	-2.817499	0.689956	1.770405	C	-2.749880	0.950699	1.764951	C	-3.132999	1.178568	1.586469	C	-3.122177	1.229450	1.620091
H	-3.095812	1.705690	1.448836	H	-2.942814	1.984179	1.438157	H	-3.359410	2.097895	1.020543	H	-3.350624	2.134652	1.034219
H	-3.358879	0.463540	2.706427	H	-3.299673	0.776520	2.705586	H	-3.699503	1.199738	2.534323	H	-3.685379	1.276448	2.568655
C	-0.822691	1.735547	2.580758	C	-0.669696	1.816824	2.576718	C	-1.172147	2.239365	2.433284	C	-1.160323	2.329074	2.406778
H	0.178160	1.409731	2.891163	H	0.297313	1.401091	2.886648	H	-0.220401	1.911371	2.875034	H	-0.205277	2.029100	2.858910
H	-1.386079	2.046360	3.478159	H	-1.207012	2.167772	3.473933	H	-1.807090	2.625214	3.249924	H	-1.797204	2.752018	3.202848
C	-0.716837	2.895234	1.612158	C	-0.459178	2.969286	1.615190	C	-0.922531	3.326493	1.409707	C	-0.917847	3.371362	1.335339
H	-1.714617	3.254867	1.310107	H	-1.422471	3.401555	1.298148	H	-1.862113	3.619320	0.909410	H	-1.860837	3.641889	0.829809
H	-0.192097	3.739015	2.096995	H	0.117104	3.769434	2.110841	H	-0.514643	4.223052	1.911252	H	-0.510158	4.289638	1.794375
C	-0.290728	3.214121	-0.698112	C	0.000000	3.233530	-0.701020	C	-0.014174	3.555213	-0.770058	C	0.019226	3.552483	-0.834121
H	-0.188747	4.296452	-0.502564	H	0.170402	4.309653	-0.526703	H	0.044964	4.643151	-0.587178	H	0.080604	4.640276	-0.655891
H	-1.329829	3.015648	-1.017422	H	-1.048670	3.092738	-1.017985	H	-0.951548	3.346150	-1.317386	H	-0.908160	3.347520	-1.399073
C	0.689956	2.817499	-1.770405	C	0.950699	2.749880	-1.764951	C	1.178568	3.132999	-1.586469	C	1.229450	3.122177	-1.620091
H	0.463540	3.358879	-2.706427	H	0.776520	3.299673	-2.705586	H	1.199738	3.699503	-2.534323	H	1.276448	3.685379	-2.568655
H	1.705690	3.095812	-1.448836	H	1.984179	2.942814	-1.438157	H	2.097895	3.359410	-1.020543	H	2.134652	3.350624	-1.034219
C	1.735547	0.822691	-2.580758	C	1.816824	0.669696	-2.576718	C	2.239365	1.172147	-2.433284	C	2.329074	1.160323	-2.406778
H	2.046360	1.386079	-3.478159	H	2.167772	1.207012	-3.473933	H	2.625214	1.807090	-3.249924	H	2.752018	1.797204	-3.202848
H	1.409731	-0.178160	-2.891163	H	1.401091	-0.297313	-2.886648	H	1.911371	0.220401	-2.875034	H	2.029100	0.205277	-2.858910
C	2.895234	0.716837	-1.612158	C	2.969286	0.459178	-1.615190	C	3.326493	0.922531	-1.409707	C	3.371362	0.917847	-1.335339
H	3.739015	0.192097	-2.096995	H	3.769434	-0.117104	-2.110841	H	4.223052	0.514643	-1.911252	H	4.289638	0.510158	-1.794375
H	3.254867	1.714617	-1.310107	H	3.401555	1.422471	-1.298148	H	3.619320	1.862113	-0.909410	H	3.641889	1.860837	-0.829809
C	3.214121	0.290728	0.698112	C	3.233530	-0.000000	0.701020	C	3.555213	0.014174	0.770058	C	3.552483	-0.019226	0.834121
H	3.015648	1.329829	1.017422	H	3.092738	1.048670	1.017985	H	3.346150	0.951548	1.317386	H	3.347520	0.908160	1.399073
H	4.296452	0.188747	0.502564	H	4.309653	-0.170402	0.526703	H	4.643151	-0.044964	0.587178	H	4.640276	-0.080604	0.655891
O	1.416934	-0.592792	1.979135	O	1.360296	-0.735270	1.961848	O	1.746962	-1.078416	1.853436	O	1.731895	-1.138241	1.884172
O	-0.000000	-2.461218	0.468663	O	-0.242636	-2.484727	0.480463	O	-0.000000	-2.839159	0.451957	O	-0.000000	-2.843578	0.393599
O	-0.592792	-1.416934	-1.979135	O	-0.735270	-1.360296	-1.961848	O	-1.078416	-1.746962	-1.853436	O	-1.138241	-1.731895	-1.884172
O	-2.461218	0.000000	-0.468663	O	-2.484727	0.242636	-0.480463	O	-2.839159	0.000000	-0.451957	O	-2.843578	0.000000	-0.393599
C	2.817499	-0.689956	1.770405	C	2.749880	-0.950699	1.764951	C	3.132999	-1.178568	1.586469	C	3.122177	-1.229450	1.620091
H	3.095812	-1.705690	1.448836	H	2.942814	-1.984179	1.438157	H	3.359410	-2.097895	1.020543	H	3.350624	-2.134652	1.034219
H	3.358879	-0.463540	2.706427	H	3.299673	-0.776520	2.705586	H	3.699503	-1.199738	2.534323	H	3.685379	-1.276448	2.568655
C	0.822691	-1.735547	2.580758	C	0.669696	-1.816824	2.576718	C	1.172147	-2.239365	2.433284	C	1.160323	-2.329074	2.406778
H	-0.178160	-1.409731	2.891163	H	-0.297313	-1.401091	2.886648	H	0.220401	-1.911371	2.875034	H	0.205277	-2.029100	2.858910
H	1.386079	-2.046360	3.478159	H	1.207012	-2.167772	3.473933	H	1.807090	-2.625214	3.249924	H	1.797204	-2.752018	3.202848
C	0.716837	-2.895234	1.612158	C	0.459178	-2.969286	1.615190	C	0.922531	-3.326493	1.409707	C	0.917847	-3.371362	1.335339
H	1.714617	-3.254867	1.310107	H	1.422471	-3.401555	1.298148	H	1.862113	-3.619320	0.909410	H	1.860837	-3.641889	0.829809
H	0.192097	-3.739015	2.096995	H	-0.117104	-3.769434	2.110841	H	0.514643	-4.223052	1.911252	H	0.510158	-4.289638	1.794375
C	0.290728	-3.214121	-0.698112	C	-0.000000	-3.233530	-0.701020	C	0.014174	-3.555213	-0.770058	C	-0.019226	-3.552483	-0.834121
H	0.188747	-4.296452	-0.502564	H	-0.170402	-4.309653	-0.526703	H	-0.044964	-4.643151	-0.587178	H	-0.080604	-4.640276	-0.655891
H	1.329829	-3.015648	-1.017422	H	1.048670	-3.092738	-1.017985	H	0.951548	-3.346150	-1.317386	H	0.908160	-3.347520	-1.399073
C	-0.689956	-2.817499	-1.770405	C	-0.950699	-2.749880	-1.764951	C	-1.178568	-3.132999	-1.586469	C	-1.229450	-3.122177	-1.620091
H	-0.463540	-3.358879	-2.706427	H	-0.776520	-3.299673	-2.705586	H	-1.199738	-3.699503	-2.534323	H	-1.276448	-3.685379	-2.568655
H	-1.705690	-3.095812	-1.448836	H	-1.984179	-2.942814	-1.438157	H	-2.097895	-3.359410	-1.020543	H	-2.134652	-3.350624	-1.034219
C	-1.735547	-0.822691	-2.580758	C	-1.816824	-0.669696	-2.576718	C	-2.239365	-1.172147	-2.433284	C	-2.329074	-1.160323	-2.406778
H	-2.046360	-1.386079	-3.478159	H	-2.167772	-1.207012	-3.473933	H	-2.625214	-1.807090	-3.249924	H	-2.752018	-1.797204	-3.202848
H	-1.409731	0.178160	-2.891163	H	-1.401091	0.297313	-2.886648	H	-1.911371	-0.220401	-2.875034	H	-2.029100	-0.205277	-2.858910
C	-2.895234	-0.716837	-1.612158	C	-2.969286	-0.459178	-1.615190	C	-3.326493	-0.922531	-1.409707	C	-3.371362	-0.917847	-1.335339
H	-3.739015	-0.192097	-2.096995	H	-3.769434	0.117104	-2.110841	H	-4.223052	-0.514643	-1.911252	H	-4.289638	-0.510158	-1.794375
H	-3.254867	-1.714617	-1.310107	H	-3.401555	-1.422471	-1.298148	H	-3.619320	-1.862113	-0.909410	H	-3.641889	-1.860837	-0.829809
C	-3.214121	-0.290728	0.698112	C	-3.233530	0.000000	0.701020	C	-3.555213	-0.014174	0.770058	C	-3.552483	0.019226	0.834121
H	-3.015648	-1.329829	1.017422	H	-3.092738	-1.048670	1.017985	H	-3.346150	-0.951548	1.317386	H	-3.347520	-0.908160	1.399073
H	-4.296452	-0.188747	0.502564	H	-4.309653	0.170402	0.526703	H	-4.643151	0.044964	0.587178	H	-4.640276	0.080604	0.655891

Table S5. Optimized geometries of [Li(3^{6}Adamanzane)]$^{0/+}$ at CAM-B3LYP (Li,N,C: cc-pVDZ and H: aug-cc-pVDZ) level of theory.

Li(3^{6}Adamanzane) (S_4)				Li(3^{6}Adamanzane)$^+$ (S_4)			
N	1.165907	1.106903	1.128132	N	1.164614	1.108750	1.128407
C	0.569111	2.433495	1.366884	C	0.565005	2.434886	1.367459
H	1.316962	3.101090	1.839330	H	1.308047	3.103350	1.842218
H	-0.238910	2.317884	2.099851	H	-0.247545	2.314384	2.095372
C	0.000000	3.113740	0.121492	C	0.000000	3.113978	0.118106
H	0.779091	3.255756	-0.639495	H	0.780781	3.245097	-0.643123
H	-0.282099	4.135316	0.422255	H	-0.275294	4.138011	0.410546
C	-1.256560	2.491865	-0.491433	C	-1.259453	2.491609	-0.492011
H	-2.014158	2.400097	0.297295	H	-2.013623	2.396939	0.299893
H	-1.674319	3.200434	-1.234566	H	-1.678933	3.199538	-1.232279
N	-1.106903	1.165907	-1.128132	N	-1.108750	1.164614	-1.128407
C	-2.433495	0.569111	-1.366884	C	-2.434886	0.565005	-1.367459
H	-2.317884	-0.238910	-2.099851	H	-2.314384	-0.247545	-2.095372
H	-3.101090	1.316962	-1.839330	H	-3.103350	1.308047	-1.842218
C	-3.113740	0.000000	-0.121492	C	-3.113978	0.000000	-0.118106
H	-4.135316	-0.282099	-0.422255	H	-4.138011	-0.275294	-0.410546
H	-3.255756	0.779091	0.639495	H	-3.245097	0.780781	0.643123
C	-2.491865	-1.256560	0.491433	C	-2.491609	-1.259453	0.492011
H	-2.400097	-2.014158	-0.297295	H	-2.396939	-2.013623	-0.299893
N	-1.165907	-1.106903	1.128132	N	-1.164614	-1.108750	1.128407
C	-0.569111	-2.433495	1.366884	C	-0.565005	-2.434886	1.367459
H	-1.316962	-3.101090	1.839330	H	-1.308047	-3.103350	1.842218
H	0.238910	-2.317884	2.099851	H	0.247545	-2.314384	2.095372
C	-0.000000	-3.113740	0.121492	C	-0.000000	-3.113978	0.118106
H	0.282099	-4.135316	0.422255	H	0.275294	-4.138011	0.410546
H	-0.779091	-3.255756	-0.639495	H	-0.780781	-3.245097	-0.643123
C	1.256560	-2.491865	-0.491433	C	1.259453	-2.491609	-0.492011
H	1.674319	-3.200434	-1.234566	H	1.678933	-3.199538	-1.232279
H	2.014158	-2.400097	0.297295	H	2.013623	-2.396939	0.299893
N	1.106903	-1.165907	-1.128132	N	1.108750	-1.164614	-1.128407
C	2.433495	-0.569111	-1.366884	C	2.434886	-0.565005	-1.367459
H	2.317884	0.238910	-2.099851	H	2.314384	0.247545	-2.095372
H	3.101090	-1.316962	-1.839330	H	3.103350	-1.308047	-1.842218
C	3.113740	-0.000000	-0.121492	C	3.113978	-0.000000	-0.118106
H	4.135316	0.282099	-0.422255	H	4.138011	0.275294	-0.410546
H	3.255756	-0.779091	0.639495	H	3.245097	-0.780781	0.643123
C	2.491865	1.256560	0.491433	C	2.491609	1.259453	0.492011
H	3.200434	1.674319	1.234566	H	3.199538	1.678933	1.232279
H	2.400097	2.014158	-0.297295	H	2.396939	2.013623	-0.299893
C	1.291390	0.323514	2.368695	C	1.291946	0.324231	2.368799
H	1.984829	0.829635	3.069723	H	1.985534	0.827915	3.069481
H	1.782601	-0.619119	2.096270	H	1.780458	-0.617715	2.092154
C	0.000000	0.000000	3.134857	C	0.000000	0.000000	3.137165
H	-0.254096	0.832404	3.807969	H	-0.253371	0.831247	3.810069
H	0.254096	-0.832404	3.807969	H	0.253371	-0.831247	3.810069
C	-1.291390	-0.323514	2.368695	C	-1.291946	-0.324231	2.368799
H	-1.984829	-0.829635	3.069723	H	-1.985534	-0.827915	3.069481
H	-1.782601	0.619119	2.096270	H	-1.780458	0.617715	2.092154
C	-0.323514	1.291390	-2.368695	C	-0.324231	1.291946	-2.368799
H	0.619119	1.782601	-2.096270	H	0.617715	1.780458	-2.092154
H	-0.829635	1.984829	-3.069723	H	-0.827915	1.985534	-3.069481
C	0.000000	0.000000	-3.134857	C	0.000000	0.000000	-3.137165
H	0.832404	0.254096	-3.807969	H	0.831247	0.253371	-3.810069
H	-0.832404	-0.254096	-3.807969	H	-0.831247	-0.253371	-3.810069
C	0.323514	-1.291390	-2.368695	C	0.324231	-1.291946	-2.368799
H	-0.619119	-1.782601	-2.096270	H	-0.617715	-1.780458	-2.092154
H	0.829635	-1.984829	-3.069723	H	0.827915	-1.985534	-3.069481
Li	0.000000	0.000000	0.000000	Li	0.000000	0.000000	0.000000

Table S6. Optimized geometries of 9-Crown-3, [2.1.1]Cryptand, *o*-Me_2-1.1.1, 24-Crown-8, and 3^6Adamanzane ligands at CAM-B3LYP level.

9-Crown-3			
C,O: cc-pVTZ and H: aug-cc-pVTZ			
O	-1.618818	-0.348142	-0.502650
O	0.507809	1.575768	-0.502619
O	1.110895	-1.227699	-0.502629
C	-1.592437	0.686087	0.449678
C	0.201963	-1.721868	0.449683
C	-0.801001	1.872227	-0.076169
C	1.390460	1.035919	0.449633
C	2.022077	-0.242490	-0.076259
C	-1.220966	-1.629807	-0.076305
H	-1.190883	0.335768	1.402142
H	-2.613870	1.028529	0.647633
H	0.304387	-1.198834	1.402116
H	0.416181	-2.777634	0.647775
H	-1.300155	2.264759	-0.959920
H	-0.800267	2.658190	0.690869
H	0.886496	0.863223	1.402188
H	2.197690	1.749369	0.647450
H	2.611598	-0.006517	-0.960022
H	2.702349	-0.636087	0.690803
H	-1.901978	-2.022285	0.690685
H	-1.311202	-2.258315	-0.960097

[2.1.1]Cryptand			
C,O,N: cc-pVTZ and H: aug-cc-pVTZ			
O	-0.848285	-0.297414	1.898418
O	-2.132823	-1.118353	-1.974183
O	2.756547	-0.106300	-0.061726
O	1.609829	2.703112	-0.279032
N	0.792997	-2.241140	0.051222
N	-1.778982	1.365914	-0.165073
C	0.805436	-1.949789	1.488470
C	-2.335907	1.391912	1.173590
C	-0.027912	-1.412359	-0.827164
C	-2.725608	1.158220	-1.239443
C	2.149964	-2.431774	-0.441133
C	-0.742582	2.349400	-0.435359
C	-0.526708	-1.649769	2.140012
C	-2.200359	0.071461	1.923403
C	-1.432140	-1.952645	-1.066979
C	-3.153839	-0.287668	-1.467962
C	2.895543	-1.195286	-0.947140
C	0.504395	2.150217	0.419503
C	3.406820	1.064418	-0.509426
C	2.871756	2.291235	0.197964
H	1.466855	-1.110524	1.726684
H	1.218187	-2.833026	1.980492
H	-3.397919	1.670398	1.156583
H	-1.825857	2.158526	1.757593
H	0.444957	-1.379003	-1.807595
H	-0.114302	-0.388341	-0.479712
H	-2.273813	1.504420	-2.167735
H	-3.643950	1.751595	-1.092417
H	2.141928	-3.142048	-1.273390
H	2.728566	-2.896795	0.356475
H	-1.104897	3.384294	-0.337085
H	-0.426387	2.221948	-1.468373
H	-1.312894	-2.311568	1.767776
H	-0.436028	-1.822701	3.218256
H	-2.560000	0.197342	2.953129
H	-2.812911	-0.704893	1.457492
H	-1.370022	-2.947982	-1.510715
H	-1.994140	-2.044804	-0.138617
H	-3.578627	-0.719444	-0.558185
H	-3.948488	-0.278305	-2.217921
H	3.953877	-1.458186	-1.074528
H	2.520040	-0.898981	-1.932347
H	0.412445	2.642308	1.394225
H	0.655132	1.091720	0.597135
H	3.252281	1.191775	-1.586279
H	4.486616	0.983142	-0.328920
H	2.844216	2.116835	1.277964
H	3.561732	3.115082	0.009143

o-Me_2-1.1.1			
C,O: cc-pVDZ and H: aug-cc-pVDZ			
C	0.000000	0.000000	2.771729
C	0.000000	0.000000	4.297867
C	0.000000	0.000000	-2.771729
C	0.000000	0.000000	-4.297867
O	0.929208	0.908580	-2.258786
O	0.322249	-1.259008	-2.258786
O	-1.251457	0.350428	-2.258786
O	1.998915	-1.902769	0.000000
O	0.648389	2.682495	0.000000
O	-2.647303	-0.779726	0.000000
O	0.322249	-1.259008	2.258786
O	-1.251457	0.350428	2.258786
O	0.929208	0.908580	2.258786
C	-2.305777	-0.596866	2.332081
C	-3.250338	-0.327127	1.185295
C	1.669790	-1.698428	2.332081
C	1.908469	-2.651312	1.185295
C	0.635987	2.295295	2.332081
C	1.341869	2.978438	1.185295
C	0.635987	2.295295	-2.332081
C	1.341869	2.978438	-1.185295
C	1.908469	-2.651312	-1.185295
C	1.669790	-1.698428	-2.332081
C	-3.250338	-0.327127	-1.185295
C	-2.305777	-0.596866	-2.332081
H	-0.712420	-0.743460	4.677565
H	-0.287645	0.988703	4.677565
H	1.000065	-0.245243	4.677565
H	1.000065	-0.245243	-4.677565
H	-0.287645	0.988703	-4.677565
H	-0.712420	-0.743460	-4.677565
H	-2.843070	-0.495491	3.291376
H	-1.906693	-1.614992	2.238754
H	1.850643	-2.214425	3.291376
H	2.351970	-0.843749	2.238754
H	0.992427	2.709916	3.291376
H	-0.445277	2.458740	2.238754
H	1.850643	-2.214425	-3.291376
H	2.351970	-0.843749	-2.238754
H	-2.843070	-0.495491	-3.291376
H	-1.906693	-1.614992	-2.238754
H	1.071726	-3.371474	1.124712
H	2.841849	-3.220985	1.364675
H	1.071726	-3.371474	-1.124712
H	2.841849	-3.220985	-1.364675
H	-3.455645	0.757595	1.124712
H	-4.210380	-0.850621	1.364675
H	-3.455645	0.757595	-1.124712
H	-4.210380	-0.850621	-1.364675
H	2.383919	2.613879	1.124712
H	1.368531	4.071606	1.364675
H	2.383919	2.613879	-1.124712
H	1.368531	4.071606	-1.364675
H	0.992427	2.709916	-3.291376

24-Crown-8			
C,O: cc-pVDZ and H: aug-cc-pVDZ			
O	0.105630	-1.886198	0.600203
O	3.681170	-1.659339	0.546496
O	-3.177261	-2.783817	-0.509822
O	5.580430	0.486209	-0.369828
O	-4.776386	-0.271793	-0.100246
O	2.768227	1.156989	-0.720512
O	-3.113996	1.954326	0.221946
O	-0.313559	2.671649	0.289643
C	1.407119	-2.035415	0.075893
C	-0.885200	-2.368789	-0.280343
C	2.398740	-1.588943	1.127074
C	-2.248182	-2.112939	0.325406
C	4.698281	-1.046428	1.311522
C	-4.535566	-2.644237	-0.152551
C	5.849160	-0.664933	0.403869
C	-5.187600	-1.434274	-0.786785
C	4.825187	0.287352	-1.554287
C	-4.970916	0.921225	-0.822220
C	3.778973	1.367978	-1.682134
C	-4.499683	2.077994	0.020851
C	1.717097	2.093616	-0.788258
C	-2.564413	2.975177	1.022833
C	0.821106	1.844120	0.404355
C	-1.163546	2.580796	1.411712
H	1.597518	-3.087696	-0.204965
H	1.536191	-1.412110	-0.827229
H	-0.809067	-1.868352	-1.263294
H	-0.757599	-3.453833	-0.449837
H	2.173440	-0.552456	1.427723
H	2.328569	-2.231111	2.024317
H	-2.464772	-1.035092	0.377918
H	-2.282803	-2.527403	1.349704
H	5.049131	-1.736109	2.103349
H	4.312469	-0.129007	1.789300
H	-5.041399	-3.552487	-0.510846
H	-4.651295	-2.596861	0.945278
H	6.723996	-0.413682	1.020083
H	6.121472	-1.521789	-0.238158
H	-6.290524	-1.529618	-0.748238
H	-4.881648	-1.384280	-1.847623
H	5.502557	0.340135	-2.425054
H	4.331447	-0.693740	-1.540315
H	-6.040492	1.061580	-1.070860
H	-4.397206	0.890863	-1.766927
H	3.348800	1.342595	-2.702008
H	4.243881	2.359358	-1.529021
H	-5.028746	2.069006	0.992862
H	-4.740860	3.027839	-0.494114
H	1.140627	1.973543	-1.724557
H	2.106055	3.128057	-0.765183
H	-2.551961	3.934215	0.471946
H	-3.168313	3.110804	1.940251
H	1.378409	2.059723	1.335558
H	0.516180	0.783131	0.431844
H	-1.184639	1.544937	1.794105
H	-0.796792	3.241843	2.219326

3^6adamanzane			
C,N: cc-pVDZ and H: aug-cc-pVDZ			
N	-1.151407	1.223568	1.056943
C	-2.450707	0.645150	1.353251
H	-3.135260	1.403204	1.800049
H	-2.321241	-0.127345	2.121064
C	-3.152439	0.000000	0.155711
H	-3.312105	0.738810	-0.641528
H	-4.165810	-0.278010	0.487256
C	-2.522040	-1.277704	-0.411784
H	-2.425903	-2.004882	0.407607
H	-3.257229	-1.722783	-1.125161
N	-1.223568	-1.151407	-1.056943
C	-0.645150	-2.450707	-1.353251
H	0.127345	-2.321241	-2.121064
H	-1.403204	-3.135260	-1.800049
C	-0.000000	-3.152439	-0.155711
H	0.278010	-4.165810	-0.487256
H	-0.738810	-3.312105	0.641528
C	1.277704	-2.522040	0.411784
H	1.722783	-3.257229	1.125161
H	2.004882	-2.425903	-0.407607
N	1.151407	-1.223568	1.056943
C	2.450707	-0.645150	1.353251
H	3.135260	-1.403204	1.800049
H	2.321241	0.127345	2.121064
C	3.152439	-0.000000	0.155711
H	4.165810	0.278010	0.487256
H	3.312105	-0.738810	-0.641528
C	2.522040	1.277704	-0.411784
H	3.257229	1.722783	-1.125161
H	2.425903	2.004882	0.407607
N	1.223568	1.151407	-1.056943
C	0.645150	2.450707	-1.353251
H	-0.127345	2.321241	-2.121064
H	1.403204	3.135260	-1.800049
C	0.000000	3.152439	-0.155711
H	-0.278010	4.165810	-0.487256
H	0.738810	3.312105	0.641528
C	-1.277704	2.522040	0.411784
H	-1.722783	3.257229	1.125161
H	-2.004882	2.425903	-0.407607
C	-0.246354	1.290623	2.188843
H	-0.573460	2.066930	2.921834
H	0.716903	1.633229	1.797648
C	0.000000	0.000000	2.972986
H	-0.844828	-0.206908	3.647242
H	0.844828	0.206908	3.647242
C	0.246354	-1.290623	2.188843
H	0.573460	-2.066930	2.921834
H	-0.716903	-1.633229	1.797648
C	-1.290623	-0.246354	-2.188843
H	-1.633229	0.716903	-1.797648
H	-2.066930	-0.573460	-2.921834
C	0.000000	0.000000	-2.972986
H	-0.206908	0.844828	-3.647242
H	0.206908	-0.844828	-3.647242
C	1.290623	0.246354	-2.188843
H	1.633229	-0.716903	-1.797648
H	2.066930	0.573460	-2.921834

Table S7. Optimized geometries of K([10]aneN$_4$)$_2$ and K[2.2.2]Cryptand species at CAM-B3LYP (M = K,N,C,O: cc-pVDZ and H: aug-cc-pVDZ) level of theory.

K([10]aneN$_4$)$_2$				Methylated-K[2.2.2]Cryptand				Ethylated-K[2.2.2]Cryptand			
K	0.000000	0.000000	0.000000	K	0.000000	0.000000	0.000000	K	-0.000675	0.217609	-0.000129
N	0.092855	2.131055	2.044653	O	2.208489	-1.298791	1.372353	O	0.117489	-2.548660	-1.362012
H	0.370004	2.925008	1.464440	O	2.229031	-1.263212	-1.372353	O	-0.101267	-2.550687	1.361654
N	2.131055	-0.092855	2.044653	O	-2.208489	-1.298791	-1.372353	O	-2.292185	1.273983	1.321174
H	2.925008	-0.370004	1.464440	O	-2.229031	-1.263212	1.372353	O	-2.332378	1.175550	-1.391369
N	-0.092855	-2.131055	2.044653	O	0.020542	2.562003	1.372353	O	2.283496	1.289720	-1.320897
H	-0.370004	-2.925008	1.464440	O	-0.020542	2.562003	-1.372353	O	2.323432	1.189547	1.391674
N	-2.131055	0.092855	2.044653	N	0.000000	0.000000	-3.007697	N	-0.036256	0.050711	2.943972
H	-2.925008	0.370004	1.464440	N	-0.000000	0.000000	3.007697	N	0.035502	0.053070	-2.943546
C	1.102502	1.930123	3.079195	C	0.845156	2.279440	2.498159	C	2.431102	0.713826	-2.606084
H	0.664322	1.308806	3.872122	H	1.125026	3.205479	3.020701	H	3.230668	1.218938	-3.167810
H	1.392658	2.879586	3.571427	H	1.781182	1.794742	2.166302	H	2.721391	-0.349077	-2.507469
C	2.366353	1.256537	2.552751	C	0.067204	1.394193	3.448879	C	1.147977	0.895735	-3.387717
H	2.772836	1.859290	1.725292	H	0.500116	1.466622	4.466563	H	1.356573	0.726485	-4.465122
H	3.128433	1.277964	3.358407	H	-0.950221	1.802821	3.508460	H	0.857867	1.950310	-3.282803
C	1.930123	-1.102502	3.079195	C	1.551475	-1.871647	2.498159	C	-0.547371	-2.347435	-2.600843
H	1.308806	-0.664322	3.872122	H	2.213513	-2.577041	3.020701	H	-0.576645	-3.285092	-3.178117
H	2.879586	-1.392658	3.571427	H	0.663701	-2.439920	2.166302	H	-1.592200	-2.040647	-2.413994
C	1.256537	-2.366353	2.552751	C	1.173804	-0.755297	3.448879	C	0.207356	-1.318805	-3.415184
H	1.859290	-2.772836	1.725292	H	1.020074	-1.166424	4.466563	H	-0.094377	-1.408739	-4.479509
H	1.277964	-3.128433	3.358407	H	2.036399	-0.078495	3.508460	H	1.270247	-1.586996	-3.365477
C	-1.102502	-1.930123	3.079195	C	-2.396631	-0.407793	2.498159	C	-1.797528	1.721875	-2.591820
H	-0.664322	-1.308806	3.872122	H	-3.338539	-0.628438	3.020701	H	-2.589457	2.218372	-3.174563
H	-1.392658	-2.879586	3.571427	H	-2.444883	0.645178	2.166302	H	-1.044813	2.494238	-2.348807
C	-2.366353	-1.256537	2.552751	C	-1.241008	-0.638896	3.448879	C	-1.232629	0.601277	-3.434847
H	-2.772836	-1.859290	1.725292	H	-1.520190	-0.300198	4.466563	H	-1.119439	0.955438	-4.479832
H	-3.128433	-1.277964	3.358407	H	-1.086178	-1.724326	3.508460	H	-1.984016	-0.199229	-3.451226
C	-1.930123	1.102502	3.079195	C	0.380568	3.749450	0.661333	C	3.520142	1.548396	-0.653952
H	-1.308806	0.664322	3.872122	H	1.460888	3.706581	0.431123	H	4.050069	0.582343	-0.524314
H	-2.879586	1.392658	3.571427	C	-0.380568	3.749450	-0.661333	C	3.202412	2.103615	0.727492
C	-1.256537	2.366353	2.552751	H	-1.460888	3.706581	-0.431123	H	2.664053	3.060749	0.591601
H	-1.859290	2.772836	1.725292	C	3.056834	-2.204307	0.661333	C	-0.289372	-3.743470	-0.700111
H	-1.277964	3.128433	3.358407	H	2.479549	-3.118456	0.431123	H	-1.391189	-3.723868	-0.591143
N	-0.092855	-2.131055	-2.044653	C	3.437403	-1.545143	-0.661333	C	0.314003	-3.741954	0.698648
H	-0.370004	-2.925008	-1.464440	H	3.940437	-0.588125	-0.431123	H	1.415648	-3.714510	0.589687
N	-2.131055	0.092855	-2.044653	C	-3.437403	-1.545143	0.661333	C	-3.216050	2.084366	-0.726242
H	-2.925008	0.370004	-1.464440	H	-3.940437	-0.588125	0.431123	H	-2.682709	3.044218	-0.589589
N	0.092855	2.131055	-2.044653	C	-3.056834	-2.204307	-0.661333	C	-3.530436	1.526120	0.654739
H	0.370004	2.925008	-1.464440	H	-2.479549	-3.118456	-0.431123	H	-4.054799	0.557157	0.524266
N	2.131055	-0.092855	-2.044653	C	2.396631	-0.407793	-2.498159	C	0.563078	-2.345389	2.600087
H	2.925008	-0.370004	-1.464440	H	3.338539	-0.628438	-3.020701	H	0.599487	-3.283138	3.176820
C	-1.102502	-1.930123	-3.079195	H	2.444883	0.645178	-2.166302	H	1.605539	-2.031000	2.412650
H	-0.664322	-1.308806	-3.872122	C	1.241008	-0.638896	-3.448879	C	-0.198362	-1.322446	3.415324
H	-1.392658	-2.879586	-3.571427	H	1.520190	-0.300198	-4.466563	H	0.104545	-1.410647	4.479447
C	-2.366353	-1.256537	-2.552751	H	1.086178	-1.724326	-3.508460	H	-1.259400	-1.597966	3.366076
H	-2.772836	-1.859290	-1.725292	C	-0.845156	2.279440	-2.498159	C	1.785047	1.732297	2.592223
H	-3.128433	-1.277964	-3.358407	H	-1.125026	3.205479	-3.020701	H	2.573676	2.234149	3.174830
C	-1.930123	1.102502	-3.079195	H	-1.781182	1.794742	-2.166302	H	1.027112	2.499598	2.349313
H	-1.308806	0.664322	-3.872122	C	-0.067204	1.394193	-3.448879	C	1.227899	0.607922	3.435392
H	-2.879586	1.392658	-3.571427	H	-0.500116	1.466622	-4.466563	H	1.112056	0.961525	4.480274
C	-1.256537	2.366353	-2.552751	H	0.950221	1.802821	-3.508460	H	1.984870	-0.187308	3.452064
H	-1.859290	2.772836	-1.725292	C	-1.551475	-1.871647	-2.498159	C	-2.436132	0.694875	2.605377
H	-1.277964	3.128433	-3.358407	H	-2.213513	-2.577041	-3.020701	H	-3.240014	1.192843	3.167341
C	1.102502	1.930123	-3.079195	H	-0.663701	-2.439920	-2.166302	H	-2.718064	-0.370092	2.504869
H	0.664322	1.308806	-3.872122	C	-1.173804	-0.755297	-3.448879	C	-1.154839	0.885330	3.388036
H	1.392658	2.879586	-3.571427	H	-1.020074	-1.166424	-4.466563	H	-1.362841	0.713973	4.465213
C	2.366353	1.256537	-2.552751	H	-2.036399	-0.078495	-3.508460	H	-0.872018	1.941948	3.283948
H	2.772836	1.859290	-1.725292	C	0.059876	4.998940	1.476460	C	4.406429	2.536587	-1.442726
H	3.128433	1.277964	-3.358407	H	0.500426	4.954722	2.479161	C	5.674524	1.925548	-2.031538
C	1.930123	-1.102502	-3.079195	H	-1.027626	5.115222	1.590829	H	3.787012	2.987441	-2.230817
H	1.308806	-0.664322	-3.872122	H	0.459912	5.900079	0.997014	H	4.681740	3.380120	-0.797202
H	2.879586	-1.392658	-3.571427	C	-0.059876	4.998940	-1.476460	H	6.248002	2.671629	-2.598549
C	1.256537	-2.366353	-2.552751	H	-0.500426	4.954722	-2.479161	H	5.452521	1.088358	-2.709532
H	1.859290	-2.772836	-1.725292	H	1.027626	5.115222	-1.590829	H	6.332296	1.533127	-1.241666
H	1.277964	-3.128433	-3.358407	H	-0.459912	5.900079	-0.997014	C	4.496683	2.324389	1.543483
				C	-4.299271	-2.551324	-1.476460	C	4.711808	3.758820	2.018582
				H	-4.040702	-2.910743	-2.479161	H	4.464696	1.641122	2.403835
				H	-4.943726	-1.667661	-1.590829	H	5.367019	1.997905	0.955739
				H	-4.879662	-3.348335	-0.997014	H	5.630003	3.847082	2.616085
				C	-4.359147	-2.447615	1.476460	H	3.871669	4.112796	2.633125
				H	-3.916099	-3.447562	1.590829	H	4.795631	4.457186	1.173374
				H	-5.339574	-2.551744	0.997014	C	-4.422215	2.508422	1.444703
				C	4.359147	-2.447615	-1.476460	C	-5.687857	1.890048	2.031124
				H	4.541128	-2.043979	-2.479161	H	-3.805787	2.960490	2.234409
				H	3.916099	-3.447562	-1.590829	H	-4.700884	3.352055	0.800716
				H	5.339574	-2.551744	-0.997014	H	-6.265472	2.632178	2.599112
				C	4.299271	-2.551324	1.476460	H	-5.462291	1.052617	2.707662
				H	4.040702	-2.910743	2.479161	H	-6.343044	1.495945	1.239940
				H	4.943726	-1.667661	1.590829	C	-4.511675	2.298964	-1.541701
				H	4.879662	-3.348335	0.997014	C	-4.734052	3.732426	-2.016359
				H	-4.541128	-2.043979	2.479161	H	-4.476703	1.616004	-2.402188
								H	-5.380141	1.968122	-0.953660
								H	-5.652910	3.816327	-2.613468
								H	-3.895922	4.090698	-2.631146
								H	-4.820967	4.430120	-1.170909
								C	-0.105345	-5.004399	1.487328
								C	1.055863	-5.854933	1.994754
								H	-0.729369	-4.675891	2.329591
								H	-0.767933	-5.626325	0.870275
								H	0.695296	-6.719483	2.568793
								H	1.727489	-5.276884	2.645918
								H	1.666423	-6.241074	1.165512
								C	0.138891	-5.002267	-1.489792
								C	-1.016280	-5.860343	-1.998309
								H	0.760962	-4.668780	-2.331536
								H	0.805505	-5.620196	-0.873084
								H	-0.649600	-6.721805	-2.573110
								H	-1.691818	-5.286373	-2.649034
								H	-1.624267	-6.251538	-1.169538

Table S8. Harmonic vibrational frequencies of $[M(9\text{-Crown-3})_2]^{0/+}$ and $[M[2.1.1]Cryptand]^{0/+}$ species at B3LYP level (M=Li/Na,C,O: cc-pVTZ and H: aug-cc-pVTZ). B3LYP optimized geometries were used for frequency calculations.

$Li(9\text{-Crown-3})_2$ (S_6)	$Li(9\text{-Crown-3})_2^+$ (S_6)	$Na(9\text{-Crown-3})_2$ (S_6)	$Na(9\text{-Crown-3})_2^+$ (S_6)	Li[2.1.1]Cryptand (C_1)	$[Li[2.1.1]Cryptand]^+$ (C_2)	Na[2.1.1]Cryptand (C_2)	$[Na[2.1.1]Cryptand]^+$ (C_2)
47.0	45.7	-5.0	14.5	38.6	-49.2	-5.6	48.7
75.6	74.6	-4.3	14.5	57.7	44.6	25.1	71.5
75.6	74.6	27.0	26.9	64.9	69.4	37.5	122.2
103.0	100.8	78.6	78.7	93.1	88.1	44.3	124.9
103.0	100.8	92.6	92.1	105.0	112.0	56.6	140.6
109.9	106.5	92.6	92.1	136.3	116.8	63.8	143.3
169.7	177.8	167.7	172.4	145.7	142.9	82.8	149.5
169.7	177.8	167.8	172.4	156.1	159.1	87.9	157.4
175.6	179.2	172.3	177.7	166.7	168.0	92.7	171.1
175.6	179.2	172.3	177.7	204.7	208.6	102.0	177.0
226.2	227.8	173.3	184.2	211.6	218.2	118.4	204.9
226.2	227.8	173.4	184.2	221.1	226.3	127.3	224.5
228.2	229.1	211.4	214.2	233.1	242.4	145.8	232.1
228.2	229.1	211.4	214.2	249.7	252.2	158.2	243.7
273.9	285.2	219.3	221.5	267.6	270.1	163.0	248.0
275.5	286.3	219.4	221.5	271.6	277.8	169.5	270.5
328.7	328.3	248.7	254.1	279.8	296.2	181.1	282.5
328.7	328.3	271.8	285.2	295.5	300.4	190.7	288.8
353.1	356.0	272.7	285.5	313.2	310.4	209.9	293.3
360.3	362.6	336.9	343.1	340.1	329.2	246.4	299.4
365.1	364.6	342.0	345.5	345.3	344.6	252.7	325.7
380.5	384.2	377.3	384.3	351.8	351.9	270.5	342.6
391.4	392.6	379.8	385.8	364.7	367.6	276.6	351.2
391.4	392.6	385.3	387.7	375.5	383.0	288.3	364.4
393.0	394.5	385.3	387.7	382.5	384.0	288.6	376.8
393.0	394.5	386.5	389.0	389.6	386.3	325.1	378.9
413.1	431.2	386.5	389.0	395.1	386.4	337.2	386.5
542.8	543.3	537.2	541.3	410.4	390.4	348.1	400.1
542.8	543.3	537.2	541.3	421.6	418.2	352.2	409.7
543.5	546.9	539.6	542.4	515.4	515.1	375.0	514.1
543.5	546.9	539.6	542.4	532.1	532.0	376.9	533.6
606.4	605.9	597.7	598.4	549.8	549.5	438.2	537.6
608.1	607.5	597.9	598.5	567.0	569.5	442.6	548.4
796.4	797.2	796.8	798.6	584.7	570.6	496.7	552.9
796.4	797.2	796.8	798.6	600.0	598.0	497.0	582.7
798.6	799.6	797.1	799.5	609.7	600.3	530.0	593.3
798.6	799.6	797.1	799.5	735.2	736.2	548.8	730.2
829.5	831.8	818.6	821.3	740.4	737.0	580.4	732.5
834.8	836.0	820.5	824.5	802.7	804.6	596.9	796.7
889.8	891.3	889.5	891.6	811.8	809.0	735.9	805.2
891.3	892.0	890.5	891.8	817.3	811.7	740.7	820.9
899.5	900.2	891.5	892.6	849.0	844.1	809.8	831.8
899.5	900.2	891.5	892.6	898.5	898.7	818.0	888.0
900.5	900.8	892.0	892.8	903.0	904.3	834.5	902.8
900.5	900.8	892.0	892.8	914.1	913.7	845.9	903.2
1005.1	1008.1	1008.5	1009.0	917.0	919.1	852.2	906.7
1008.3	1008.1	1008.5	1009.0	929.6	933.1	880.0	918.3
1008.3	1010.0	1009.6	1010.2	938.7	936.6	882.9	921.7
1010.4	1010.0	1009.6	1010.2	943.3	943.0	903.0	934.3
1010.4	1012.2	1010.6	1015.9	949.5	956.8	914.6	940.1
1015.1	1014.5	1017.4	1017.9	1018.4	1019.3	915.6	1015.5
1049.8	1051.2	1054.6	1056.7	1019.6	1021.1	931.2	1016.8
1050.0	1051.5	1055.1	1056.7	1030.3	1030.1	989.1	1023.8
1093.7	1105.0	1097.5	1112.2	1039.5	1038.0	994.7	1029.5
1093.7	1105.0	1097.5	1112.2	1049.4	1049.1	1000.1	1050.1
1099.4	1108.7	1105.7	1114.9	1056.7	1059.8	1002.9	1054.0
1099.4	1108.7	1105.7	1114.9	1065.8	1061.9	1032.8	1061.5
1136.0	1135.6	1136.0	1136.2	1070.9	1072.4	1034.5	1068.9
1136.9	1136.6	1136.3	1136.6	1074.7	1076.7	1043.6	1068.9
1175.8	1176.5	1174.4	1176.5	1078.2	1084.8	1047.5	1074.8
1175.8	1176.5	1174.4	1176.5	1088.1	1085.6	1062.9	1074.8
1177.1	1177.6	1175.5	1177.0	1096.7	1095.7	1069.4	1098.7
1177.1	1177.6	1175.5	1177.0	1100.1	1103.7	1074.5	1105.7
1269.2	1271.6	1272.8	1275.5	1112.6	1116.2	1078.9	1113.3
1270.0	1271.8	1273.1	1275.7	1114.5	1120.6	1099.4	1115.4
1281.3	1283.0	1286.1	1288.4	1138.4	1133.5	1110.8	1119.7
1281.3	1283.0	1286.1	1288.4	1141.1	1139.7	1123.9	1141.3
1281.4	1283.3	1286.3	1288.4	1188.6	1190.3	1125.2	1184.4
1281.4	1283.3	1286.3	1288.4	1191.4	1191.3	1125.6	1186.0
1293.5	1293.2	1291.5	1292.4	1196.6	1199.4	1139.6	1189.4
1293.5	1293.2	1291.5	1292.4	1206.4	1208.1	1142.6	1200.8
1293.6	1294.3	1292.4	1293.2	1257.1	1256.0	1188.6	1254.5
1293.6	1294.3	1292.4	1293.2	1264.6	1265.1	1194.6	1266.2
1316.3	1318.4	1315.5	1318.7	1271.4	1271.3	1212.1	1266.3
1317.8	1318.9	1317.6	1319.0	1275.7	1277.6	1218.5	1272.7
1386.3	1387.6	1384.9	1385.8	1280.8	1282.5	1222.0	1277.4
1389.1	1388.7	1386.7	1386.5	1282.2	1291.1	1237.6	1282.5
1408.1	1407.9	1405.7	1406.9	1291.4	1295.4	1238.4	1294.8
1408.1	1407.9	1405.9	1406.9	1300.8	1303.4	1259.0	1306.6
1409.0	1410.0	1408.2	1408.4	1304.0	1305.9	1260.6	1309.4
1409.6	1410.6	1408.2	1408.4	1307.4	1308.4	1272.1	1312.9
1410.9	1410.7	1409.1	1409.2	1309.5	1313.8	1279.4	1316.0
1410.9	1410.7	1409.1	1409.2	1315.9	1314.1	1283.4	1321.1
1421.7	1423.0	1420.0	1421.8	1318.3	1318.7	1296.5	1322.4
1421.7	1423.0	1420.0	1421.8	1326.2	1329.5	1302.4	1332.0
1422.2	1424.0	1421.0	1421.8	1379.8	1380.5	1314.2	1375.0
1422.2	1424.0	1421.0	1421.8	1385.7	1386.2	1329.1	1387.3
1490.1	1497.2	1492.4	1499.2	1394.4	1395.4	1337.5	1387.9
1491.7	1497.2	1492.4	1499.2	1397.4	1397.0	1342.8	1395.7
1491.7	1497.3	1492.4	1500.1	1407.7	1406.7	1357.4	1404.1
1492.0	1497.3	1492.4	1500.1	1413.6	1413.6	1365.2	1407.5
1492.0	1499.0	1493.2	1503.1	1414.6	1416.0	1371.3	1414.2
1496.5	1500.8	1497.1	1503.3	1416.5	1417.3	1375.2	1414.5
1499.3	1506.1	1498.6	1504.8	1419.2	1419.0	1384.2	1417.7
1499.3	1506.1	1498.6	1504.8	1424.5	1424.2	1396.4	1420.7
1500.5	1506.9	1499.2	1505.6	1426.3	1431.0	1400.9	1427.9
1500.5	1506.9	1499.2	1505.6	1434.2	1431.3	1402.2	1428.0
1525.4	1532.7	1523.3	1531.7	1434.7	1434.8	1412.5	1433.4
1525.7	1533.1	1523.8	1531.9	1447.3	1446.1	1418.3	1446.9
3006.1	3033.9	2999.3	3024.5	1487.8	1493.6	1419.4	1487.5
3006.1	3033.9	2999.4	3024.5	1488.7	1493.7	1421.2	1487.9
3006.6	3034.1	2999.6	3025.2	1489.7	1494.9	1440.9	1491.9
3006.6	3034.1	2999.6	3025.2	1492.0	1495.1	1447.7	1492.4
3007.7	3034.1	3000.0	3025.2	1492.9	1495.9	1447.9	1493.6
3007.9	3034.1	3000.0	3025.2	1493.9	1497.7	1458.2	1495.3
3019.8	3040.9	3008.0	3034.7	1499.7	1510.0	1459.7	1502.4
3019.8	3040.9	3008.0	3034.7	1504.5	1511.1	1467.8	1503.1
3020.1	3041.1	3008.4	3034.7	1505.4	1512.0	1467.9	1503.8
3020.1	3041.1	3008.4	3034.7	1507.6	1512.8	1473.5	1504.2
3022.5	3046.1	3010.7	3040.0	1511.9	1517.1	1474.3	1516.9
3022.6	3047.3	3011.5	3040.7	1514.2	1518.8	1487.1	1521.8
3044.3	3071.8	3046.5	3068.0	1521.2	1520.3	1496.0	1522.2
3044.3	3071.8	3046.5	3068.0	1524.0	1526.4	1677.8	1525.7
3044.4	3071.9	3046.6	3068.1	2939.4	2962.5	2806.3	2965.1
3044.4	3071.9	3046.6	3068.1	2944.8	2962.7	2812.8	2965.3
3050.3	3080.8	3052.7	3075.3	2948.8	2969.5	2883.1	2971.6
3054.6	3080.8	3057.5	3075.3	2952.9	2969.8	2886.0	2971.8
3101.6	3114.1	3076.4	3093.4	2964.5	2981.4	2916.4	2978.8
3101.6	3114.1	3076.4	3093.4	2965.0	2981.6	2916.7	2979.0
3102.1	3114.2	3076.5	3093.8	2973.4	3000.2	2927.6	2998.1
3102.1	3114.2	3076.5	3093.8	2976.8	3000.8	2928.1	2998.1
3102.2	3115.8	3077.6	3098.4	2978.1	3005.0	2983.2	3004.0
3102.2	3115.9	3078.1	3098.8	2988.5	3007.1	2983.5	3004.3
				2996.3	3037.3	2985.1	3007.0

				3007.0 3011.6 3015.4 3020.1 3020.6 3024.0 3026.2 3033.2 3051.7 3055.5 3063.7 3066.6 3074.7 3082.9 3085.8 3088.1 3100.5	3037.9 3039.0 3039.1 3039.6 3040.1 3048.1 3058.3 3068.5 3068.6 3072.9 3073.6 3086.5 3086.7 3095.2 3095.9 3101.0 3101.2	2986.3 3009.5 3010.3 3020.0 3020.2 3059.2 3059.3 3071.7 3073.3 3088.9 3096.4 3096.5 3096.8 3098.1 3106.1 3185.2 3212.4	3007.8 3032.0 3032.5 3035.9 3035.9 3035.9 3036.3 3046.8 3052.5 3074.9 3075.4 3084.9 3084.9 3089.7 3090.0 3096.2 3097.0

Table S9. Harmonic vibrational frequencies of M(*o*-Me_2-1.1.1)$^{0/+}$, M(24-Crown-8)$^{0/+}$, and Li(3^6Adamanzane)$^{0/+}$ species at B3LYP level (M=Li/Na/K,C,O,N: cc-pVDZ and H: aug-cc-pVDZ). B3LYP optimized geometries were used for frequency calculations.

Li(*o*-Me_2-1.1.1) (C_1)	Li(*o*-Me_2-1.1.1)$^+$ (C_1)	Na(*o*-Me_2-1.1.1) (C_{2h})	Na(*o*-Me_2-1.1.1)$^+$ (C_{2h})	Na(24-Crown-8) (S_4)	Na(24-Crown-8)$^+$ (S_4)	K(24-Crown-8) (S_4)	K(24-Crown-8)$^+$ (S_4)	Li(3^6Adamanzane) (S_4)	Li(3^6Adamanzane)$^+$ (S_4)
34.4	30.6	41.5	43.5	41.7	41.5	-3.6	17.1	103.7	103.3
40.4	33.7	58.2	62.6	42.7	41.8	23.0	24.5	115.7	115.8
54.8	39.4	58.2	62.6	42.7	41.8	38.9	37.2	115.7	115.8
62.0	55.6	73.5	77.7	47.9	46.6	39.5	37.2	124.7	124.5
69.4	57.7	73.5	77.7	67.8	65.9	39.5	38.7	156.3	158.0
89.3	74.4	85.2	87.8	74.7	70.5	50.0	51.0	170.4	168.6
100.8	82.5	104.9	110.0	76.0	71.3	68.3	64.1	171.3	168.6
115.9	117.8	105.0	110.0	83.0	85.2	85.3	90.3	171.3	174.2
134.7	139.2	118.9	128.5	83.0	85.2	85.3	90.3	224.1	226.2
143.8	141.3	119.0	128.5	107.3	106.3	108.2	110.2	236.9	237.3
149.4	141.9	149.5	151.4	140.0	146.9	111.7	124.1	236.9	237.3
160.1	165.5	149.5	151.4	145.4	152.7	119.2	132.9	242.3	242.1
164.9	176.9	163.5	166.1	145.4	152.7	119.2	132.9	266.0	266.1
173.3	181.2	179.4	181.2	154.8	154.9	123.1	135.2	266.0	266.1
177.2	183.9	179.4	181.2	164.1	167.7	133.4	141.9	273.0	277.9
202.1	193.4	181.0	183.6	164.1	167.7	133.4	141.9	287.5	288.9
202.9	207.4	181.0	186.8	164.2	175.8	145.5	143.4	298.1	303.7
211.5	211.4	181.9	186.8	186.6	189.8	182.8	183.3	298.1	303.7
232.0	216.5	198.2	200.9	186.6	189.8	190.8	190.0	317.4	319.0
236.8	232.4	199.9	210.0	190.8	194.5	191.5	190.0	321.7	323.5
241.9	234.2	230.9	234.7	193.9	200.6	191.5	195.2	336.5	339.2
245.3	239.4	230.9	234.7	246.5	251.5	214.5	224.2	336.5	339.2
252.0	240.6	237.9	241.2	252.8	251.6	227.1	228.3	362.3	363.7
272.4	279.0	242.2	246.0	253.1	254.2	227.1	228.3	405.3	407.2
276.2	284.8	274.1	277.2	253.1	254.2	232.8	232.5	411.2	411.6
282.9	285.8	274.1	277.2	272.4	276.8	275.8	278.7	428.9	429.4
283.7	286.4	278.9	280.4	283.0	288.6	279.8	282.0	428.9	429.4
289.4	289.9	279.7	283.3	283.0	288.6	282.8	288.5	446.3	445.6
297.2	291.9	286.3	288.9	301.0	303.7	282.8	288.5	461.3	460.4
305.6	293.0	286.3	288.9	305.2	307.3	294.0	296.7	461.3	460.4
342.7	325.3	326.3	326.7	311.6	313.8	294.0	296.7	495.8	495.9
348.7	338.4	333.8	332.8	311.6	313.8	295.8	298.4	515.5	518.0
390.0	398.4	394.9	395.9	324.8	326.8	319.6	323.5	515.5	518.0
395.9	400.2	394.9	395.9	359.6	362.6	361.7	364.5	518.7	523.8
407.5	406.8	394.9	396.2	378.5	380.3	379.3	382.2	566.7	575.3
408.3	407.9	394.9	396.2	378.5	380.3	379.3	382.2	567.4	575.3
467.9	477.1	473.9	478.5	388.4	388.3	389.3	391.0	567.4	575.4
482.9	484.0	485.3	485.2	520.3	520.6	510.2	510.9	624.3	624.0
491.2	488.8	485.3	485.2	520.3	520.6	516.2	516.8	645.3	645.7
492.8	494.0	487.8	489.4	521.1	523.2	516.2	516.8	710.8	712.1
495.3	495.3	487.8	489.4	523.9	524.6	524.4	527.2	710.8	712.1
502.0	498.5	492.6	496.0	580.4	579.7	573.3	570.6	733.0	733.7
567.4	568.1	565.9	566.4	580.4	580.2	576.6	575.3	780.6	781.0
574.9	575.3	571.6	572.6	581.0	580.3	576.6	575.3	798.9	800.6
604.3	612.8	614.3	614.4	581.0	580.3	579.7	577.4	798.9	800.6
608.0	618.4	614.3	614.4	813.6	814.1	816.8	816.6	813.4	813.7
631.3	627.9	617.5	618.6	814.7	815.5	816.8	816.6	833.8	834.1
633.2	630.7	617.6	618.6	814.7	815.5	816.9	816.8	866.4	868.5
763.9	764.7	759.8	760.8	819.1	819.2	819.5	819.9	866.4	868.5
768.6	769.8	764.7	765.5	832.5	833.1	830.1	830.2	877.8	881.6
836.4	843.3	839.3	838.7	845.1	845.2	847.4	847.4	888.9	890.0
842.6	845.0	839.3	838.7	845.1	845.2	847.4	847.4	888.9	890.0
847.0	847.4	840.9	840.7	864.4	863.4	871.2	870.7	902.2	903.3
872.3	870.5	875.2	875.8	913.0	915.9	915.1	917.5	907.8	909.9
881.7	879.2	875.3	875.8	924.1	926.1	926.4	927.4	920.0	920.1
889.5	888.5	891.7	891.9	924.1	926.1	929.3	929.8	931.1	933.2
905.0	895.7	891.7	891.9	929.5	928.8	929.3	929.8	955.5	956.1
921.7	938.6	932.1	937.1	932.5	933.7	937.8	941.2	956.0	957.5
940.8	945.2	939.4	940.8	932.5	933.7	937.8	941.2	956.0	957.5
945.1	947.7	939.4	940.8	934.7	935.3	941.5	942.0	980.9	980.0
956.0	955.7	954.4	954.2	937.2	939.8	945.5	950.0	1000.4	1001.4
966.6	965.4	957.9	958.9	1045.5	1046.1	1052.0	1051.3	1000.4	1001.4
968.6	967.6	957.9	958.9	1045.5	1046.1	1052.4	1051.3	1010.2	1012.3
971.5	968.5	969.2	976.4	1046.2	1047.1	1052.4	1052.2	1041.1	1044.2
977.7	977.0	969.2	976.4	1051.3	1050.1	1056.8	1055.6	1041.1	1044.2
981.8	980.3	978.7	978.9	1066.9	1064.8	1072.0	1072.1	1056.9	1058.4
1051.8	1054.9	1057.4	1057.8	1066.9	1064.8	1072.8	1072.1	1062.9	1062.4
1062.9	1060.1	1057.4	1057.8	1068.3	1066.6	1072.8	1073.3	1086.2	1086.8
1065.2	1074.4	1066.5	1079.4	1070.3	1067.6	1074.7	1073.7	1093.0	1092.3
1076.6	1074.9	1066.5	1079.4	1080.7	1080.3	1089.7	1088.7	1093.0	1092.3
1079.0	1079.1	1082.0	1081.3	1080.7	1088.7	1089.7	1091.7	1100.4	1101.3
1082.2	1080.1	1082.0	1081.3	1080.8	1090.5	1091.0	1097.0	1101.9	1104.9
1090.7	1083.1	1085.0	1082.7	1087.0	1090.5	1092.4	1097.0	1104.5	1106.9
1092.5	1093.2	1091.7	1090.9	1114.6	1123.2	1118.1	1124.4	1104.5	1106.9
1096.0	1102.5	1104.3	1103.1	1122.0	1123.2	1120.3	1124.4	1115.3	1114.4
1102.5	1105.5	1104.3	1103.7	1122.0	1129.0	1120.3	1127.0	1145.4	1144.2
1108.7	1105.6	1104.5	1103.7	1129.8	1129.6	1126.6	1132.1	1145.4	1144.2
1112.3	1110.9	1104.8	1106.0	1135.3	1141.2	1136.0	1143.1	1149.6	1149.2
1124.6	1137.3	1124.4	1137.6	1143.4	1149.7	1148.4	1151.1	1190.5	1192.6
1132.9	1137.5	1130.3	1138.1	1143.4	1149.7	1148.4	1151.1	1190.5	1192.6
1133.2	1141.4	1130.3	1138.1	1153.3	1154.6	1152.2	1151.9	1194.7	1196.9
1135.4	1143.2	1134.6	1138.9	1156.6	1156.2	1152.4	1155.3	1227.5	1228.1
1141.4	1148.7	1134.6	1138.9	1158.2	1159.3	1152.4	1155.3	1242.3	1244.1
1156.3	1159.1	1136.0	1143.1	1158.2	1159.3	1153.3	1156.0	1242.3	1244.1
1161.1	1164.9	1158.4	1167.1	1159.8	1162.8	1158.1	1158.7	1255.3	1258.5
1170.3	1172.3	1158.4	1167.1	1247.4	1248.4	1245.3	1246.0	1277.8	1279.0
1178.0	1182.9	1165.6	1179.6	1247.4	1248.4	1245.6	1246.0	1280.5	1282.3
1179.1	1192.7	1165.6	1179.6	1248.1	1249.0	1245.6	1246.2	1280.5	1282.3
1211.6	1220.9	1211.6	1217.1	1249.7	1249.9	1247.6	1247.6	1286.9	1288.5
1223.6	1233.3	1222.8	1227.5	1257.9	1261.3	1255.3	1258.3	1289.2	1292.2
1242.5	1244.2	1246.7	1247.3	1260.4	1261.6	1257.9	1259.4	1290.6	1293.6
1245.6	1246.1	1246.7	1247.3	1260.4	1263.2	1257.9	1260.0	1290.6	1295.0
1252.4	1256.4	1253.6	1255.4	1261.0	1263.2	1259.1	1260.0	1291.0	1295.0
1255.9	1257.9	1256.5	1258.9	1273.9	1276.7	1273.6	1278.0	1315.9	1318.3
1261.6	1259.0	1256.5	1258.9	1279.4	1281.6	1280.8	1284.3	1320.0	1322.8
1264.8	1265.7	1260.0	1261.9	1279.4	1281.6	1280.8	1284.3	1323.0	1328.0
1271.8	1269.7	1273.4	1275.8	1289.3	1292.3	1289.8	1294.1	1328.1	1330.3
1278.6	1278.1	1274.3	1277.3	1299.2	1302.2	1300.4	1303.2	1328.1	1330.3
1279.2	1279.1	1274.3	1277.3	1301.7	1305.7	1304.2	1308.1	1330.3	1332.6
1283.6	1286.7	1288.5	1291.7	1301.7	1305.7	1304.2	1308.1	1363.3	1363.3
1289.5	1291.0	1290.6	1293.5	1304.5	1307.8	1306.5	1310.0	1366.6	1367.0
1302.1	1294.2	1290.6	1293.5	1352.5	1353.1	1349.8	1349.6	1366.6	1367.0
1357.8	1358.6	1360.0	1360.1	1357.4	1357.8	1355.3	1356.0	1373.5	1374.4
1359.5	1360.2	1360.0	1360.1	1357.4	1357.8	1355.3	1356.0	1377.6	1379.3
1368.0	1363.5	1360.8	1362.8	1367.1	1368.0	1364.3	1366.0	1377.6	1379.3
1381.4	1383.3	1381.6	1383.8	1382.5	1382.8	1375.8	1376.4	1393.6	1395.5
1387.4	1388.5	1389.0	1389.9	1389.3	1389.4	1385.0	1384.9	1393.6	1395.5
1388.4	1390.4	1389.8	1389.9	1389.3	1389.4	1385.0	1384.9	1395.4	1396.3
1393.8	1394.7	1389.8	1395.0	1394.4	1395.1	1389.5	1390.7	1402.0	1402.0
1396.1	1401.6	1394.1	1401.6	1405.9	1408.4	1406.8	1409.3	1402.5	1402.8
1400.1	1404.1	1397.9	1402.7	1407.4	1408.9	1408.8	1410.3	1406.7	1409.2
1404.0	1406.3	1405.1	1406.0	1407.4	1408.9	1408.8	1410.3	1406.7	1409.2
1410.7	1408.0	1405.1	1406.0	1414.1	1414.8	1412.4	1412.9	1412.0	1412.2
1431.4	1436.8	1434.2	1438.1	1434.8	1438.1	1437.7	1440.9	1412.0	1412.2
1434.2	1439.4	1436.6	1440.4	1438.4	1441.3	1440.8	1443.5	1417.5	1418.6
1444.3	1441.4	1436.6	1440.4	1438.4	1441.3	1440.8	1443.5	1420.6	1422.4
1452.5	1458.7	1451.3	1458.1	1443.2	1446.3	1444.7	1446.9	1422.4	1423.6
1453.6	1459.1	1451.3	1458.1	1451.2	1456.7	1452.7	1457.9	1452.2	1457.2
1454.2	1459.7	1452.1	1458.8	1452.1	1457.0	1452.9	1458.3	1452.2	1457.4
1455.1	1460.1	1452.1	1458.8	1455.9	1459.0	1454.2	1458.9	1452.3	1457.4
1456.8	1462.1	1456.6	1463.7	1455.9	1459.0	1454.2	1458.9	1452.5	1458.1
1456.9	1463.4	1459.2	1464.8	1460.3	1468.1	1460.7	1466.5	1461.1	1468.2
1460.7	1468.1	1459.2	1464.8	1461.8	1468.1	1461.7	1466.8	1461.7	1469.3
1463.4	1468.8	1464.3	1469.4	1461.8	1468.1	1461.7	1466.8	1463.8	1470.3
1465.5	1470.2	1464.9	1469.6	1463.9	1468.5	1463.5	1467.2	1463.8	1470.3

1467.3	1472.5	1467.2	1473.2	1467.7	1474.2	1468.2	1473.9	1466.1	1472.4
1468.4	1472.5	1467.2	1473.2	1470.0	1476.2	1469.8	1475.1	1466.3	1473.3
1468.7	1476.5	1467.5	1473.4	1470.0	1476.2	1469.8	1475.1	1469.2	1477.1
1469.3	1476.6	1467.5	1473.4	1473.2	1478.2	1472.6	1476.6	1470.9	1477.1
1471.0	1485.0	1477.5	1486.1	1479.8	1488.9	1477.9	1485.9	1472.2	1477.8
1477.1	1485.7	1477.5	1486.2	1483.0	1489.9	1480.9	1486.9	1472.2	1478.1
1481.1	1489.5	1477.5	1486.2	1483.0	1489.9	1480.9	1486.9	1476.5	1488.0
2959.0	2979.1	2964.4	2991.0	1485.3	1491.4	1482.6	1487.9	1476.5	1488.0
2960.0	2986.6	2964.4	2991.0	2966.4	2991.6	2955.6	2985.3	1483.3	1491.4
2965.6	2989.7	2964.7	2991.1	2966.5	2991.6	2955.9	2985.3	1488.8	1493.1
2967.5	2996.9	2971.5	2997.4	2966.5	2991.7	2955.9	2985.3	2928.3	2962.3
2975.3	3003.1	2971.5	2997.4	2967.2	2991.7	2956.7	2985.4	2929.6	2962.6
2983.2	3008.3	2972.3	2997.5	2973.3	3002.5	2965.1	2992.1	2929.6	2962.6
3008.0	3024.6	3009.3	3035.8	2973.3	3002.9	2965.4	2992.6	2930.0	2962.7
3008.6	3028.8	3009.3	3035.8	2973.7	3002.9	2965.4	2992.6	2931.5	2967.8
3009.3	3033.6	3010.3	3035.8	2973.7	3003.2	2965.9	2993.2	2933.7	2968.0
3010.3	3034.6	3010.3	3037.2	2982.3	3009.9	2973.2	2999.4	2933.7	2968.0
3010.5	3040.2	3010.4	3037.2	2982.8	3010.2	2973.6	2999.9	2935.2	2968.4
3010.6	3040.6	3010.8	3037.4	2982.8	3010.2	2973.6	2999.9	2943.6	2973.7
3015.4	3042.4	3017.3	3043.8	2983.8	3010.9	2974.7	3000.6	2943.7	2973.7
3015.6	3044.0	3017.4	3043.8	2999.4	3022.5	2989.8	3017.1	2943.7	2974.0
3016.6	3044.1	3017.4	3044.2	2999.4	3022.5	2989.8	3017.1	2944.3	2975.2
3020.1	3045.5	3017.5	3047.2	3000.5	3023.0	2990.7	3017.1	3015.1	3047.2
3032.9	3056.4	3017.8	3047.2	3000.7	3023.9	2990.7	3017.7	3017.0	3047.2
3033.0	3056.5	3017.8	3047.2	3019.1	3041.4	3011.4	3033.0	3017.0	3047.4
3035.6	3059.5	3028.5	3054.4	3019.1	3041.7	3011.5	3033.4	3017.0	3048.0
3036.3	3063.2	3029.3	3054.4	3019.1	3041.7	3011.5	3033.4	3017.9	3048.0
3089.5	3107.3	3099.0	3114.9	3019.4	3042.3	3012.3	3034.0	3018.8	3049.2
3092.6	3107.3	3099.6	3114.9	3025.2	3048.2	3017.3	3038.2	3043.2	3068.6
3094.2	3113.2	3099.6	3114.9	3025.5	3049.2	3017.7	3039.2	3043.2	3068.6
3095.3	3113.2	3099.9	3114.9	3025.5	3049.2	3017.7	3039.2	3058.0	3072.3
3107.4	3116.8	3101.3	3115.0	3025.6	3049.8	3018.0	3040.0	3058.5	3074.7
3107.7	3116.8	3101.3	3115.0	3052.6	3071.0	3038.9	3058.2	3058.5	3074.7
3124.0	3145.7	3120.6	3145.1	3052.8	3071.0	3038.9	3058.2	3059.7	3076.1
3124.1	3145.8	3120.6	3145.1	3052.9	3071.0	3039.0	3058.3	3069.2	3085.1
3132.5	3148.3	3120.9	3145.1	3052.9	3071.2	3039.2	3058.3	3072.8	3085.1
3132.6	3148.3	3120.9	3145.1	3104.0	3112.4	3083.6	3097.7	3072.8	3085.8
				3104.0	3112.4	3083.6	3097.7	3075.3	3086.3
				3104.0	3112.4	3083.6	3097.8	3079.9	3089.2
				3104.2	3112.4	3083.8	3097.8	3080.6	3091.5
								3080.6	3095.1
								3080.8	3095.1
								3085.2	3096.4
								3088.8	3106.0
								3088.8	3106.0
								3092.0	3106.5

Table S10. Harmonic vibrational frequencies of 9-Crown-3, [2.1.1]Cryptand, *o*-Me_2-1.1.1, 24-Crown-8, and 3^6Adamanzane species at B3LYP level. B3LYP optimized geometries were used for frequency calculations.

9-Crown-3	[2.1.1]Cryptand	*o*-Me_2-1.1.1	24-Crown-8	3^6Adamanzane
C,O: cc-pVTZ and H: aug-cc-pVTZ	C,O,N: cc-pVTZ and H: aug-cc-pVTZ	C,O: cc-pVDZ and H: aug-cc-pVDZ	C,O: cc-pVDZ and H: aug-cc-pVDZ	C,N: cc-pVDZ and H: aug-cc-pVDZ
143.1	42.8	30.9	24.2	80.0
143.5	57.3	44.7	26.6	116.2
192.3	65.1	46.0	35.1	116.2
193.0	84.2	46.0	37.2	119.8
249.5	94.5	68.8	53.4	164.4
309.3	102.2	68.8	54.3	166.2
375.9	129.8	118.3	62.3	166.2
376.6	144.5	118.3	73.8	170.2
389.1	161.6	130.1	74.1	208.3
536.1	168.5	130.1	83.2	212.5
537.2	180.3	132.9	87.3	214.7
590.7	190.4	150.7	110.8	214.7
806.6	204.0	150.7	112.5	271.3
806.6	235.4	153.3	121.1	282.0
806.7	255.1	160.8	128.6	296.3
884.5	274.2	160.8	144.4	298.1
884.5	278.5	186.0	149.0	298.1
899.7	291.9	231.2	156.5	317.4
1018.0	312.8	231.2	159.5	317.4
1018.1	333.6	254.8	173.4	323.8
1031.1	338.5	259.9	181.5	334.0
1073.9	341.4	279.2	207.5	334.0
1139.1	358.1	279.9	213.9	355.4
1139.5	381.9	279.9	222.0	378.6
1158.9	421.7	290.8	232.3	404.1
1184.8	446.1	293.9	269.4	425.8
1185.0	464.8	293.9	275.5	425.8
1278.7	483.1	326.5	290.1	443.2
1293.5	497.6	326.6	319.9	467.9
1293.6	521.4	385.3	335.4	467.9
1298.8	530.6	385.3	352.7	501.1
1298.8	580.0	385.8	359.5	526.1
1319.2	626.0	385.8	400.1	526.1
1382.3	748.8	458.3	420.3	532.7
1402.9	764.6	463.3	429.0	615.5
1408.3	780.6	463.3	470.9	628.2
1408.4	810.4	487.5	510.4	712.8
1418.4	822.1	487.5	521.6	712.8
1418.5	833.3	493.9	542.8	726.0
1485.2	837.5	558.1	551.6	778.5
1485.2	877.7	561.1	563.9	801.4
1488.6	895.4	603.7	575.3	801.4
1497.2	923.3	603.7	812.1	816.4
1498.2	926.6	614.2	824.5	843.9
1527.6	943.8	614.2	826.3	874.8
2954.8	969.5	755.3	832.6	874.8
2954.8	979.6	759.3	836.7	887.5
2955.0	987.1	841.7	849.7	887.5
2987.9	1010.0	841.7	866.2	888.7
2988.0	1045.1	844.9	884.5	902.7
2992.6	1050.6	879.0	893.3	906.3
3031.3	1055.8	879.0	905.3	921.0
3031.7	1065.3	890.1	924.5	929.6
3049.9	1069.0	890.1	950.0	952.0
3086.5	1078.0	941.3	952.8	952.0
3086.6	1084.5	941.3	1000.2	966.9
3087.8	1094.9	943.6	1032.7	1004.8
	1107.1	948.5	1037.9	1005.6
	1118.9	964.1	1051.9	1005.6
	1122.3	967.9	1059.1	1023.2
	1127.8	967.9	1068.7	1062.2
	1134.0	977.6	1070.9	1062.2
	1147.2	977.6	1078.0	1063.5
	1155.5	1076.8	1080.5	1068.5
	1193.7	1076.8	1093.2	1098.9
	1200.8	1079.0	1096.4	1098.9
	1203.8	1082.0	1113.8	1103.2
	1211.0	1082.0	1125.0	1105.9
	1248.7	1096.9	1129.6	1113.2
	1260.6	1096.9	1132.2	1113.2
	1269.3	1097.6	1139.4	1139.1
	1272.7	1100.3	1142.3	1142.4
	1276.3	1101.2	1143.5	1165.9
	1280.0	1101.2	1149.1	1167.2
	1291.2	1108.0	1155.6	1167.2
	1311.4	1137.5	1157.2	1222.3
	1318.9	1144.3	1162.4	1222.8
	1319.7	1144.3	1165.5	1222.8
	1327.8	1162.2	1167.6	1226.3
	1337.8	1162.2	1172.0	1245.3
	1349.6	1176.8	1174.3	1245.3
	1352.8	1187.8	1179.6	1251.7
	1369.4	1187.8	1210.3	1276.3
	1372.1	1189.8	1219.6	1276.3
	1380.0	1194.1	1221.8	1281.9
	1387.3	1194.1	1239.4	1282.8
	1390.9	1201.3	1246.2	1293.1
	1394.2	1239.8	1249.2	1297.7
	1399.1	1241.3	1256.3	1297.7
	1404.0	1241.3	1260.1	1305.7
	1415.2	1252.4	1280.2	1318.1
	1418.4	1255.4	1282.5	1318.4
	1425.4	1255.4	1283.1	1324.8
	1435.4	1282.1	1286.6	1324.8
	1441.5	1282.1	1291.5	1329.1
	1442.7	1282.7	1294.5	1329.8
	1474.6	1290.1	1301.3	1364.6
	1485.1	1290.8	1306.7	1366.9
	1485.5	1290.8	1323.3	1366.9
	1488.5	1355.4	1329.5	1371.5
	1490.2	1355.4	1350.7	1376.9
	1493.6	1357.6	1351.4	1376.9
	1498.5	1379.0	1364.1	1392.4
	1501.6	1383.7	1368.2	1397.5
	1506.1	1386.4	1377.6	1397.5
	1507.9	1387.3	1384.9	1401.3
	1510.4	1387.3	1394.5	1409.8
	1522.6	1393.6	1400.8	1409.8
	1527.4	1403.7	1413.9	1411.7
	1530.1	1403.7	1425.1	1416.2
	2891.7	1428.6	1425.9	1416.2
	2915.9	1432.5	1440.8	1416.4
	2946.4	1432.5	1447.2	1425.0
	2952.4	1446.8	1452.2	1425.8
	2959.5	1446.8	1453.9	1457.0
	2960.9	1448.0	1455.0	1458.8
	2976.5	1455.2	1455.8	1458.8
	2976.8	1455.2	1459.0	1461.6
	2986.6	1456.2	1460.4	1463.7
	2989.1	1456.2	1463.5	1464.9
	2997.0	1458.7	1466.0	1465.5

	2998.1 3002.5 3012.3 3015.7 3020.5 3026.6 3031.2 3037.2 3052.5 3054.3 3060.5 3065.6 3068.1 3073.3 3088.9 3135.1 3139.8	1460.9 1467.1 1467.1 1467.7 1467.7 1477.8 1478.8 1478.8 2944.1 2944.1 2944.3 2953.0 2953.0 2953.6 2994.8 2994.8 2996.0 2996.0 2996.1 2998.2 3002.9 3003.2 3003.2 3005.1 3005.1 3005.6 3041.4 3041.5 3105.9 3105.9 3105.9 3106.2 3106.5 3106.5 3129.2 3129.2 3129.3 3129.3	1469.8 1479.6 1481.6 1483.1 1491.6 1495.6 1499.9 1505.5 1507.2 2950.0 2953.6 2958.3 2959.2 2960.5 2965.9 2968.3 2968.6 2973.3 2976.6 2976.9 2979.0 2983.4 2988.3 2995.4 2996.4 2997.4 3004.9 3006.2 3008.7 3012.1 3013.9 3016.6 3016.9 3028.9 3029.1 3035.3 3045.4 3073.9 3075.5 3078.8 3095.9	1465.5 1469.5 1471.1 1471.9 1474.4 1474.4 1475.3 1480.8 1480.8 1486.7 1488.4 2838.6 2838.7 2838.7 2838.8 2844.8 2845.3 2845.3 2846.1 2866.2 2866.4 2866.4 2871.2 3026.6 3026.7 3027.6 3027.7 3027.7 3028.3 3047.5 3047.5 3048.1 3050.9 3050.9 3055.0 3067.3 3071.2 3071.2 3073.8 3090.4 3090.4 3090.7 3091.4 3107.8 3109.6 3112.2 3112.2

Table S11. Harmonic vibrational frequencies of K([10]aneN$_4$)$_2$, Methylated-K[2.2.2]Cryptand, and Ethylated-K[2.2.2]Cryptand species at B3LYP level (M=Na/K,C,O,N: cc-pVDZ and H: aug-cc-pVDZ). B3LYP optimized geometries were used for frequency calculations.

K([10]aneN$_4$)$_2$	Methylated-K[2.2.2]Cryptand	Ethylated-K[2.2.2]Cryptand
-3.0	-34.7	10.6
26.9	-19.7	10.7
26.9	-19.3	23.0
60.8	-9.9	31.0
66.8	49.5	44.7
66.8	50.2	44.7
79.7	52.6	64.9
80.2	74.6	70.0
125.6	75.5	71.5
132.5	75.7	71.5
133.7	80.8	74.8
133.7	82.4	76.7
146.1	99.7	76.7
148.2	100.4	81.4
155.7	101.2	81.4
199.5	104.6	92.5
201.7	104.8	92.5
220.0	134.0	97.8
220.0	146.7	98.0
224.5	146.7	98.2
224.5	152.6	119.2
258.2	154.5	142.9
258.2	163.6	144.7
259.6	164.1	144.7
259.6	181.9	154.0
275.1	182.2	154.0
281.4	187.7	172.5
287.1	201.8	176.0
289.8	214.3	186.1
319.2	215.4	186.1
320.8	230.0	198.8
339.5	232.4	201.5
339.5	233.3	201.5
341.9	259.2	214.0
341.9	268.2	215.8
401.7	268.5	215.8
405.8	306.2	221.1
462.7	306.8	227.8
464.4	337.7	227.8
532.7	339.7	237.1
532.7	346.5	237.1
533.3	347.1	250.0
533.3	349.6	276.9
579.9	355.0	295.1
585.8	355.3	295.1
712.0	375.3	301.4
727.1	386.9	313.6
739.1	387.2	313.7
739.1	412.9	335.5
756.8	420.3	335.5
756.8	420.3	343.2
781.0	460.3	344.5
804.5	464.4	351.5
844.2	464.5	351.5
844.2	500.9	359.9
848.0	506.9	368.2
848.0	507.0	368.2
852.0	518.7	375.4
855.0	526.4	391.8
887.6	526.5	391.8
893.0	565.8	414.3
897.3	573.8	420.4
898.1	578.6	420.4
902.4	578.8	473.2
902.8	585.5	482.0
944.4	585.6	482.0
944.4	767.8	508.5
946.9	768.4	512.1
946.9	831.8	512.1
1017.7	831.8	535.9
1017.7	835.1	541.9
1018.2	835.2	541.9
1018.2	842.2	577.3
1023.1	852.9	584.6
1023.6	866.5	584.6
1037.5	866.5	585.6
1038.3	891.6	587.3
1069.4	914.1	587.3
1070.2	914.1	754.0
1102.1	927.5	758.1
1102.1	927.7	761.5
1102.5	939.2	761.5
1102.5	940.9	765.8
1128.4	940.9	765.8
1128.6	946.8	778.8
1159.9	948.8	787.1
1159.9	948.8	844.4
1160.5	980.8	844.4
1160.5	985.3	857.9
1165.9	985.3	860.2
1166.0	1035.5	860.2
1189.1	1041.5	889.3
1189.3	1042.0	901.8
1222.8	1042.1	901.8
1225.5	1055.3	904.4
1255.0	1055.6	916.0
1255.0	1058.1	916.0
1258.9	1060.3	936.1
1258.9	1060.3	941.3
1266.1	1073.7	941.3
1266.4	1085.7	943.1
1279.8	1091.3	943.1
1280.2	1094.9	1003.1
1297.4	1095.0	1003.1
1297.4	1099.6	1008.4
1297.4	1107.5	1010.9
1297.4	1108.3	1011.8
1314.6	1108.3	1015.0
1315.0	1112.3	1015.0
1358.4	1112.3	1019.2
1358.6	1122.1	1019.2
1376.7	1122.2	1047.4
1376.7	1123.3	1048.0
1378.4	1132.3	1048.0
1378.4	1134.5	1050.2
1378.7	1134.6	1050.2
1379.7	1175.4	1052.6
1392.9	1175.8	1052.7
1392.9	1178.8	1063.0
1393.2	1179.4	1063.0
1393.6	1208.4	1074.7
1393.8	1209.6	1074.7
1393.8	1209.8	1075.5
1405.8	1258.0	1075.5
1411.5	1258.7	1088.3
1456.6	1272.1	1091.5

1457.6	1272.1	1098.6
1458.6	1276.3	1098.6
1459.7	1276.4	1107.5
1459.7	1295.7	1109.0
1460.1	1295.9	1109.0
1460.1	1296.3	1110.7
1460.8	1319.7	1110.7
1472.7	1319.9	1112.0
1472.7	1323.5	1120.5
1472.9	1325.3	1120.5
1472.9	1328.2	1122.8
1472.9	1328.3	1131.7
1472.9	1329.0	1131.7
1480.3	1329.3	1133.8
1480.9	1330.4	1172.6
1488.2	1342.2	1172.7
1488.2	1342.2	1175.5
1488.6	1343.7	1175.5
1488.6	1376.2	1188.4
1488.9	1379.0	1192.2
1491.9	1379.2	1192.2
1494.5	1385.0	1252.4
1495.3	1385.7	1252.9
2928.4	1385.8	1252.9
2928.4	1396.1	1257.2
2928.4	1396.1	1258.6
2928.6	1397.1	1271.7
2928.6	1397.2	1271.7
2928.6	1397.3	1273.2
2928.8	1405.3	1273.3
2929.0	1405.5	1276.0
2948.5	1405.7	1278.3
2948.6	1408.9	1278.3
2949.9	1423.2	1280.1
2949.9	1429.5	1281.3
2950.1	1429.6	1281.3
2950.1	1432.2	1305.3
2951.9	1435.2	1305.3
2953.9	1435.3	1305.9
3026.1	1453.4	1320.1
3026.7	1453.5	1320.1
3027.6	1454.7	1320.2
3027.6	1454.9	1321.9
3027.7	1455.0	1325.8
3028.0	1462.4	1325.8
3028.1	1462.5	1338.9
3028.1	1462.9	1338.9
3063.9	1463.0	1340.6
3064.3	1466.9	1364.4
3072.5	1466.9	1364.4
3072.5	1467.3	1366.0
3073.7	1474.3	1373.3
3073.7	1474.5	1373.3
3083.4	1477.8	1374.1
3083.6	1479.4	1378.7
3383.6	1479.7	1378.7
3385.9	1480.1	1380.7
3385.9	1485.8	1391.5
3405.2	1486.7	1391.5
3407.7	1486.9	1399.0
3407.7	1491.3	1399.2
3410.0	1513.8	1399.2
3410.8	1514.8	1399.6
	2932.2	1401.0
	2932.2	1401.0
	2932.6	1402.4
	2932.7	1404.1
	2939.6	1404.2
	2941.9	1407.8
	2961.9	1423.1
	2962.6	1426.5
	2962.7	1426.5
	2977.5	1437.9
	2977.8	1437.9
	2977.8	1438.3
	2994.7	1455.9
	2995.0	1455.9
	2995.2	1458.6
	2995.4	1458.6
	2995.4	1458.6
	2995.7	1461.4
	3040.3	1461.4
	3041.0	1465.4
	3041.0	1466.1
	3043.9	1466.1
	3044.3	1466.2
	3044.3	1467.1
	3051.8	1467.2
	3054.1	1467.2
	3054.2	1468.9
	3054.5	1474.5
	3060.9	1474.5
	3060.9	1474.8
	3092.6	1477.6
	3092.9	1477.6
	3093.7	1478.1
	3093.7	1478.4
	3094.8	1480.6
	3094.9	1480.7
	3122.4	1489.2
	3124.8	1490.5
	3124.9	1490.5
	3125.6	1494.1
	3127.9	1494.9
	3127.9	1494.9
	3130.2	2945.6
	3130.4	2945.6
	3130.4	2945.7
	3141.7	2945.7
	3142.1	2952.0
	3142.1	2954.5
		2958.5
		2959.2
		2959.2
		2973.4
		2973.6
		2973.6
		2988.0
		2988.2
		2988.4
		2988.4
		2988.6
		2988.6
		3021.4
		3021.5
		3021.5
		3021.7
		3021.9
		3021.9
		3048.2
		3048.4
		3048.4
		3049.3
		3049.8
		3049.8
		3052.6
		3053.2

		3053.2 3053.9 3054.4 3054.4 3076.4 3076.4 3076.4 3077.7 3078.0 3078.0 3084.3 3084.7 3086.2 3086.2 3087.0 3087.0 3097.9 3098.2 3098.2 3101.4 3101.4 3101.4 3104.0 3104.0 3104.1 3104.1 3104.2 3104.2

Table S12. VEEs (eV) for Li(9-Crown-3)$_2$ at the KT, D2, P3, and P3+ levels of theory with the H: d-aug-cc-pVDZ, Li,C,O: DZ basis set. The states are ordered according to P3+ excitation energies.

Approximate Superatomic orbital	Final State (S_6)	VEE (eV)			
		KT	D2	P3	P3+
1S	1^2A_g	0.000	0.000	0.000	0.000
1P	1^2A_u	0.122	0.123	0.125	0.124
1P	1^2E_u	0.191	0.229	0.228	0.228
1D	2^2A_g	0.396	0.416	0.421	0.420
1D	1^2E_g	0.492	0.577	0.576	0.576
1D	2^2E_g	0.538	0.638	0.639	0.638
1F	2^2A_u	0.851	0.973	0.977	0.976
1F	2^2E_u	0.863	0.990	0.993	0.993
1F	3^2E_u	0.901	1.049	1.051	1.050
2S	3^2A_g	1.041	1.103	1.111	1.110
1F	3^2A_u	0.958	1.123	1.126	1.126
1F	4^2A_u	0.978	1.126	1.131	1.130
2P	4^2E_u	1.163	1.228	1.234	1.233
2P	5^2A_u	1.347	1.308	1.318	1.317
2D	4^2A_g	1.500	1.408	1.423	1.421
1G	3^2E_g	1.296	1.484	1.489	1.488
1G	4^2E_g	1.314	1.495	1.500	1.499
1G	5^2A_g	1.325	1.525	1.529	1.529
2D	5^2E_g	1.680	1.667	1.668	1.667
2D	6^2E_g	1.741	1.715	1.717	1.717

Table S13. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Li(9-Crown-3)$_2^+$ at Li(9-Crown-3)$_2$ CAM-B3LYP geometry, from electron propagator methods using the H: d-aug-cc-pVDZ, Li,C,O: cc-pVDZ basis set. All valence electrons correlated.

Final State (S_6)	Li(9-Crown-3)$_2^+$						
	KT	D2		P3		P3+	
	VEAE	VEAE	PS	VEAE	PS	VEAE	PS
^2A_g	-1.653	-1.893	0.991	-1.902	0.989	-1.901	0.989
^2A_u	-1.531	-1.770	0.991	-1.777	0.989	-1.777	0.989
^2E_u	-1.462	-1.664	0.993	-1.674	0.991	-1.673	0.991
^2A_g	-1.257	-1.477	0.992	-1.481	0.991	-1.481	0.991
^2E_g	-1.161	-1.316	0.994	-1.326	0.993	-1.325	0.993
^2E_g	-1.115	-1.255	0.995	-1.263	0.994	-1.263	0.994
^2A_u	-0.802	-0.920	0.996	-0.925	0.995	-0.925	0.995
^2E_u	-0.790	-0.903	0.996	-0.909	0.995	-0.908	0.995
^2E_u	-0.752	-0.844	0.997	-0.851	0.996	-0.851	0.996
^2A_u	-0.695	-0.770	0.997	-0.776	0.997	-0.775	0.997
^2A_u	-0.675	-0.767	0.997	-0.771	0.996	-0.771	0.996
^2A_g	-0.612	-0.790	0.993	-0.791	0.993	-0.791	0.993
^2E_u	-0.490	-0.665	0.994	-0.668	0.993	-0.668	0.993
^2E_g	-0.357	-0.409	0.998	-0.413	0.998	-0.413	0.998
^2E_g	-0.339	-0.398	0.998	-0.402	0.997	-0.402	0.997
^2A_g	-0.328	-0.368	0.998	-0.373	0.998	-0.372	0.998
^2A_u	-0.306	-0.585	0.990	-0.584	0.988	-0.584	0.988
^2A_g	-0.153	-0.485	0.988	-0.479	0.987	-0.480	0.987
^2E_g	0.027	-0.226	0.991	-0.234	0.989	-0.234	0.989
^2E_g	0.088	-0.178	0.990	-0.185	0.989	-0.184	0.989

Table S14. VEEs (eV) for Na(9-Crown-3)$_2$ at the KT, D2, P3, and P3+ levels of theory with the H: d-aug-cc-pVDZ, Na,C,O: cc-pVDZ basis set. The states are ordered according to P3+ excitation energies.

Approximate Superatomic orbital	Final State (S_6)	VEE (eV)			
		KT	D2	P3	P3+
1S	1^2A_g	0.000	0.000	0.000	0.000
1P	1^2A_u	0.118	0.120	0.122	0.122
1P	1^2E_u	0.180	0.216	0.215	0.215
1D	2^2A_g	0.354	0.358	0.363	0.362
1D	1^2E_g	0.467	0.545	0.544	0.543
1D	2^2E_g	0.526	0.627	0.626	0.626
1F	2^2A_u	0.799	0.907	0.910	0.910
1F	2^2E_u	0.812	0.925	0.928	0.927
1F	3^2E_u	0.864	1.003	1.004	1.004
2S	3^2A_g	1.014	1.067	1.074	1.074
1F	3^2A_u	0.939	1.103	1.107	1.106
1F	4^2A_u	1.002	1.131	1.135	1.135
2P	4^2E_u	1.148	1.202	1.207	1.207
2D	4^2A_g	1.465	1.348	1.364	1.363
2P	5^2A_u	1.471	1.400	1.411	1.410
1G	3^2E_g	1.237	1.411	1.416	1.416
1G	4^2E_g	1.261	1.428	1.432	1.432
1G	5^2A_g	1.282	1.470	1.475	1.474
2D	5^2E_g	1.672	1.653	1.654	1.654
2D	6^2E_g	1.742	1.706	1.707	1.707

Table S15. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Na(9-Crown-3)$_2^+$ at Na(9-Crown-3)$_2$ CAM-B3LYP geometry, from electron propagator methods using the H: d-aug-cc-pVDZ, Na,C,O: cc-pVDZ basis set. All valence electrons correlated.

Final State (S_6)	Na(9-Crown-3)$_2^+$						
	KT	D2		P3		P3+	
	VEAE	VEAE	PS	VEAE	PS	VEAE	PS
^2A_g	-1.609	-1.839	0.991	-1.848	0.990	-1.847	0.990
^2A_u	-1.491	-1.719	0.991	-1.726	0.990	-1.725	0.990
^2E_u	-1.429	-1.623	0.993	-1.633	0.991	-1.632	0.991
^2A_g	-1.255	-1.481	0.992	-1.485	0.990	-1.485	0.990
^2E_g	-1.142	-1.294	0.994	-1.304	0.993	-1.304	0.993
^2E_g	-1.083	-1.212	0.995	-1.222	0.994	-1.221	0.994
^2A_u	-0.810	-0.932	0.995	-0.938	0.994	-0.937	0.995
^2E_u	-0.797	-0.914	0.996	-0.920	0.995	-0.920	0.995
^2E_u	-0.745	-0.836	0.997	-0.844	0.996	-0.843	0.996
^2A_u	-0.670	-0.736	0.998	-0.741	0.997	-0.741	0.997
^2A_u	-0.607	-0.708	0.996	-0.713	0.995	-0.712	0.995
^2A_g	-0.595	-0.772	0.993	-0.774	0.992	-0.773	0.992
^2E_u	-0.461	-0.637	0.994	-0.641	0.992	-0.640	0.993
^2E_g	-0.372	-0.428	0.998	-0.432	0.997	-0.431	0.997
^2E_g	-0.348	-0.411	0.998	-0.416	0.997	-0.415	0.997
^2A_g	-0.327	-0.369	0.998	-0.373	0.998	-0.373	0.998
^2A_g	-0.144	-0.491	0.988	-0.484	0.986	-0.484	0.986
^2A_u	-0.138	-0.439	0.989	-0.437	0.987	-0.437	0.988
^2E_g	0.063	-0.186	0.991	-0.194	0.989	-0.193	0.989
^2E_g	0.133	-0.133	0.990	-0.141	0.989	-0.140	0.989

Table S16. VEEs (eV) for Li[2.1.1]Cryptand at the KT, D2, P3, and P3+ levels of theory with the H: d-aug-cc-pVDZ, Li,C,O,N: cc-pVDZ basis set. The states are ordered according to P3+ excitation energies.

Approximate Superatomic orbital	Final State (C_2)	VEE (eV)			
		KT	D2	P3	P3+
1S	1^2A	0.000	0.000	0.000	0.000
1P	2^2A	0.136	0.148	0.149	0.148
1P	1^2B	0.162	0.188	0.189	0.188
1P	2^2B	0.198	0.248	0.245	0.245
1D	3^2A	0.452	0.532	0.530	0.530
1D	4^2A	0.453	0.533	0.531	0.531
1D	5^2A	0.470	0.548	0.547	0.547
1D	3^2B	0.490	0.590	0.589	0.589
1D	4^2B	0.502	0.603	0.602	0.601
1F	6^2A	0.824	0.953	0.954	0.953
1F	5^2B	0.833	0.974	0.973	0.972
1F	7^2A	0.856	0.996	0.997	0.997
1F	6^2B	0.863	1.012	1.012	1.011
1F	8^2A	0.875	1.024	1.025	1.025
1F	7^2B	0.878	1.024	1.026	1.025
1F	9^2A	0.895	1.057	1.057	1.057

Table S17. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Li[2.1.1]Cryptand$^+$ at Li[2.1.1]Cryptand CAM-B3LYP geometry, from electron propagator methods using the H: d-aug-cc-pVDZ, Li,C,O,N: cc-pVDZ basis set. All valence electrons correlated.

Final State (C_2)	Li[2.1.1]Cryptand$^+$						
	KT	D2		P3		P3+	
	VEAE	VEAE	PS	VEAE	PS	VEAE	PS
^2A	-1.609	-1.868	0.990	-1.875	0.988	-1.874	0.988
^2A	-1.473	-1.720	0.991	-1.726	0.989	-1.726	0.989
^2B	-1.447	-1.680	0.991	-1.686	0.990	-1.686	0.990
^2B	-1.411	-1.620	0.992	-1.630	0.990	-1.629	0.990
^2A	-1.157	-1.336	0.993	-1.345	0.992	-1.344	0.992
^2A	-1.156	-1.335	0.993	-1.344	0.992	-1.343	0.992
^2A	-1.139	-1.320	0.993	-1.328	0.992	-1.327	0.992
^2B	-1.119	-1.278	0.994	-1.286	0.993	-1.285	0.993
^2B	-1.107	-1.265	0.994	-1.273	0.993	-1.273	0.993
^2A	-0.785	-0.915	0.995	-0.921	0.994	-0.921	0.994
^2B	-0.776	-0.894	0.995	-0.902	0.994	-0.902	0.994
^2A	-0.753	-0.872	0.995	-0.878	0.994	-0.877	0.995
^2B	-0.746	-0.856	0.996	-0.863	0.995	-0.863	0.995
^2A	-0.734	-0.844	0.996	-0.850	0.995	-0.849	0.995
^2B	-0.731	-0.844	0.996	-0.849	0.995	-0.849	0.995
^2A	-0.714	-0.811	0.996	-0.818	0.995	-0.817	0.996

Table S18. VEEs (eV) for Na[2.1.1]Cryptand at the KT, D2, P3, and P3+ levels of theory with the H: d-aug-cc-pVDZ, Na,C,O,N: cc-pVDZ basis set. The states are ordered according to P3+ excitation energies.

Approximate Superatomic orbital	Final State (C_2)	VEE (eV)			
		KT	D2	P3	P3+
1S	1^2A	0.000	0.000	0.000	0.000
1P	2^2A	0.131	0.144	0.144	0.144
1P	1^2B	0.157	0.180	0.180	0.179
1P	2^2B	0.199	0.252	0.250	0.250
1D	3^2A	0.442	0.521	0.519	0.519
1D	4^2A	0.442	0.522	0.519	0.519
1D	5^2A	0.466	0.545	0.544	0.543
1D	3^2B	0.488	0.589	0.588	0.587
1D	4^2B	0.504	0.608	0.607	0.607
1F	6^2A	0.811	0.939	0.939	0.938
1F	5^2B	0.820	0.958	0.957	0.956
1F	7^2A	0.847	0.985	0.986	0.986
1F	6^2B	0.856	1.005	1.005	1.004
1F	7^2B	0.871	1.016	1.018	1.018
1F	8^2A	0.873	1.023	1.024	1.023
1F	9^2A	0.893	1.055	1.056	1.055

Table S19. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Na[2.1.1]Cryptand$^+$ at Na[2.1.1]Cryptand CAM-B3LYP geometry, from electron propagator methods using the H: d-aug-cc-pVDZ, Na,C,O,N: cc-pVDZ basis set. All valence electrons correlated.

Final State (C_2)	Na[2.1.1]Cryptand$^+$						
	KT	D2		P3		P3+	
	VEAE	VEAE	PS	VEAE	PS	VEAE	PS
^2A	-1.600	-1.859	0.990	-1.866	0.988	-1.865	0.988
^2A	-1.469	-1.715	0.991	-1.722	0.989	-1.721	0.989
^2B	-1.443	-1.679	0.991	-1.686	0.989	-1.686	0.989
^2B	-1.401	-1.607	0.992	-1.616	0.990	-1.615	0.990
^2A	-1.158	-1.338	0.993	-1.347	0.992	-1.346	0.992
^2A	-1.158	-1.337	0.993	-1.347	0.992	-1.346	0.992
^2A	-1.134	-1.314	0.993	-1.322	0.992	-1.322	0.992
^2B	-1.112	-1.270	0.994	-1.278	0.993	-1.278	0.993
^2B	-1.096	-1.251	0.994	-1.259	0.993	-1.258	0.993
^2A	-0.789	-0.920	0.995	-0.927	0.994	-0.927	0.994
^2B	-0.780	-0.901	0.995	-0.909	0.994	-0.909	0.994
^2A	-0.753	-0.874	0.995	-0.880	0.994	-0.879	0.994
^2B	-0.744	-0.854	0.996	-0.861	0.995	-0.861	0.995
^2B	-0.729	-0.843	0.996	-0.848	0.995	-0.847	0.995
^2A	-0.727	-0.836	0.996	-0.842	0.995	-0.842	0.995
^2A	-0.707	-0.804	0.996	-0.810	0.995	-0.810	0.995

Table S20. VEEs (eV) for Li(*o*-Me_2-1.1.1) at the D2 level of theory with the H: d-aug-cc-pVDZ, Li,C,O: cc-pVDZ basis set.

Approximate Superatomic orbital	Final State (C_{3h})	VEE (eV)
1S	$1^2A'$	0.000
1P	$1^2A''$	0.153
1P	$1^2E'$	0.181
1D	$1^2E''$	0.459
1D	$2^2A'$	0.490
1D	$2^2E'$	0.515
1F	$3^2E'$	0.866
1F	$2^2A''$	0.873
1F	$3^2A'$	0.875
1F	$2^2E''$	0.878
1F	$4^2A'$	0.934

Table S21. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Li(*o*-Me_2-1.1.1)$^+$ at Li(*o*-Me_2-1.1.1) CAM-B3LYP geometry, from D2 electron propagator method using the H: d-aug-cc-pVDZ, Li,C,O: cc-pVDZ basis set. All valence electrons correlated.

Final State (C_{3h})	VEAE	PS
$^2A'$	-1.722	0.991
$^2A''$	-1.569	0.992
$^2E'$	-1.541	0.992
$^2E''$	-1.263	0.994
$^2A'$	-1.232	0.994
$^2E'$	-1.207	0.994
$^2E'$	-0.856	0.996
$^2A''$	-0.849	0.996
$^2E''$	-0.844	0.996
$^2A'$	-0.847	0.995
$^2A'$	-0.788	0.996

Table S22. VEEs (eV) for Na(*o*-Me_2-1.1.1) at the D2 level of theory with the H: d-aug-cc-pVDZ, Na,C,O: cc-pVDZ basis set.

Approximate Superatomic orbital	Final State (C_{3h})	VEE (eV)
1S	$1^2A'$	0.000
1P	$1^2E'$	0.168
1P	$1^2A''$	0.187
1D	$1^2E''$	0.473
1D	$2^2A'$	0.498
1D	$2^2E'$	0.503
1F	$3^2A'$	0.858
1F	$3^2E'$	0.872
1F	$2^2A''$	0.881
1F	$2^2E''$	0.882
1F	$4^2A'$	0.930

Table S23. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Na(*o*-Me_2-1.1.1)$^+$ at Na(*o*-Me_2-1.1.1) CAM-B3LYP geometry, from D2 electron propagator method using the H: d-aug-cc-pVDZ, Na,C,O: cc-pVDZ basis set. All valence electrons correlated.

Final State (C_{3h})	VEAE	PS
^{2}A'	-1.723	0.991
^{2}E'	-1.555	0.992
^{2}A"	-1.536	0.992
^{2}E"	-1.250	0.994
^{2}E'	-1.220	0.994
^{2}A'	-1.225	0.994
^{2}E'	-0.851	0.996
^{2}E"	-0.841	0.996
^{2}A"	-0.842	0.996
^{2}A'	-0.865	0.994
^{2}A'	-0.793	0.996

Table S24. VEEs (eV) for Na([24]Crown-8) at the D2 level of theory with the H: d-aug-cc-pVDZ, Na,C,O: cc-pVDZ basis sets.

Approximate Superatomic orbital	Final State (S_4)	VEE (eV)
1S	1^2A	0.000
1P	1^2E	0.149
1P	1^2B	0.203
1D	2^2B	0.403
1D	2^2A	0.489
1D	2^2E	0.494
1D	3^2B	0.507
1F	3^2A	0.842
1F	3^2E	0.863
1F	4^2A	0.892
1F	4^2E	0.901
1F	4^2B	0.917

Table S25. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Na([24]Crown-8)$^+$ at Na([24]Crown-8) CAM-B3LYP geometry, from D2 electron propagator method using the H: d-aug-cc-pVDZ, Na,C,O: cc-pVDZ basis set. All valence electrons correlated.

Final State (S_4)	VEAE	PS
^{2}A	-1.731	0.991
^{2}E	-1.582	0.992
^{2}B	-1.528	0.993
^{2}B	-1.328	0.993
^{2}A	-1.242	0.994
^{2}E	-1.237	0.994
^{2}B	-1.224	0.994
^{2}A	-0.889	0.995
^{2}E	-0.868	0.995
^{2}A	-0.839	0.996
^{2}E	-0.830	0.996
^{2}B	-0.814	0.996

Table S26. VEEs (eV) for K([24]Crown-8) at the D2 level of theory with the H: d-aug-cc-pVDZ, K,C,O: cc-pVDZ basis set.

Approximate Superatomic orbital	Final State (S_4)	VEE (eV)
1S	1^2A	0.000
1P	1^2E	0.139
1P	1^2B	0.171
1D	2^2B	0.370
1D	2^2A	0.458
1D	3^2B	0.461
1D	2^2E	0.468
1F	3^2A	0.791
1F	3^2E	0.793
1F	4^2A	0.832
1F	4^2E	0.861
1F	4^2B	0.883

Table S27. Vertical electron attachment energies (VEAE) and pole strengths (PS) of K([24]Crown-8)$^+$ at K([24]Crown-8) CAM-B3LYP geometry, from D2 electron propagator method using the H: d-aug-cc-pVDZ, K,C,O: cc-pVDZ basis set. All valence electrons correlated.

Final State (S_4)	VEAE	PS
^{2}A	-1.669	0.991
^{2}E	-1.530	0.992
^{2}B	-1.498	0.993
^{2}B	-1.299	0.993
^{2}B	-1.208	0.994
^{2}A	-1.211	0.994
^{2}E	-1.201	0.994
^{2}E	-0.876	0.995
^{2}A	-0.878	0.995
^{2}A	-0.837	0.996
^{2}E	-0.808	0.996
^{2}B	-0.786	0.996

Table S28. VEEs (eV) for Li[3^{6}adamanzane] at the D2 level of theory with the H: d-aug-cc-pVDZ, Li,C,N: cc-pVDZ basis set.

Approximate Superatomic orbital	Final State (S_4)	VEE (eV)
1S	1^{2}A	0.000
1P	1^{2}B	0.143
1P	1^{2}E	0.153
1D	2^{2}B	0.516
1D	2^{2}E	0.518
1D	2^{2}A	0.565
1D	3^{2}B	0.566
1F	3^{2}A	0.949
1F	3^{2}E	0.982
1F	4^{2}A	0.987
1F	4^{2}B	0.989
1F	4^{2}E	0.995

Table S29. Vertical electron attachment energies (VEAE) and pole strengths (PS) of Li[3^{6}adamanzane]$^+$ at Li[3^{6}adamanzane] CAM-B3LYP geometry, from D2 electron propagator method using the H: d-aug-cc-pVDZ, Li,C,N: cc-pVDZ basis set. All valence electrons correlated.

Final State (S_4)	VEAE	PS
^{2}A	-1.865	0.988
^{2}B	-1.722	0.989
^{2}E	-1.712	0.989
^{2}E	-1.347	0.992
^{2}B	-1.349	0.992
^{2}B	-1.299	0.993
^{2}A	-1.300	0.993
^{2}A	-0.916	0.994
^{2}E	-0.883	0.995
^{2}A	-0.878	0.995
^{2}E	-0.870	0.995
^{2}B	-0.876	0.995

Table S30. Point group symmetries, bond distances, and average 1S → 1P, 1S → 1D, and 1S → 1F EPT VEE (eV) of the complexes reported in the present work.

Structure	Bond lengths			Average 1S → 1P VEE			Average 1S → 1D VEE			Average 1S → 1F VEE		
	M-O	M-N	C-H	D2	P3	P3+	D2	P3	P3+	D2	P3	P3+
Li(9-Crown-3)	2.076		1.088-1.093									
Na(9-Crown-3)	2.569		1.089-1.095									
Li(9-Crown-3)$_2$	2.078		1.087-1.093	0.194	0.194	0.193	0.569	0.570	0.570	1.043	1.046	1.045
Li(9-Crown-3)$_2^+$	2.087		1.087-1.091									
Na(9-Crown-3)$_2$	2.366		1.089-1.093	0.184	0.184	0.184	0.540	0.541	0.540	1.000	1.002	1.002
Na(9-Crown-3)$_2^+$	2.376		1.089-1.093									
Li[2.1.1]Cryptand	2.091, 2.148	2.259	1.087-1.099	0.195	0.194	0.194	0.561	0.560	0.560	1.006	1.006	1.006
Li[2.1.1]Cryptand$^+$	2.076, 2.112	2.307	1.087-1.098									
Na[2.1.1]Cryptand	2.248, 2.278	2.313	1.088-1.101	0.192	0.191	0.191	0.557	0.555	0.555	0.997	0.998	0.997
Na[2.1.1]Cryptand$^+$	2.256, 2.290	2.380	1.088-1.098									
Li(*o*-Me$_2$-1.1.1)	2.435, 2.706,		1.098-1.106	0.172			0.488			0.881		
Li(*o*-Me$_2$-1.1.1)$^+$	2.441, 2.715		1.096-1.105									
Na(*o*-Me$_2$-1.1.1)	2.565, 2.581		1.098-1.106	0.174			0.490			0.882		
Na(*o*-Me$_2$-1.1.1)$^+$	2.575, 2.586		1.097-1.104									
Na(24-Crown-8)	2.505		1.097-1.106	0.167			0.477			0.883		
Na(24-Crown-8)$^+$	2.498, 2.542		1.097-1.105									
K(24-Crown-8)	2.766, 2.875		1.099-1.105	0.150			0.445			0.831		
K(24-Crown-8)$^+$	2.801, 2.871		1.098-1.105									
Li(3^{6}Adz)		1.964	1.097-1.109	0.150			0.537			0.983		
Li(3^{6}Adz)$^+$		1.964	1.097-1.107									

Table S31. Total number of H atoms in the solvation shell, EPT (D2/P3+) VIE (eV), and average 1S → 1P and 1S → 1D EPT (D2/P3+) VEE (eV), and $\Sigma r_{(M\cdots H)}$ (Å) of the Rydberg-type complexes collected from literature.

Species	No of H atoms	Method	Basis set[a]		EPT VIE	EPT 1S → 1P VEE	EPT 1S → 1D VEE	$\Sigma r_{(M\cdots H)}$	Reference
			C, N, O, M=Li/Na/K	H					
$Li(NH_3)_4$	12	P3+	TZ	DATZ	2.837	0.719	1.412	31.759	1
$Na(NH_3)_4$	12	P3+	TZ	DATZ	2.711	0.656	1.329	36.272	1
$Li(C_{20}H_{20})$	20	P3+	TZ	DATZ	2.350	0.398	0.956	65.618	2
$Na(C_{20}H_{20})$	20	P3+	TZ	DATZ	2.270	0.382	0.878	66.049	2
$Li(en)_2$	16	P3+	TZ	DATZ	2.478	0.458	1.042	36.130	3
$Na(en)_2$	16	P3+	TZ	DATZ	2.453	0.484	1.047	55.605	3
$K(en)_2$	16	P3+	TZ	DATZ	2.448	0.544	1.065	-	3
Li(12-Crown-4)	16	P3+	TZ	DATZ	2.538	-	-	54.797	3
Li(15-Crown-5)	20	P3+	DZ	DADZ	1.957	0.221	0.626	74.385	3
Na(15-Crown-5)	20	P3+	DZ	DADZ	2.582	-	-	80.789	3
K(15-Crown-5)	20	P3+	DZ	DADZ	2.583	-	-	-	3
Na(18-Crown-6)	24	P3+	DZ	DADZ	2.345	-	-	102.764	3
K(18-Crown-6)	24	P3+	DZ	DADZ	2.328	-	-	-	3
$Li([9]aneN_3)_2$	30	P3+	DZ	DADZ	2.093	0.313	0.729	104.251	4
$Na([9]aneN_3)_2$	30	P3+	DZ	DADZ	2.063	0.311	0.721	110.947	4
$Li[18]aneN_6$	30	P3+	DZ	DADZ	2.142	0.345	0.780	105.800	4
$Na[18]aneN_6$	30	P3+	DZ	DADZ	2.138	0.352	0.787	108.954	4
Li[1.1.1]Cryptand	24	P3+	DZ	DADZ	1.948	0.182	0.593	80.383	4
Na[2.2.2]Cryptand	36	D2	DZ	DADZ	1.669	0.137	0.436	153.445	4
$Na(Tren)_2$	36	P3+	DZ	DADZ	2.011	0.291	0.686	140.325	5
$K(Tren)_2$	36	P3+	DZ	DADZ	1.959	0.282	0.659	-	5
Na(Azacryptand)	42	P3+	DZ	DADZ	1.767	0.114	0.494	176.224	5
K(Azacryptand)	42	P3+	DZ	DADZ	1.751	0.100	0.485	-	5
Na(TriPip222)	48	D2	DZ	DADZ	1.694	0.161	0.448	196.525	5
K(TriPip222)	48	D2	DZ	DADZ	1.680	0.156	0.442	-	5

[a] TZ = cc-pVTZ, DZ = cc-pVDZ, DATZ = d-aug-cc-pVTZ, DADZ = d-aug-cc-pVDZ

Table S32. CAM-B3LYP VIE (eV) and average TD-DFT 1S→1P and 1S→1D VEE (eV) of the Rydberg-type complexes. Structures were collected from references listed in Table S31.

Complex	VIE	Average 1S → 1P VEE	Average 1S → 1D VEE
$Li(NH_3)_4$	3.021	0.776	1.441
$Li(C_{20}H_{20})$	2.460	0.379	0.982
$Li(en)_2$	2.621	0.489	1.057
Li(12-Crown-4)	2.684	-	-
Li(15-Crown-5)	2.077	0.236	0.607
$Li([9]aneN_3)_2$	2.258	0.357	0.797
$Li[18]aneN_6$	2.306	0.422	0.874
Li[1.1.1]Cryptand	2.039	0.166	0.560
$Li(9\text{-Crown-}3)_2$	2.002	0.198	0.540
Li[2.1.1]Cryptand	1.965	0.192	0.549
$Li(o\text{-}Me_2\text{-}1.1.1)$	1.821	0.176	0.452
$Li(3^6adamanzane)$	1.946	0.114	0.502
$Na(NH_3)_4$	2.915	0.735	1.384
$Na(C_{20}H_{20})$	2.372	0.394	0.895
$Na(en)_2$	2.605	0.530	1.061
Na(15-Crown-5)	2.840	-	-
Na(18-Crown-6)	2.594	-	-
$Na([9]aneN_3)_2$	2.225	0.356	0.785
$Na[18]aneN_6$	2.304	0.405	0.863
Na[2.2.2]Cryptand	1.760	0.132	0.399
$Na(Tren)_2$	2.208	0.338	0.780
Na(Azacrypt)	1.894	0.163	0.546
Na(TriPip222)	1.784	0.157	0.431
$Na(9\text{-Crown-}3)_2$	1.958	0.193	0.510
Na[2.1.1]Cryptand	1.960	0.189	0.548
$Na(o\text{-}Me_2\text{-}1.1.1)$	1.822	0.178	0.455
Na(24-Crown-8)	1.835	0.171	0.446
$K(en)_2$	2.633	0.630	1.118
K(15-Crown-5)	2.889	-	-
K(18-Crown-6)	2.571	-	-
$K(Tren)_2$	2.145	0.334	0.736
K(Azacrypt)	1.883	0.152	0.540
K(TriPip222)	1.783	0.153	0.437
K(24-Crown-8)	1.775	0.154	0.409

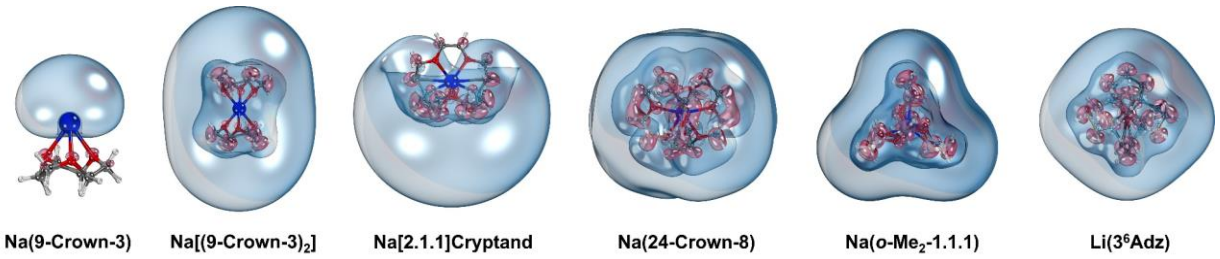

Figure S1. Contours of singly occupied molecular orbitals of Na(9-Crown-3)$_{n=1,2}$, Na[2.1.1]Cryptand, Na(24-Crown-8), Na(*o*-Me$_2$-1.1.1), and Li(3^{6}Adz) complexes. A threshold of 70% was applied for the contours. Molecular orbitals of corresponding Li- or K-complexes have similar shapes.

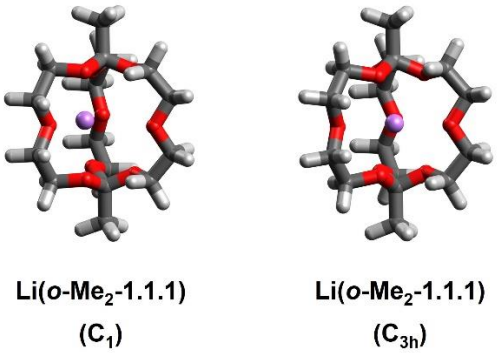

Figure S2. C_1 and C_{3h} geometries of Li(*o*-Me$_2$-1.1.1).

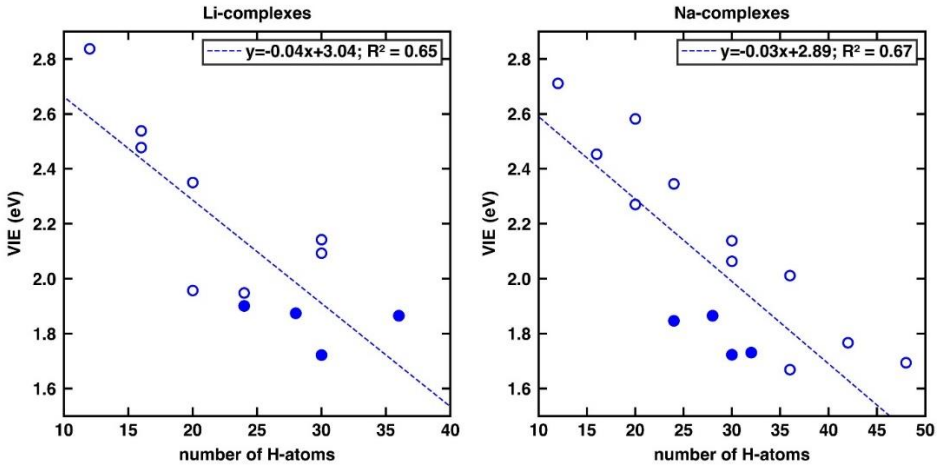

Figure S3. EPT VIE (eV) vs. number of H-atoms in the solvation shell of Li- and Na-complexes. The open circles correspond to the literature values, whereas the closed circles represent the values report in the present work. The literature EPT VIEs and the number of H-atoms of corresponding complexes are listed in the Table S31.

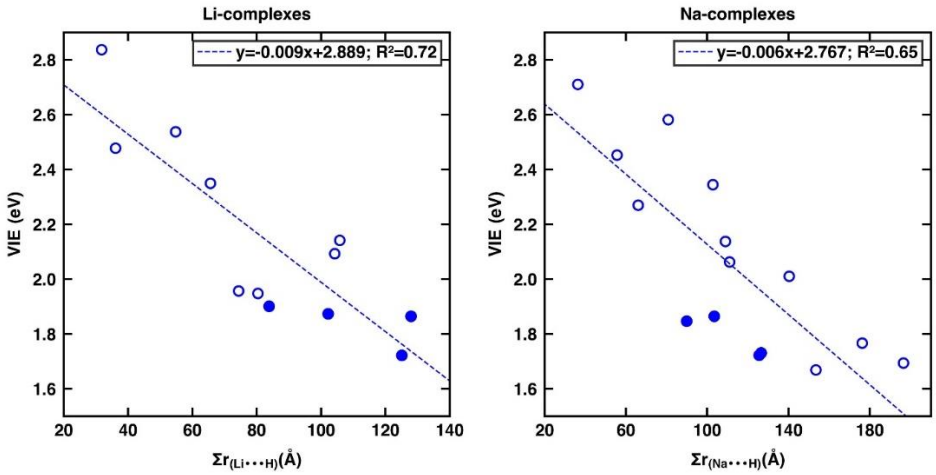

Figure S4. EPT VIE (eV) vs. the $\Sigma r_{(M\cdots H)}$ (Å) of Li- and Na-complexes. The open circles correspond to the literature values, whereas the closed circles represent the values report in the present work. The literature EPT VIEs and $\Sigma r_{(M\cdots H)}$ of corresponding complexes are listed in the Table S31.

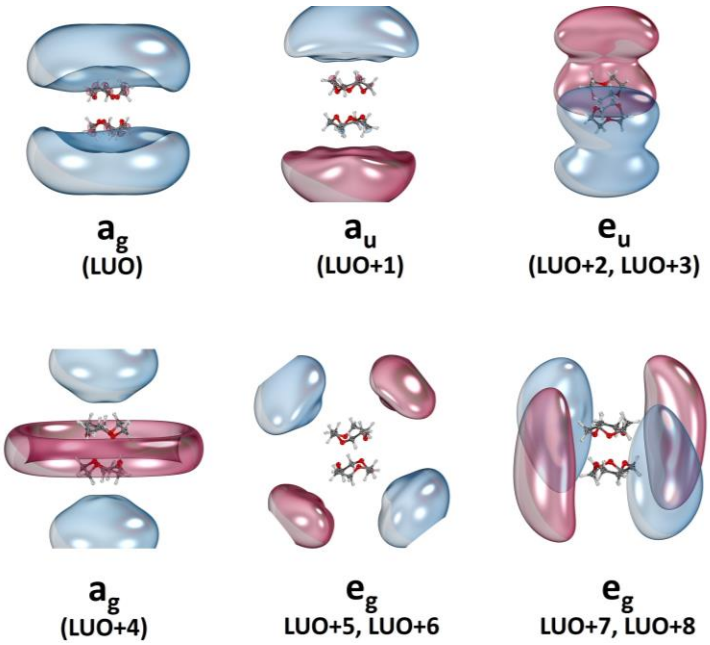

Figure S5. Lowest unoccupied orbitals (LUOs) of $(9\text{-crown-3})_2$ obtained under the geometry of $Li(9\text{-crown-3})_2$. A threshold of 70% was applied for orbital plots.

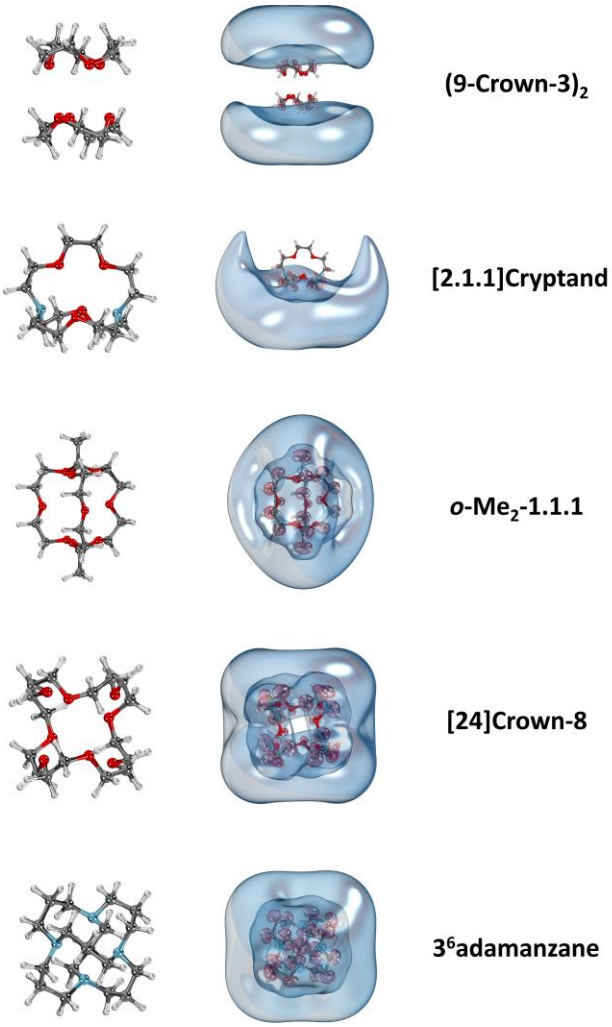

Figure S6. Lowest unoccupied orbitals (LUOs) of the (9-crown-3)$_2$, [2.1.1]Cryptand, *o*-Me$_2$-1.1.1, 24-Crown-8, and 3^{6}adamanzane (blue color). The LUOs of (9-crown-3)$_2$, [2.1.1]Cryptand, and 3^{6}adamanzane obtained at geometries of their corresponding Li-complexes. The LUOs of *o*-Me$_2$-1.1.1 and 24-Crown-8 obtained at the geometries of their corresponding Na-complexes. A threshold of 70% was applied for orbital plots.

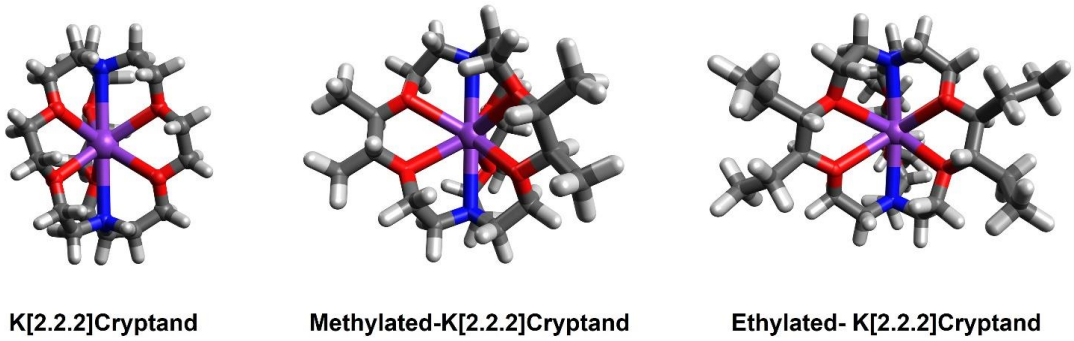

Figure S7. Geometries of K[2.2.2]Cryptand, Methylated-K[2.2.2]Cryptand, and Ethylated-K[2.2.2]Cryptand complexes.

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