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

Electric Field Induced Intra-Molecular Self-Redox: Superalkali Li_3N_3Mg as Candidate for NLO Molecular Switches

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Contents

Li_3N_3Mg	F_z = 0.0000 au		
Li	-0.6474027	-1.39037866	1.69577348
Li	1.53229778	0.13573683	1.69190155
Li	-0.88156587	1.2576162	1.69314341
N	0.51371096	-0.73422422	0.22892741
N	0.37746219	0.81213662	0.22888524
N	-0.89330421	-0.0793265	0.22802115
Mg	0.00041082	0.0000813	-1.67027432
	F_z = -0.0010 au		
Li	-0.651602	-1.400138	1.686254
Li	1.541369	0.136551	1.6832
Li	-0.887245	1.266262	1.684413
N	0.51381	-0.733404	0.238131
N	0.37756	0.811793	0.237714
N	-0.892225	-0.078894	0.237977
Mg	-0.000058	-0.000528	-1.671311
	F_z = -0.0020 au		
Li	-0.6563	-1.410098	1.676706
Li	1.552462	0.137487	1.673457
Li	-0.893678	1.275263	1.674786
N	0.51345	-0.732938	0.247951
N	0.377294	0.811263	0.247567
N	-0.891644	-0.078852	0.247752
Mg	0.000025	-0.000484	-1.671841
	F_z = -0.0030 au		
Li	-0.661493	-1.421125	1.666782
Li	1.564711	0.138524	1.663329
Li	-0.900786	1.285224	1.664783
N	0.513106	-0.732484	0.258011
N	0.377041	0.810753	0.257655
N	-0.891078	-0.078808	0.257772
Mg	0.000107	-0.000443	-1.671954
	F_z = -0.0040 au		
Li	-0.667036	-1.432927	1.656935
Li	1.577773	0.139638	1.653315
Li	-0.908358	1.295878	1.654868
N	0.512824	-0.732095	0.267877
N	0.376835	0.810328	0.267545
N	-0.890593	-0.078765	0.267606
Mg	0.000164	-0.000415	-1.671768
	F_z = -0.0050 au		
Li	-0.673061	-1.445907	1.646137
Li	1.591906	0.140876	1.642614
Li	-0.916536	1.307547	1.64408

N	0.512924	-0.732107	0.277651
N	0.376925	0.810426	0.277292
N	-0.89062	-0.078731	0.277415
Mg	0.000071	-0.000462	-1.668811

F_z = -0.0060 au

Li	-0.678969	-1.458521	1.63595
Li	1.605841	0.142074	1.632288
Li	-0.924599	1.318931	1.633829
N	0.512881	-0.732057	0.286355
N	0.376896	0.810378	0.286017
N	-0.890556	-0.078725	0.28609
Mg	0.000115	-0.000439	-1.664151

F_z = -0.0070 au

Li	-0.684197	-1.46973	1.627289
Li	1.618161	0.143147	1.623578
Li	-0.931717	1.329041	1.625141
N	0.512989	-0.732189	0.292421
N	0.376977	0.810541	0.292086
N	-0.890723	-0.078731	0.292152
Mg	0.00012	-0.000437	-1.656289

F_z = -0.0072 au

Li	-0.685551	-1.472706	1.625344
Li	1.621318	0.143433	1.621753
Li	-0.933543	1.331707	1.623225
N	0.513059	-0.732205	0.293276
N	0.377037	0.810598	0.292915
N	-0.890751	-0.078716	0.293047
Mg	0.000039	-0.000470	-1.653182

F_z = -0.0074 au

Li	-0.686060	-1.473839	1.624455
Li	1.622505	0.143547	1.620920
Li	-0.934225	1.332724	1.622357
N	0.513129	-0.732275	0.293439
N	0.377090	0.810686	0.293065
N	-0.890839	-0.078717	0.293233
Mg	0.000010	-0.000485	-1.651092

F_z = -0.0076 au

Li	-0.687372	-1.476660	1.623406
Li	1.625585	0.143820	1.619895
Li	-0.935996	1.335252	1.621297
N	0.513275	-0.732455	0.293239
N	0.377209	0.810911	0.292855
N	-0.891069	-0.078733	0.293031
Mg	-0.000023	-0.000494	-1.647344

F_z = -0.0078 au

Li	-0.686863	-1.475575	1.623395
Li	1.624403	0.143716	1.619846
Li	-0.935321	1.334296	1.621306
N	0.513335	-0.732573	0.292673
N	0.377236	0.811016	0.292297
N	-0.891204	-0.078745	0.292475
Mg	0.000022	-0.000493	-1.645615

F_z = -0.0080 au

Li	-0.686327	-1.474461	1.624318
Li	1.623161	0.143605	1.620758
Li	-0.934617	1.333316	1.622264
N	0.513415	-0.732708	0.290696
N	0.37728	0.811148	0.290324
N	-0.891351	-0.078753	0.290517
Mg	0.000048	-0.000506	-1.642499

F_z = -0.0082 au

Li	-0.685933	-1.473694	1.62606
Li	1.622208	0.143534	1.622617
Li	-0.934069	1.332617	1.624058
N	0.513629	-0.732948	0.287356
N	0.377439	0.811441	0.286956
N	-0.891646	-0.078762	0.287219
Mg	-0.000018	-0.000546	-1.637888

F_z = -0.0084 au

Li	-0.684856	-1.471478	1.629451
Li	1.619631	0.143321	1.626152
Li	-0.932594	1.330609	1.627518
N	0.513918	-0.733277	0.2822
N	0.377655	0.811841	0.281763
N	-0.892044	-0.078776	0.282117
Mg	-0.000102	-0.000599	-1.632824

F_z = -0.0085 au

Li	-0.683061	-1.46772	1.632146
Li	1.615343	0.142993	1.629108
Li	-0.930062	1.327159	1.630232
N	0.514237	-0.733625	0.279132
N	0.377922	0.812276	0.278642
N	-0.892515	-0.078815	0.279106
Mg	-0.000255	-0.000626	-1.631987

F_z = -0.0086 au

Li	-0.681639	-1.464726	1.635825
Li	1.611975	0.142703	1.632858
Li	-0.928129	1.324459	1.633956

N	0.514402	-0.733821	0.274546
N	0.378041	0.812507	0.274035
N	-0.892748	-0.078823	0.274549
Mg	-0.000293	-0.000657	-1.629391

F_z = -0.0088 au

Li	-0.676865	-1.454652	1.645339
Li	1.600634	0.141757	1.642678
Li	-0.921566	1.31533	1.643574
N	0.51498	-0.734504	0.262887
N	0.378479	0.813313	0.262301
N	-0.893594	-0.078874	0.262993
Mg	-0.000459	-0.000729	-1.623393

F_z = -0.0090 au

Li	-0.67031	-1.440717	1.660516
Li	1.585103	0.14043	1.658079
Li	-0.912603	1.302731	1.658843
N	0.515587	-0.735261	0.245489
N	0.378938	0.814186	0.244835
N	-0.894526	-0.07894	0.245679
Mg	-0.00058	-0.000787	-1.617064

F_z = -0.0092 au

Li	-0.663865	-1.426396	1.677604
Li	1.570505	0.139058	1.674323
Li	-0.90404	1.290039	1.675589
N	0.515553	-0.735987	0.227331
N	0.378829	0.814586	0.226984
N	-0.895374	-0.079202	0.227107
Mg	0	-0.000457	-1.612561

F_z = -0.0094 au

Li	-0.661484	-1.421356	1.686822
Li	1.564905	0.138575	1.683632
Li	-0.900801	1.285494	1.684836
N	0.515586	-0.736004	0.217145
N	0.378853	0.814615	0.216787
N	-0.895396	-0.079197	0.216948
Mg	-0.000054	-0.000485	-1.609793

F_z = -0.0096 au

Li	-0.657542	-1.4133	1.697273
Li	1.555239	0.137821	1.694733
Li	-0.895275	1.278086	1.69555
N	0.515893	-0.73595	0.206165
N	0.379127	0.814781	0.205588
N	-0.895363	-0.079085	0.206268
Mg	-0.000471	-0.000711	-1.609198

F_z = -0.0098 au

Li	-0.65780800	-1.41351300	1.70006600
Li	1.55626800	0.13783500	1.69696800
Li	-0.89578800	1.27842400	1.69811000
N	0.51549300	-0.73587100	0.20323400
N	0.37878300	0.81445700	0.20286700
N	-0.89523900	-0.07918600	0.20305000
Mg	-0.00010000	-0.00050400	-1.60791700

F_z = -0.0100 au

Li	-0.656692	-1.411101	1.703536
Li	1.553679	0.137589	1.700387
Li	-0.894295	1.276256	1.701523
N	0.515398	-0.735762	0.199739
N	0.378716	0.814326	0.199393
N	-0.895108	-0.079186	0.199545
Mg	-0.000088	-0.000481	-1.607745

Li_3N_3Be F_z = 0.0000 au

Li	-1.50291100	0.56032800	1.19868800
Li	0.26535500	-1.58144300	1.19950500
Li	1.23637000	1.02037500	1.20046800
N	-0.68906200	-0.56900500	-0.19673900
N	0.83715700	-0.31226800	-0.19586400
N	-0.14818100	0.88118500	-0.19550500
Be	0.00104100	0.00070800	-1.66980700

Li_3N_3Ca F_z = 0.0000 au

Li	1.487491	-0.464501	-2.02321
Li	-0.341958	1.522742	-2.020811
Li	-1.147001	-1.056356	-2.022203
N	0.650877	0.59902	-0.588732
N	-0.844201	0.263432	-0.588794
N	0.19401	-0.863319	-0.588662
Ca	-0.00002	0.000021	1.5281

Table S1. Total Energy (E_{tot}, au), Relative Energy (E_{rel}, kcal/mol), Energies of HOMOs (ε_{HOMO}, in eV), and HOMO-LUMO Gaps (ε_{gap}, in eV), Vertical Ionization Potential (VIP, in eV), Natural Popular Analysis Charge (NPA, $Q_{Li3\ ring}$ and Q_{Mg}, |e|) of Li_3N_3Mg at CCSD(T)/6-311+G(3df)//MP2/6-311+G(3df) level in presence and absence of OEEF ($F_z \times 10^{-4}$)

Field	E_{tot}	E_{rel}	ε_{HOMO}	ε_{gap}	VIP	Q_{Li3}	Q_{Mg}
0	-386.0114	0.000	-3.641	2.630	5.30	1.697	0.804
-10	-386.0102	-0.721	-3.579	2.618	5.25	1.628	0.875
-20	-386.0095	-1.179	-3.527	2.601	5.21	1.562	0.949
-30	-386.0092	-1.367	-3.486	2.576	5.19	1.494	1.021
-40	-386.0094	-1.237	-3.460	2.539	5.15	1.423	1.096
-50	-386.0102	-0.698	-3.452	2.484	5.11	1.347	1.178
-60	-386.0121	0.460	-3.469	2.413	5.08	1.264	1.266
-70	-386.0155	2.620	-3.517	2.340	5.05	1.179	1.367
-72	-386.0165	3.222	-3.531	2.327	5.05	1.158	1.389
-80	-386.0218	6.583	-3.602	2.294	5.05	1.068	1.483
-82	-386.0237	7.726	-3.624	2.295	5.04	1.040	1.512
-84	-386.0255	8.857	-3.647	2.300	5.03	1.008	1.544
-85	-386.0262	9.312	-3.661	2.305	5.02	0.993	1.559
-86	-386.0267	9.650	-3.675	2.314	5.00	0.974	1.578
-87	-386.0267	9.629	-3.690	2.326	4.96	0.940	1.593
-88	-386.0257	8.984	-3.705	2.342	4.89	0.926	1.614
-90	-386.0180	4.179	-3.741	2.391	4.60	0.875	1.657
-92	-386.0071	-2.643	-3.781	2.451	4.23	0.832	1.696
-94	-386.0032	-5.126	-3.817	2.492	4.08	0.808	1.718
-95	-386.0023	-5.666	-3.839	2.521	4.04	0.794	1.729
-96	-386.0025	-5.556	-3.858	2.536	4.03	0.787	1.736
-98	-386.0037	-4.786	-3.892	2.552	4.03	0.779	1.744
-100	-386.0054	-3.719	-3.929	2.567	4.04	0.771	1.751

Table S2. T_1 diagnostics for the energies of both field-free $Li_3^{2+}N_3^{3-}Mg^{+}$ and $Li_3^{+}N_3^{3-}Mg^{2+}$ under F_z of -0.0086 or -0.0100 au obtained at CCSD(T)/6-311+G(3df) level

	$Li_3^{2+}N_3^{3-}Mg^{+}$	$Li_3^{+}N_3^{3-}Mg^{2+}$	
		F_z = -0.0086	F_z = -0.0100
T_1 diagnostic	0.0448	0.1390	0.390

Table S3. Dipole moment ($\mu_0(F)$), Static First Hyperpolarizabilities ($\beta_0(F)$) at MP2/6-311+G(3df) level, Dipole Moment between Ground State and Crucial Excited State ($\Delta\mu_0$), Oscillator Strength f_0, and Transition energy (ΔE) of Crucial Excited States of $Li_3N_3Mg(n)$ in presence of OEEF ($F_z \times 10^{-4}$) of Li_3N_3Mg at the TD-M06-2X/6-311+G(3df) level

$Li_3N_3Mg(n)$	$\mu_0(F)$ [au]	$\mu_z(F)$ [au]	$\beta_{zzz}(F)$ [au]	$\beta_0(F)$ [au]	$\Delta\mu_z(F)$ [au]	ΔE [eV]	f_0	Major Contribution
n = 0	0.742	0.742	-52297	34986	3.041	0.9609	0.2179	H → L
n = 10	0.534	0.533	-77699	51958	3.041	0.9609	0.2179	H → L
n = 20	0.336	0.336	-103847	69355	3.034	0.9531	0.2148	H → L
n = 30	0.158	0.158	-130046	86692	3.035	0.9438	0.2129	H → L
n = 40	0.012	0.011	-155115	103164	3.052	0.9325	0.2128	H → L
n = 50	-0.095	-0.095	-177516	117790	3.097	0.9185	0.2158	H → L
n = 60	-0.158	-0.158	-195609	129544	3.202	0.8995	0.2259	H → L
n = 70	-0.172	-0.172	-205391	135994	3.430	0.8673	0.2500	H → L
n = 72	-0.166	-0.166	-205872	136397	3.579	0.8431	0.2645	H → L
n = 80	-0.109	-0.109	-194717	129571	3.757	0.8148	0.2818	H → L
n = 82	-0.064	-0.064	-185073	123489	3.861	0.7996	0.2921	H → L
n = 84	0.006	0.006	-170878	114385	4.000	0.7768	0.3047	H → L
n = 86	0.107	0.107	-150817	101225	4.075	0.7629	0.3106	H → L

[a] H for HOMO, L for LUMO

Table S4. Total Energy (E_{tot}, au), Relative Energy (E_{rel}, kcal/mol), Energies of HOMOs (ε_{HOMO}, in eV), and HOMO-LUMO Gaps (ε_{gap}, in eV), Vertical Ionization Potential (VIP, in eV), Natural Popular Analysis Charge (NPA, $Q_{Li3\ ring}$ and Q_{Be}, |e|) of Li_3N_3Be under OEEF ($F_z \times 10^{-4}$) at MP2/6-311+G(3df) level.

Field	E_{tot}	E_{rel}	ε_{HOMO}	ε_{gap}	VIP	Q_{Li3}	Q_{Be}
0	-200.9881	0.000	-3.684	-2.891	6.086	1.448	0.819
-5	-200.9866	-0.919	-3.704	-2.893	4.788	1.405	0.859
-10	-200.9851	-1.842	-3.726	-2.895	4.775	1.353	0.906
-15	-200.9837	-2.757	-3.748	-2.897	4.826	1.312	0.944
-20	-200.9825	-3.500	-3.746	-2.887	4.842	1.319	0.946
-25	-200.9812	-4.304	-3.767	-2.884	4.802	1.285	0.977
-30	-200.9800	-5.063	-3.793	-2.882	4.752	1.285	0.977
-35	-200.9789	-5.761	-3.822	-2.882	4.684	1.494	1.021
-40	-200.9779	-6.362	-3.860	-2.890	4.590	1.423	1.096
-41	-200.9778	-6.464	-3.869	-2.893	4.566	1.122	1.118
-42	-200.9776	-6.557	-3.881	-2.903	4.522	1.096	1.137
-43	-200.9775	-6.637	-3.892	-2.909	4.493	1.077	1.151
-44	-200.9774	-6.700	-3.902	-2.918	4.460	1.057	1.166
-45	-200.9784	-6.067	-4.091	-3.362	4.228	0.824	1.282
-50	-200.9803	-4.865	-4.168	-3.447	4.284	0.811	1.289
-55	-200.9824	-3.545	-4.239	-3.414	4.340	0.804	1.294
-60	-200.9847	-2.136	-4.310	-3.342	4.398	0.798	1.299
-65	-200.9870	-0.650	-4.380	-3.264	4.455	0.795	1.304
-70	-200.9895	0.910	-4.455	-3.188	6.396	0.792	1.308
-75	-200.9921	2.543	-4.530	-3.114	4.574	0.784	1.319
-80	-200.9949	4.254	-4.610	-3.044	4.636	0.781	1.324
-85	-200.9977	6.048	-4.693	-2.978	4.699	0.780	1.329
-90	-201.0007	7.937	-4.781	-2.918	4.766	0.778	1.335
-95	-201.0039	9.928	-4.873	-2.864	4.834	0.777	1.341
-100	-200.9772	-6.811	-4.029	-3.300	4.183	0.834	1.270

Table S5. Total Energy (E_{tot}, au), Relative Energy (E_{rel}, kcal/mol), Energies of HOMOs (ε_{HOMO}, in eV), and HOMO-LUMO Gaps (ε_{gap}, in eV), Vertical Ionization Potential (VIP, in eV), Natural Popular Analysis Charge (NPA, $Q_{Li3\ ring}$ and Q_{Ca}, |e|) of Li_3N_3Ca in presence of OEEF ($F_z \times 10^{-4}$) at MP2/6-311+G(3df) level.

Field	E_{tot}	E_{rel}	ε_{HOMO}	ε_{gap}	VIP	Q_{Li3}	Q_{Ca}
0	-863.3706	0.000	-3.195	-2.311	3.896	1.342	1.190
-5	-863.3699	-0.445	-3.205	-2.317	3.854	1.288	1.245
-10	-863.3693	-0.833	-3.217	-2.322	3.809	1.233	1.297
-15	-863.3688	-1.142	-3.234	-2.327	3.761	1.173	1.356
-20	-863.3685	-1.337	-3.256	-2.332	3.708	1.108	1.420
-25	-863.3685	-1.362	-3.285	-2.340	3.650	1.035	1.490
30	-863.3689	-1.109	-3.324	-2.357	3.584	0.958	1.562
-31	-863.3690	-1.007	-3.334	-2.363	3.573	0.938	1.579
-32	-863.3692	-0.880	-3.345	-2.370	3.560	0.917	1.598
-33	-863.3695	-0.725	-3.358	-2.381	3.548	0.898	1.616
-34	-863.3698	-0.536	-3.372	-2.395	3.539	0.872	1.636
-35	-863.3706	-0.052	-3.400	-2.421	3.538	0.836	1.662
-36	-863.3706	-0.038	-3.408	-2.439	3.534	0.820	1.672
-37	-863.3711	0.272	-3.428	-2.467	3.540	0.801	1.686
-38	-863.3716	0.616	-3.449	-2.495	3.551	0.786	1.696
-39	-863.3722	0.987	-3.469	-2.522	3.564	0.775	1.703
-40	-863.3728	1.381	-3.489	-2.549	3.578	0.767	1.709
-45	-863.3763	3.573	0.000	0.000	3.655	0.744	1.724
-50	-863.3802	6.005	-3.689	-2.664	3.734	0.727	1.739
-55	-863.3844	8.615	-3.798	-2.597	3.816	0.720	1.745
-60	-863.3888	11.398	-3.914	-2.530	3.901	0.717	1.751
-65	-863.3935	14.374	-4.038	-2.473	3.992	0.723	1.750
-70	-863.3986	17.566	-4.171	-2.426	4.090	0.728	1.748
-75	-863.4041	20.998	-4.312	-2.388	4.197	0.737	1.744
-80	-863.4100	24.682	-4.460	-2.358	4.313	0.749	1.737
-85	-863.4163	28.621	-4.615	-2.336	4.439	0.764	1.728
-90	-863.4229	32.808	-4.775	-2.318	4.575	0.763	1.738
-95	-863.4300	37.231	-4.939	-2.305	4.720	0.780	1.727
-100	-863.4374	41.875	-5.107	-2.296	4.874	0.799	1.715

Table S6. Dipole moment (μ_0, au), Static First Hyperpolarizabilities (β_0, au) of $Li_3N_3Be(n)$ and $Li_3N_3Ca(n)$ under OEEF ($F_z \times 10^{-4}$) at MP2/6-311+G(3df) level

	μ_0	μ_z	β_{zzz}	β_0		μ_0	μ_z	β_{zzz}	β_0
$Li_3N_3Be(n)$					$Li_3N_3Ca(n)$				
n = 0	2.909	2.909	138638	96564	n = 0	1.488	-1.488	-324610	237929
n = 5	2.943	2.943	138638	96564	n = 5	1.340	-1.340	-304922	224170
n = 10	2.937	2.937	138638	96564	n = 10	1.126	-1.126	-290181	213858
n = 15	2.879	2.879	138252	96319	n = 15	0.825	-0.825	-287717	212351
n = 20	2.622	2.622	107014	73178	n = 20	0.384	-0.384	-371869	272203
n = 25	2.499	2.499	102324	69717	n = 25	0.294	0.294	-389129	284344
n = 30	2.335	2.335	100846	68670	n = 30	1.488	1.488	-441255	320735
n = 35	2.093	2.093	105360	72163	n = 31	1.819	1.819	-473826	343239
n = 40	1.685	1.685	120018	83423	n = 32	2.225	2.225	-510178	368075
n = 41	1.561	1.561	124926	87203	n = 33	2.723	2.723	-544936	391496
n = 42	1.345	1.345	137060	96550	n = 34	3.300	3.300	-574206	410915
n = 43	1.155	1.155	144485	102289	n = 35	3.957	3.957	-595203	424607
n = 44	0.922	0.922	153086	108959	n = 36	4.627	4.627	-610089	434184
n = 45	3.581	-3.581	201192	161299	n = 37	5.234	5.234	-621183	441222
n = 50	4.044	-4.044	180312	148598	n = 38	5.724	5.724	-646051	456615
n = 55	4.361	-4.361	170224	142447	n = 39	6.114	6.114	-652582	460537
n = 60	4.618	-4.618	167086	140527	n = 40	6.434	6.434	-653386	460998
n = 65	4.856	-4.856	167800	120920	n = 45	7.429	7.429	-650572	459331
n = 70	5.087	-5.087	-15823	9083	n = 50	8.046	8.046	-644802	455850
n = 75	5.326	-5.326	175112	145673	n = 55	8.589	8.589	-636335	450653
n = 80	5.582	-5.582	180565	149093	n = 60	9.164	9.164	-625628	443970
n = 85	5.865	-5.865	186739	153017	n = 65	9.815	9.815	-599057	427029
n = 90	6.179	-6.179	194233	157634	n = 70	10.546	10.546	-584593	417623
					n = 75	11.335	11.335	-304922	224170
					n = 80	12.150	12.150	-290181	213858
					n = 90	13.731	13.731	-287717	212351