Supporting Information

From Electride-like Super Alkali Earth Atom to Superalkalide or Superalkali Electride: $M(HF)_3M$ (M = Na or Li) as Field-Induced Excellent Inorganic NLO Molecular Switches

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Optimized Cartesian coordinates at the MP2/6-311+G(3df,3pd) level.

$Na(HF)_3Na$

1 C_{3h}

F	-1.553508	-0.816084	0.000000
F	1.483503	-0.937335	0.000000
F	0.070004	1.753419	0.000000
Na	0.000000	0.000000	1.753986
Na	0.000000	0.000000	-1.753986
H	2.323508	-0.519946	0.000000
H	-0.711467	2.272190	0.000000
H	-1.612041	-1.752244	0.000000

2 C_{3v}

F	-1.88243476	-1.08682421	-0.56369219
F	0.00000000	2.17364843	-0.56369219
F	1.88243476	-1.08682421	-0.56369219
Na	0.00000000	0.00000000	-1.38840447
Na	0.00000000	0.00000000	2.68362337
H	-0.00001936	1.85739523	0.32409375
H	1.60856113	-0.92868085	0.32409375
H	-1.60854178	-0.92871438	0.32409375

3 C_{3v}

F	-1.70824303	0.98625457	0.50297338
F	-0.00000000	-1.97250914	0.50297338
F	1.70824303	0.98625457	0.50297338
Na	0.00000000	0.00000000	1.68542789
Na	0.00000000	0.00000000	-2.82017843
H	0.00002457	-1.60266344	-0.36600840
H	1.38793497	0.80135300	-0.36600840
H	-1.38795954	0.80131044	-0.36600840

4 C_{3v}

F	1.55858449	0.89985460	-0.50050479
F	-1.55857874	0.89988114	-0.50050619
F	0.00000369	-1.79971892	-0.50050686
Na	-0.00000929	-0.00001751	3.06657429
Na	-0.00000836	-0.00001642	-1.99402815
H	-1.28876237	0.74406383	0.38427585
H	0.00003290	-1.48813926	0.38427398
H	1.28873770	0.74409254	0.38427756

5 C_{3v}

F	1.99760124	1.15422486	-0.60499400
F	-1.99794560	1.15328776	-0.60505056
F	0.00027475	-2.30732210	-0.60494687
Na	0.00010621	-0.00016777	2.68251738
Na	0.00008960	-0.00021500	-1.06860058
H	-1.80327531	1.04141217	0.30825415
H	-0.00020638	-2.08284212	0.30836410
H	1.80335550	1.04162218	0.30831208

$Li(HF)_3Li$

1 C_{3h}

F	-1.34185039	0.77471768	0.00000000
F	0.00000000	-1.54943537	0.00000000
F	1.34185039	0.77471768	0.00000000
Li	0.00000000	0.00000000	1.36998402
Li	0.00000000	0.00000000	-1.36998402
H	0.83366812	-2.01200133	0.00000000
H	1.32561021	1.72797844	0.00000000
H	-2.15927833	0.28402289	0.00000000

2 C_{3v}

F	0.32595415	1.62841702	-0.25634459
F	1.24730198	-1.09647813	-0.25633958
F	-1.57324208	-0.53192924	-0.25635332
Li	0.00000488	-0.00000043	-1.14064054
Li	-0.00000855	0.00001285	2.81647363
H	0.91823991	-0.80720297	0.63128588
H	-1.15815092	-0.39174712	0.63127233
H	0.23979561	1.19882589	0.63127994

3 C_{3v}

F	-1.43869899	0.83063325	0.25876455
F	-0.00000000	-1.66126650	0.25876455
F	1.43869899	0.83063325	0.25876455
Li	0.00000000	0.00000000	1.16794636
Li	0.00000000	0.00000000	-2.85919737
H	0.00458838	-1.27576019	-0.63762992
H	1.10254655	0.64185375	-0.63762992
H	-1.10713493	0.63390644	-0.63762992

4 C_{3v}

F	-1.43680253	0.82653111	0.28079814
F	0.00260913	-1.65756982	0.28079779
F	1.43419423	0.83104235	0.28079734
Li	-0.00000132	0.00000107	1.26246126
Li	0.00000638	-0.00000057	-3.02984903
H	0.00200435	-1.40059753	-0.63428484
H	1.21194181	0.70203625	-0.63428453
H	-1.21395204	0.69855714	-0.63428347

5 C_{3v}

F	-1.41879148	0.81819411	0.23531340
F	0.00085773	-1.63788361	0.23539077
F	1.41803642	0.81962433	0.23538192
Li	-0.00003976	0.00001301	1.12388197
Li	-0.00011742	0.00005632	-2.76110712
H	0.00029631	-1.07894123	-0.63218833
H	0.93416438	0.53983731	-0.63220873
H	-0.93440618	0.53909977	-0.63231121

Table S1. Distances of M-M (L, in Å) and NPA charge of M1 and M2 (Q_{M1} and Q_{M2}, in |e|) with increasing external electric field strength (F_z, $\times10^{-4}$ au).

Field	Na(HF)$_3$Na			Field	Li(HF)$_3$Li		
	L	Q_{Na1}	Q_{Na2}		L	Q_{Li1}	Q_{Li2}
30	3.751	-0.448	0.754	45	3.885	0.462	0.957
25	3.788	-0.440	0.772	40	3.893	0.412	0.958
20	3.832	-0.428	0.793	35	3.900	0.368	0.959
15	3.890	-0.411	0.816	30	3.908	0.327	0.959
10	3.966	-0.387	0.842	25	3.915	0.288	0.960
5	4.072	-0.348	0.874	20	3.923	0.250	0.961
0	4.216	-0.297	0.907	15	3.931	0.213	0.962
-5	4.354	-0.255	0.930	10	3.937	0.175	0.962
-10	4.461	-0.229	0.942	5	3.948	0.139	0.963
-15	4.542	-0.213	0.950	0	4.027	0.103	0.963
-20	4.608	-0.209	0.954	-5	3.969	0.068	0.964
-25	4.666	-0.202	0.958	-10	3.981	0.032	0.965
-30	4.717	-0.201	0.960	-15	3.994	-0.004	0.965
-35	4.764	-0.203	0.961	-20	4.006	-0.041	0.966
-40	4.809	-0.206	0.962	-25	4.020	-0.078	0.966
-45	4.854	-0.211	0.963	-30	4.033	-0.115	0.968
-50	4.901	-0.218	0.963	-35	4.050	-0.153	0.968
-55	4.949	-0.227	0.963	-40	4.067	-0.192	0.970
-60	5.001	-0.237	0.963	-45	4.084	-0.231	0.970
-65	5.061	-0.252	0.962	-50	4.103	-0.270	0.970
-70	3.751	-0.448	0.754	-55	4.124	-0.310	0.971
				-60	4.145	-0.351	0.971
				-65	4.169	-0.393	0.971
				-70	4.195	-0.436	0.972
				-75	4.224	-0.479	0.972
				-80	4.257	-0.525	0.970
				-85	4.292	-0.590	0.971
				-90	4.339	-0.643	0.971
				-95	4.407	-0.708	0.970
				-100	4.541	-0.797	0.966

Table S2. 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 energy (VIE, in eV), and electron tunneling ionization (ω, s^{-1}) of $Na(HF)_3Na$ with respect to OEEF (F_z, $\times 10^{-4}$ au).

Field	E_{tot}	E_{rel}	ε_{HOMO}	ε_{gap}	VIE	ω
25	-624.7436	0.315	-4.718	4.887	4.961	1.62×10^{-7}
20	-624.7438	0.228	-4.709	4.866	4.953	1.03×10^{-13}
15	-624.7439	0.144	-4.699	4.841	4.942	4.70×10^{-24}
10	-624.7440	0.076	-4.685	4.807	4.926	1.06×10^{-44}
5	-624.7441	0.023	-4.666	4.763	4.903	1.06×10^{-106}
0	-624.7441	0.000	-4.639	4.701	4.868	-
-5	-624.7441	0.036	-4.597	4.612	4.810	1.06×10^{-103}
-10	-624.7439	0.141	-4.551	4.520	4.746	2.56×10^{-41}
-15	-624.7437	0.287	-4.511	4.443	4.688	6.72×10^{-21}
-20	-624.7434	0.446	-4.479	4.383	4.645	7.29×10^{-11}
-25	-624.7431	0.625	-4.446	4.326	4.607	6.48×10^{-5}
-30	-624.7429	0.809	-4.421	4.280	4.574	5.37×10^{1}
-35	-624.7425	1.006	-4.396	4.235	4.541	3.30×10^{2}
-40	-624.7422	1.220	-4.371	4.192	4.512	3.81×10^{4}
-45	-624.7418	1.446	-4.346	4.151	4.487	1.46×10^{6}
-50	-624.7414	1.708	-4.320	4.108	4.458	2.71×10^{7}
-55	-624.7410	1.997	-4.292	4.062	4.428	2.96×10^{8}
-60	-624.7404	2.325	-4.263	4.016	4.397	2.15×10^{9}
-65	-624.7398	2.704	-4.231	3.966	4.365	1.16×10^{10}
-70	-624.7391	3.166	-4.194	4.194	4.328	4.96×10^{10}

Table S3. 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 energy (VIE, in eV), and electron tunneling ionization (ω, s^{-1}) of $Li(HF)_3Li$ with respect to OEEF (F_z, $\times 10^{-4}$ au).

Field	E_{tot}	E_{rel}	ε_{HOMO}	ε_{gap}	VIE	ω
45	-315.9531	0.988	-5.624	4.394	6.035	4.60×10^{-1}
40	-315.9536	0.709	-5.551	4.499	5.951	5.87×10^{-3}
35	-315.9539	0.505	-5.505	4.628	5.885	1.64×10^{-5}
30	-315.9541	0.352	-5.474	4.771	5.831	5.38×10^{-9}
25	-315.9543	0.235	-5.454	4.922	5.784	6.01×10^{-14}
20	-315.9545	0.146	-5.441	5.076	5.741	1.93×10^{-21}
15	-315.9546	0.080	-5.434	5.229	5.702	5.21×10^{-34}
10	-315.9547	0.034	-5.430	5.377	5.663	3.13×10^{-59}
5	-315.9547	0.008	-5.431	5.517	5.563	1.32×10^{-132}
0	-315.9547	0.000	-5.437	5.625	5.595	-
-5	-315.9547	0.008	-5.446	5.501	5.563	1.32×10^{-132}
-10	-315.9547	0.034	-5.458	5.336	5.532	1.42×10^{-56}
-15	-315.9546	0.075	-5.471	5.158	5.501	2.65×10^{-31}
-20	-315.9545	0.135	-5.487	4.974	5.471	1.01×10^{-18}
-25	-315.9544	0.211	-5.505	4.786	5.440	3.37×10^{-11}
-30	-315.9542	0.303	-5.526	4.597	5.412	3.28×10^{-6}
-35	-315.9540	0.418	-5.547	4.404	5.381	1.20×10^{-2}
-40	-315.9538	0.549	-5.571	4.211	5.350	5.49×10^{0}
-45	-315.9536	0.703	-5.597	4.019	5.320	6.34×10^{2}
-50	-315.9533	0.878	-5.624	3.828	5.289	2.79×10^{4}
-55	-315.9530	1.078	-5.654	3.637	5.257	6.12×10^{5}
-60	-315.9526	1.304	-5.686	3.448	5.225	7.98×10^{6}
-65	-315.9522	1.560	-5.721	3.262	5.192	6.98×10^{7}
-70	-315.9518	1.852	-5.758	3.077	5.158	4.48×10^{8}
-75	-315.9512	2.191	-5.797	2.896	5.122	2.25×10^{9}
-80	-315.9506	2.585	0.971	0.966	5.083	9.29×10^{9}
-85	-315.9498	3.057	-5.889	2.549	5.038	3.31×10^{10}
-90	-315.9489	3.672	-5.946	2.392	4.986	1.05×10^{11}
-95	-315.9473	4.625	-6.016	2.254	4.913	3.21×10^{11}
-100	-315.9440	6.697	-6.103	2.149	4.777	1.11×10^{12}

Table S4. Calculated values of static electronic first hyperpolarizabilities (β_0^e) of $M(HF)_3M$ with respect to M-M distance.

$Na(HF)_3Na$		$Li(HF)_3Li$	
Na-Na Distance (Å)	β_0^e (a.u.)	Na-Na Distance (Å)	β_0^e (a.u.)
3.751	1851	3.885	4984
3.788	1583	3.893	4935
3.832	1223	3.900	4867
3.890	751	3.908	4792
3.966	45	3.915	4711
4.027	1162	3.923	4625
4.216	3400	3.931	4535
4.354	6500	3.937	4435
4.461	9778	3.948	4336
4.506	11727	3.957	4240
4.542	12838	3.969	4130
4.608	15798	3.981	4019
4.666	18821	3.994	3904
4.717	21787	4.006	3779
4.764	24871	4.020	3649
4.809	27993	4.027	3589
4.854	31495	4.033	3513
4.901	35200	4.050	3365
4.949	39322	4.067	3210
5.001	43976	4.084	3044
5.061	49348	4.103	2866
		4.124	2675
		4.145	2467
		4.169	2240
		4.195	1989
		4.224	1703
		4.257	1376

Table S5. Calculated wavelengthes of λ_{max} and λ_2 of $Na(HF)_3Na$ at different methods with 6-311++G (3df, 3pd) basis set.

	$Na(HF)_3Na$					
	TD-M062X	TD-LC-BLYP	TD-B3LYP	TD-CAM-B3LYP	TD-WB97XD	TD-PBEPBE
λ_{max}						
1	688	709	663	683	777	662
2	456	436	446	440	461	451
3	458	433	449	441	462	455
4	487	458	476	467	488	481
λ_2						
1	822	829	763	791	890	772
2	514	494	575	527	507	582
3	564	535	682	596	536	697
4	679	640	866	742	621	882

Table S6. Calculated wavelengthes of λ_{max} and λ_2 of Li(HF)$_3$Li at different methods with 6-311++G (3df, 3pd) basis set.

	Na(HF)$_3$Na					
	TD-M062X	TD-LC-BLYP	TD-B3LYP	TD-CAM-B3LYP	TD-WB97XD	TD-PBEPBE
λ_{max}						
1	679	731	672	697	755	666
2	427	391	418	403	412	432
3	439	405	429	416	425	437
5	393	359	395	376	384	409
λ_2						
1	715	769	721	740	800	730
2	516	458	512	481	470	534
3	533	467	524	490	476	545
5	473	442	503	469	463	529

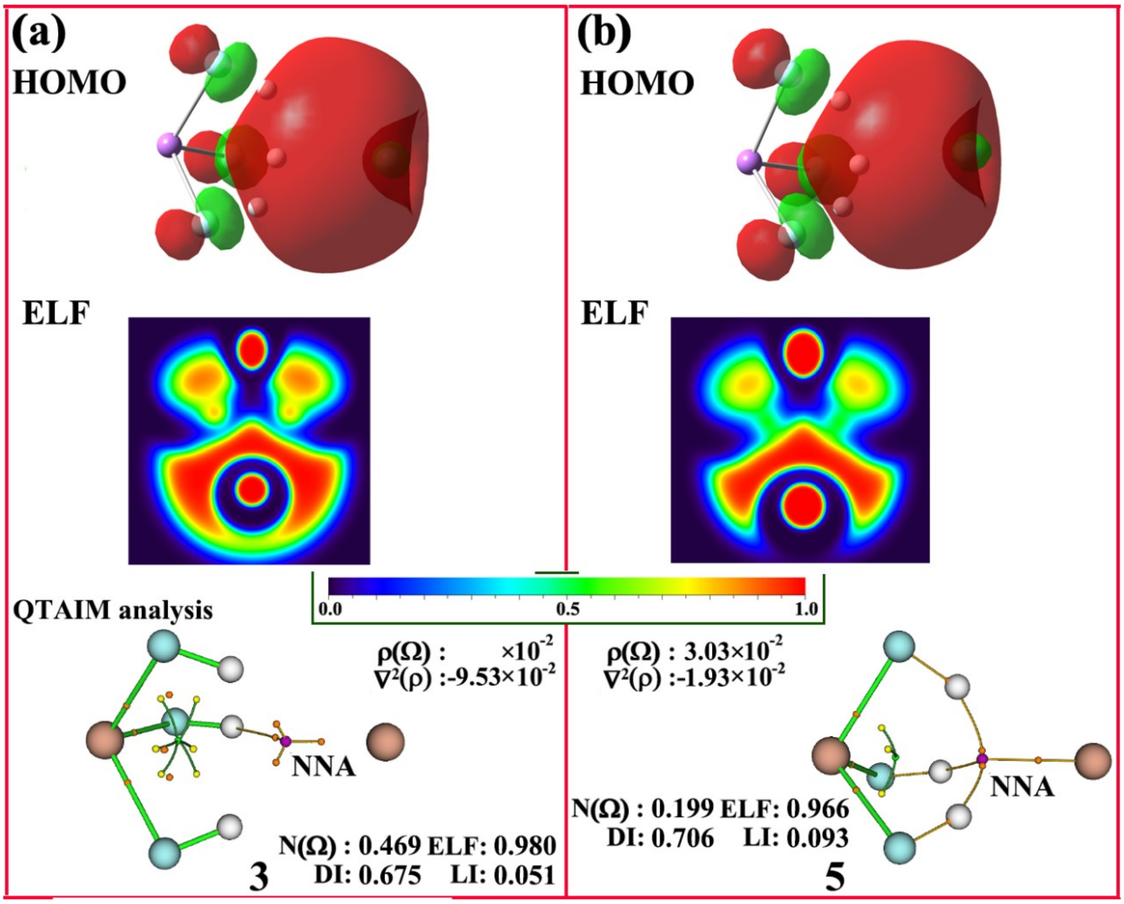

Fig. S1. QTAIM analysis of **3** and **5** of $Li(HF)_3Li$