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

Switching from Electride-like Molecule to Molecular Electride K-$F_6C_6H_6$ Driven by Oriented External Electric Field

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Contents

1 K-$F_6C_6H_6$ in presence of F_z = -0.0050 a.u.

C	1.24697476	0.66547996	-1.31793531
C	-1.24697411	0.66547898	-1.31793513
C	-0.00000006	-1.49263175	-1.22552652
C	0.00000030	1.43239708	-0.89849111
C	1.27166788	-0.76817414	-0.80499412
C	-1.27166886	-0.76817502	-0.80499387
K	-0.00000027	0.11576614	2.86378142
F	2.36562912	1.33056448	-0.86690618
F	0.00000021	1.60622740	0.48457302
F	1.37231170	-0.76709372	0.58528717
F	-2.36562805	1.33056371	-0.86690600
F	-0.00000004	-2.76253498	-0.69126230
F	-1.37231212	-0.76709399	0.58528762
H	0.00000026	2.43148167	-1.34117305
H	2.15229840	-1.29307505	-1.18328992
H	1.28175731	0.63893494	-2.41519395
H	-1.28175681	0.63893421	-2.41519372
H	-0.00000002	-1.58037950	-2.32009429
H	-2.15229958	-1.29307549	-1.18328989

2 field-free K-$F_6C_6H_6$

C	0.66216861	-1.32152344	1.24208816
C	0.66216861	-1.32152344	-1.24208816
C	-1.48729516	-1.23060891	0.00000000
C	1.43221990	-0.89230857	-0.00000000
C	-0.76836784	-0.79933186	1.27166289
C	-0.76836784	-0.79933186	-1.27166289
K	0.12588775	3.00935344	0.00000000
F	1.33230949	-0.90698097	2.37145402
F	1.60707508	0.48173815	-0.00000000
F	-0.76836784	0.58210212	1.37283347
F	1.33230949	-0.90698097	-2.37145402
F	-2.77148405	-0.73335129	-0.00000000
F	-0.76836784	0.58210212	-1.37283347
H	2.42931215	-1.34163264	-0.00000000
H	-1.29269410	-1.18441455	2.15079587
H	0.62381362	-2.41969489	1.25600140
H	0.62381362	-2.41969489	-1.25600140
H	-1.54984498	-2.32775783	0.00000000
H	-1.29269410	-1.18441455	-2.15079587

3 K-$F_6C_6H_6$ in presence of F_z = 0.0030 a.u.

C	1.23216925	0.65782825	-1.29229631
C	-1.23222138	0.65793012	-1.29217960
C	0.00006408	-1.47529155	-1.20184492
C	0.00004130	1.42820051	-0.87891962
C	1.26764602	-0.76542198	-0.78659772
C	-1.26757833	-0.76543128	-0.78678478
K	-0.00011362	0.10822439	2.62464269
F	2.36676873	1.33089688	-0.87794236
F	0.00005664	1.65185352	0.51792148
F	1.40927905	-0.78774479	0.62061121
F	-2.36674364	1.33089698	-0.87747204
F	0.00000018	-2.76479281	-0.70299112
F	-1.40933221	-0.78783955	0.62039842
H	0.00007646	2.42099297	-1.33898309
H	2.14379581	-1.28836810	-1.18151918
H	1.23276642	0.61199181	-2.40315639
H	-1.23310159	0.61228147	-2.40304666
H	0.00009332	-1.52422472	-2.31224877
H	-2.14366648	-1.28838717	-1.18184741

4 K-$F_6C_6H_6$ in presence of $F_z = 0.0050$ a.u.

C	1.24697476	0.66547996	-1.31793531
C	-1.24697411	0.66547898	-1.31793513
C	-0.00000006	-1.49263175	-1.22552652
C	0.00000030	1.43239708	-0.89849111
C	1.27166788	-0.76817414	-0.80499412
C	-1.27166886	-0.76817502	-0.80499387
K	-0.00000027	0.11576614	2.86378142
F	2.36562912	1.33056448	-0.86690618
F	0.00000021	1.60622740	0.48457302
F	1.37231170	-0.76709372	0.58528717
F	-2.36562805	1.33056371	-0.86690600
F	-0.00000004	-2.76253498	-0.69126230
F	-1.37231212	-0.76709399	0.58528762
H	0.00000026	2.43148167	-1.34117305
H	2.15229840	-1.29307505	-1.18328992
H	1.28175731	0.63893494	-2.41519395
H	-1.28175681	0.63893421	-2.41519372
H	-0.00000002	-1.58037950	-2.32009429
H	-2.15229958	-1.29307549	-1.18328989

Table S1. C-F bond lengths (B_{C-F}, in Å) and NPA charges of M (Q_M, in |e|) in M@$F_6C_6H_6$ (M= Li, Na, K) with increasing external electric field strength (F_z, $\times 10^{-4}$ a.u.).

Field	Li-$F_6C_6H_6$		Na-$F_6C_6H_6$		K-$F_6C_6H_6$	
	B_{C-F}	Q_{Li}	B_{C-F}	Q_{Na}	B_{C-F}	Q_K
-55			2.545	0.043	2.789	0.034
-50	2.096	0.057	2.537	0.043	2.803	0.035
-45	2.104	0.057	2.550	0.044	2.815	0.036
-40	2.110	0.057	2.565	0.043	2.828	0.037
-35	2.117	0.057	2.580	0.043	2.840	0.038
-30	2.123	0.056	2.596	0.043	2.853	0.039
-25	2.130	0.056	2.612	0.007	2.891	0.039
-20	2.136	0.055	2.630	0.041	2.878	0.040
-15	2.142	0.054	2.650	0.040	2.891	0.041
-10	2.147	0.053	2.672	0.039	2.905	0.040
-5	2.154	0.052	2.699	0.038	2.917	0.040
0	2.154	0.051	2.727	0.036	2.928	0.039
5	2.155	0.050	2.764	0.034	2.940	0.038
10	2.156	0.049	2.809	0.031	2.950	0.036
15	2.159	0.048	2.875	0.028	2.950	0.034
20	-	-	-	-	2.929	0.032
25	2.100	0.332	-	-	2.950	0.035
30	2.162	0.312	-	-	2.609	0.890
35	1.900	0.911	3.557	0.008	2.615	0.898
40	1.903	0.912	2.628	0.339	2.624	0.904
45	1.907	0.913	2.748	0.330	2.631	0.909
50	1.910	0.913	2.325	0.932	2.639	0.912
55	1.914	0.914	2.330	0.935	2.649	0.915
60	1.918	0.913	2.337	0.938	2.658	0.918
65	1.922	0.913	2.344	0.940	2.668	0.917
70	1.926	0.913	2.351	0.942	2.678	0.922
80	1.935	0.913	2.367	0.945	2.701	0.925
90	1.944	0.913	2.384	0.947	2.727	0.928
100	1.955	0.910	2.404	0.950		

Table S2. Total energy (E_{tot}, au), relative energy (E_{rel}, kcal/mol), Interaction energy (E_{int}, 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 K-$F_6C_6H_6$ with respect to OEEF (F_z, $\times 10^{-4}$ au).

Field	E_{tot}	E_{rel}	E_{int}	ε_{HOMO}	ε_{gap}	VIE	ω
-55	-1429.1866	-20.18	-11.45	-0.151	2.684	4.207	1.37×10^{9}
-50	-1429.1830	-17.91	-10.57	-0.146	2.747	4.103	$4{,}11 \times 10^{8}$
-45	-1429.1795	-15.75	-9.72	-0.142	2.816	4.002	9.11×10^{7}
-40	-1429.1762	-13.67	-8.91	-0.138	2.891	3.902	1.34×10^{7}
-35	-1429.1731	-11.69	-8.12	-0.134	2.970	3.806	1.09×10^{6}
-30	-1429.1700	-9.79	-7.36	-0.131	3.053	3.712	3.68×10^{4}
-25	-1429.1671	-7.95	-6.57	-0.128	3.148	3.640	2.24×10^{2}
-20	-1429.1644	-6.23	-5.88	-0.123	3.216	3.529	2.06×10^{-1}
-15	-1429.1617	-4.56	-5.18	-0.120	3.245	3.441	9.75×10^{-7}
-10	-1429.1592	-2.97	-4.49	-0.116	3.140	3.354	1.77×10^{-17}
-5	-1429.1567	-1.45	-3.81	-0.113	2.998	3.269	5.73×10^{-50}
0	-1429.1544	0.00	-3.15	-0.109	2.849	3.186	
5	-1429.1523	1.37	-2.51	-0.106	2.696	3.104	6.43×10^{-45}
10	-1429.1502	2.66	-1.89	-0.102	2.539	3.023	1.80×10^{-12}
15	-1429.1483	3.86	-1.31	-0.099	2.375	2.941	9.34×10^{-2}
20	-1429.1466	4.95	-0.78	-0.095	2.194	2.853	2.01×10^{4}
25	-1429.1451	5.84	-0.41	-0.092	2.039	2.790	2.15×10^{7}
30	-1429.1514	1.93	-6.69	-0.105	2.727	2.954	2.03×10^{8}
35	-1429.1548	-0.25	-9.13	-0.108	2.889	3.018	2.41×10^{9}
40	-1429.1584	-2.50	-11.66	-0.111	3.048	3.087	1.48×10^{10}
45	-1429.1621	-4.83	-14.14	-0.114	3.201	3.157	5.95×10^{10}
50	-1429.1660	-7.23	-16.66	-0.117	3.338	3.230	1.77×10^{11}
55	-1429.1699	-9.69	-19.16	-0.120	3.438	3.304	4.23×10^{11}
60	-1429.1739	-12.21	-21.71	-0.124	3.507	3.383	8.57×10^{11}
65	-1429.1739	-12.20	-21.58	-0.123	3.503	3.348	2.70×10^{12}
70	-1429.1822	-17.42	-26.64	-0.130	3.619	3.540	2.55×10^{12}
80	-1429.1909	-22.86	-31.39	-0.137	3.730	3.703	5.60×10^{12}
90	-1429.1999	-28.50	-35.73	-0.143	3.846	3.871	1.11×10^{13}

Table S3. Total energy (E_{tot}, au), relative energy (E_{rel}, kcal/mol), Interaction energy (E_{int}, 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-$F_6C_6H_6$ with respect to OEEF (F_z, $\times 10^{-4}$ au).

Field	E_{tot}	E_{rel}	E_{int}	ε_{HOMO}	ε_{gap}	VIE	ω
-45	-837.2796	-15.89	-11.78	-0.150	3.619	4.132	3.09×10^{7}
-40	-837.2765	-13.93	-10.89	-0.147	3.697	4.052	3.35×10^{6}
-35	-837.2734	-12.03	-10.02	-0.144	3.776	3.974	1.85×10^{5}
-30	-837.2705	-10.17	-9.17	-0.142	3.845	3.897	3.77×10^{3}
-25	-837.2676	-8.36	-8.33	-0.139	3.853	3.820	1.57×10^{1}
-20	-837.2648	-6.60	-7.49	-0.136	3.760	3.744	4.01×10^{-3}
-15	-837.2621	-4.88	-6.66	-0.133	3.639	3.669	3.81×10^{-9}
-10	-837.2594	-3.21	-5.84	-0.130	3.510	3.593	2.91×10^{-21}
-5	-837.2568	-1.58	-5.02	-0.127	3.382	3.523	5.70×10^{-58}
0	-837.2543	0.00	-4.22	-0.124	3.237	3.443	
5	-837.2518	1.53	-3.43	-0.121	3.089	3.365	5.79×10^{-53}
10	-837.2495	3.01	-2.66	-0.118	2.939	3.289	1.79×10^{-16}
15	-837.2472	4.43	-1.92	-0.114	2.764	3.201	2.71×10^{-4}
25	-837.2471	4.50	-3.35	-0.101	2.146	3.151	2.04×10^{5}
30	-837.2452	5.70	-2.49	-0.101	2.146	3.141	2.70×10^{7}
35	-837.2574	-1.93	-14.37	-0.122	3.479	3.440	4.46×10^{7}
40	-837.2596	-3.34	-15.99	-0.124	3.599	3.482	5.62×10^{8}
45	-837.2620	-4.83	-17.71	-0.127	3.718	3.529	3.87×10^{9}
50	-837.2644	-6.38	-19.45	-0.129	3.832	3.577	1.77×10^{10}
55	-837.2671	-8.02	-21.33	-0.131	3.945	3.634	5.81×10^{10}
60	-837.2697	-9.70	-23.18	-0.134	4.043	3.689	1.57×10^{11}
65	-837.2725	-11.45	-25.08	-0.136	4.127	3.749	3.54×10^{11}
70	-837.2754	-13.27	-27.08	-0.139	4.175	3.814	6.92×10^{11}
80	-837.2814	-17.02	-31.02	-0.145	4.221	3.942	2.05×10^{12}
90	-837.2878	-21.01	-35.09	-0.150	4.267	4.082	4.53×10^{12}

Table S4. Total energy (E_{tot}, au), relative energy (E_{rel}, kcal/mol), Interaction energy (E_{int}, 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-$F_6C_6H_6$ with respect to OEEF (F_z, $\times 10^{-4}$ au).

Field	E_{tot}	E_{rel}	E_{int}	ε_{HOMO}	ε_{gap}	VIE	ω
-55	-991.6934	-18.37	-9.10	-0.164	3.383	4.605	
-50	-991.6903	-16.40	-8.33	-0.161	3.464	4.502	1.92×10^{7}
-45	-991.6873	-14.50	-7.59	-0.158	3.547	4.403	3.03×10^{6}
-40	-991.6844	-12.67	-6.87	-0.155	3.634	4.310	2.82×10^{5}
-35	-991.6815	-10.89	-6.16	-0.152	3.722	4.219	1.27×10^{4}
-30	-991.6788	-9.17	-5.47	-0.149	3.811	4.133	1.89×10^{2}
-25	-991.6702	-3.80	-1.87	-0.182	-9.470	4.979	1.18×10^{-7}
-20	-991.6736	-5.89	-4.13	-0.143	3.962	3.968	5.86×10^{-5}
-15	-991.6711	-4.34	-3.48	-0.140	3.943	3.890	1.46×10^{-11}
-10	-991.6687	-2.84	-2.85	-0.138	3.851	3.815	6.91×10^{-25}
-5	-991.6664	-1.39	-2.23	-0.135	3.741	3.744	3.28×10^{-65}
0	-991.6642	0.00	-1.62	-0.133	3.625	3.676	
5	-991.6620	1.33	-1.03	-0.130	3.512	3.614	6.13×10^{-61}
10	-991.6600	2.60	-0.47	-0.128	3.404	3.558	1.06×10^{-20}
15	-991.6581	3.80	0.06	-0.127	3.312	3.516	1.61×10^{-7}
35	-991.6523	7.48	1.20	-0.125	3.121	3.467	3.44×10^{7}
40	-991.6516	7.86	1.37	-0.099	1.983	3.049	1.99×10^{10}
45	-991.6507	8.43	1.57	-0.100	1.953	3.044	1.31×10^{11}
50	-991.6626	0.97	-7.83	-0.121	3.228	3.309	1.06×10^{11}
55	-991.6661	-1.23	-10.27	-0.123	3.371	3.375	2.80×10^{11}
60	-991.6697	-3.49	-12.77	-0.126	3.515	3.446	6.10×10^{11}
65	-991.6734	-5.79	-15.27	-0.129	3.660	3.517	1.17×10^{12}
70	-991.6772	-8.16	-17.78	-0.132	3.801	3.590	2.02×10^{12}
80	-991.6849	-13.04	-22.81	-0.138	4.079	3.742	4.78×10^{12}
90	-991.6930	-18.11	-27.82	-0.144	4.197	3.899	9.07×10^{12}

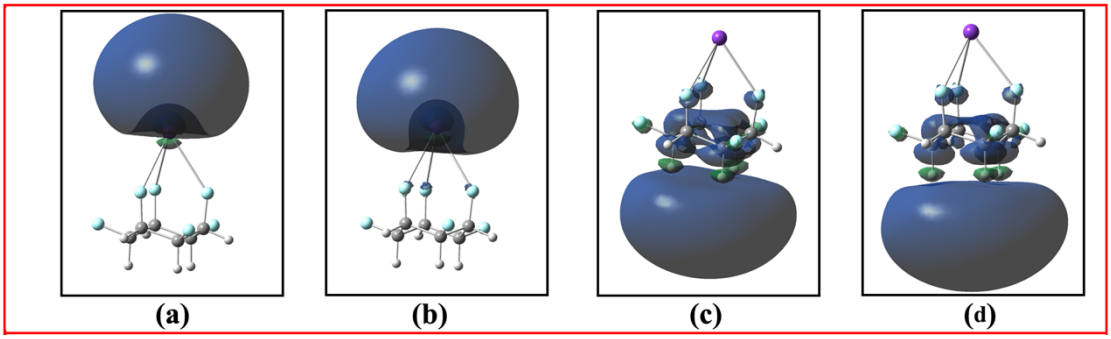

Fig. S1. Spin density maps of K-$F_6C_6H_6$. (a) for **4**, (b) for **1**, (c) for **2**, (d) for **3**.

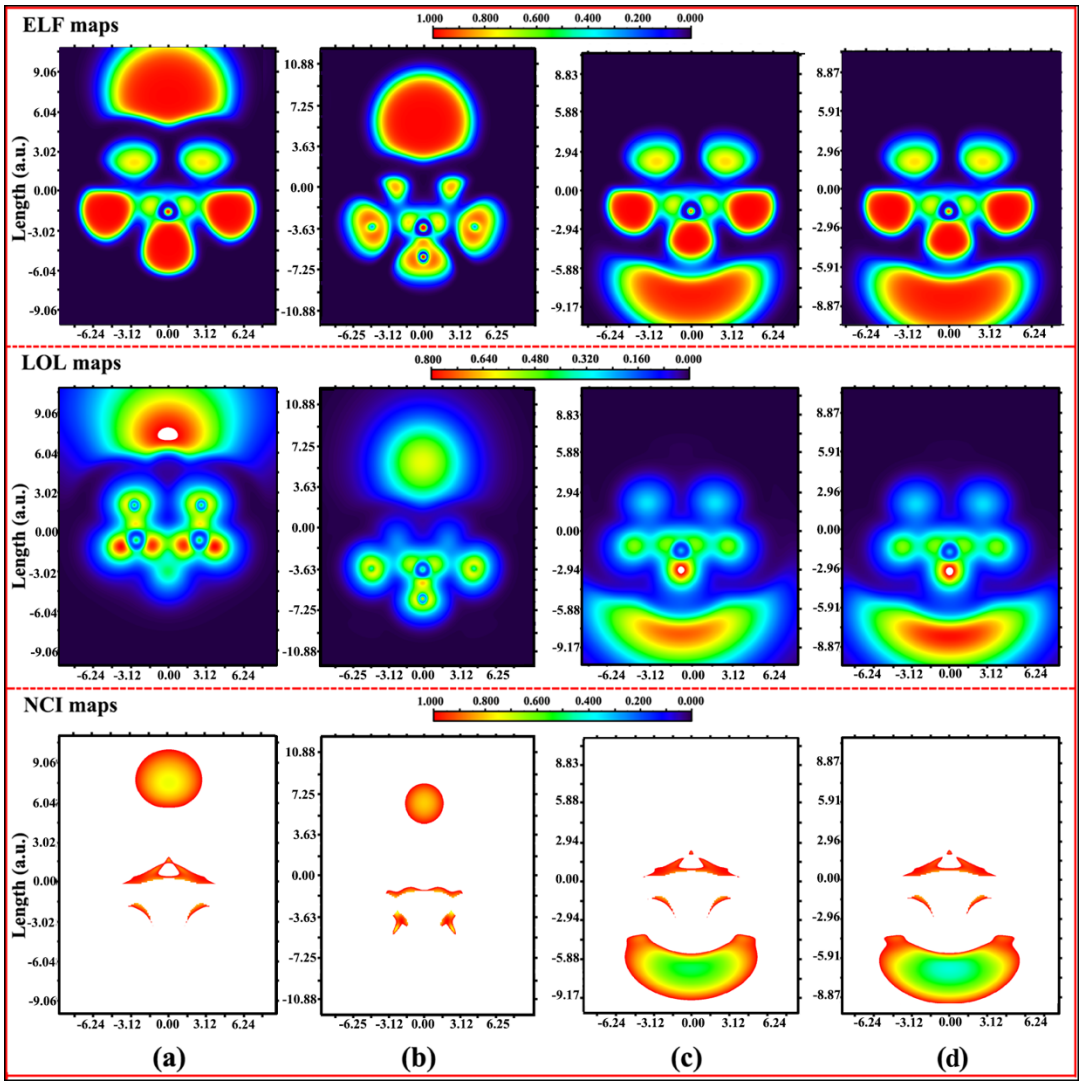

Fig. S2. ELF, LOL, and NCI maps for Li-$F_6C_6H_6$ optimized in presence of OEEF. (a) for **4** (F_z = -0.0050), (b) for **1** (F_z = 0), (c) for **2** (F_z = 0.0050), (d) for **3** (F_z = 0.0080).

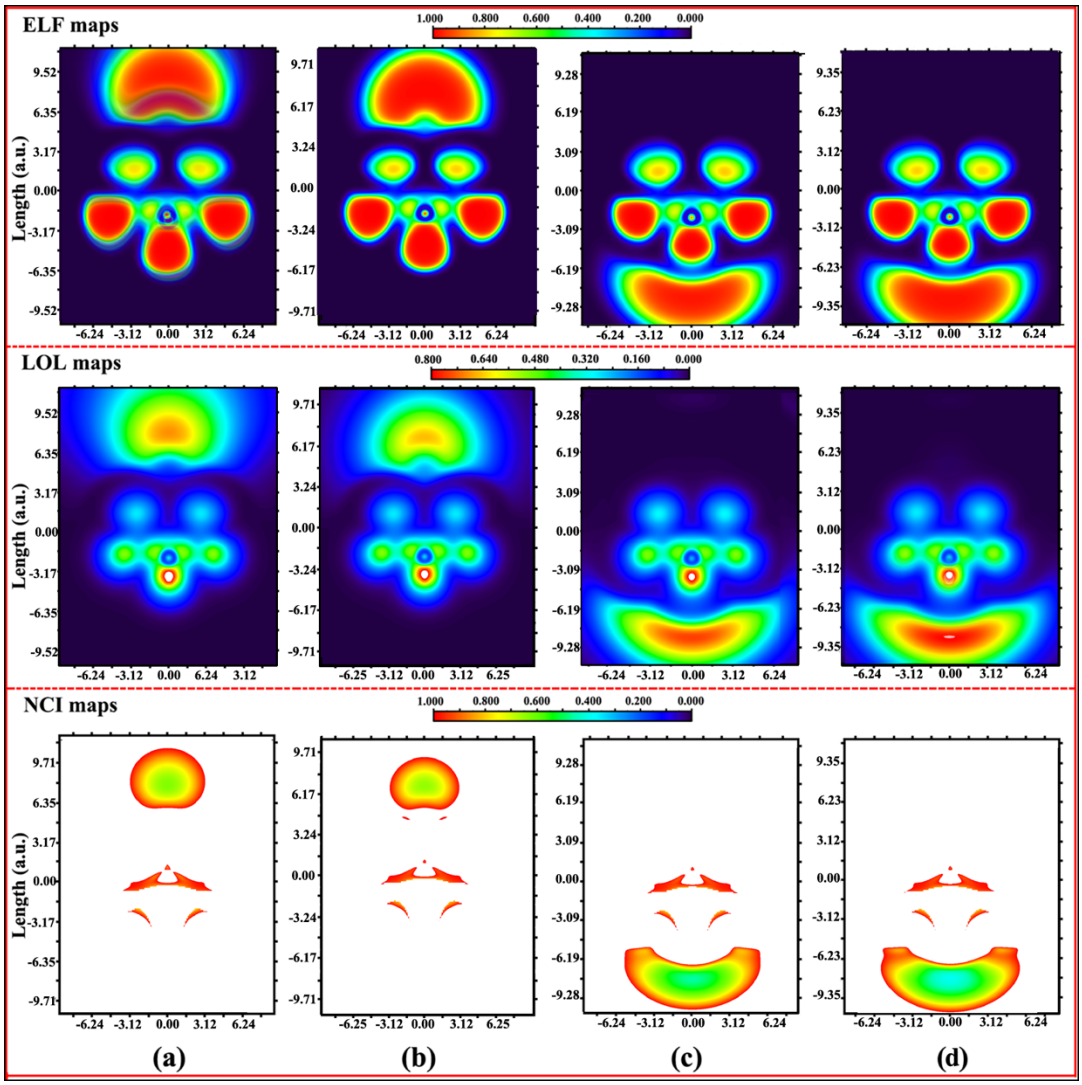

Fig. S3. ELF, LOL, and NCI maps for Na-$F_6C_6H_6$ optimized in presence of OEEF. (a) for **4** (F_z = -0.0050), (b) for **1** (F_z = 0), (c) for **2** (F_z = 0.0035), (d) for **3** (F_z = 0.0070).

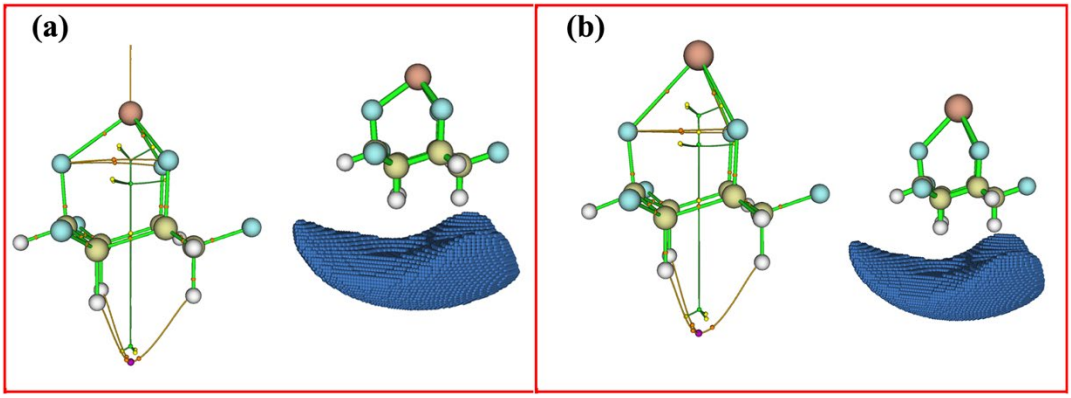

Fig. S4. QTAIM topological analysis and corresponding basin representations of Li-$F_6C_6H_6\cdots e^-$ (a, F_z = 0.0080) and Na-$F_6C_6H_6$ (b, F_z = 0.0070 a. u.).