Supplementary Information

Long-range Charge Transfer Driven by External Electric Field in Alkalides M-LCaL-M (M = Li or Na, L = all-*cis* 1,2,3,4,5,6-Hexafluorocyclohexane): Facially Polarized Janus-type Second Order Nonlinear Molecular Optical Switches

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Contents

Table S1 Point group(*PG*), distance L between alkali atoms, bond length R_1, R_2, R_3, R_4 (Å) for Li^--$LCa^{2+}L$-Li^- under different external electric fields (*EEF*, $\times10^{-4}$, au) at M06-2X/6-311++G(2d,2p) level..…… ……..S3

Table S2 Point group(*PG*), distance L between alkali atoms, bond length R_1, R_2, R_3, R_4 (Å) for Na^--$LCa^{2+}L$-Na^- under different external electric fields (*EEF*, $\times10^{-4}$, a.u.) at M06-2X/6-311++G(2d,2p) level..…… ……..S4

Table S3 Stactic electronic first hyperpolarizability(β_0^0, au) of M^--$LCa^{2+}L$-M^- (M = Li or Na, L = $C_6F_6H_6$) under different external electric fields (*EEF*,$\times10^{-4}$, au) at M06-2X/6-311++G(2d,2p) level.……..……..…… …… S5

Table S4 Selected frequency-dependence first hyperpolarizability β(-2ω, ω, ω) and β(-ω, ω, 0) under different external electric field (*EEF*s, $\times10^{-4}$, au) for Li^--$LCa^{2+}L$-Li^- at M06-2X/6-311++G(2d,2p)

level. ..…… ……...S6

Table S5 Selected frequency-dependence first hyperpolarizability β(-2ω, ω, ω) and β(-ω, ω, 0) under different external electric field (*EEF*s, $\times10^{-4}$, au) for Na^--$LCa^{2+}L$-Na^- at M06-2X/6-311++G(2d,2p)

level. ..…… ……...S7

Table S1. Point group(*PG*), distance L between alkali atoms, bond length R_1, R_2, R_3, R_4 (Å) for Na^--$LCa^{2+}L$-Na^- under different external electric fields (*EEF*, $\times 10^{-4}$, a.u.) at M06-2X/6-311++G(2d,2p) level.

EEF	*PG*	L	R_1	R_2	R_3	R_4
0	C_{2h}	14.32	2.81	2.29	2.29	2.81
1	C_{3v}	14.26	2.82	2.29	2.29	2.80
2	C_{3v}	14.26	2.82	2.29	2.29	2.79
3	C_{3v}	14.26	2.83	2.30	2.29	2.79
4	C_{3v}	14.26	2.84	2.30	2.28	2.78
5	C_{3v}	14.26	2.85	2.30	2.28	2.77
6	C_{3v}	14.26	2.86	2.30	2.28	2.77
7	C_{3v}	14.26	2.86	2.30	2.28	2.76
8	C_{3v}	14.26	2.87	2.31	2.28	2.75
9	C_{3v}	14.26	2.88	2.31	2.27	2.74
10	C_{3v}	14.27	2.89	2.31	2.27	2.74
11	C_{3v}	14.27	2.89	2.31	2.27	2.73
12	C_{3v}	14.27	2.90	2.31	2.27	2.72
13	C_{3v}	14.27	2.91	2.31	2.27	2.71
14	C_{3v}	14.27	2.92	2.32	2.27	2.71
15	C_{3v}	14.28	2.93	2.32	2.26	2.70
16	C_{3v}	14.28	2.93	2.32	2.26	2.70
17	C_{3v}	14.28	2.94	2.32	2.26	2.69
18	C_{3v}	14.29	2.95	2.32	2.26	2.69
19	C_{3v}	14.29	2.96	2.33	2.26	2.69
20	C_{3v}	14.29	2.96	2.33	2.26	2.69

Table S2. Point group(*PG*), distance L between alkali atoms, bond length R_1, R_2, R_3, R_4 (Å) for Na^--$LCa^{2+}L$-Na^- under different external electric fields (*EEF*, $\times 10^{-4}$, a.u.) at M06-2X/6-311++G(2d,2p) level

EEF	*PG*	*L*	R_1	R_2	R_3	R_4
0	C_{2h}	14.62	2.99	2.29	2.29	2.99
1	C_{3v}	14.61	2.98	2.29	2.29	2.98
2	C_{3v}	14.61	3.00	2.29	2.29	2.99
3	C_{3v}	14.61	3.01	2.30	2.29	2.97
4	C_{3v}	14.61	3.01	2.30	2.28	2.97
5	C_{3v}	14.62	3.02	2.30	2.28	2.96
6	C_{3v}	14.62	3.02	2.30	2.28	2.95
7	C_{3v}	14.62	3.03	2.30	2.28	2.95
8	C_{3v}	14.62	3.03	2.31	2.28	2.94
9	C_{3v}	14.62	3.04	2.31	2.28	2.94
10	C_{3v}	14.62	3.04	2.31	2.27	2.93
11	C_{3v}	14.62	3.05	2.31	2.27	2.93
12	C_{3v}	14.63	3.04	2.31	2.27	2.93
13	C_{3v}	14.63	3.06	2.31	2.27	2.92
14	C_{3v}	14.63	3.06	2.32	2.27	2.91
15	C_{3v}	14.64	3.07	2.32	2.27	2.91
16	C_{3v}	14.64	3.07	2.32	2.27	2.91
17	C_{3v}	14.64	3.07	2.32	2.27	2.90
18	C_{3v}	14.65	3.08	2.32	2.26	2.90
19	C_{3v}	14.65	3.09	2.33	2.26	2.90
20	C_{3v}	14.66	3.09	2.33	2.26	2.89

Table S3. Stactic electronic first hyperpolarizability(β_0^0, au) of M^--$LCa^{2+}L$-M^- (M = Li or Na, L = $C_6F_6H_6$) under different external electric fields (*EEF*,$\times 10^{-4}$, au) at M06-2X/6-311++G(2d,2p) level.

EEF	β_0	
	Li^--$LCa^{2+}L$-Li^-	Na^--$LCa^{2+}L$-Na^-
0	0	0
1	3986	5804
2	7939	12177
3	11833	18306
4	15649	24740
5	19363	30699
6	22973	37019
7	26476	43195
8	29889	49124
9	33238	54713
10	36552	59173
11	39869	62501
12	43215	64231
13	46581	63997
14	49926	61690
15	53129	57909
16	55988	53572
17	58221	49606
18	59550	47334
19	59824	47492
20	0	50454

Table S4. Selected frequency-dependence first hyperpolarizability $\beta(-2\omega, \omega, \omega)$ and $\beta(-\omega, \omega, 0)$ under different external electric field (*EEF*s, $\times 10^{-4}$, au) for Li^{-}-LCa^{2+}L-Li^{-} at M06-2X/6-311++G(2d,2p) level.

EEF	$\beta(-2\omega, \omega, \omega)$					$\beta(-\omega, \omega, 0)$				
	0.0000	0.0005	0.0010	0.0015	0.0020	0.0000	0.0005	0.0010	0.0015	0.0020
4	15649	15655	15671	15688	15738	15649	15651	15656	15666	15679
8	29889	29900	29933	29988	30065	29899	29893	29903	29922	29947
12	43215	43231	43281	43364	43481	43215	43220	43237	43264	43303
16	55988	56011	56080	56194	56356	55988	55996	56019	56057	56110
19	59824	59850	59928	60058	60241	59824	59833	59859	59902	59963
20	59156	59183	59262	59394	59580	59156	59165	59192	59235	59297

Table S5. Selected frequency-dependence first hyperpolarizability $\beta(-2\omega, \omega, \omega)$ and $\beta(-\omega, \omega, 0)$ under different external electric field (*EEF*s, $\times 10^{-4}$, au) for Na^{-}-$LCa^{2+}L$-Na^{-} at M06-2X/6-311++G(2d,2p) level.

EEF	$\beta(-2\omega, \omega, \omega)$					$\beta(-\omega, \omega, 0)$				
	0.0000	0.0005	0.0010	0.0015	0.0020	0.0000	0.0005	0.0010	0.0015	0.0020
4	24740	24751	24784	24840	24918	24740	24743	24755	24734	24799
8	49124	49147	49216	49331	49492	49124	49132	49155	49193	49246
12	64231	64263	64360	64523	64752	64231	64241	64274	64328	64403
16	53572	53605	53701	53863	54090	53572	53583	53615	53669	53744
19	47492	47525	47626	47795	48032	47492	47503	47537	47592	47671
20	50454	50490	50600	50782	51039	50454	50466	50503	50563	50648