Supporting Information

Design of a Novel Series of Donor-Acceptor Frameworks via Superalkali-Superhalogen Assemblage to Improve the Nonlinear Optical Responses

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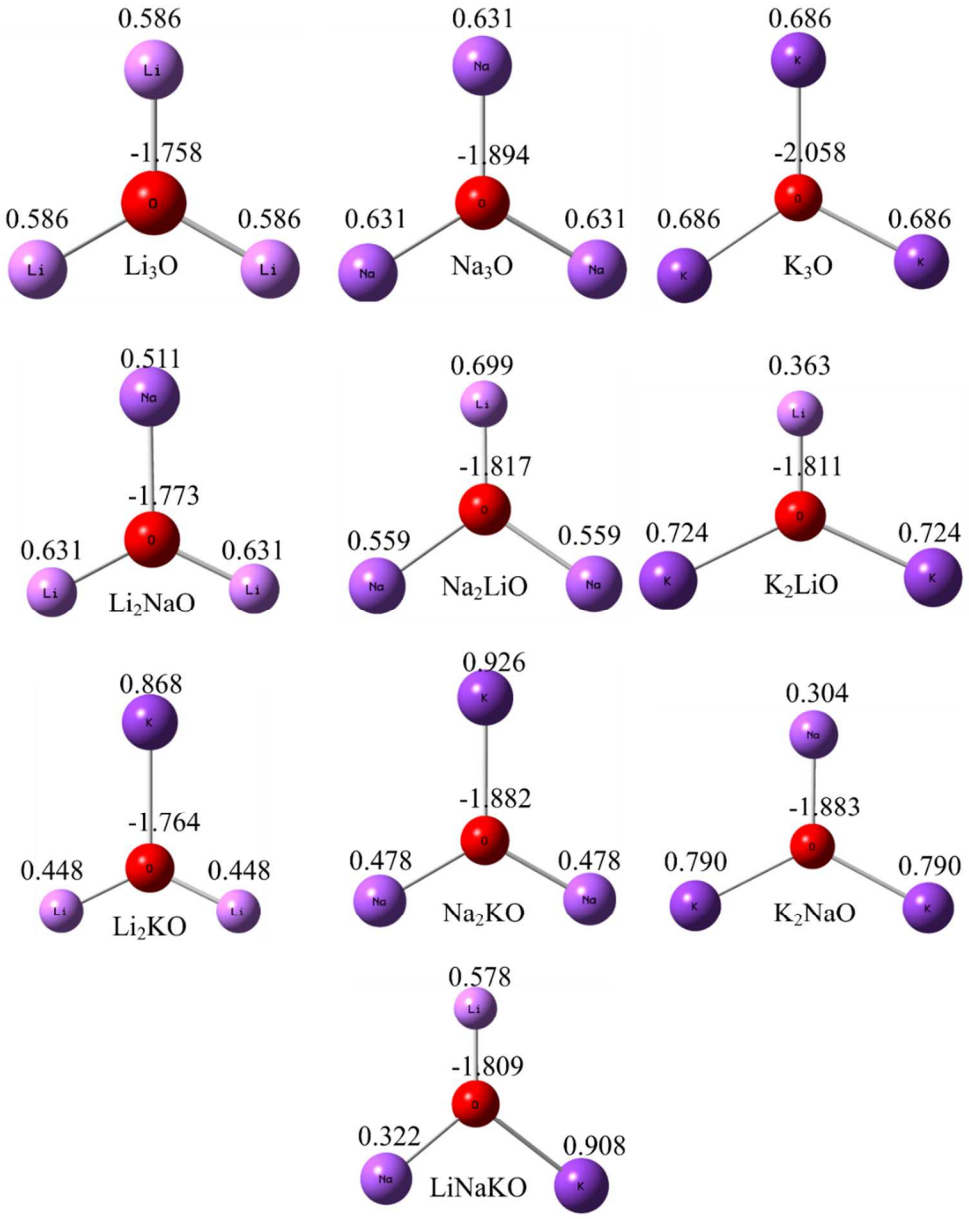

Figure S1. The optimized geometry together with the NBO charges of the superalkalis M_3O.

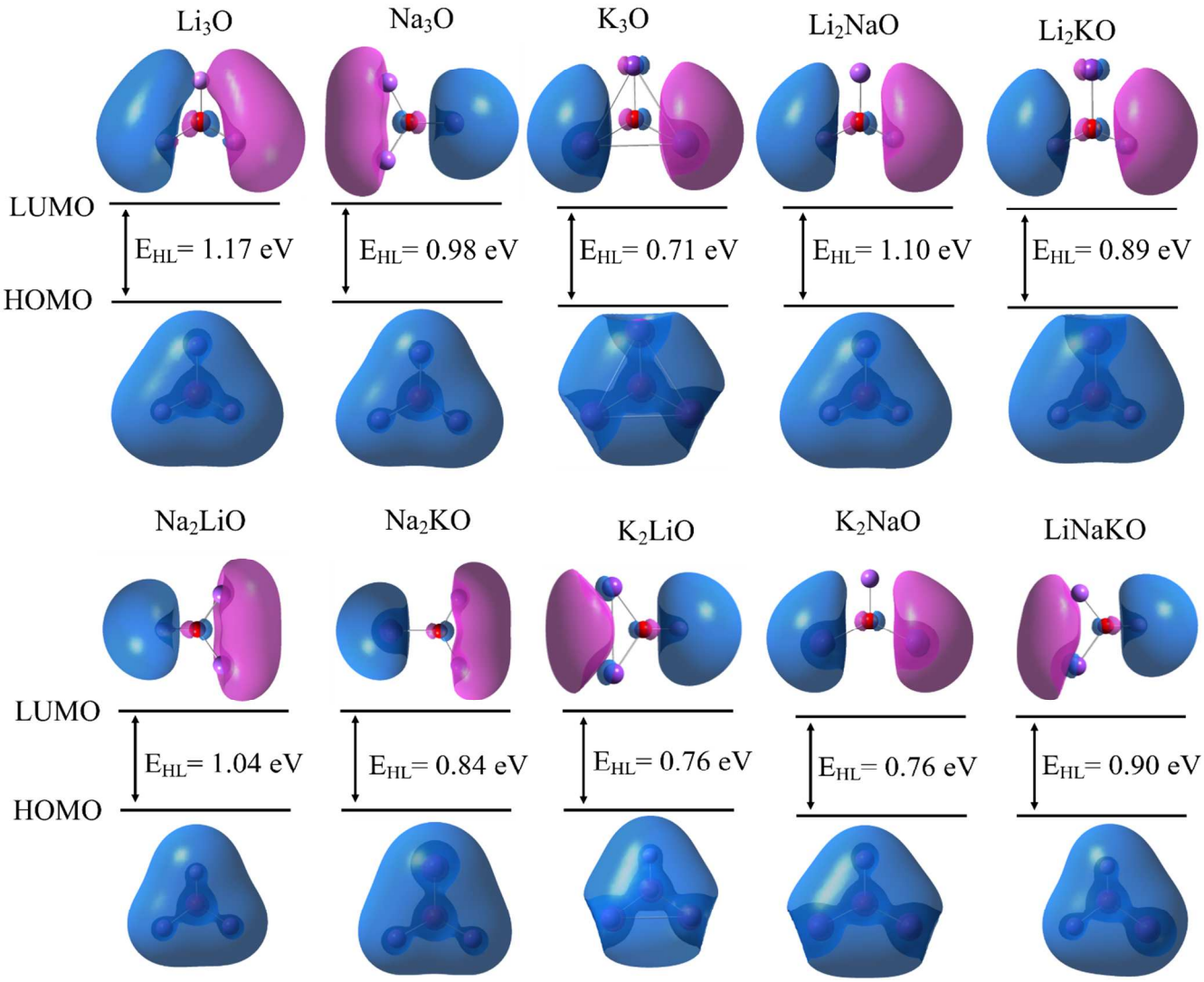

Figure S2. The HOMO, LUMO, and E_{HL} of all the superalkalies M_3O. These orbitals are drawn with an isosurface value of 0.004 e/b^3.

Table S1. Geometrical parameters (bond lengths and bond angles) and real lowest vibrational frequencies (ν_1) of the superalkalis M_3O.

Superalkalis (point group)	(Li-O) (Å)	(Na-O) (Å)	(K-O) (Å)	<LiOLi> (º)	<NaONa> (º)	<KOK> (º)	<LiONa> (º)	<LiOK> (º)	<NaOK> (º)	ν_1 (cm^{-1})
$Li_3O(D_3h)$	1.69	-	-	120.0	-	-	-	-	-	32
$Na_3O(D_3h)$	-	2.06	-	-	120.0	-	-	-	-	35
$K_3O(D_3h)$	-	-	2.38	-	-	120.0	-	-	-	71
$Li_2NaO(C_2V)$	1.68	2.08	-	126.9	-	-	116.5	-	-	46
$Li_2KO(C_2V)$	1.68	-	2.37	112.5	-	-	-	119.7	-	55
$Na_2LiO(C_2V)$	1.66	2.08	-	-	110.3	-	124.8	-	-	54
$Na_2KO(C_2V)$	-	2.07	2.34	-	105.0	-	-	-	127.4	13
$K_2LiO(C_2V)$	1.67	-	2.38	-	-	129.2	-	115.4	-	75
$K_2NaO(C_2V)$	-	2.08	2.37	-	-	131.4	-	-	114.2	85
LiNaKO(Cs)	1.66	2.10	2.36	-	-	-	108.1	133.1	118.6	85

Table S2. Binding energy per atom (E_{bin}), electronic spatial extent $\langle R^2 \rangle$, and IPs for the superalkalis M_3O. ([a] The IP values calculated at MP2 and CCSD(T) are reported in Ref. (57)).

Superalkalis	E_{bin} (kcal mol^{-1})	$<R^2>$ (a.u.)	IP (eV)			
			M06/6-31+g(d)	MP2[a]	CCSD(T)[a]	Exp.
Li_3O	-69.21	235.9	3.54	3.48	3.55	3.54
Na_3O	-55.03	568.1	3.06	3.18	3.26	-
K_3O	-51.72	4228.1	2.49	2.74	2.84	-
Li_2NaO	-64.85	235.9	3.38	3.38	3.45	-
Li_2KO	-64.34	380.2	3.16	3.16	3.24	-
Na_2LiO	-60.17	351.0	3.22	3.30	3.37	-
Na_2KO	-54.28	817.7	2.90	3.02	3.12	-
K_2LiO	-58.62	1025.0	2.81	2.94	3.01	-
K_2NaO	-53.19	1283.7	2.70	2.86	2.98	-
LiNaKO	-59.55	774.9	3.03	3.11	3.19	-

Table S3. Calculated EA for the Al_{13} cluster. All calculations were performed adopting the 6-31g+(d) basis set. |Δ| is the deviation with respect to the experimental data.[91]

DFT Functional	EA (eV)	|Δ| (eV)
PBE	2.93	19
TPSS	2.93	19
BPW91	3.04	16
BP86	3.02	17
MN12L	3.18	12
B3LYP	3.05	16
B3P86	2.86	21
B3PW91	3.11	14
BMK	3.11	14
HSE06	3.09	15
M06	3.45	5
M06L	3.12	14
M062X	3.40	6
MPW1B95	3.32	8
PBE1	3.12	14
TPSSh	3.12	14
WB97XD	3.12	14
LC-WPBE	3.28	9
M11	3.14	13
CAM-B3LYP	3.13	14
Exp.[91]	3.62±0.06	-