The supplementary information for

Designing a new class of excess electron compounds with unique electronic structures and extremely large nonlinear optical responses

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1. Tables

Table S1 The symmetry, the distance between Ca and Li ($d_{Ca\text{-}Li}$, in Å), Li^+-F distance ($d_{Ca\text{-}F}$, in Å), and distance between Li^- and H ($d_{Li\text{-}H}$, in Å) for Ca-**1**-Li optimized by using M06-2X method and different basis sets.

Basis sets	Symmetry	$d_{Ca\text{-}Li}$	$D_{Ca\text{-}F}$	$D_{Li\text{-}H}$
6-31G	C_{3v}	7.481	2.392	2.952
6-31G(d)	C_{3v}	7.986	2.574	3.300
6-31+G(d)	C_{3v}	8.225	2.743	3.345
6-31+G(d,p)	$\boldsymbol{C_{3v}}$	8.224	2.742	3.344
6-31++G(d,p)	C_{3v}	8.224	2.742	3.344
6-311+G(d)	C_{3v}	7.511	2.379	3.047
6-311++G(d,p)	$\boldsymbol{C_{3v}}$	**7.510**	**2.377**	**3.045**
6-311++G(2d,2p)	C_{3v}	7.514	2.383	3.058
6-311++G(3df,3pd)	$\boldsymbol{C_{3v}}$	**7.480**	**2.371**	**3.044**

Table S2 The dipole moments (μ_0, in au), polarizabilities (α_0, in au) first hyperpolarizabilities (β_0, in au) of Ca-**1**-Li calculated by using M06-2X method and different basis sets.

Basis sets	μ_0	α_0	β_0
6-31g	0.325	788	1263260
6-31G(d)	0.254	979	889322
6-31+G(d)	0.643	878	1403449
6-31+G(d,p)	0.677	870	1394763
6-31++G(d,p)	0.707	850	1282893
6-311+G(d)	0.805	770	882447
6-311++G(d,p)	0.828	774	916498
6-311++G(2d,2p)	**0.764**	**830**	**993965**
6-311++G(3df,3pd)	**0.818**	**841**	**1063915**

Table S3 Symmetries, distances between the nether M and axial F atoms ($d_{M\text{-}F}$, in Å), distances between the upper M' and axial H atoms ($d_{M'\text{-}H}$, in Å), distances between the M and M' atoms ($d_{M\text{-}M'}$, in Å), NPA charges on M (Q_M, in |e|) and M' ($Q_{M'}$, in |e|), VIE values (in eV), and complexation energies (E_c, in kcal/mol) of the M-**1**-M' (M = Be, Mg, and Ca; M' = Li, Na, and K) compounds.

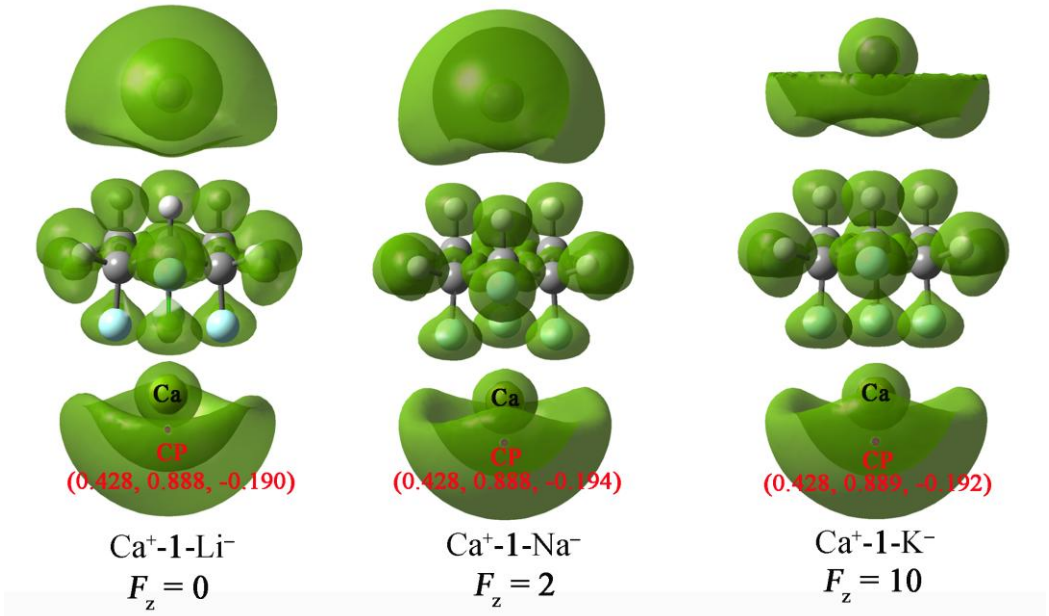
Complex	Symmetry	$d_{M\text{-}F}$	$d_{M'\text{-}H}$	$d_{M\text{-}M'}$	Q_M	$Q_{M'}$	VIE	E_c
Be-**1**-Li	C_{3v}	3.124	3.451	8.754	-0.005	0.029	6.110	-1.59
Be-**1**-Na	C_{3v}	3.136	3.402	8.712	-0.007	0.027	5.893	-2.19
Be-**1**-K	C_{3v}	3.132	3.608	8.929	-0.007	0.056	5.007	-2.83
Mg-**1**-Li	C_{3v}	3.206	3.374	8.765	0.016	0.019	6.006	-2.14
Mg-**1**-Na	C_{3v}	3.156	3.344	8.673	0.042	-0.010	5.862	-2.92
Mg-**1**-K	C_{3v}	3.241	3.632	9.084	-0.001	0.054	5.013	-3.14
Ca-**1**-Li	C_{3v}	2.377	3.045	7.510	0.604	-0.282	5.058	-14.22
Ca-**1**-Na	C_{3v}	2.529	3.346	7.996	0.198	-0.116	5.150	-11.25
Ca-**1**-K	C_{3v}	2.568	3.673	8.393	0.146	-0.047	4.753	-10.59

Table S4. Frequency-dependant first hyperpolarizabilities $\beta(-2\omega, \omega, \omega)$ and $\beta(-\omega, \omega, 0)$ of the Ca^{+}-**1**-M'^{-} (M' = Li, Na, and K) compounds under the critical electric field F_z (in 10^{-4} au).

Ca^{+}-**1**-M'^{-}	F_z	$\beta(-2\omega, \omega, \omega)$			$\beta(-\omega, \omega, 0)$		
		0.000	0.005	0.010	0.000	0.005	0.010
Ca^{+}-**1**-Li^{-}	0	5.97×10^{4}	7.01×10^{4}	7.87×10^{4}	5.97×10^{4}	7.65×10^{5}	6.96×10^{5}
Ca^{+}-**1**-Na^{-}	2	4.72×10^{5}	5.73×10^{5}	1.03×10^{6}	4.72×10^{5}	8.33×10^{5}	1.91×10^{6}
Ca^{+}-**1**-K^{-}	10	7.02×10^{5}	4.80×10^{5}	2.27×10^{6}	7.02×10^{5}	1230172	3.07×10^{5}

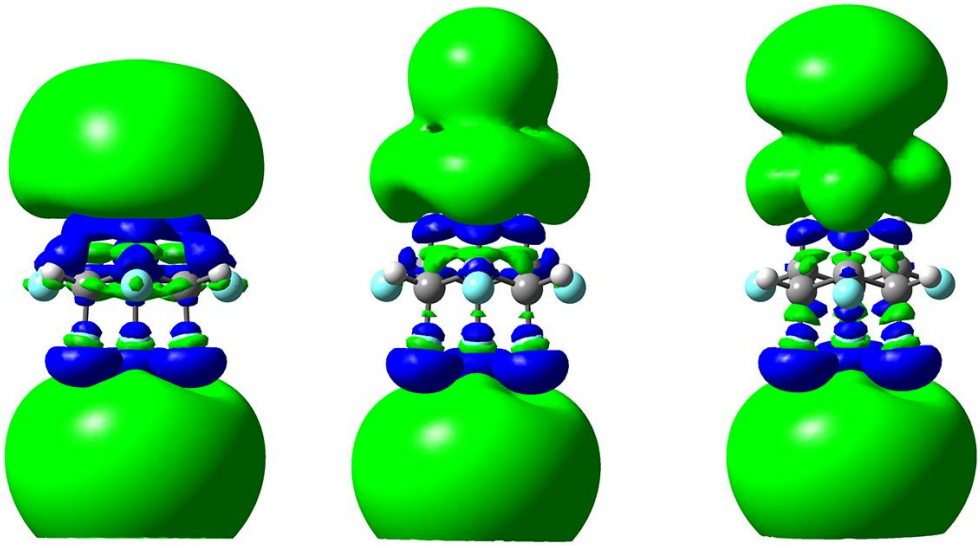
2. Figures

Fig. S1 Electron localization function (ELF = 0.75) isosurface pictures with the critical points (CP) in the relevant basins for Ca^{+}-**1**-M'^{-} (M' = Li, Na, and K) under the critical electric field F_z. The real space function values (density of all electrons, ELF, laplacian of the electron density $\nabla^2\rho$) at the CP of ELF are also shown.



Ca^{+}-**1**-Li^{-} $F_z = 0$ | Ca^{+}-**1**-Na^{-} $F_z = 2$ | Ca^{+}-**1**-K^{-} $F_z = 10$

Fig. S2 Isosurface maps of β_{zzz} density $-z\rho_{zz}^{2}(\mathbf{r})$ for Ca^{+}-**1**-M'^{-} (M' = Li, Na, and K) under the critical electric field F_z with the same isovalue of 80.00, where green and blue surfaces denote positive and negative densities, respectively.

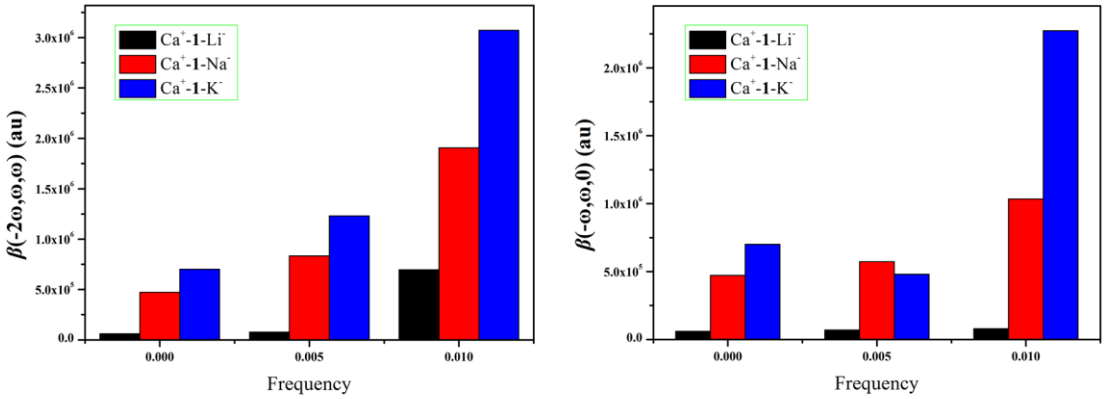


Ca^{+}-**1**-Li^{-} $\boldsymbol{F}_z = 0$

Ca^{+}-**1**-Na^{-} $\boldsymbol{F}_z = 2$

Ca^{+}-**1**-K^{-} $\boldsymbol{F}_z = 10$

Fig. S3 Frequency-dependent first hyperpolarizability $\beta(-2\omega,\omega,\omega)$ and $\beta(-\omega,\omega,0)$ of Ca^{+}-**1**-M'^{-} (M' = Li, Na, and K) under F_z.



3. Cartesian coordinates

(1) The optimized structure of Ca^{+}-1-Li^{-} without F_z

C	1.23096800	0.71070000	-1.09287000
C	0.00000000	1.44924700	-0.63650100
C	-1.23096800	0.71070000	-1.09287000
C	-1.25508500	-0.72462400	-0.63650100
C	0.00000000	-1.42140000	-1.09287000
C	1.25508500	-0.72462400	-0.63650100
H	0.00000000	2.48140700	-0.98800900
H	1.21865800	0.70359300	-2.20948000
H	-2.14896200	-1.24070400	-0.98800900
H	0.00000000	-1.40718500	-2.20948000
H	2.14896200	-1.24070400	-0.98800900
H	-1.21865800	0.70359300	-2.20948000
F	-1.34070200	-0.77405500	0.79633900
F	0.00000000	1.54810900	0.79633900
F	1.34070200	-0.77405500	0.79633900
F	2.36123400	1.36325900	-0.66851200
F	0.00000000	-2.72651800	-0.66851200
F	-2.36123400	1.36325900	-0.66851200
Li	0.00000000	0.00000000	-4.90967600
Ca	0.00000000	0.00000000	2.59994300

(2) The optimized structure of Ca^{+}-1-Na^{-} under $F_z = 2 \times 10^{-4}$ au

C	-1.23281000	0.70906500	-0.78668300
C	-0.00039600	1.44832200	-0.32984800
C	1.23242600	0.70963200	-0.78648000
C	1.25577800	-0.72651000	-0.32650300
C	0.00029700	-1.42778400	-0.78070900
C	-1.25556700	-0.72708600	-0.32667000
H	-0.00059800	2.47969000	-0.68311200
H	-1.22739300	0.70544100	-1.90058600
H	2.14979900	-1.24298600	-0.67664900
H	0.00038500	-1.43005400	-1.89427400
H	-2.14930900	-1.24397900	-0.67691000
H	1.22718900	0.70601300	-1.90039500
F	1.33817100	-0.77013000	1.10290900
F	-0.00054900	1.54545300	1.09926200
F	-1.33811000	-0.77069800	1.10272300
F	-2.36248500	1.36044100	-0.35985000
F	0.00056900	-2.72831300	-0.34287500
F	2.36174200	1.36151500	-0.35947000
Ca	-0.00008600	0.00274200	2.92788000
Na	0.00094700	0.03922700	-4.78329000

(3) The optimized structure of Ca^{+}-1-K^{-} under $F_z = 10 \times 10^{-4}$ au

C	0.00009500	1.41716500	-0.44922100
C	1.25590000	0.71965300	0.01059500
C	1.23372400	-0.72163700	-0.43607900
C	0.00000600	-1.45570400	0.02797900
C	-1.23355900	-0.72162500	-0.43647300
C	-1.25586400	0.71966800	0.01019000
H	2.14931200	1.23283800	-0.34634300
H	0.00025100	1.41642400	-1.56209700
H	0.00005800	-2.49091900	-0.31398800
H	-1.23475600	-0.73149900	-1.54889000
H	-2.14915500	1.23286000	-0.34704500
H	1.23527200	-0.73153300	-1.54848200
F	-0.00022000	-1.53579800	1.45590900
F	1.33899700	0.77604200	1.43730500
F	-1.33942300	0.77607600	1.43686400
F	0.00003600	2.72081300	-0.02124400
F	-2.36202300	-1.36876900	-0.00037900
F	2.36204300	-1.36878800	0.00038000
Ca	-0.00060400	0.02526100	3.28125900
K	-0.00008900	0.08946900	-4.96446000