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

Novel Inorganic Aromatic Mixed-Valent Superalkali Electrides CaN_3Ca: Alkaline-Earth-Based High-Sensitive Multi-State Nonlinear Optical Molecular Switch

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Contents

CaN_3Ca (D_{3h})

N	0.00000000	0.87985560	0.00000000
N	0.76197714	-0.43992780	0.00000000
N	-0.76197714	-0.43992780	0.00000000
Ca	0.00000000	0.00000000	2.03126698
Ca	0.00000000	0.00000000	-2.03126698

CaN_3Ca (C_{3v})

N	-0.00000000	0.87712973	-0.04890368
N	-0.75961662	-0.43856486	-0.04890368
N	0.75961662	-0.43856486	-0.04890368
Ca	0.00000000	0.00000000	-2.01621761
Ca	0.00000000	0.00000000	2.06756647

MgN_3Mg (D_{3h})

N	0.00000000	0.91721200	0.00000000
N	0.79432900	-0.45860600	0.00000000
N	-0.79432900	-0.45860600	0.00000000
Mg	0.00000000	0.00000000	1.79780000
Mg	0.00000000	0.00000000	-1.79780000

MgN_3Mg (C_{3v})

N	-0.78572904	0.45364087	-0.03662530
N	0.00000000	-0.90728175	-0.03662530
N	0.78572904	0.45364087	-0.03662530
Mg	-0.00000000	-0.00000000	-1.78057440
Mg	-0.00000000	-0.00000000	1.84559043

BeN_3Be (D_{3h})

N	0.00000000	0.92246100	0.00000000
N	0.79887500	-0.46123100	0.00000000
N	-0.79887500	-0.46123100	0.00000000
Be	0.00000000	0.00000000	1.35473200
Be	0.00000000	0.00000000	-1.35473200

BeN_3Be (C_{3v})

N	0.00000000	0.90977608	-0.02257123
N	-0.78788920	-0.45488804	-0.02257123
N	0.78788919	-0.45488804	-0.02257123
Be	0.00000000	0.00000000	-1.30935477
Be	0.00000000	0.00000000	1.42785372

Table S1. Static first hyperpolarizability (β_0, au) of **1** and **3** of CaN_3Ca at the MP2/6-311+G(3df) level in different applied electric fields (*EEF*, au).

EEF	**1**	**3**
0.0001	23503	23503
0.0005	24308	24308
0.0007	25362	25362
0.0010	27876	27876
0.0012	30390	30390
0.0015	36113	36113
0.0020	56880	56880

Table S2. Optimized structural parameters (in Å), point group (PG), characteristic vibrational frequencies (ω_c, in cm^{-1}), vertical ionization energy (VIE, in eV), energies of HOMOs (ε_{HOMO}, in eV), and HOMO-LUMO gaps (ε_{gap}, in eV) of MN_3M (M = Be, Mg, and Ca).

	Structural Parameters						ω_c	VIE	ε_{HOMO}	ε_{gap}
	PG	M1-N	M2-N	N-N	L_1[a]	L_2[b]				
M = Ca										
1	C_{3v}	2.291	2.154	1.519	2.068	2.016	611	3.90	-3.89	1.78
2	D_{3h}	2.214	2.214	1.524	2.031	2.031	883	3.62	-3.23	3.01
3	C_{3v}	2.154	2.291	1.519	2.016	2.068	611	3.90	-3.89	1.78
M = Mg										
1	C_{3v}	2.089	1.965	1.571	1.882	1.743	699	5.59	-5.70	4.05
2	D_{3h}	2.018	2.018	1.589	1.798	1.798	923	5.46	-5.03	2.81
3	C_{3v}	1.965	2.089	1.571	1.743	1.882	699	5.59	-5.70	4.05
M = Be										
1	C_{3v}	1.712	1.576	1.576	1.450	1.287	923	6.53	-12.13	-11.02
2	D_{3h}	1.639	1.639	1.598	1.305	1.305	1590	6.23	-12.34	-12.00
3	C_{3v}	1.576	1.712	1.576	1.287	1.450	923	6.53	-12.13	-11.02

[a] Distance of M1-centroid of the N_3^{3-} ring, [b] Distance of M2-centroid of the N_3^{3-} ring.

Table S3 Distances of Ca-centroid of the N_3^{3-} ring (L_1 and L_2, in Å) of **1** under the effect of external electric fields (*EEF*s).

EEF/ (10^4 au)	L_1	L_2	*EEF*/ (10^4 au)	L_1	L_2
0	2.116	1.967	65	2.075	1.998
1	2.116	1.967	70	2.071	2.001
2	2.116	1.967	75	2.065	2.005
3	2.116	1.967	80	2.057	2.009
4	2.115	1.969	85	2.045	2.014
5	2.114	1.969	90	2.017	2.027
6	2.114	1.970	95	2.002	2.035
7	2.114	1.970	100	1.995	2.040
8	2.113	1.970	105	1.990	2.044
9	2.113	1.971	110	1.987	2.047
10	2.112	1.971	115	1.985	2.050
11	2.110	1.972	120	1.983	2.054
12	2.110	1.972	125	1.981	2.056
13	2.109	1.973	130	1.980	2.059
14	2.109	1.973	135	1.978	2.062
15	2.108	1.974	140	1.977	2.065
16	2.108	1.974	145	1.975	2.068
17	2.107	1.975	150	1.974	2.071
18	2.106	1.975	155	1.973	2.074
19	2.106	1.975	160	1.971	2.077
20	2.105	1.976	165	1.970	2.080
25	2.102	1.978	170	1.969	2.083
30	2.099	1.980	175	1.968	2.086
35	2.096	1.983	180	1.966	2.089
40	2.093	1.985	185	1.965	2.092
45	2.090	1.988	190	1.964	2.095
50	2.087	1.990	195	1.963	2.099
60	2.083	1.993	200	1.962	2.102

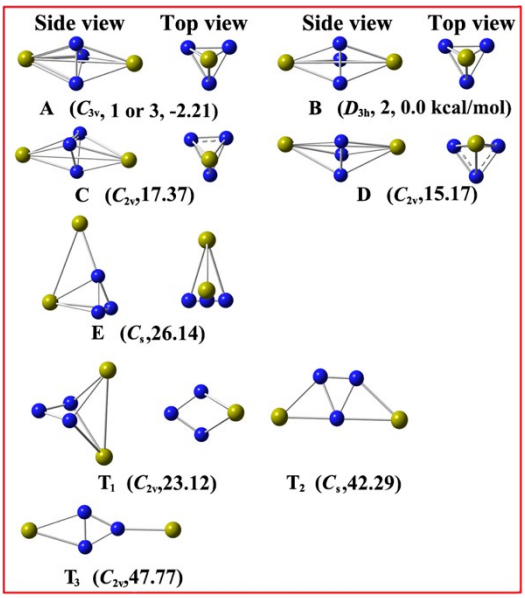

Fig. S1. Isomers of CaN3Ca at the B3LYP/6-311+G(3df) level. Relative energy in parentheses. T_1 ~ T_3 are transition states due to an imaginary frequency of each of them.

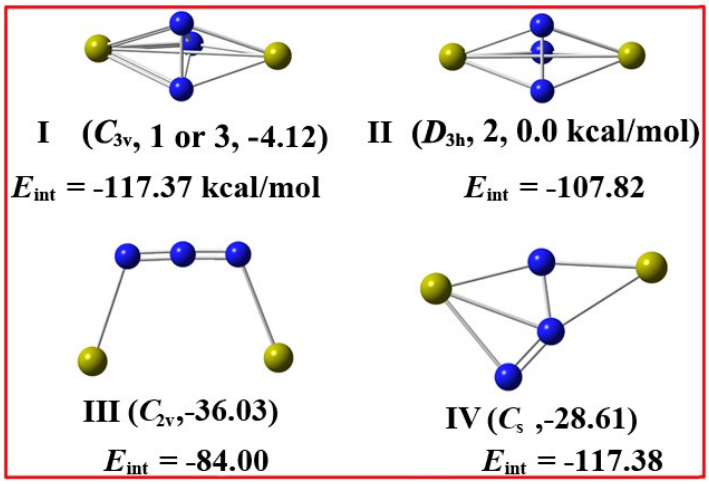

Fig. S2. Relative energies and interaction energies for linear and cyclic Ca2N3 compounds at the CCSD(T) /6-311+G(3df)//B3LYP/6-311+G(3df) level.

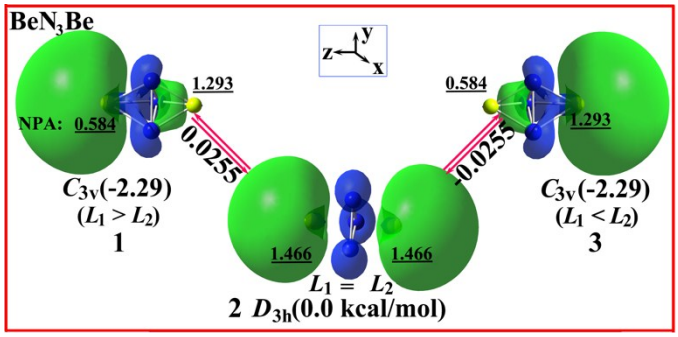

Fig. S3. Different configurations (**1**, **2**, and **3**) of BeN_3Be. . Underlined values are NPA charges. Molecular orbitals at the isovalue of 0.02 au.

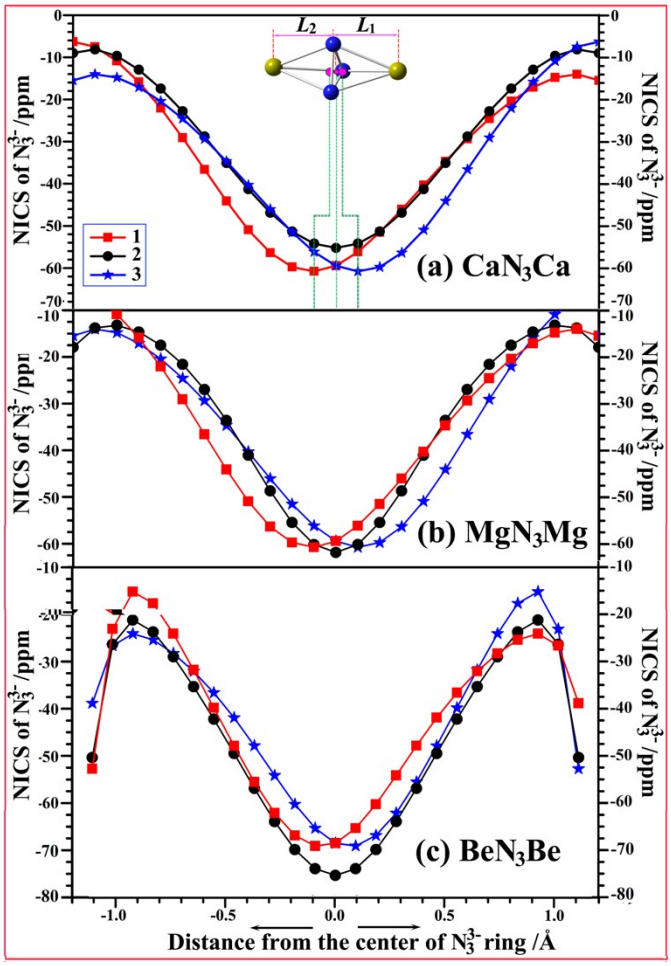

Fig. S4. Relationship between NICS values and distance from the center of the N_3 subunit in **1**, **2**, and **3**.