Supporting Information

Theoretical insights into single-pole quadruple-throw (SP4T) inorganic nonlinear optics molecular switch of $Na(HCN)_3Na$: from superalkali to superalkalides

Zhi-Jun Wang[a], Yin-Feng Wang[*,a], Jia-Mei Zeng[a], Wen Zhang[a], Xue-Xia Liu[a], Jia Li[a], Zhi-Ru Li[*,b]

[a.] *Jiangxi Province Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering. Jinggangshan University, Ji'an, Jiangxi 343009 (P.R. China). E-mail: cyclont@yeah.net*

[b.] *Institute of Theoretical Chemistry, Jilin University, Changchun 130023 (P.R. China) E-mail: lzr@jlu.edu.cn*

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Optimized Cartesian coordinates at the MP2/6-311+G(3df,3pd) level.

$Na(HCN)_3Na$

1 D_{3h}

Na	0.00000000	0.00000000	1.96214529
Na	0.00000000	-0.00000000	-1.96214529
C	-2.74349518	-1.58395768	0.00000000
C	0.00000000	3.16791537	0.00000000
C	2.74349518	-1.58395768	0.00000000
N	0.00000000	2.00184019	0.00000000
N	-1.73364446	-1.00092010	0.00000000
N	1.73364446	-1.00092010	0.00000000
H	3.66673967	-2.11699314	0.00000000
H	-3.66673967	-2.11699314	-0.00000000
H	0.00000000	4.23398628	0.00000000

2 C_{3v}

Na	3.75841187	-0.00046224	0.00026655
Na	-2.33858407	0.00009357	-0.00015826
C	0.11564042	-1.77425474	-1.41739038
C	0.11556798	-0.34022641	2.24512516
C	0.11619634	2.11503343	-0.82823149
N	-1.01038218	-0.29475051	1.94673122
N	-1.01026570	-1.53844021	-1.22872307
N	-1.00946065	1.83306748	-0.71754141
H	1.16959612	2.30969747	-0.90472521
H	1.16933812	-1.93653936	-1.54723548
H	1.16929128	-0.37155371	2.45048264

3 C_{3v}

C	1.30264329	-0.06014141	3.19620303
C	1.25252363	2.81757172	-1.55060293
C	1.28447454	-2.73906955	-1.66540023
N	0.93636763	1.83631727	-1.01078224
N	0.96642111	-0.03972004	2.08231189
N	0.95561661	-1.78488396	-1.08609457
H	1.57087653	-3.61665401	-2.19813392
H	1.59585026	-0.07888542	4.22073414
H	1.52711475	3.71993823	-2.04690926
Na	-0.47256733	-0.00358333	0.00272174
Na	-3.86748064	-0.01610360	0.01955683

2a C_{3v}

Na	-3.64536500	0.00128000	0.00290200
Na	2.19400100	-0.00010500	-0.00206900

C	-0.11120500	2.31404600	-0.14009800
C	-0.10937200	-1.03624000	2.07352500
C	-0.11538800	-1.27931500	-1.93442800
N	1.02669900	-0.91744500	1.83529500
N	1.02492300	2.04856300	-0.12438700
N	1.02019600	-1.13119800	-1.71092000
H	-1.17692000	-1.37403700	-2.07722000
H	-1.17341400	2.48184800	-0.14985600
H	-1.17160100	-1.11111600	2.22400000

3a C_{3v}

Na	-0.05002200	0.03672100	3.16767200
Na	-0.00133300	-0.00316400	-0.26999200
C	-3.11172600	-0.15680100	-0.39657800
C	1.43729900	2.75493300	-0.36144000
C	1.70024000	-2.61655600	-0.30704700
N	1.12552600	2.12513800	-1.29200300
N	-2.39354700	-0.12973800	-1.31479300
N	1.32719600	-2.03204200	-1.24449200
H	2.04374500	-3.15494900	0.54749900
H	-3.77238500	-0.18187400	0.44065600
H	1.72443200	3.33473200	0.48676200

$Li(HCN)_3Li$

2 C_{3v}

C	1.11830035	1.98330739	0.32268934
C	1.15888026	-1.95952177	0.32509860
C	-2.27684654	-0.02306537	0.32439455
N	0.89859177	-1.52108646	-0.72353079
N	0.86740257	1.53796028	-0.72533946
N	-1.76650445	-0.01892057	-0.72399518
H	-2.75325628	-0.02705485	1.28049215
H	1.35238933	2.39913033	1.27841821
H	1.40185185	-2.36899035	1.28134561
Li	-0.00044709	-0.00098496	-1.63925616
Li	0.00064091	0.00329186	3.48482518

3 C_{3v}

C	-2.67907583	-1.33400838	-0.45111695
C	2.49494593	-1.65210373	-0.45238826
C	0.18348514	2.98644873	-0.45203083
N	1.55536225	-1.03031523	-0.16431055
N	-1.67021601	-0.83204214	-0.16361624
N	0.11429408	1.86185979	-0.16402667

H	0.24751111	4.02568117	-0.67909821
H	-3.61124264	-1.79796360	-0.67799664
H	3.36314080	-2.22676871	-0.67967766
Li	0.00005614	-0.00042811	0.76928565
Li	0.00273619	0.00059960	3.76860204

$K(HCN)_3K$

2 C_{3v}

C	0.04971604	-0.91437906	2.04831019
C	0.05026448	-1.31838968	-1.81520395
C	0.04968378	2.23257767	-0.23321805
N	1.20092868	-1.20700027	-1.66161062
N	1.20039198	-0.83703527	1.87511441
N	1.20022663	2.04318225	-0.21311292
H	-1.02130584	2.33410841	-0.24409842
H	-1.02140456	-0.95554554	2.14065957
H	-1.02084087	-1.37773747	-1.89719439
K	2.96897145	0.00034303	0.00002305
K	-4.18188016	-0.00001177	-0.00009841

Table S1. Convergence of β_{zzz}^{SOS} (and β_0^{SOS}) as a function of the number of excited states (N) of **2** of $Na(HCN)_3Na$ at M06-2X/6-311++G(3df,3pd) level.

CES	$\Delta\mu_i^z$	μ_{0i}^z	ΔE	f_0	$\beta_{zzz}^{C\text{-}SOS}$	$\beta_{zzz}^{CT\text{-}SOS}$	$\Sigma\beta_{zzz}^{C}$	β_{zzz}^{SOS}	β_{zzz}^{e}	β_0^{SOS}	β_0^{e}
	N = 250										
4	-4.1770	-1.7403	1.4563	0.1081	-26501	15284	-38638	-16711	-7255	3333	10940
7	-4.0964	-2.3899	1.9470	0.2725	-27421						
	N = 200										
4	-4.1856	-1.7366	1.4568	0.1076	-26423	15193	-38766	-16922	-7255	3436	10940
7	-4.1158	-2.3889	1.9467	0.2722	-27535						
	N = 150										
4	-4.1856	-1.7366	1.4568	0.1076	-26424	15193	-38766	-16865	-7255	3429	10940
7	-4.1158	-2.3889	1.9467	0.2722	-27535						
	N = 100										
4	-4.1856	-1.7366	1.4568	0.1076	-26424	15193	-38766	-16965	-7255	3446	10940
7	-4.1158	-2.3889	1.9467	0.2722	-27536						
	N = 50										
4	-4.1856	-1.7366	1.4568	0.1076	-26424	15193	-38766	-16110	-7255	2398	10940
7	-4.1158	-2.3889	1.9467	0.2722	-27535						

Table S2. Crucial excited state (CES) and its z-component of transition dipole moment (μ_{0i}^{z}), variation of z-component of dipole moment between ground state and CES ($\Delta\mu_z$, a.u), transition energy (ΔE, eV) of CES, oscillator strength (f_0), static first hyperpolarizability (β_0, a.u.) and it z-component (β_{zzz}, a.u.) and their values obtained by sum-over-states calculation (β_0^{SOS} and β_{zzz}^{SOS}, a.u.), contribution of individual CES to β_{zzz}^{SOS} ($\beta_{zzz}^{C\text{-}SOS}$, a.u.), and cross term contribution between two CESs ($\beta_{zzz}^{CT\text{-}SOS}$) of **2** of $Na(HCN)_3Na$ using different methods with 6-311++G(3df,3pd) basis set.

CES	$\Delta\mu_z$	μ_{0i}^{z}	ΔE	f_0	$\beta_{zzz}^{C\text{-}SOS}$	$\beta_{zzz}^{CT\text{-}SOS}$	β_{zzz}^{SOS}	β_{zzz}^{e}	β_0^{SOS}	β_0^{e}
M06-2X										
4	-4.1856	1.7366	1.4568	0.1076	-26424	15193	-16965	-7255	3446	10940
7	-4.1158	-2.3889	1.9467	0.2722	-27536					
PBE0										
4	-3.5984	-2.2777	1.4845	0.1887	-37635	22804	-9608	-7255	8578	10940
10	1.3287	-2.4242	2.2094	0.3181	7106					
B3LYP										
4	-3.4252	2.2120	1.4174	0.1699	-37059	15813	-28665	-7255	13634	10940
10	-1.3309	-2.1953	2.1681	0.2560	-6062					
CAM-B3LYP										
4	-4.2242	2.0870	1.5313	0.1634	-34859	18081	-9539	-7255	6195	10940
8	-1.1707	-2.3835	2.1989	0.3060	-6111					
LC-BLYP										
4	-4.9230	1.9908	1.7744	0.1723	-27532	25236	-2685	-7255	16678	10940
7	-0.3365	2.4981	2.2706	0.3472	-1809					
WB97X-D										
3	3.2341	-2.5192	1.6550	0.2573	33291	-26979	-2775	-7255	21006	10940
7	-1.9103	-2.3386	2.2907	0.3069	-8845					

Table S3. Crucial excited state (CES) and its z-component of transition dipole moment (μ_{0i}^{z}), variation of z-component of dipole moment between ground state and CES ($\Delta\mu_z$, a.u), transition energy (ΔE, eV) of CES, oscillator strength (f_0) and its z-component (f_0^{z}), static first hyperpolarizability (β_0, a.u.) and it z-component (β_{zzz}, a.u.) and their values obtained by sum-over-states calculation (β_0^{SOS} and β_{zzz}^{SOS}, a.u.), contribution of individual CES to β_{zzz}^{SOS} ($\beta_{zzz}^{C\text{-}SOS}$, a.u.), and cross term contribution between two CESs ($\beta_{zzz}^{CT\text{-}SOS}$) of **2** of $Na(HCN)_3Na$ using PBE0 method with different basis sets.

CES	$\Delta\mu_z$	μ_{0i}^{z}	ΔE	f_0	$\beta_{zzz}^{C\text{-}SOS}$	$\beta_{zzz}^{CT\text{-}SOS}$	β_{zzz}^{SOS}	β_{zzz}^{e}	β_0^{SOS}	β_0^{e}
6-311++G(3df,3pd)										
4	-3.5984	-2.2777	1.4845	0.1887	-37635	22804	-9608	-7255	8578	10940
10	1.3287	-2.4242	2.2094	0.3181	7106					
6-311++G(2d,2p)										
4	-3.6172	2.2880	1.4845	0.1904	-38173	10045	-12018	-7255	6521	10940
10	1.0358	-2.4003	2.2120	0.3124	5419					
aug-cc-pVTZ										
4	-3.5936	-2.2765	1.4857	0.1886	-37484	21685	-11046	-7255	6215	10940
10	0.8719	-2.3965	2.2105	0.3110	4552					
aug-pc-2										
4	-3.5925	2.2858	1.4857	0.1902	-37779	21897	-12244	-7255	5337	10940
10	0.2223	-2.4096	2.2239	0.3164	1159					
ma-TZVP										
4	-3.6821	-2.2837	1.4844	0.1896	-38718	22781	-11939	-7255	6554	10940
10	0.5802	-2.3959	2.2075	0.3105	3036					
POL										
4	-3.6148	-2.2865	1.4813	0.1897	-38265	22641	10997	-7255	6926	10940
10	1.3682	-2.3870	2.2043	0.3077	7128					

Table S4. Crucial excited state (CES) and its z-component of transition dipole moment (μ_{0i}^{z}), variation of z-component of dipole moment between ground state and CES ($\Delta\mu_z$, a.u), transition energy (ΔE, eV) of CES, oscillator strength (f_0), static first hyperpolarizability (β_0, a.u.) and it z-component (β_{zzz}, a.u.) and their values obtained by sum-over-states calculation (β_0^{SOS} and β_{zzz}^{SOS}, a.u.), contribution of individual CES to β_{zzz}^{SOS} ($\beta_{zzz}^{C\text{-}SOS}$, a.u.), and cross term contribution between two CESs ($\beta_{zzz}^{CT\text{-}SOS}$) of **2** of $Na(HCN)_3Na$ using CAM-B3LYP method with different basis sets.

CES	$\Delta\mu_z$	μ_{0i}^{z}	ΔE	f_0	$\beta_{zzz}^{C\text{-}SOS}$	$\beta_{zzz}^{CT\text{-}SOS}$	β_{zzz}^{SOS}	β_{zzz}^{e}	β_0^{SOS}	β_0^{e}
6-311++G(3df,3pd)										
4	-4.2242	2.0870	1.5313	0.1634	-34859	18081	-9539	-7255	6195	10940
8	-1.1707	-2.3835	2.1989	0.3060	-6111					
6-311++G(2d,2p)										
4	-4.2100	2.1006	1.5346	0.1659	-35046	17853	-11184	-7255	4691	10940
8	-1.2229	-2.3731	2.1995	0.3035	-6324					
aug-cc-pVTZ										
4	-4.1900	2.0908	1.5292	0.1638	-34799	17389	-10197	-7255	4988	10940
8	-1.4944	-2.3635	2.1927	0.3001	-7713					
aug-pc-2										
4	-4.2125	2.0926	1.5301	0.1642	-35006	17616	-10681	-7255	4131	10940
8	-1.8960	-2.3693	2.2052	0.3033	-9723					
ma-TZVP										
4	-4.2907	2.1019	1.5371	0.1664	-35646	18340	-11133	-7255	4562	10940
8	-1.6309	-2.3686	2.1955	0.3018	-8433					
POL										
4	-4.2502	2.1048	1.5277	0.1658	-35843	18813	-10586	-7255	4987	10940
8	-0.9268	2.3639	2.1975	0.3008	-4764					

Table S5. Crucial excited state (CES) and its z-component of transition dipole moment (μ_{0i}^{z}), variation of z-component of dipole moment between ground state and CES ($\Delta\mu_z$, a.u), transition energy (ΔE, eV) of CES, oscillator strength (f_0) and its z-component (f_0^z), static first hyperpolarizability (β_0, a.u.) and it z-component (β_{zzz}, a.u.) and their values obtained by sum-over-states calculation (β_0^{SOS} and β_{zzz}^{SOS}, a.u.), contribution of individual CES to β_{zzz}^{SOS} ($\beta_{zzz}^{C\text{-}SOS}$, a.u.), and cross term contribution between two CESs ($\beta_{zzz}^{CT\text{-}SOS}$) at PBE0/6-311++G(3df,3pd). level

	CES	$\Delta\mu_z$	μ_{0i}^{z}	ΔE	f_0	f_0^z	$\beta_{zzz}^{C\text{-}SOS}$	$\beta_{zzz}^{CT\text{-}SOS}$	β_{zzz}^{SOS}	β_{zzz}	β_0^{SOS}	β_0
	$Na(HCN)_3Na$											
	11	0.0000	-2.5101	1.6439	0.2538	0.2538	0.00					
1	19	0.0000	-1.4876	2.1523	0.1167	0.1167	0.00	0.00	0.00	0.00	188	417
	13,14	0.000	0.000	1.7267	0.3178	0.0000	0.00					
	4	-5.2780	-1.8715	1.5523	0.1332	0.1332	-34082					
2a	10	1.6686	2.3587	2.2709	0.3096	0.3096	7997	20271	-9925	-6633	6113	10603
	8,9	-2.6386	0.0035	2.2146	0.3231	0.0000	-0.32					
	4	-3.5984	-2.2777	1.4845	0.1887	0.1887	-37635					
	10	1.3287	-2.4242	2.2094	0.3181	0.3181	7106	22804				
2	8,9	4.8301	0.0007	2.1836	0.2387	0.0000	0.01		-9608	-7255	8578	10940
	11,12	6.9324	0.0024	2.3660	0.1328	0.0000	0.04					
	9	1.7820	2.8250	2.1734	0.4251	0.4249	13375					
3a	7,8	-0.2509	0.0584	2.0999	0.2691	0.0002	-0.88		15206	9488	16804	8988
	10	2.7266	2.6999	2.0139	0.3597	0.3597	21771					
3	8,9	-7.0148	-0.0050	1.7021	0.1100	0.0000	-0.46		39459	5785	50104	3620
	11,12	-1.0820	0.0022	2.0676	0.2888	0.0000	-0.06					
	$Li(HCN)_3Li$											
	3	3.2262	-2.6624	1.5842	0.2751	0.2751	40482					
2	10	-2.6205	-1.9288	2.3733	0.2163	0.2163	-7689	-38233	-5396	-6818	7703	135
	8,9	2.8684	0.0007	2.2813	0.2964	0.0000	0.00					
	7	8.9446	-1.5799	1.6349	0.1000	0.1000	37110					
	10	-3.7399	-1.9820	2.1076	0.2029	0.2028	-14694	-27678				
3	8,9	5.6566	0.0019	1.7521	0.1119	0.0000	0.03		28264	2845	39105	1418
	11,12	-0.0426	0.0131	2.1238	0.2316	0.0000	-0.00					
	$K(HCN)_3K$											
	4	4.4207	2.1395	1.1650	0.1306	0.1306	66237					
	10	-4.3533	3.0808	1.7092	0.3975	0.3975	-62837	-33902				
2	5,6	-1.9802	-0.0012	1.4299	0.1140	0.0000	-0.01		-54413	-24437	14709	26375
	11,12	-4.4579	0.0115	1.9430	0.1947	0.0000	-0.83					

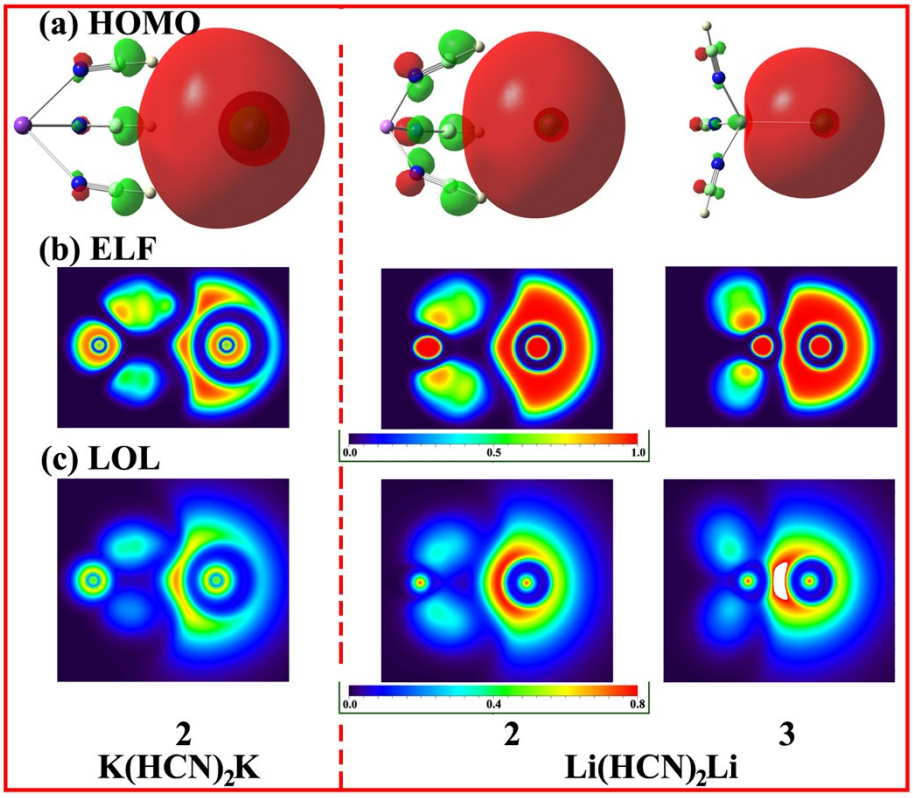

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Fig. S1. HOMOs, ELF and LOL maps of $M(HCN)_3M$. (M = Li or K) (a) HOMO, (b) ELF, and (b) LOL. HOMOs have the isovalue of 0.02 a.u.