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Static second hyperpolarizability of inverse sandwich compounds (M_1-C_5H_5-M_2) of alkali (M_1=Li, Na, K) and alkaline earth metals (M_2= Be, Mg, Ca)

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Supplementary Information

Table S1: HF/6-311++G(d,p) calculated second hyperpolarizability (10^4 au) obtained at different field strengths (au)

	0.0007 au		0.0008 au		0.0009 au		0.0010 au	
	γ_{zzzz}	γ_{av}	γ_{zzzz}	γ_{av}	γ_{zzzz}	γ_{av}	γ_{zzzz}	γ_{av}
Li-Cp-Be	24.1	11.8	24.11	11.8	24.2	11.8	24.1	11.8
Na-Cp-Be	334	651	336	654	340	658	344	662
K-Cp-Be	267	86.9	270	87.6	273	88.4	277	89.2
Li-Cp-Mg	59.4	31.5	59.6	31.6	59.9	31.7	60.2	31.8
K-Cp-Mg	294	109	299	111	304	112	310	113

Table S2: Axial components and the average value of second hyperpolarizability (10^6 au) of M_1-Cp-M_2 complexes calculated using the finite field method and cubic response function at the HF/6-311++G(d,p) level

	HF				Cubic response			
	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{av}	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{av}
Li-Cp-Be	0.06	0.06	0.24	0.11	0.06	0.06	0.24	0.12
Li-Cp-Mg	0.22	0.22	0.59	0.31	0.22	0.22	0.59	0.31
Li-Cp-Ca	3.63	3.63	18.51	6.89	3.46	3.46	16.23	6.29
Na-Cp-Be	6.16	6.16	3.57	6.63	6.02	6.02	3.52	6.54
Na-Cp-Mg	0.43	0.43	3.92	1.21	0.43	0.43	3.73	1.17
Na-Cp-Ca	8.78	8.78	91.94	28.77	8.39	8.39	112.02	32.52
K-Cp-Be	0.27	0.27	2.70	0.87	0.27	0.27	2.57	0.85
K-Cp-Mg	0.54	0.54	2.99	1.10	0.54	0.54	2.80	1.06
K-Cp-Ca	10.16	10.16	244.87	63.75	9.58	9.58	219.34	57.21

Table S3: Axial components and the average value of second hyperpolarizability (10^6 au) of M_1-Cp-M_2 complexes obtained at HF and MP2 levels for the 6-311++G(d,p) basis set

	HF				MP2			
	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{av}	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{av}
Li-Cp-Be	0.06	0.06	0.24	0.11	0.09	0.09	0.35	0.17
Li-Cp-Mg	0.22	0.22	0.59	0.31	0.19	0.19	0.81	0.34
Li-Cp-Ca	3.63	3.63	18.51	6.89	3.03	3.03	43.48	11.83
Na-Cp-Be	6.16	6.16	3.57	6.63	1.33	1.33	0.24	7.91
Na-Cp-Mg	0.43	0.43	3.92	1.21	0.38	0.38	7.61	1.99
Na-Cp-Ca	8.78	8.78	91.94	28.77	7.37	7.37	77.54	26.65
K-Cp-Be	0.27	0.27	2.70	0.87	0.26	0.26	16.44	3.09
K-Cp-Mg	0.54	0.54	2.99	1.10	0.40	0.40	15.42	2.90
K-Cp-Ca	10.16	10.16	244.87	63.75	4.00	4.00	253.44	55.64

Table S4: γ_{zzzz} (10^6 au) of Cp-M_1 and M_1-Cp-M_2 complexes obtained at the MP2/6-311++G(3df,3pd) level

Complexes	γ_{zzzz}
Li-Cp	0.04
Na-Cp	0.08
K-Cp	6.01
Li-Cp-Be	0.32
Li-Cp-Mg	0.80
Li-Cp-Ca	42.65
Na-Cp-Be	22.07
Na-Cp-Mg	6.91
Na-Cp-Ca	131.44
K-Cp-Be	17.81
K-Cp-Mg	16.49
K-Cp-Ca	201.12

Table S5: MP2 Calculated longitudinal component of first hyperpolarizability (β_{zzz}, 10^3 au) of M_1-Cp-M_2 complexes obtained at BS-I (6311++G(3df,3pd)), BS-II (Sadlej's Pol), BS-III (Def2-TZVPPD) and BS-IV (aug-cc-pVTZ) basis sets

	BSSE corrected β_{zzz}				BSSE uncorrected β_{zzz}				%BSSE effect			
	BS-I	BS-II	BS-III	BS-IV	BS-I	BS-II	BS-III	BS-IV	BS-I	BS-II	BS-III	BS-IV
Li-Cp-Be	0.079	-0.3913	-0.46531	0.1563	0.114	0.1089	0.01638	0.014	30.70	459.32	2940.72	-1016.43
Li-Cp-Mg	0.282	-0.1511	0.14069	0.343	0.324	0.3563	0.3996	0.05474	12.96	142.40	64.79	-526.59
Li-Cp-Ca	49.925	47.0288	47.7363	49.198	50.351	47.502	48.216	48.78584	0.84	0.99	0.99	-0.84
Na-Cp-Be	264.183	237.8004	234.5509	240.195	264.215	237.832	234.641	240.1644	0.01	0.01	0.03	-0.01
Na-Cp-Mg	12.506	12.8913	12.6552	13.34	12.565	12.9622	12.764	13.28147	0.46	0.54	0.85	-0.44
Na-Cp-Ca	665.148	626.8224	649.474	660.769	665.537	626.901	649.769	660.3295	0.05	0.012	0.04	-0.06
K-Cp-Be	76.488	75.6458	74.1146	75.843	77.016	75.805	74.911	75.4791	0.68	0.21	1.06	-0.48
K-Cp-Mg	66.155	63.5033	63.81067	66.319	66.708	63.65	64.701	65.7918	0.82	0.23	1.37	-0.80
K-Cp-Ca	313.551	368.0207	326.1991	307.072	314.501	368.211	327.051	306.0662	0.30	0.05	0.26	-0.32

Table S6: %BSSE effect on γ_{zzzz} and β_{zzz} obtained at HF level for different basis sets

Complexes	6-31++G(d,p)	6-311++G	6-311++G(3df,3pd)	aug-cc-pVTZ*
		γ_{zzzz}		
Li-Cp-Be	24.42	43.68	43.10	50.42
Li-Cp-Mg	28.77	35.42	35.62	37.59
		β_{zzz}		
Li-Cp-Be	19.68	8.02	2.75	15.23
Li-Cp-Mg	7.44	2.38	0.62	2.28

*without '*f*' type diffuse function for Li, Be, C and Mg

Table S7: Static and dynamic (1064 nm) second hyperpolarizability (10^6 au) IDRI $\gamma(-\omega;\omega,-\omega,\omega)$, DC-Kerr $\gamma(-\omega;-\omega,0,0)$, SHG $\gamma(-2\omega;\omega,\omega,0)$, THG $\gamma(-3\omega;\omega,\omega,\omega)$ of M_1-Cp-M_2 complexes obtained at the HF/6-311++G(d,p) level

Complexes	$\gamma(0;0,0,0,0)$	$\gamma(-\omega;\omega,-\omega,\omega,)$	$\gamma(-2\omega;\omega,\omega,0,)$	$\gamma(-\omega;\omega,0,0,)$	$\gamma(-3\omega;\omega,\omega,\omega,)$
Li-Cp-Be	0.11	0.17	0.22	0.14	0.55
Li-Cp-Mg	0.31	0.64	0.99	0.43	-81.31
Li-Cp-Ca	6.89	-29.82	161.16	47.79	101.57
Na-Cp-Be	6.63				
Na-Cp-Mg	1.21			2.22	
Na-Cp-Ca	28.77	-80.14	234.56	-4.63	-33.60
K-Cp-Be	0.87	6.41	29.97	1.51	-58.52
K-Cp-Mg	1.10	12.11	96.32	1.96	104.72
K-Cp-Ca	63.75			-12.74	

*The missing data in some cases arises from the convergence failure problem.