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

Electronic Structure and Second Hyperpolarizability of Alkaline Earth Metal Complexes End-capped With NA_2 (A=H, Li, Na)

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Table S1. Longitudinal component of second hyperpolarizability (γ_{xxxx}, **10^4 au**) and the average second hyperpolarizability (γ_{av}, **10^4 au**) of complexes (**Scheme 1(A-C))** obtained at the CAM-B3LYP/6-311++G(3df,3pd) level for different electric field strength (**au**)

Molecules	**0.000033**		**0.000133**		**0.000233**		**0.000333(Default)**		**0.000433**		**0.000500**		**0.000567**	
	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}
1a	4.50	2.77	4.50	2.78	4.50	2.78	4.50	2.78	4.50	2.78	4.50	2.78	4.50	2.78
1b	98.30	65.15	98.69	65.14	99.59	65.08	101.24	64.95	103.82	64.94	105.52	65.13	105.16	64.87
1c	204.12	169.88	204.30	169.94	204.37	169.63	204.51	168.74	204.54	167.60	204.51	167.15	204.49	167.02
2a	8.18	5.39	8.18	5.40	8.18	5.40	8.18	5.40	8.18	5.40	8.18	5.40	8.18	5.40
2b	270.32	121.86	270.77	122.02	271.80	122.43	272.99	122.89	273.95	123.25	273.78	123.25	271.02	122.58
2c	625.87	323.18	626.43	323.14	626.94	323.24	627.76	323.37	629.35	347.87	644.66	319.86	424.51	223.50
3a	13.23	8.65	13.23	8.65	13.23	8.65	13.24	8.65	13.24	8.65	13.24	8.65	13.24	8.65
3b	504.47	182.26	504.75	182.27	505.24	182.41	506.09	182.65	507.00	182.92	507.68	183.13	508.31	183.33
3c	1341.50	517.73	1342.61	518.11	1344.45	518.61	1347.16	519.35	1350.92	520.39	1353.78	521.21	1357.08	522.14
4a	22.73	15.25	22.76	15.26	22.77	15.26	22.79	15.26	22.79	15.26	22.80	15.31	22.80	14.78
4b	812.33	337.55	812.92	337.67	813.95	338.00	815.52	338.50	817.74	339.20	819.54	339.78	821.60	340.46
4c	1886.24	794.98	1888.71	795.62	1896.90	797.80	2009.43	823.35	1894.35	798.56	1900.86	800.06	1903.92	801.05
5a	31.30	20.93	31.30	20.93	31.31	20.93	31.32	20.93	31.33	20.94	31.34	20.94	31.35	20.95
5b	1343.01	450.95	1344.94	4514.29	1348.37	452.31	1353.42	453.57	1357.96	454.67	1357.04	453.37	1349.13	452.39
5c	3049.72	1004.05	3264.44	1123.02	3258.56	1136.36	3265.75	1138.44	3278.62	1144.01	3288.25	1145.80	3308.87	1151.11
6a	47.28	43.22	47.28	43.23	47.32	47.28	47.36	43.33	47.41	43.38	47.45	43.40	47.50	43.41
6b	2681.69	947.99	2683.59	948.57	2688.88	950.10	2695.94	952.19	2706.09	955.13	2714.19	957.51	2723.25	960.17
6c	5909.13	2061.23	5352.30	1954.68	5438.68	1987.97	5574.78	2025.11	5629.93	2023.96	5628.04	2015.83	5619.29	2015.65

Table S2. Longitudinal component of second hyperpolarizability (γ_{xxxx}, **10^7 au)** and the average second hyperpolarizability (γ_{av}, **10^7 au**) of complexes (**Scheme 2C)** obtained at the CAM-B3LYP/6-311++G(3df,3pd) level for different electric field strength (**au**)

n	**0.000033**		**0.000133**		**0.000233**		**0.000333(Default)**		**0.000433**		**0.000500**		**0.000567**	
	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}
							$Na_2N\text{-}(Mg)_n\text{-}NNa_2$							
3	3.67	1.09	3.67	1.09	3.68	1.09	3.69	1.10	3.70	1.10	3.71	1.11	3.72	1.11
4	7.70	2.03	7.71	2.03	7.73	2.04	7.77	2.04	7.80	2.05	7.84	2.06	7.88	2.07
5	13.59	3.32	13.61	3.33	13.66	3.34	13.74	3.36	13.85	3.38	13.94	3.40	14.04	3.42
6	21.07	4.92	21.12	4.93	21.23	4.95	21.40	4.99	21.64	5.04	21.83	5.08	22.05	5.13
7	30.04	6.70	30.04	6.79	30.24	6.83	30.56	6.90	30.99	6.99	31.35	7.07	31.77	7.16
							$Na_2N\text{-}(Ca)_n\text{-}NNa_2$							
3	15.45	4.71	15.42	4.71	15.37	4.70	15.42	4.70	15.43	4.71	15.47	4.69	15.71	4.75
4	29.68	6.98	30.33	8.29	30.82	8.53	30.97	8.51	32.11	8.72	-----	-----	31.27	8.60
5	54.17	13.78	52.46	13.45	53.88	13.74	53.41	13.64	53.54	13.70	54.41	13.87	55.07	14.03
6	81.41	19.86	81.36	19.85	82.33	20.05	82.60	20.10	84.69	20.60	83.77	20.40	85.70	20.79
7	114.74	27.13	113.29	26.81	115.31	27.24	117.75	27.92	120.67	28.24	121.48	28.44	124.91	29.26

Scheme 3 (Optimized structures along with geometrical parameters of non-linear metal complexes**)**

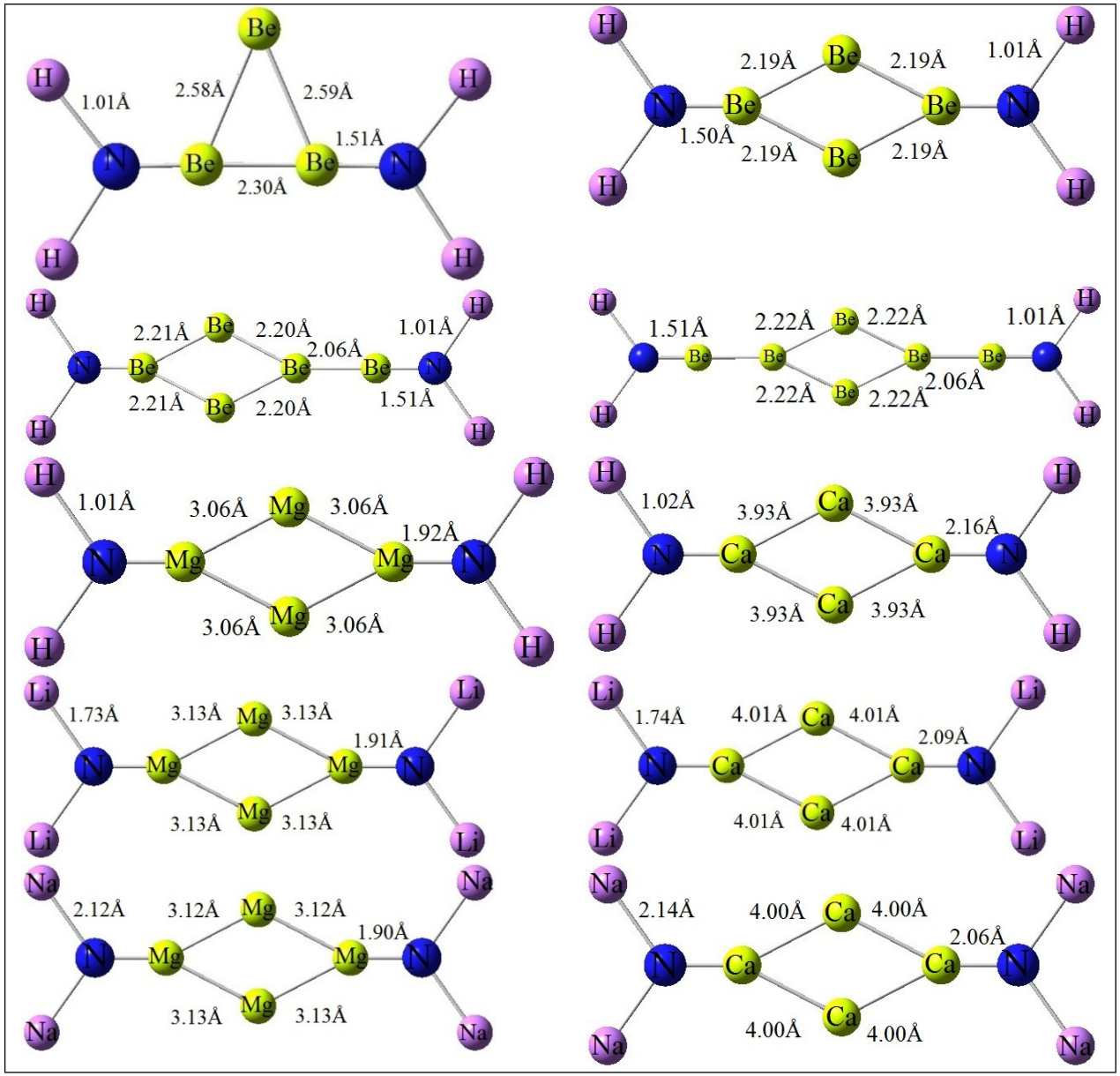

Table S3 B3LYP/6-311++G(d, p) optimized energy (a.u.), relative energy (ΔE, kcal/mol), longitudinal component of linear polarizability (α_{xx}, **10^2 au**) and of second hyperpolarizability (γ_{xxxx}, **10^4 au**)[a] of linear structures and non-linear structural isomers.

	Linear structures			**Non-linear Isomers**			
Molecules	**Energy**	α_{xx}	γ_{xxxx}	**Energy**	α_{xx}	γ_{xxxx}	**ΔE**
$Be_3(NH_2)_2$	-156.250666843	0.97	10.45	-156.208061655	1.56	15.70/2.30[b]	26.735
$Be_4(NH_2)_2$	-170.968491260	1.26	16.99	-170.954940625	1.82	22.28	8.503
$Be_5(NH_2)_2$	-185.686167293	1.56	23.17	-185.678090180	2.30	26.78/9.00[b]	5.068
$Be_6(NH_2)_2$	-200.403786408	1.85	29.21	-200.400040106	2.79	44.85	2.351
$Mg_4(NH_2)_2$	-912.391572038	4.46	188.98	-912.396377770	3.06	76.27	-3.015
$Mg_4(NLi_2)_2$	-940.060484065	8.69	3238.86	-940.066103242	5.97	904.50	-3.526
$Mg_4(NNa_2)_2$	-1559.08295552	12.87	7766.52	-1559.08824972	8.80	2154.89	-3.322
$Ca4(NH_2)_2$	-2822.35484769	12.03	886.70	-2822.37487804	5.93	238.09	-12.579
$Ca4(NLi_2)_2$	-2850.02044187	22.45	18244.60	-2850.03929508	10.79	3890.08	-11.830
$Ca4(NNa_2)_2$	-3469.04858800	31.12	30975.50	-3469.06601699	15.01	8360.35	-10.937

[a]The linear and non-linear polarizabilities are calculated at the **CAM-B3LYP** Level for the **6-311++G(3df,3pd)** basis set.

[b]The quantity in the parentheses refers to the magnitude of first hyperpolarizability (β_{xxx}) in 10^2 au.

Table S4 The B3LYP/ 6-311++G(d,p) calculated binding energy (**ΔE,** kJ/mol)[a] of the complexes (**Schemes 2A)** with increasing chain length.

n	ΔE	n	ΔE	n	ΔE
$Be_n(NH_2)_2$		**$Mg_n(NH_2)_2$**		**$Ca_n(NH_2)_2$**	
		B3LYP			
2	-640.41	**2**	-185.41	**2**	-273.19
3	-759.42	**3**	-193.59	**3**	-282.83
4	-876.74	**4**	-200.49	**4**	-292.33
5	-988.15	**5**	-206.61	**5**	-301.42
6	-1109.09	**6**	-212.56	**6**	-310.86
7	-1226.05	**7**	-218.28	**7**	-320.04
		CAM-B3LYP			
2	-668.73	**2**	-215.75	**2**	-298.58
3	-791.51	**3**	-225.20	**3**	-310.95
4	-912.09	**4**	-232.52	**4**	-322.55
5	-986.53	**5**	-238.60	**5**	-333.28
6	-1151.43	**6**	-244.24	**6**	-339.40
7	-1271.89	**7**	-249.51	**7**	-354.11

[a] **$2M+N_2+2H_2 = M_n(NH_2)_2$** (M= Be, Mg and Ca)

Table S5 The DFT/ 6-311++G(d,p) calculated results of binding energy (**ΔE,** kJ/mol)[a] of the complexes (**Schemes 2B** and **2C)** with increasing chain length

n	**ΔE**	**n**	**ΔE**	**n**	**ΔE**
$Mg_n(NLi_2)_2$		**$Ca_n(NLi_2)_2$**		**$Ca_n(NNa_2)_2$**	
			B3LYP		
2	-390.97	**2**	-466.73	**2**	-71.73
3	-397.12	**3**	-474.18	**3**	-80.31
4	-402.43	**4**	-483.48	**4**	-89.77
5	-407.64	**5**	-492.45	**5**	-98.96
6	-412.87	**6**	-501.37	**6**	-107.83
7	-418.14	**7**	-510.32	**7**	-116.79
			CAM-B3LYP		
2	-402.63	**2**	-466.56	**2**	-45.09
3	-408.01	**3**	-475.61	**3**	-54.44
4	-413.15	**4**	-486.80	**4**	-65.88
5	-417.90	**5**	-497.06	**5**	-75.82
6	-422.70	**6**	-507.17	**6**	-86.29
7	-427.27	**7**	-516.52	**7**	-96.32

[a] **$2M+N_2+4A=M_n(NA_2)_2$** (A = Li and Na)

Table S6 Calculated results of dipole polarizability anisotropy (**Δα, 10^2 au)**

obtained for molecules of **Schemes 1(A-C)** at the CAM-B3LYP level for different basis sets.

		6-311++G(3df,3pd)			
1a	0.17	**1b**	0.54	**1c**	0.49
2a	0.24	**2b**	0.98	**2c**	1.40
3a	0.37	**3b**	1.61	**3c**	2.75
4a	0.31	**4b**	1.57	**4c**	2.75
5a	0.51	**5b**	2.53	**5c**	4.68
6a	0.87	**6b**	3.78	**6c**	6.84
		aug-pc-2			
1a	0.17	**1b**	0.54	**1c**	0.49
2a	0.24	**2b**	0.98	**2c**	1.40
3a	0.37	**3b**	1.62	**3c**	2.78
4a	0.30	**4b**	1.59	**4c**	2.83
5a	0.52	**5b**	2.56	**5c**	4.78
6a	0.89	**6b**	3.83	**6c**	7.03

Table S7. Longitudinal component of polarizability (a_{xx},**10^2 au**), second hyperpolarizability (γ_{xxxx}, **10^4 au**) and average second hyperpolarizability (γ_{av}, **10^4 au**) of complexes (**Schemes 1(A-C)**) at the obtained for the **wB97XD** functional at different basis sets

	wB97XD											
	6-311++G(d,p)			**6-311++G(3df,3pd)**			**aug-cc-pVTZ[a]**			**aug-pc-2**		
X	a_{xx}	γ_{xxxx}	γ_{av}	a_{xx}	γ_{xxxx}	γ_{av}	a_{xx}	γ_{xxxx}	γ_{av}	a_{xx}	γ_{xxxx}	γ_{av}
1a	0.67	4.326	2.48	0.69	4.38	2.78	0.69	4.45	3.20	0.69	4.53	3.12
1b	1.82	95.33	70.46	1.86	97.37	64.95	1.85	82.38	59.46	1.84	92.01	66.92
1c	2.65	208.36	210.23	2.66	202.91	168.74	2.69	223.26	221.60	2.68	213.27	209.98
2a	0.89	7.65	4.62	0.91	7.67	5.40	0.92	7.970	6.13	0.92	8.17	5.99
2b	2.58	191.90	99.04	2.62	253.11	122.89	2.62	230.89	120.85	2.59	123.41	233.08
2c	4.05	558.75	762.36	5.77	536.80	323.37	4.12	588.32	394.63	4.06	573.77	373.16
3a	1.19	12.30	7.43	1.22	11.99	8.65	1.23	12.68	10.16	1.23	12.75	9.33
3b	3.49	427.14	179.45	3.55	395.38	182.65	3.54	425.45	174.83	3.49	430.97	180.02
3c	5.81	1222.96	571.81	5.77	1249.88	519.35	5.91	1268.28	609.80	5.79	1215.39	571.36
4a	1.15	22.85	14.79	1.19	24.48	15.26	1.21	24.09	18.72	1.21	24.22	19.13
4b	3.61	644.85	306.95	3.65	635.93	338.50	3.67	609.15	285.34	3.65	673.09	325.68
4c	5.73	1619.35	802.05	5.66	1578.35	823.35	5.85	1963.71	929.55	5.78	1649.86	829.11
5a	1.61	32.46	20.11	1.67	34.18	20.93	1.69	34.38	25.69	1.70	34.02	26.06
5b	4.87	1000.95	376.14	4.94	1019.66	453.57	4.96	1020.30	384.01	4.89	1060.78	401.68
5c	8.10	2636.57	1080.09	7.99	2591.61	1138.44	8.28	2871.94	1194.86	8.15	2734.80	1123.18
6a	2.63	12.25	26.78	2.75	14.03	43.33	2.68	6.68	30.11	2.79	12.57	21.37
6b	6.98	1775.96	717.17	7.09	1880.99	952.19	7.13	1909.90	807.15	958.42	2048.62	849.91
6c	10.90	4525.10	1827.54	10.86	4668.44	2025.11	11.24	4948.37	1911.10	11.12	4922.60	2031.88

[a]For Ca atom aug-pc-2 basis set has been used.

Table S8. Longitudinal component of polarizability (a_{xx}, **10^2 au**), second hyperpolarizability (γ_{xxxx}, **10^4 au**) and average second hyperpolarizability (γ_{av}, **10^4 au**) of complexes (**Schemes 1(A-C))** obtained for the **B2PLYP** functional at different basis sets

	B2PLYP											
	6-311++G(d,p)			**6-311++G(3df,3pd)**			**aug-cc-pVTZ[a]**			**aug-pc-2**		
X	a_{xx}	γ_{xxxx}	γ_{av}	a_{xx}	γ_{xxxx}	γ_{av}	a_{xx}	γ_{xxxx}	γ_{av}	a_{xx}	γ_{xxxx}	γ_{av}
1a	0.65	4.099	2.25	0.66	4.147	2.63	0.66	4.18	2.82	0.66	4.27	2.75
1b	1.71	103.32	69.84	1.74	97.64	61.01	1.74	106.72	69.60	1.74	112.29	71.91
1c	2.55	248.84	219.66	2.25	240.50	214.14	2.60	255.34	228.52	2.57	244.89	218.13
2a	0.86	7.752	4.44	0.88	7.82	5.35	0.89	8.08	5.71	0.89	8.21	5.53
2b	2.46	281.12	130.72	2.50	303.08	142.09	2.51	303.97	143.42	2.50	143.50	306.73
2c	3.99	849.99	469.13	2.97	819.79	453.66	4.06	864.93	477.65	4.02	842.91	462.30
3a	1.20	13.15	7.15	1.18	12.86	8.79	1.19	13.52	9.60	1.19	13.61	8.90
3b	3.36	552.23	209.44	3.41	581.52	216.57	3.42	576.61	215.64	3.42	584.25	216.56
3c	5.77	1834.33	745.16	5.73	1769.40	724.80	5.87	1834.33	765.68	5.81	1815.25	736.81
4a	1.12	23.09	14.54	1.19	23.20	16.22	1.20	23.48	18.77	1.20	24.00	18.67
4b	3.63	1025.56	421.44	3.69	1055.11	436.10	3.71	1040.77	439.93	3.71	1085.77	449.41
4c	6.46	2613.90	1121.19	4.19	2634.06	1142.97	1.72	2702.31	1185.30	6.54	2684.29	1175.96
5a	1.59	30.47	19.48	1.64	31.64	22.36	1.66	32.03	25.26	1.66	31.99	25.45
5b	4.81	1615.23	545.84	3.11	1678.65	566.99	4.93	1694.29	575.25	4.93	1706.25	578.57
5c	8.75	4467.47	1611.75	8.71	4476.12	1612.41	8.99	4626.70	1669.42	8.88	4569.38	1643.09
6a	2.45	51.77	44.37	2.56	52.77	48.35	2.50	45.12	45.07	2.59	51.32	61.61
6b	6.94	1025.56	1175.96	7.13	3549.09	1248.58	7.19	3583.09	1281.87	7.20	3635.82	1301.97
6c	12.27	7164.27	2651.87	12.37	7234.17	2770.52	12.68	6729.77	2468.62	12.64	7247.45	2758.30

[a]For Ca atom aug-pc-2 basis set has been used.

Table S9 The ratio[a] of γ_{xxxx} (γ_{av}) calues of complexes (**Scheme 1) o**btained by different DFT methods and basis sets

CAM-B3LYP

Complexes	**6-311++G(d,p)**		**6-311++G(3df,3pd)**		**aug-cc-pVTZ**		**aug-pc-2**	
	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}
1c	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2c	3.10	1.94	3.07	1.92	3.09	1.93	3.13	1.94
3c	6.62	3.05	6.59	3.08	6.82	3.16	6.72	3.11
4c	9.11	4.69	9.82	4.88	9.19	4.72	9.44	4.86
5c	15.64	6.60	15.97	6.75	15.86	6.72	16.26	6.88
6c	28.87	12.12	27.26	12.00	25.46	10.72	27.65	12.22

wB97XD

	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}
1c	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2c	2.68	1.78	2.64	1.76	2.63	1.78	2.69	1.78
3c	6.00	2.72	6.16	2.84	5.68	2.75	5.70	2.72
4c	7.77	3.81	7.78	3.92	8.79	4.19	7.74	3.95
5c	12.65	5.14	12.77	5.34	12.86	5.39	12.82	5.35
6c	21.72	8.69	23.01	9.61	22.16	8.62	23.08	9.68

B2PLYP

	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}	γ_{xxxx}	γ_{av}
1c	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2c	3.41	2.13	3.41	2.12	3.30	2.09	3.44	2.12
3c	7.37	3.39	7.36	3.38	7.18	3.35	7.41	3.38
4c	10.50	5.10	10.95	5.34	9.19	4.72	10.96	5.39
5c	17.95	7.34	18.61	7.53	18.12	7.30	18.66	7.53
6c	28.79	12.07	30.08	12.94	23.08	10.80	29.59	12.64

[a]Ratio of γ_{xxxx} **(**γ_{av}) refer to the quantity obtained with respect to that of complex **1c**.

Table S10 Longitudinal component of second hyperpolarizability (γ_{xxxx}, **10^4 au**) of Complexes with **n = 2 - 7 (Schemes 2A and 2B)** obtained at the **CAM-B3LYP** level for the **6-311++G(3df,3pd)** basis set

	$H_2N\text{-}(Be)_n\text{-}NH_2$	$H_2N\text{-}(Mg)_n\text{-}NH_2$	$H_2N\text{-}(Ca)_n\text{-}NH_2$	$Li_2N\text{-}(Mg)_n\text{-}NLi_2$	$Li_2N\text{-}(Ca)_n\text{-}NLi_2$
n	γ_{xxxx}	γ_{xxxx}	γ_{xxxx}	γ_{xxxx}	γ_{xxxx}
2	4.50	13.52	46.91	485.93	2566.97
3	10.45	58.85	285.08	1476.34	8633.63
4	16.99	188.98	886.70	3238.86	18244.60
5	23.34	480.23	2084.42	5668.54	31844.30
6	29.21	1045.96	4150.34	9244.70	50124.50
7	34.57	2049.08	7347.07	13566.50	71896.60

Table S11 The **c** values in the power-law dependence of the longitudinal component of second hyperpolarizability on '**n**' obtained for **Be** and **Mg** metal chain complexes (**n** = **1 - 7**) encapped by NH_2 groups . The values in parentheses are the errors in the fitting of the corresponding equations obtained from γ_{xxxx} values calculated at different methods for the 6-311++G(d,p) basis set

	H_2N-(Be)$_n$-NH_2	
	$\gamma = bn^c$	$\gamma = a + bn^c$
CAM-B3LYP	1.43(±0.0915)	1.14(±0.1033)
CCSD(T)	1.64(±0.1075)	1.74(±0.2343)
MP2	1.45(±0.0722)	1.23(±0.0906)
	H_2N-(Mg)$_n$-NH_2	
	$\gamma = bn^c$	$\gamma = a + bn^c$
CAM-B3LYP	4.33(±0.0222)	4.36(±0.0210)
CCSD(T)	4.31(±0.0248)	4.34(±0.0222)
MP2	4.13(±0.0087)	4.13(±0.0121)

Table S12 Transition energy (ΔE_{ng}, au), change in dipole moment ($\Delta\mu_{ng}$, au), oscillator strength (f_{ng}, au), state wise contribution of β_0 and β_0 (total) along with the major transitions[a] involved in the crucial excitation[b] for complexes (**Scheme 1(A-C)**) obtained at the TD-CAM-B3LYP/6-311++G(d,p) level.

Complexes	$S_0 \rightarrow S_n$	$\Delta\mu_{ng}$	ΔE_{gn}	f_{ng}	β_0 (State Wise)	β_0 (total)[a]
2a	$S_0 \rightarrow S_7$	0.022	0.205	0.49	1.25	20.72
	$S_0 \rightarrow S_4$	0.299	0.173	0.33	19.05	
	$S_0 \rightarrow S_5$	0.323	0.177	0.23	0.419	
2b	$S_0 \rightarrow S_3$	3.606	0.088	0.17	904.84	1518.39
	$S_0 \rightarrow S_7$	5.138	0.104	0.08	365.41	
	$S_0 \rightarrow S_9$	4.222	0.106	0.07	248.14	
2c	$S_0 \rightarrow S_4$	2.645	0.066	0.16	1481.22	2939.87
	$S_0 \rightarrow S_8$	3.402	0.083	0.15	879.68	
	$S_0 \rightarrow S_7$	3.009	0.080	0.10	578.97	
4a	$S_0 \rightarrow S_1$	1.210	0.116	0.18	139.53	296.45
	$S_0 \rightarrow S_3$	1.486	0.135	0.21	126.83	
	$S_0 \rightarrow S_4$	0.289	0.136	0.27	30.90	
4b	$S_0 \rightarrow S_1$	1.492	0.066	0.21	1110.58	2791.76
	$S_0 \rightarrow S_3$	3.678	0.083	0.17	1093.52	
	$S_0 \rightarrow S_5$	4.010	0.085	0.09	587.66	
4c	$S_0 \rightarrow S_2$	0.385	0.055	0.28	659.50	3137.65
	$S_0 \rightarrow S_6$	0.874	0.073	0.09	471.80	
	$S_0 \rightarrow S_8$	4.979	0.075	0.21	2006.35	
5a	$S_0 \rightarrow S_1$	0.145	0.110	0.28	30.39	129.69
	$S_0 \rightarrow S_3$	0.615	0.125	0.30	15.51	
	$S_0 \rightarrow S_2$	0.409	0.123	0.24	84.09	
5b	$S_0 \rightarrow S_1$	0.477	0.065	0.34	592.29	764.28
	$S_0 \rightarrow S_6$	0.615	0.082	0.09	100.39	
	$S_0 \rightarrow S_7$	0.409	0.083	0.10	71.60	
5c	$S_0 \rightarrow S_3$	1.043	0.053	0.46	3243.68	6713.18
	$S_0 \rightarrow S_9$	3.998	0.073	0.22	2260.98	
	$S_0 \rightarrow S_{10}$	2.332	0.074	0.21	1208.52	

[a]In the last column the value against each complex are obtained by summing the state wise contribution of β_0.

Table S13 Transition energy (ΔE_{ng}, au), x-component of ground and excited state dipole moment (Debye), dipole moment difference ($(\Delta\mu^x)_{ng}$, au), oscillator strength ($(f^x)_{ng}$, au) along with the two state contribution of second hyperpolarizability (au) calculated from the crucial electronic transition obtained for complexes (**Scheme 1(A-C)**) at the TD-CAM-B3LYP/6-311++G(d,p) level

Complexes	Excited State Dipole Moment	Ground State Dipole Moment	$(\Delta\mu^x)_{ng}$	ΔE_{ng}	$(f^x)_{ng}$	$\left\lvert\gamma^{2L}_{xxxx}\right\rvert$
1a				0.238	0.324	7423.33
1b				0.110	0.192	123604.07
1c				0.088	0.199	405215.97
2a	1.682	1.620	0.022	0.205	0.488	35514.46
2b	9.963	0.797	3.606	0.088	0.171	1035602.14
2c	7.054	0.332	2.645	0.066	0.161	1019295.87
3a				0.178	0.621	116540.52
3b				0.084	0.334	1440423.72
3c				0.062	0.362	7724181.20
4a	1.969	1.235	0.289	0.117	0.178	75181.59
4b	5.658	1.864	1.492	0.066	0.214	245578.06
4c	2.228	1.249	0.385	0.055	0.285	8548857.95
5a	2.176	2.544	0.145	0.110	0.279	259556.58
5b	3.922	2.703	0.477	0.065	0.341	5255251.90
5c	0.221	2.873	1.043	0.053	0.463	26664879.28
6a				0.091	0.495	2120299.43
6b				0.056	0.489	23446139.41
6c				0.048	0.605	77570809.26

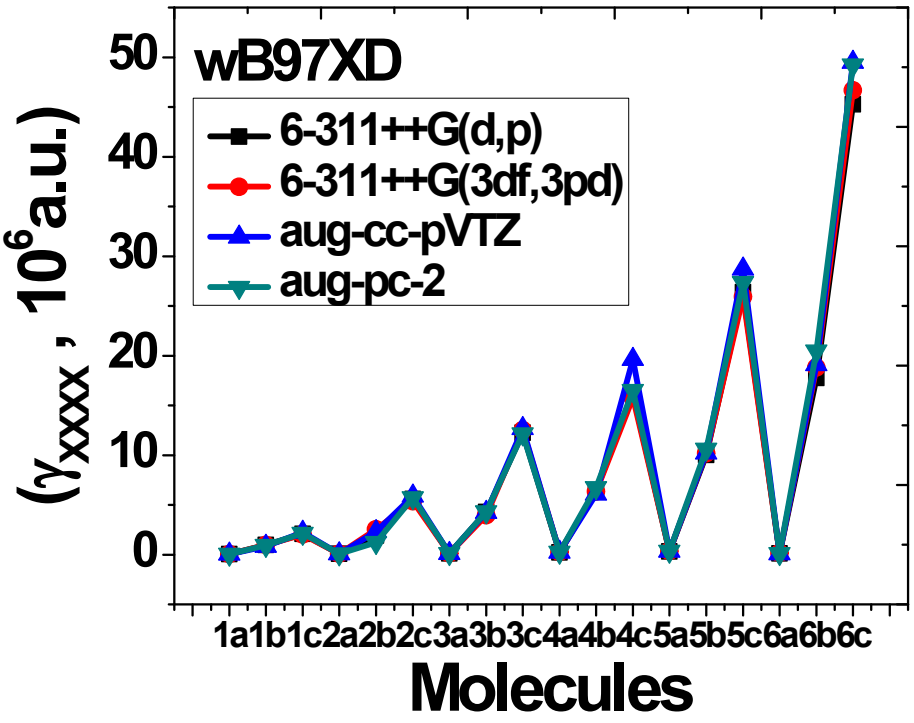

Fig.S1 Plot of γ_{xxxx} of molecules (**Scheme 1**) obtained at different basis sets for the wB97XD functional.

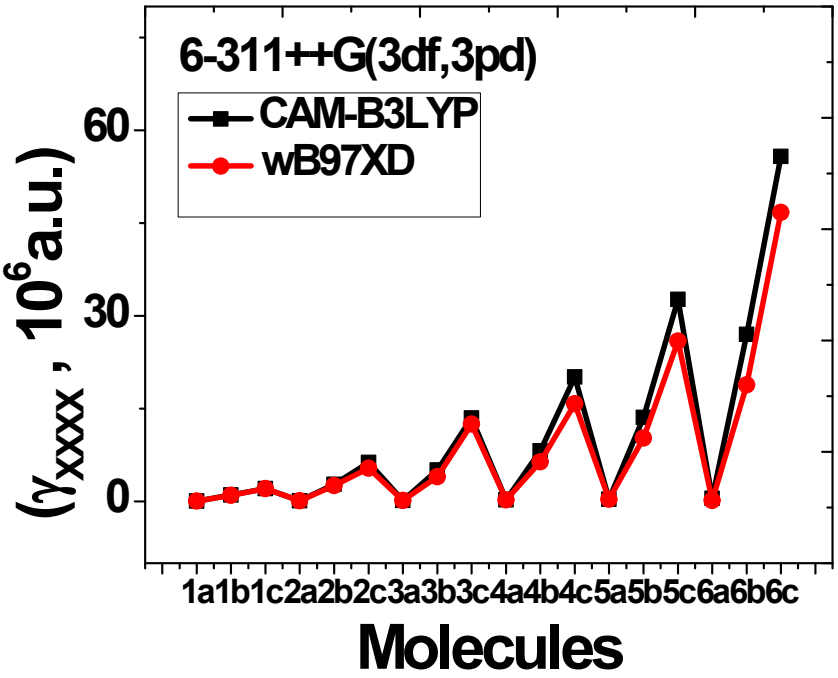

Fig. S2 Plot of γ_{xxxx} of molecules (**Scheme 1**) obtained at two different DFT functionals for the 6-311++G(3df,3pd) basis set

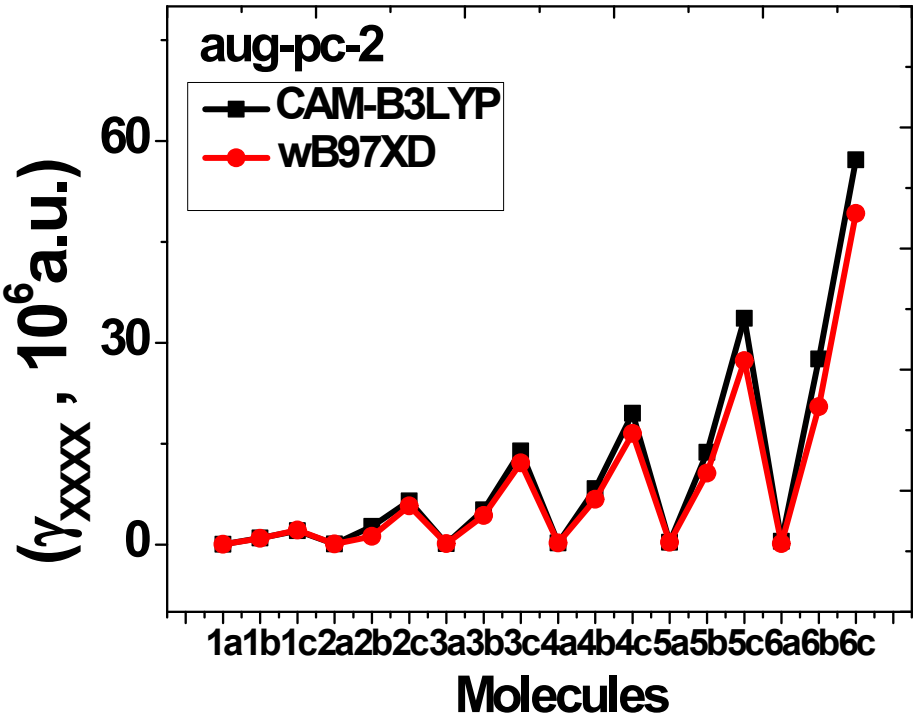

Fig. S3 Plot of γ_{xxxx} of molecules (**Scheme 1**) obtained at two different DFT functional for the aug-pc-2 basis set.

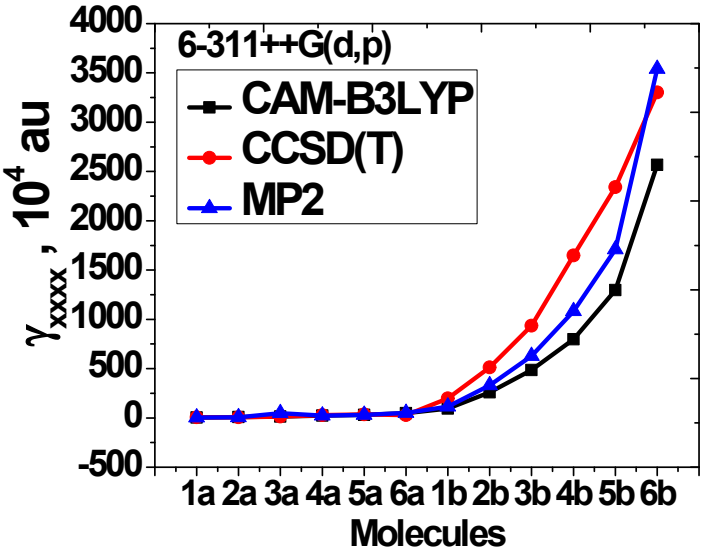

Fig. S4 The variation of γ_{xxxx} of complexes of **Schemes 1A and 1B** obtained at the CAM-B3LYP, CCSD(T), MP2 levels for 6-311++G(d,p) basis set.

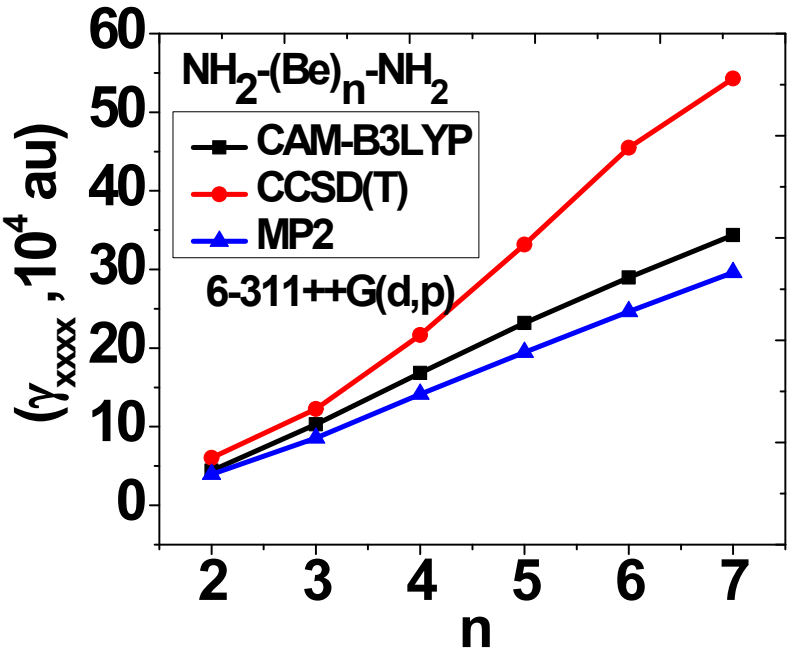

Fig.S5 The variation of γ_{xxxx} of $\mathbf{Be_n(NH_2)_2}$ [**n** = 2 - 7] complexes obtained at the CAM-B3LYP, CCSD(T) and MP2 levels for the 6-311++G(d,p) basis set.

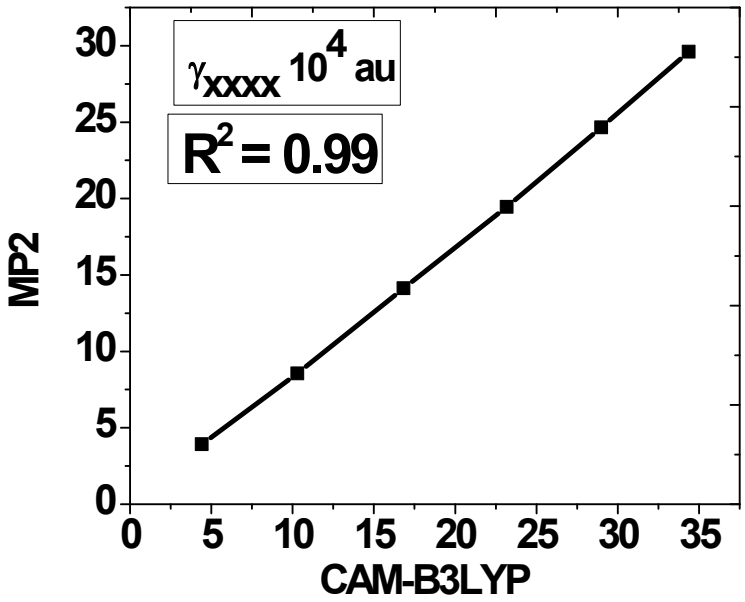

Fig. S6 The plot of MP2 γ_{xxxx} versus CAM-B3LYP γ_{xxxx} obtained for $\mathbf{Be_n(NH_2)_2}$ [**n** = **2 - 7**] complexes for the 6-311++G(d,p) basis set.

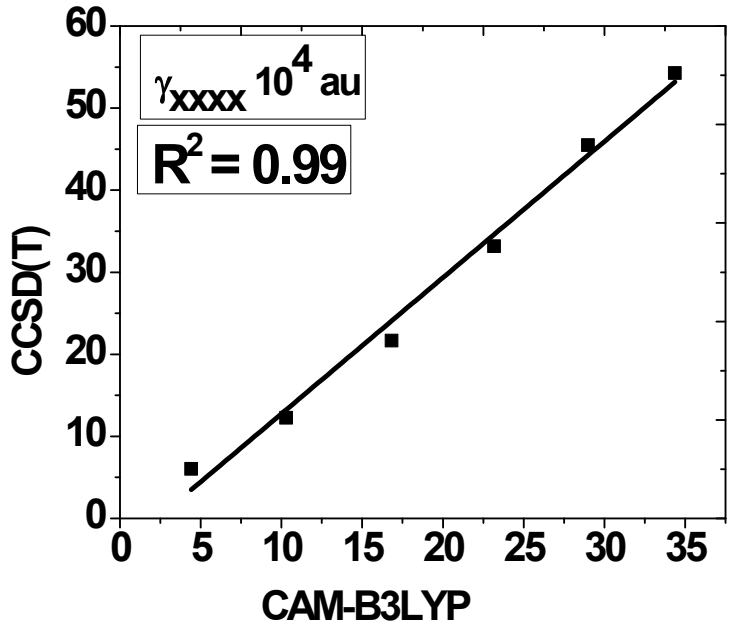

Fig. S7 The plot of CCSD(T) γ_{xxxx} versus CAM-B3LYP γ_{xxxx} obtained for $\mathbf{Be_n(NH_2)_2}$ [**n = 2 - 7**] complexes for the 6-311++G(d,p) basis set.

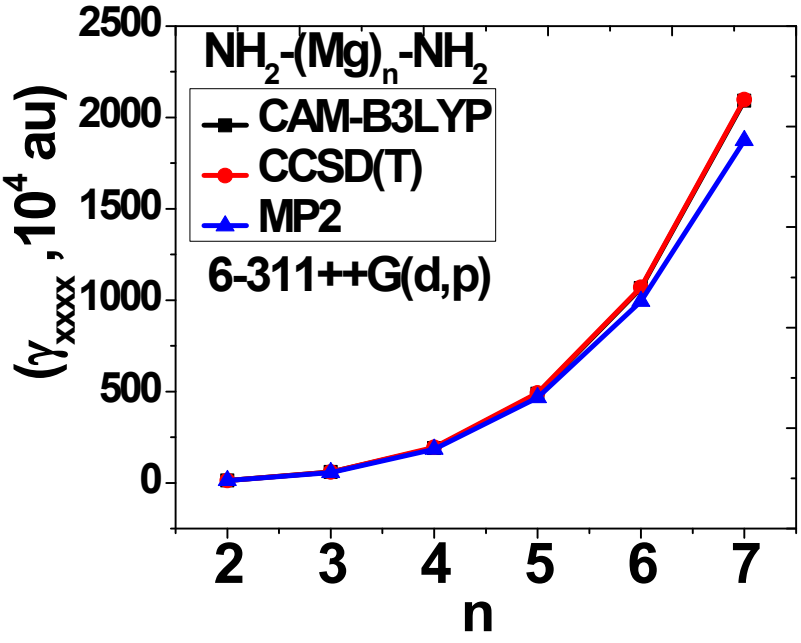

Fig. S8 The variation of γ_{xxxx} of $\mathbf{Mg_n(NH_2)_2}$ [**n = 2 - 7**] complexes obtained at the CAM-B3LYP,CCSD(T) and MP2 levels for the 6-311++G(d,p) basis set.

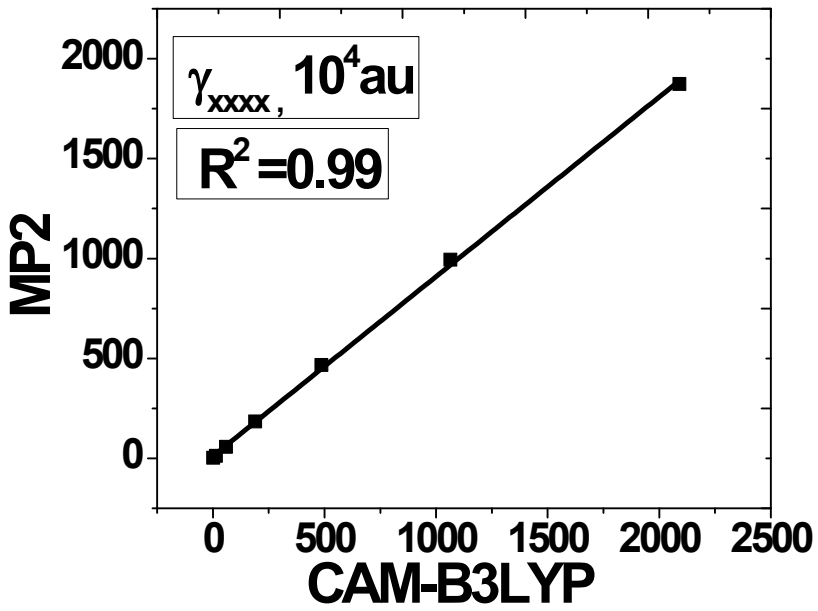

Fig. S9 The plot of MP2 γ_{xxxx} versus CAM-B3LYP γ_{xxxx} obtained for $\mathbf{Mg_n(NH_2)_2}$ [**n = 2 - 7**] complexes for the 6-311++G(d,p) basis set.

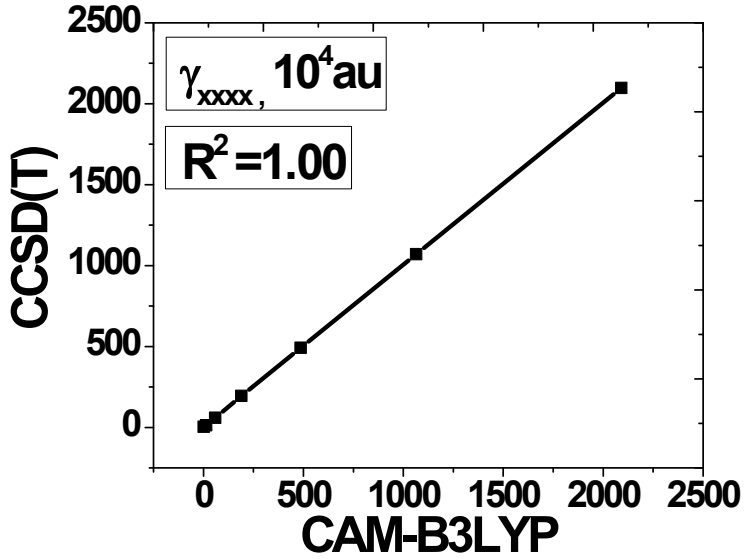

Fig. S10 The plot of CCSD(T) γ_{xxxx} versus CAM-B3LYP γ_{xxxx} obtained for $\mathbf{Mg_n(NH_2)_2}$ [**n = 2 - 7**] complexes for the 6-311++G(d,p) basis set.

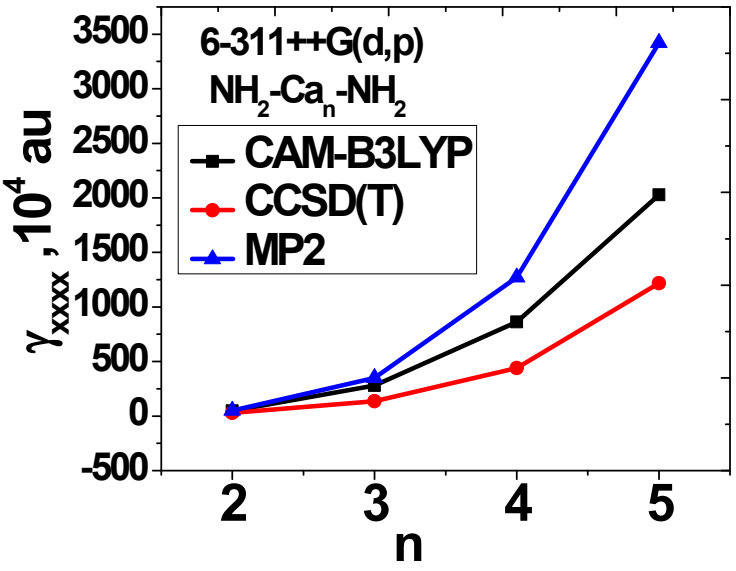

Fig. S11 The variation of γ_{xxxx} of $Ca_n(NH_2)_2$ [**n = 1 - 5**] complexes obtained at the CAM-B3LYP, CCSD(T) and MP2 levels for the 6-311++G(d,p) basis set.

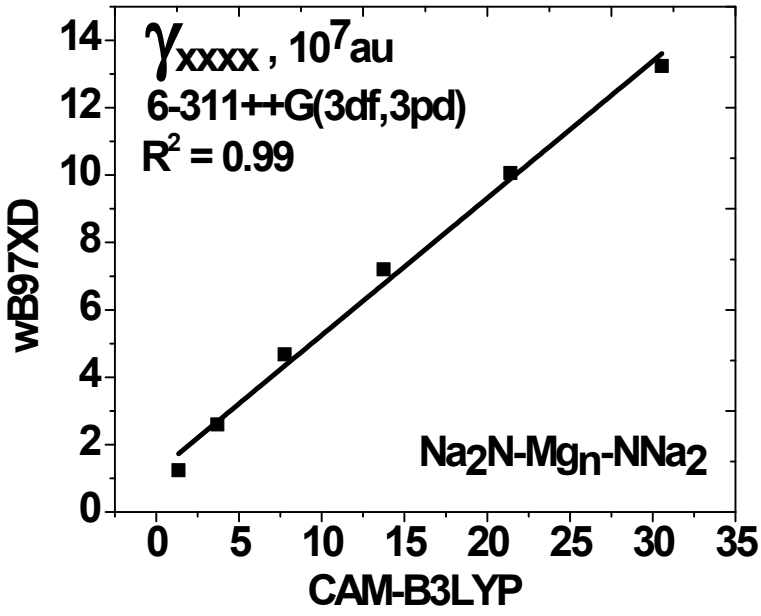

Fig. S12 The plot of wb97XD γ_{xxxx} versus CAM-B3LYP γ_{xxxx} obtained for $Mg_n(NNa_2)_2$ [**n = 2 - 7**] complexes for the 6-311++G(3df,3pd) basis set.

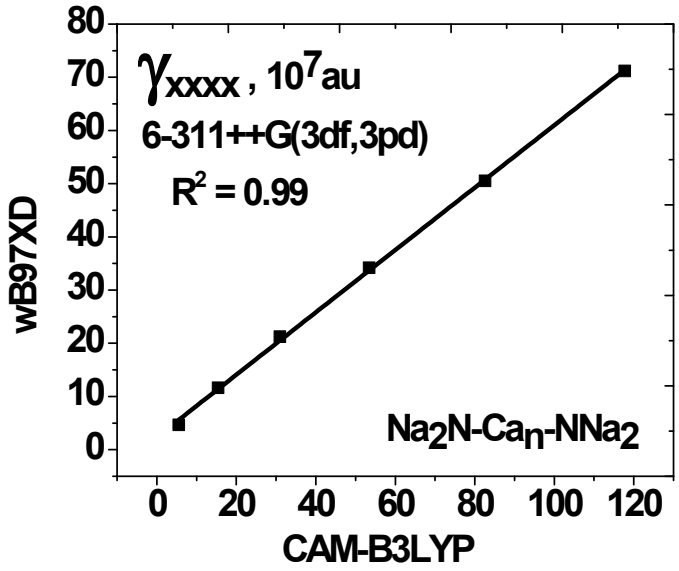

Fig. S13 The plot of wb97XD γ_{xxxx} versus CAM-B3LYP γ_{xxxx} obtained for $\mathbf{Ca_n(NNa_2)_2}$ [**n = 2 - 7**] complexes for the 6-311++G(3df,3pd) basis set.