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

Supplementary Information

Unraveling the Role of Superalkalis in Modulating Static and Dynamic Hyperpolarizabilities of Emerging Calix[4]arene

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Coordinates of optimized geometries

Calix[4]arene

C	1.31047400	-2.28438200	0.66275800
C	2.56440300	-2.01859100	0.09875500
C	2.93583000	-2.72150300	-1.04580000
C	2.08225900	-3.65423600	-1.62543500
C	0.83772800	-3.88840800	-1.05308400
C	0.42769900	-3.21480100	0.09860900
C	3.47870300	-0.95328300	0.67767500
C	3.21491400	0.42768300	0.09876500
C	3.88853900	0.83770600	-1.05291300
C	3.65435500	2.08222400	-1.62528600
C	2.72157000	2.93576800	-1.04569800
C	2.01860300	2.56433400	0.09881800
C	2.28445600	1.31044200	0.66290100
C	0.95325100	3.47858500	0.67769600
C	-0.42773500	3.21476700	0.09884100
C	-0.83778600	3.88844900	-1.05281700
C	-2.08232900	3.65433900	-1.62515000
C	-2.93590100	2.72156600	-1.04556100
C	-2.56442200	2.01853400	0.09889200
C	-1.31047500	2.28429100	0.66289900
C	-3.47871800	0.95322600	0.67779600
C	-3.21493900	-0.42769900	0.09877500
C	-3.88861400	-0.83767400	-1.05289200
C	-3.65443500	-2.08216600	-1.62532600
C	-2.72162100	-2.93572600	-1.04580700
C	-2.01862000	-2.56433300	0.09870400

C	-2.28444500	-1.31045900	0.66281200
C	-0.95326200	-3.47863200	0.67751300
O	-1.60589200	-0.98707600	1.81312600
O	-0.98697400	1.60562900	1.81311200
O	1.60617200	0.98715100	1.81338500
O	0.98709400	-1.60578500	1.81303800
H	-0.93768100	-3.40540700	1.76925100
H	-1.22515500	-4.51255300	0.44656600
H	-2.52695400	-3.90809800	-1.49039300
H	-4.61432600	-0.16462500	-1.50173900
H	-4.51266400	1.22515300	0.44700400
H	-3.40530400	0.93758400	1.76951500
H	-3.90833600	2.52697900	-1.49004400
H	-0.16473100	4.61410800	-1.50174100
H	0.93772600	3.40530200	1.76943100
H	1.22509400	4.51252700	0.44678100
H	2.52689000	3.90815300	-1.49024900
H	4.61421900	0.16466700	-1.50182900
H	3.40537100	-0.93770900	1.76940500
H	4.51262900	-1.22521300	0.44679800
H	3.90822800	-2.52683200	-1.49032700
H	0.16467500	-4.61405300	-1.50203400
H	-0.01113700	1.52446000	1.90149500
H	-1.52474600	-0.01129400	1.90187400
H	0.01130900	-1.52427800	1.90164400
H	1.52501600	0.01138100	1.90235000
H	2.38509100	-4.19457800	-2.51609100
H	4.19473400	2.38506700	-2.51591500

H	-2.38518400	4.19476900	-2.51574500
H	-4.19484700	-2.38498100	-2.51594500

Li_3O@calix[4]arene

C	0.02830800	2.62473500	0.80271200
C	-1.17746700	3.05261500	0.22926600
C	-1.12468200	3.79692900	-0.95219000
C	0.09224400	4.10387000	-1.55469600
C	1.27327700	3.67890400	-0.95734000
C	1.26725600	2.94472700	0.22904000
C	-2.51441700	2.62675700	0.80980100
C	-2.96203300	1.29822900	0.22093500
C	-3.63641900	1.28874000	-1.01298200
C	-3.99810900	0.09304400	-1.62265300
C	-3.71044900	-1.11563000	-0.99013600
C	-3.04260500	-1.15214000	0.23570000
C	-2.65871900	0.06826100	0.81803900
C	-2.64032800	-2.47561200	0.85512800
C	-1.32950300	-2.95787800	0.27852100
C	-1.34479500	-3.68175600	-0.97829200
C	-0.13928900	-4.04523700	-1.58667400
C	1.08654500	-3.69384000	-1.03060400
C	1.13400500	-2.99241900	0.23262900
C	-0.08253200	-2.64262600	0.82830700
C	2.46508200	-2.60746100	0.82687900
C	2.98515100	-1.29923900	0.26414900
C	3.80171200	-1.28627500	-0.87368000
C	4.25120700	-0.08906000	-1.43574200
C	3.88246500	1.12250600	-0.85512800

C	3.04942800	1.15577100	0.27352800
C	2.61072800	-0.05934900	0.81637400
C	2.58067800	2.48314600	0.83831400
O	1.80142300	0.00035400	1.91266900
O	-0.00040800	-1.92706400	2.01519400
O	-1.98827100	0.00187900	2.01064600
O	-0.05247200	1.89962800	1.95788800
H	2.50344900	2.42748800	1.92777100
H	3.34125500	3.23898400	0.62223800
H	4.23289900	2.05859500	-1.28034100
H	4.09529100	-2.23480000	-1.31324500
H	3.19958000	-3.39005700	0.59725500
H	2.41164600	-2.55286500	1.91914500
H	2.01370200	-3.99089600	-1.51105200
H	-2.29325600	-4.00404100	-1.39551800
H	-2.60839700	-2.39427500	1.94567600
H	-3.41712700	-3.21685600	0.62949300
H	-4.00573100	-2.05230600	-1.45328500
H	-3.89501700	2.23677900	-1.47909300
H	-2.46703900	2.58186400	1.90073300
H	-3.26209300	3.38611600	0.56300100
H	-2.05335100	4.14405500	-1.39842500
H	2.22702000	3.92734300	-1.41536600
H	-0.81612300	-1.40622100	2.13719800
H	1.22370500	-0.80527800	1.98444500
H	0.71264300	1.28171800	2.02401100
H	-1.40548900	0.78128200	2.10988100
H	0.11897600	4.68120200	-2.47246800

H	-4.52126800	0.10173100	-2.57314900
H	-0.16138100	-4.60336100	-2.51910000
H	4.89170300	-0.10333400	-2.31117500
O	0.05074900	-0.00641700	-1.79806300
Li	-1.18104700	1.10606600	-1.59162400
Li	1.71586900	0.12494000	-1.64273500
Li	-0.34622000	-1.65707000	-1.52582100

Na_3O@calix[4]arene

C	2.64158718	0.47332204	-1.18530778
C	3.33180619	-0.66149840	-0.73286359
C	4.27588316	-0.50271058	0.28361755
C	4.50151022	0.74283176	0.86694608
C	3.76703327	1.84238644	0.43224771
C	2.82902836	1.73340999	-0.59795577
C	2.96782491	-2.04063244	-1.24637863
C	1.72017227	-2.56711677	-0.54991460
C	1.83267238	-3.12559066	0.72683745
C	0.71760322	-3.57284876	1.42320308
C	-0.53444890	-3.49655887	0.82510759
C	-0.69249944	-2.95967328	-0.45008026
C	0.44153220	-2.47546132	-1.11389325
C	-2.07186831	-2.88807216	-1.08584680
C	-2.87914301	-1.67778645	-0.65348444
C	-3.82922251	-1.79165786	0.36496922
C	-4.56912647	-0.69430408	0.79641249
C	-4.33705579	0.55398674	0.22190971
C	-3.38051739	0.71803683	-0.78221716
C	-2.68395636	-0.41424696	-1.23196587

C	-3.00981856	2.10031986	-1.28248856
C	-1.77355385	2.62265837	-0.56290913
C	-1.90651026	3.17195870	0.71618246
C	-0.80227346	3.61151736	1.43415378
C	0.45954897	3.53772513	0.85606245
C	0.63763704	3.01266590	-0.42119457
C	-0.48625629	2.53505917	-1.10733575
C	2.02720126	2.94579523	-1.03501426
O	-0.27750571	1.99056645	-2.35715363
O	-1.80834118	-0.22551544	-2.26140328
O	0.25203193	-1.92006494	-2.36243712
O	1.78098078	0.29067803	-2.22927842
H	1.96110454	2.98800868	-2.12666626
H	2.57667431	3.84062115	-0.73097409
H	1.32617937	3.88191464	1.41300650
H	-2.89986007	3.25183501	1.15270833
H	-3.84091612	2.78167582	-1.08076519
H	-2.86943080	2.10021594	-2.36683004
H	-4.89598172	1.42073885	0.56392099
H	-3.99216283	-2.76321604	0.82208854
H	-1.98852242	-2.92273235	-2.17654553
H	-2.62703031	-3.78431723	-0.79662687
H	-1.40950993	-3.84809845	1.36417598
H	2.81825943	-3.20677934	1.18029272
H	2.84478579	-2.03458293	-2.33287283
H	3.79520170	-2.72361329	-1.03525161
H	4.82932683	-1.37122781	0.62989688
H	3.92408183	2.81127487	0.89701675

H	-1.16018084	-0.96147483	-2.34929183
H	-0.94905249	1.29488538	-2.50667688
H	1.13757419	1.02889383	-2.32494613
H	0.92654879	-1.22351593	-2.49508037
H	5.23416121	0.85296013	1.65866737
H	0.82121131	-3.97150295	2.42548580
H	-5.31320076	-0.80935288	1.57687573
H	-0.92048563	4.00332783	2.43752593
O	-0.04798232	0.01337911	2.67147518
Na	0.09375312	-0.05740917	4.75614481
Na	-1.80311508	0.26124140	1.67918731
Na	1.75239311	-0.22077139	1.74804704

K_3O@calix[4]arene

C	0.83818190	-2.51673264	1.91092529
C	-0.10161945	-3.37273756	1.32092237
C	-1.30847402	-3.58962556	1.98421478
C	-1.58673822	-2.96278529	3.19474129
C	-0.64920764	-2.09683174	3.74475905
C	0.57552586	-1.85429272	3.11809495
C	0.14732151	-3.96933027	-0.04985438
C	-0.13195798	-2.96430935	-1.15695667
C	-1.45551163	-2.69483637	-1.51878406
C	-1.76415858	-1.75096551	-2.48990633
C	-0.73363930	-1.07948799	-3.13856445
C	0.60059071	-1.32201549	-2.81792798
C	0.88400997	-2.25166251	-1.80684156
C	1.70402060	-0.55224892	-3.52630446
C	1.86994320	0.85764073	-2.99231315

C	1.40959035	1.95858991	-3.71700519
C	1.51898074	3.25189030	-3.21479871
C	2.06195867	3.45265714	-1.94767770
C	2.53162842	2.38092576	-1.19095893
C	2.45967554	1.09758312	-1.74540446
C	3.07890094	2.57807665	0.20773999
C	2.12138197	2.11325260	1.29519890
C	1.03433477	2.91991574	1.63534809
C	0.14511929	2.55619579	2.63992246
C	0.34456988	1.36427468	3.32680822
C	1.40075133	0.51145877	3.00040185
C	2.27379486	0.89431051	1.97459218
C	1.53774074	-0.83265295	3.69578981
O	3.28987455	0.01917634	1.65713382
O	3.00440410	0.08697996	-1.00338781
O	2.21033174	-2.43317581	-1.47263859
O	2.02243530	-2.35259270	1.24037902
H	2.57127212	-1.18730424	3.64807512
H	1.30728367	-0.70366460	4.75674734
H	-0.34478246	1.07125019	4.11417119
H	0.87958537	3.84873945	1.09398922
H	3.26670687	3.64486396	0.35840634
H	4.05081194	2.08468811	0.30964028
H	2.13407410	4.45795208	-1.54117464
H	0.97179943	1.79438383	-4.69810148
H	2.64797954	-1.10366627	-3.47076501
H	1.45238596	-0.48950969	-4.58841519
H	-0.96911376	-0.33451936	-3.89290734

H	-2.25545201	-3.22725864	-1.01104689
H	1.16322246	-4.36810289	-0.12331073
H	-0.52318877	-4.82256583	-0.18519260
H	-2.04141031	-4.25624410	1.53830049
H	-0.86442424	-1.59356576	4.68327923
H	2.81122665	-0.80994767	-1.34994806
H	3.47616678	0.11692005	0.70315936
H	2.53694461	-1.58166302	1.55923477
H	2.25714500	-2.66220314	-0.52424177
H	-2.52863068	-3.14290789	3.70128864
H	-2.79596202	-1.52105977	-2.72657519
H	1.18924297	4.09866202	-3.80923739
H	-0.70353001	3.18960477	2.86935620
O	-2.30895272	1.65549579	-0.54469300
K	-0.73837850	0.08446016	0.31932260
K	-1.64099900	3.29794273	-2.16988753
K	-4.63264614	2.16664613	-0.15127657

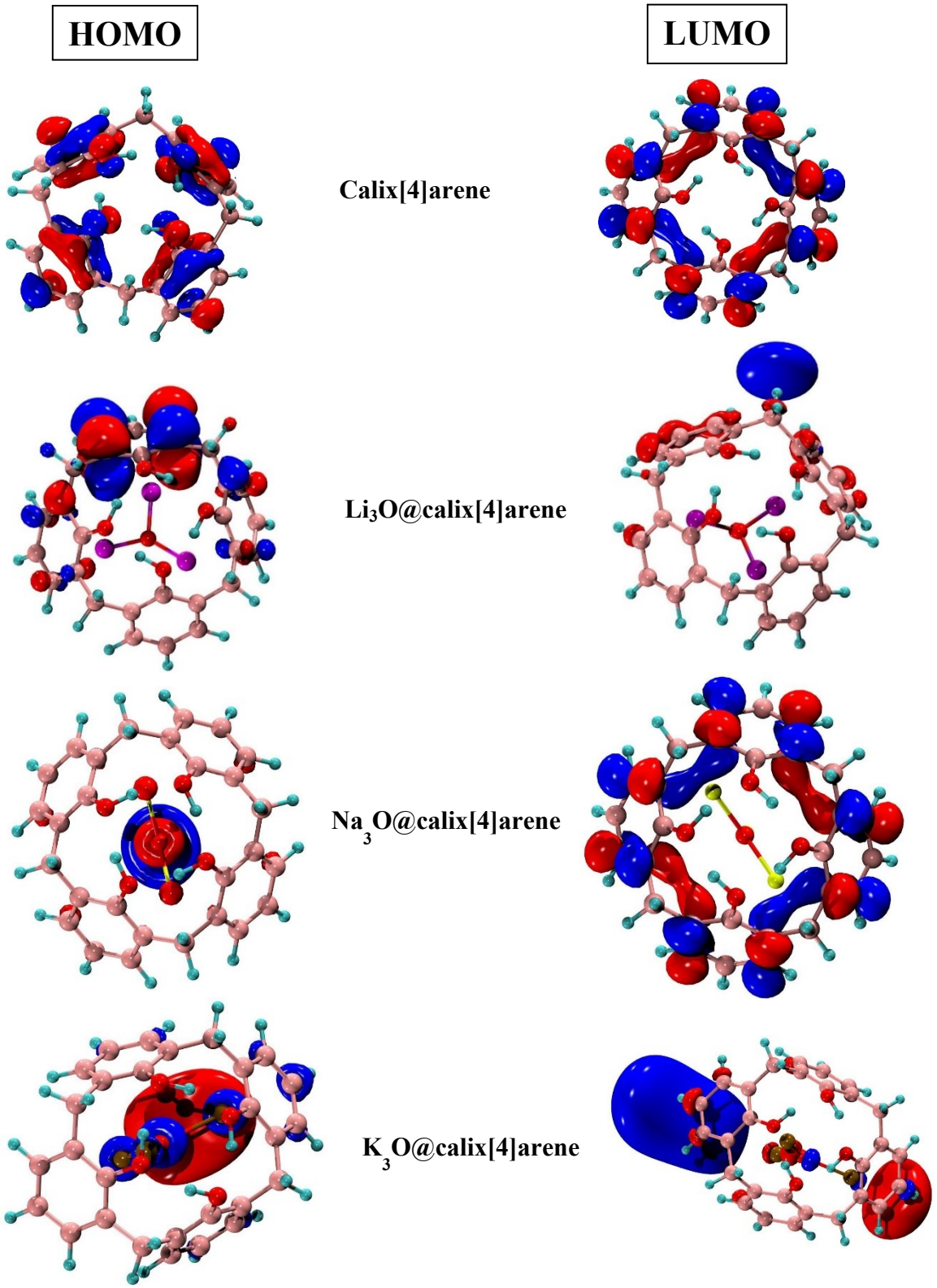


Fig. S1: Electronic densities of frontier molecular orbitals (HOMO = Highest Occupied Molecular Orbital, LUMO = Lowest Unoccupied Molecular Orbital) in M_3O@calix[4]arene complexes (isovalue = 0.03)

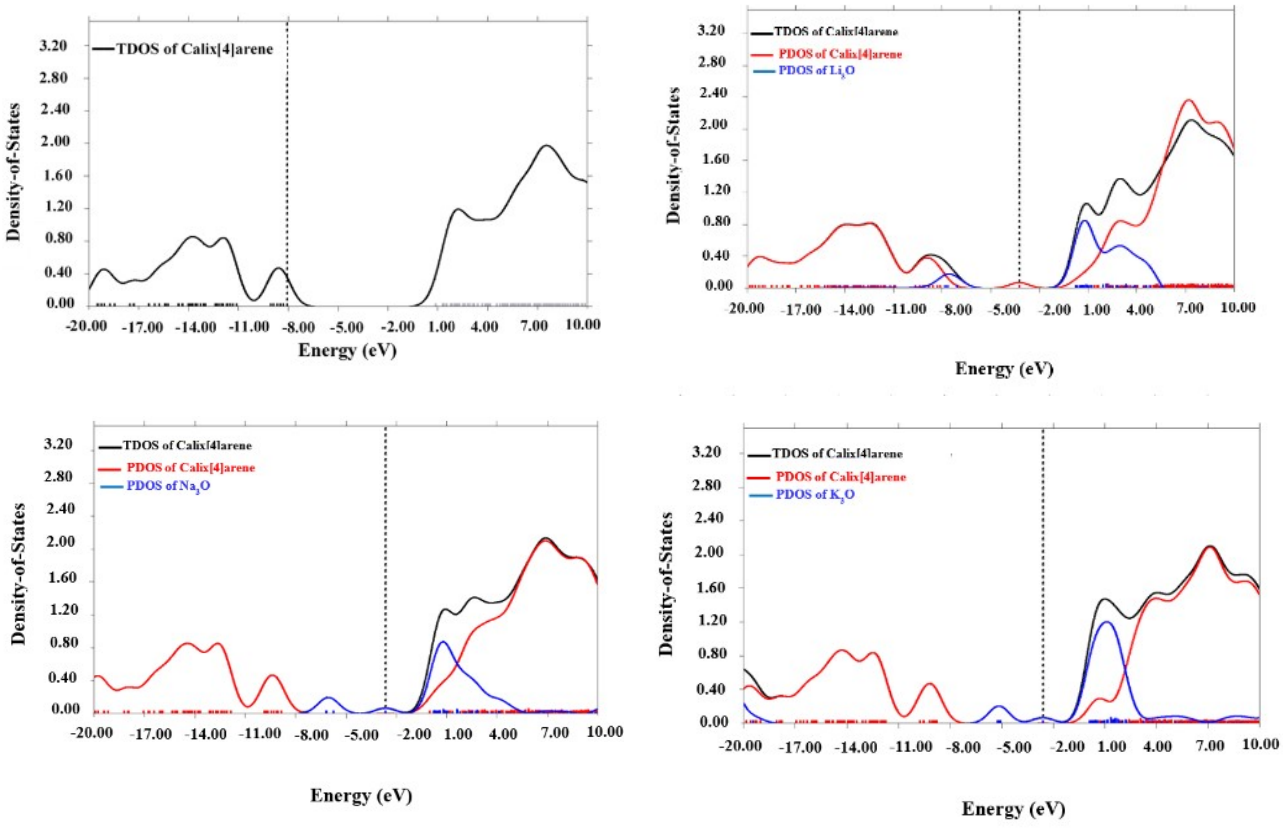
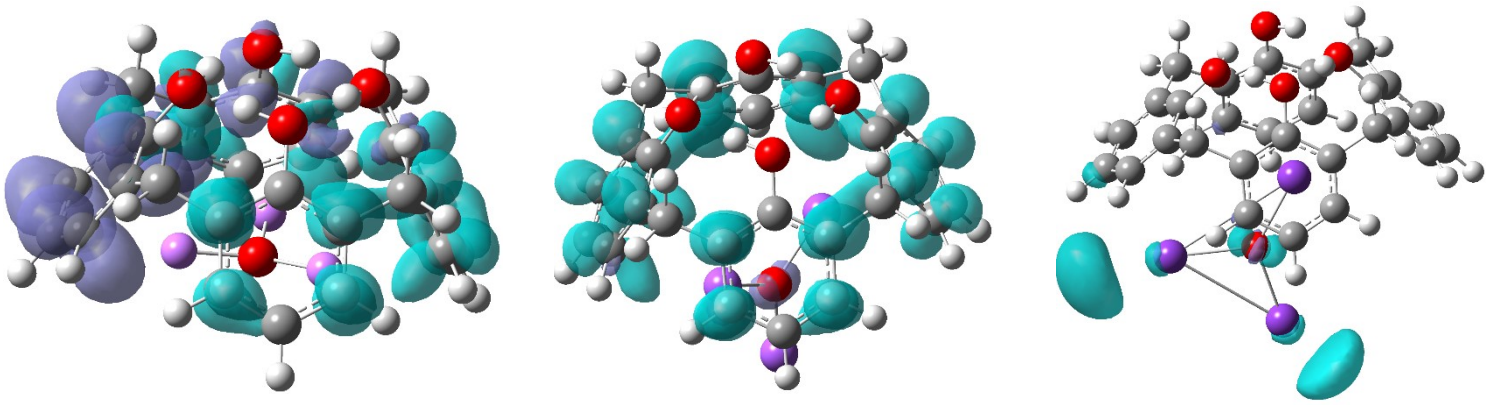


Fig. S2: Density of state (DOS) spectra of pure calix[4]arene (CX [4]) and M_3O@ calix[4]arene complexes



Li_3O@calix[4]arene **Na_3O@calix[4]arene** **K_3O@calix[4]arene**

Fig. S3: Electron Density Difference (EDD) Analysis of M_3O@calix[4]arene complexes (isosurface = 0.05 au)

Table S1 The Atoms in Molecules (AIM) topological parameters, including electron density (ρ), Laplacian of electron density (∇2ρ), electron energy density H(r) and the ratio of the kinetic electron density G(r) to potential electron density V(r) at bond critical points (BCPs) of the all SA@calix[4]arene complexes

Complex	Interaction	ρ	$\nabla^2\rho$	H r	V r	G r	$-G$ r/V r
Li_3O@calix[4]arene	Li-C	0.015	0.082	0.0032	-0.0139	0.0172	1.2374
	Li-C	0.011	0.0513	0.0020	-0.0086	0.0107	1.2441
	Li-C	0.009	0.0474	0.0022	-0.0073	0.0096	1.3150
	Li-O	0.004	0.0112	0.0003	-0.0020	0.0024	1.200
	Li-C	0.006	0.0332	0.0015	-0.0050	0.0065	1.300
Na_3O@calix[4]arene	Na-C	0.0064	0.0270	0.0011	-0.0043	0.0055	1.2790
	Na-C	0.0062	0.0265	0.0011	-0.0042	0.0054	1.2857
	Na-C	0.0062	0.0265	0.0011	-0.0042	0.0054	1.2857
	Na-C	0.0064	0.0270	0.0011	-0.0043	0.0055	1.2790
K_3O@calix[4]arene	K-C	0.0014	0.0059	0.0004	-0.0006	0.0010	1.6666
	K-C	0.0059	0.0208	0.0010	-0.0031	0.0041	1.3225
	K-C	0.0054	0.0201	0.0009	-0.0030	0.0040	1.333
	K-C	0.0051	0.0175	0.0008	-0.0027	0.0035	1.2131
	K-C	0.0053	0.0193	0.0009	-0.0030	0.0039	1.300
	O-C	0.0031	0.0070	0.0003	-0.0011	0.0014	1.2727

Table S2: Dipole moment (Debye), polarizability (au), first hyperpolarizability (au)/(esu) for superalkali doped calix[4]arenes at ωB97XD/6-31+(d, p)

Complexes	μ_t	α_o	β_o (au)	β_o (esu)
Calix[4]arene	2.05	316	550	4.75×10^{-30}
Li_3O@calix[4]arene	6.56	447	4.7×10^{4}	4.06×10^{-28}
Na_3O@calix[4]arene	11.91	905	3.6×10^{4}	3.11×10^{-28}
K_3O@calix[4]arene	11.19	863	3.5×10^{5}	3.02×10^{-27}