Optimizing Nonlinearity in $C_6O_6Li_6$-Doped Alkalides via Group I/III Doping for Unprecedented Charge Transfer and Breakthrough in Optoelectronics

Naveen Kosar*[1], Khurshid Ayub[2], Abdulaziz A. Al-Saadi[3,4], Muhammad Imran[5], and Tariq Mahmood[2,6]*

[1]Department of Chemistry, University of Management and Technology (UMT), C-11, Johar Town Lahore, Pakistan

[2]Department of Chemistry, COMSATS University Islamabad, Abbottabad Campus, Abbottabad-22060, Pakistan

[3]Chemistry Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

[4]Interdisciplinary Research Center for Refining and Advanced Chemicals, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

[5]Research Center for Advanced Materials Science (RCAMS), Chemistry Department, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

[6]Department of Chemistry, College of Science, University of Bahrain, Sakhir P.O. Box 32038, Bahrain

*Corresponding authors. E-mail address: naveen.kosar@umt.edu.pk (N.K) and mahmood@cuiatd.edu.pk

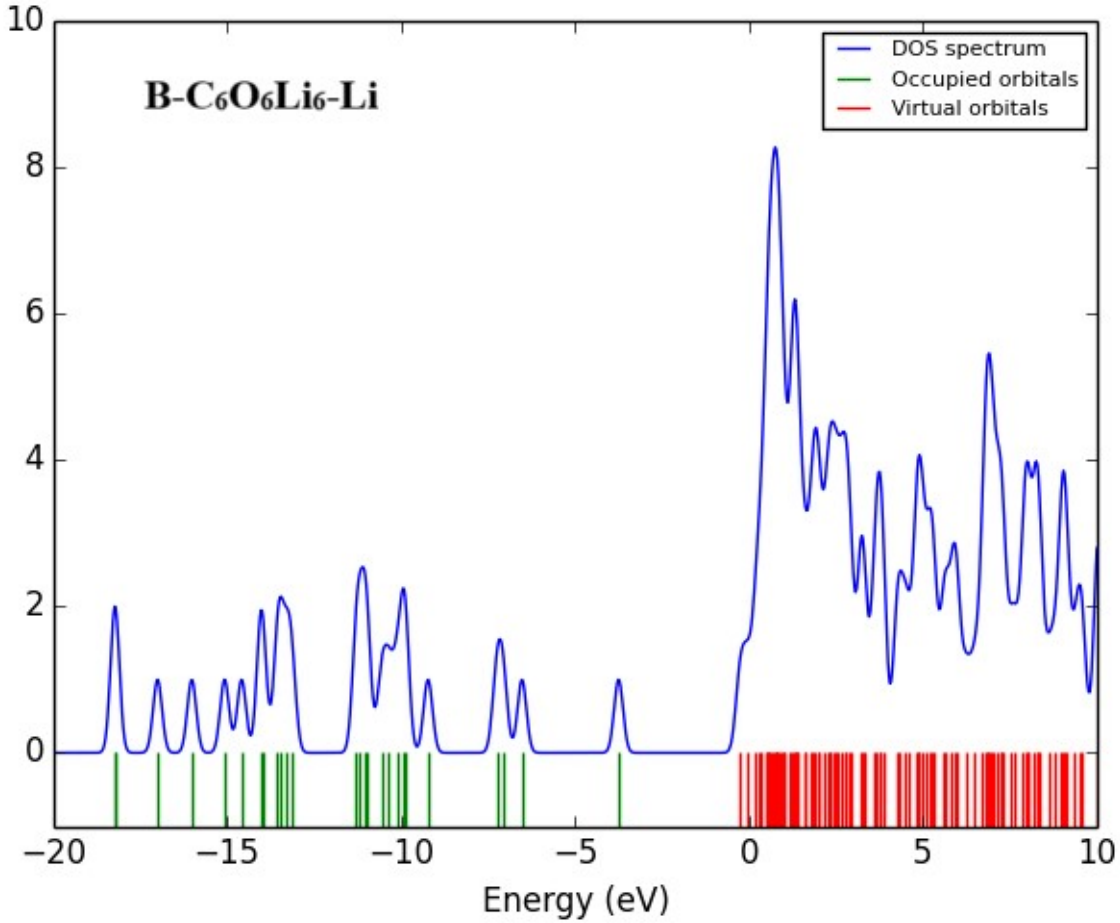
SI. Table 1: Interaction energies (E_{int} in kcal mol^{-1}) of pristine $C_6O_6Li_6$ and Group-I and Group-III on $C_6O_6Li_6$-alkalides (Group-IA = K, Na, Li and Group-IIIA = Ga, Al, B). The aug-ccPVDZ and aug-cc-PVTZ basis sets show error when implemented on K containing complexes as the atomic size of the K is out of the reach of these dunning basis sets (aug-ccPVDZ and aug-cc-PVTZ basis sets).

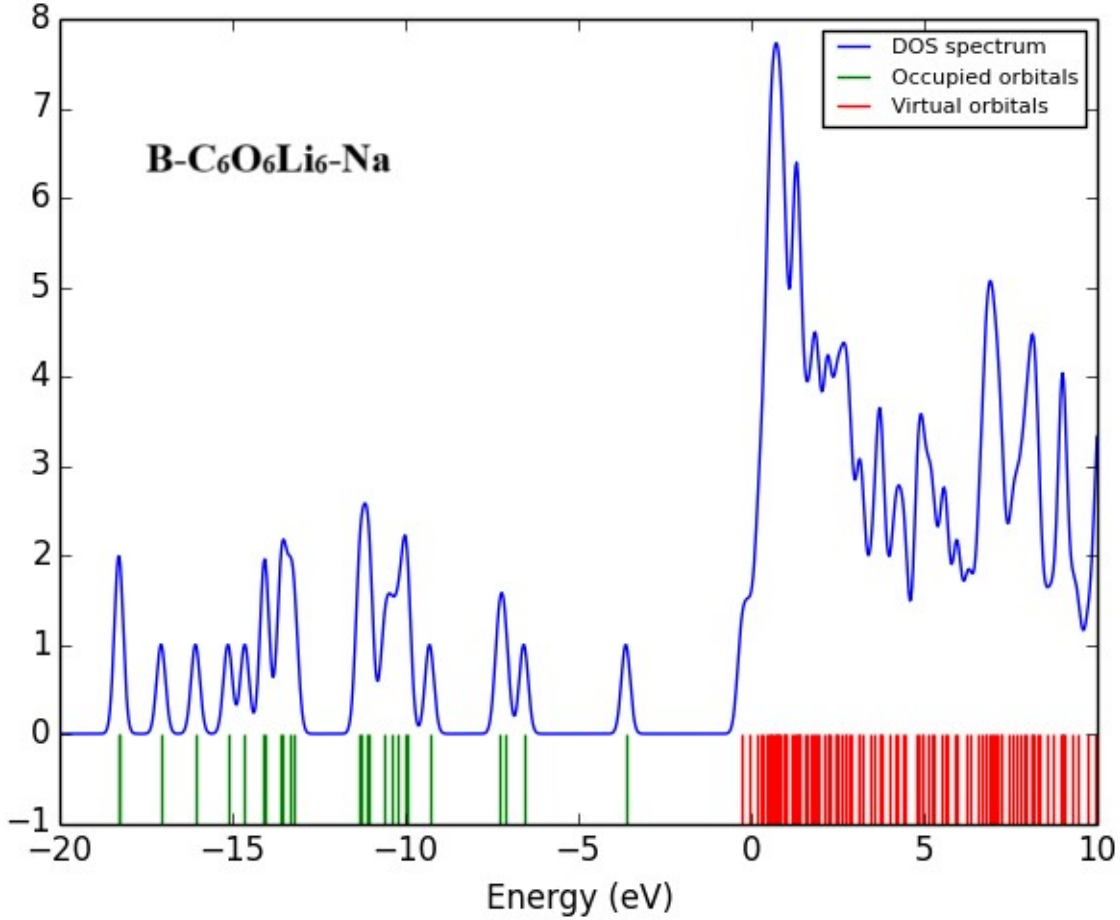
Complexes	aug-cc-PVDZ		aug-cc-PVTZ		Def2-TZVP	
	LC-BLYP	ωB97XD	LC-BLYP	ωB97XD	LC-BLYP	ωB97XD
B-$C_6O_6Li_6$-Li	-43.58	-16.01	-47.58	-41.08	-44.66	-63.61
B-$C_6O_6Li_6$-Na	-42.65	-15.32	-46.05	-30.15	-43.59	-62.56
B-$C_6O_6Li_6$-K	--	--	--	--	-37.30	-47.62
Al-$C_6O_6Li_6$-Li	-39.3	-7.51	-44.35	-36.52	-45.63	-55.95
Al-$C_6O_6Li_6$-Na	-38.67	-7.11	-43.11	-34.31	-44.90	-55.27
Al-$C_6O_6Li_6$-K	--	--	--	--	-37.86	-47.00
Ga-$C_6O_6Li_6$-Li	-34.72	-3.82	-39.07	-32.18	-35.67	-50.87
Ga-$C_6O_6Li_6$-Na	-35.08	-3.36	-37.82	-31.43	-34.92	-50.16
Ga-$C_6O_6Li_6$-K	--	--	--	--	-22.60	-43.09

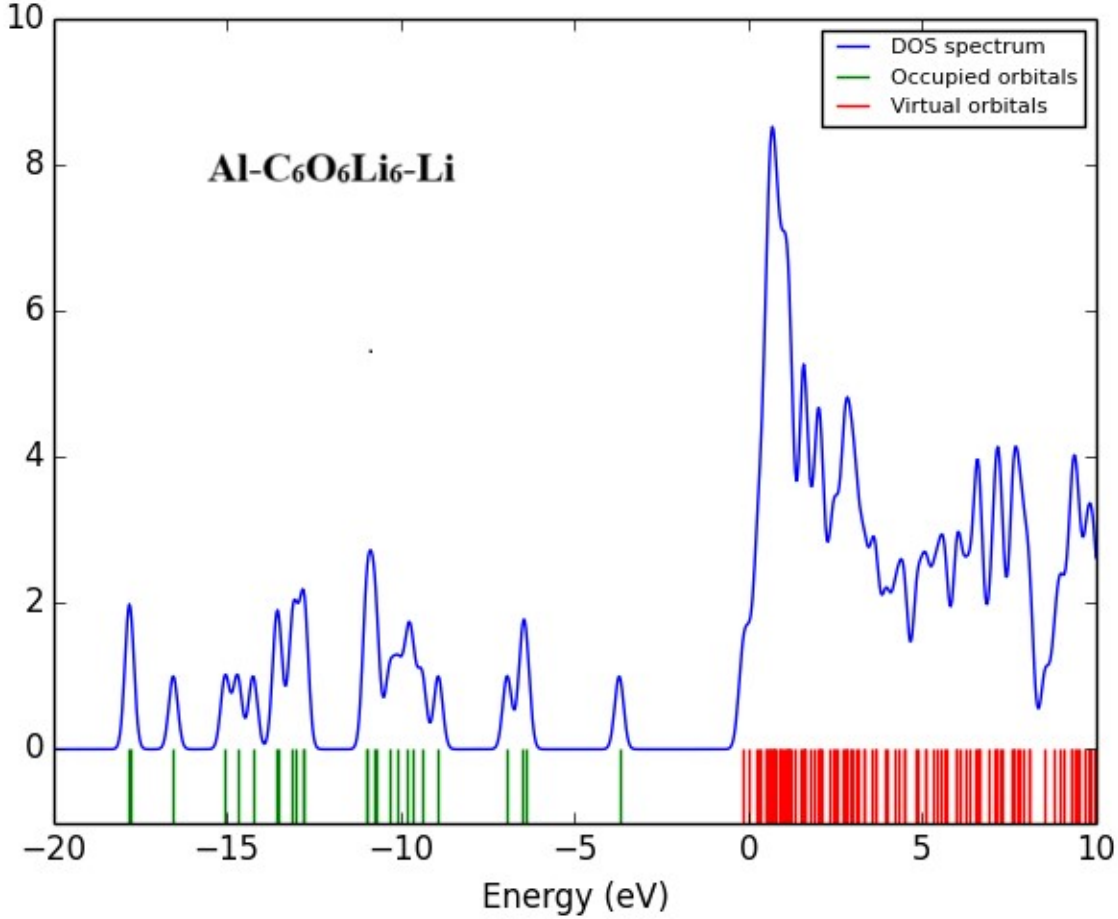
SI. Table 2: Nonlinear optical properties including dipole moment (μ in Debye), polarizability (α in au) and hyperpolarizability (β in au) of pristine $C_6O_6Li_6$ and Group-I and Group-III on $C_6O_6Li_6$-alkalides (Group-IA = K, Na, Li and Group-IIIA = Ga, Al, B). The aug-ccPVDZ and aug-cc-PVTZ basis sets show error when implemented on K containing complexes as the atomic size of the K is out of the reach of these dunning basis sets (aug-ccPVDZ and aug-cc-PVTZ basis sets).

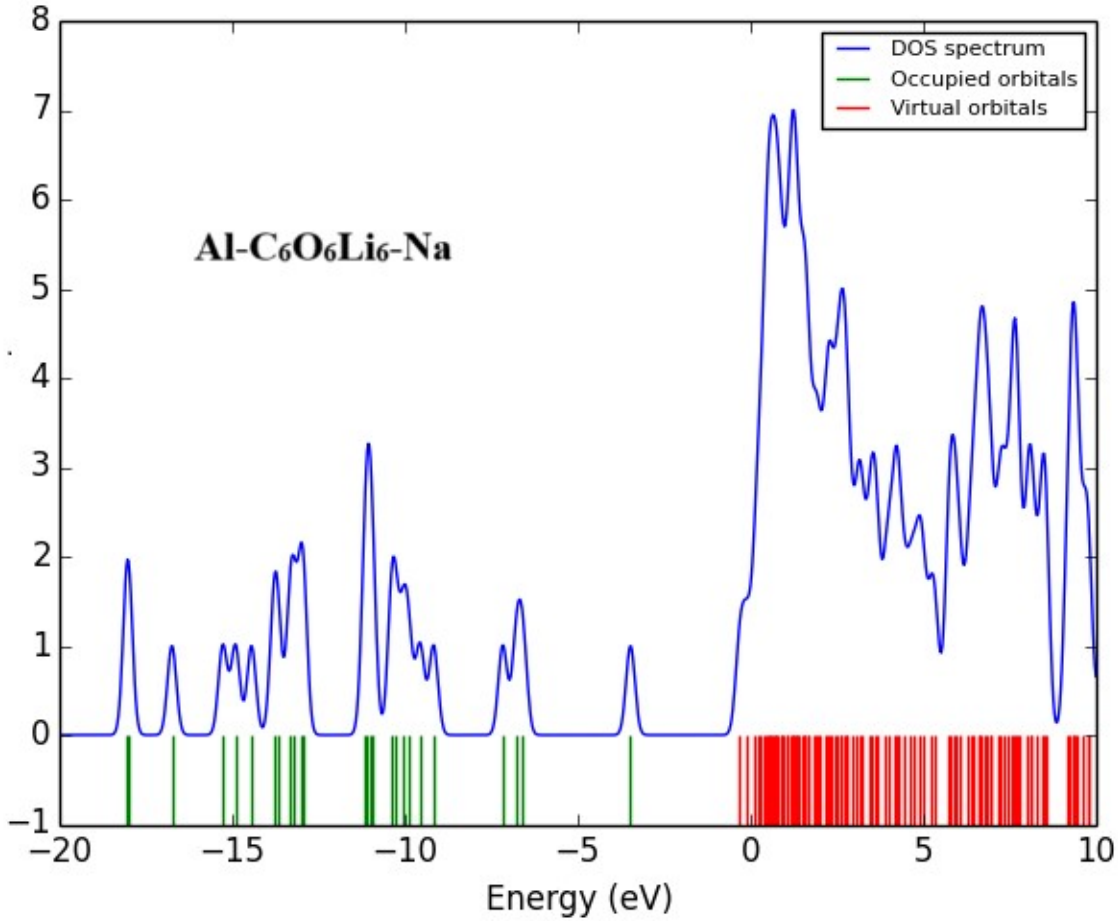
Basis sets	Density functionals	Parameters	B-$C_6O_6Li_6$-Li	B-$C_6O_6Li_6$-Na	B-$C_6O_6Li_6$-K	Al-$C_6O_6Li_6$-Li	Al-$C_6O_6Li_6$-Na	Al-$C_6O_6Li_6$-K	Ga-$C_6O_6Li_6$-Li	Ga-$C_6O_6Li_6$-Na	Ga-$C_6O_6Li_6$-K
aug-cc-PVDZ	**ωB97XD**	μ	15.50	16.25	--	16.34	17.51	--	16.51	14.43	--
		α	410	445	--	464	507	--	502	507	--
		β	1.53×10^4	1.39×10^4	--	8.22×10^3	8.89×10^2	--	9.09×10^2	8.89×10^2	--
	LC-BLYP	μ	16.90	16.68	--	16.40	16.65	--	16.51	14.43	--
		α	425	413	--	480	497	--	515	523	--
		β	1.81×10^4	1.21×10^4	--	8.22×10^3	8.93×10^2	--	9.35×10^2	8.95×10^2	--

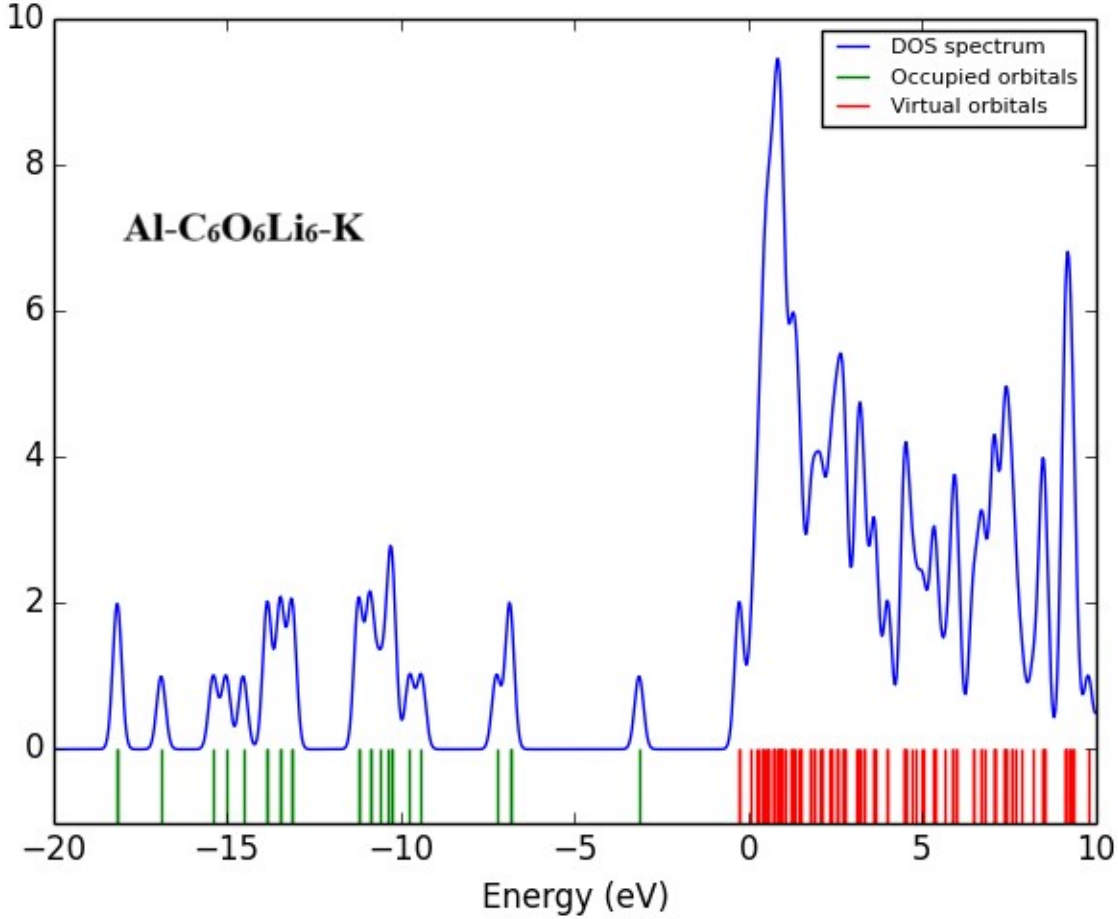
aug-cc-PVTZ	**ωB97XD**	μ	15.99	16.68	--	17.18	18.31	--	16.07	16.59	--
		α	417	454	--	474	521	--	420	473	--
		β	1.26×10^{4}	1.41×10^{4}	--	5.37×10^{3}	6.28×10^{3}	--	1.26×10^{4}	1.41×10^{4}	--
	LC-BLYP	μ	16.20	17.19	--	16.64	18.12	--	16.31	17.19	--
		α	388	422	--	436	476	--	396	438	--
		β	1.26×10^{4}	1.14×10^{4}	--	6.81×10^{3}	4.04×10^{3}	--	1.13×10^{4}	1.34×10^{4}	--
Def2-TZVP	**ωB97XD**	μ	16.01	16.66	11.78	17.10	18.38	5.11	17.06	17.56	6.00
		α	349	418	762	389	473	579	384	418	223
		β	8.67×10^{3}	5.49×10^{3}	1.36×10^{5}	1.67×10^{4}	1.16×10^{3}	1.46×10^{5}	1.64×10^{4}	3.46×10^{3}	1.37×10^{5}
	LC-BLYP	μ	15.98	17.16	17.56	16.41	17.91	15.07	16.34	17.74	6.31
		α	327	392	523	360	434	567	357	430	810
		β	6.28×10^{3}	5.26×10^{3}	1.55×10^{4}	1.28×10^{4}	2.89×10^{3}	4.67×10^{4}	1.32×10^{4}	3.61×10^{3}	1.29×10^{5}

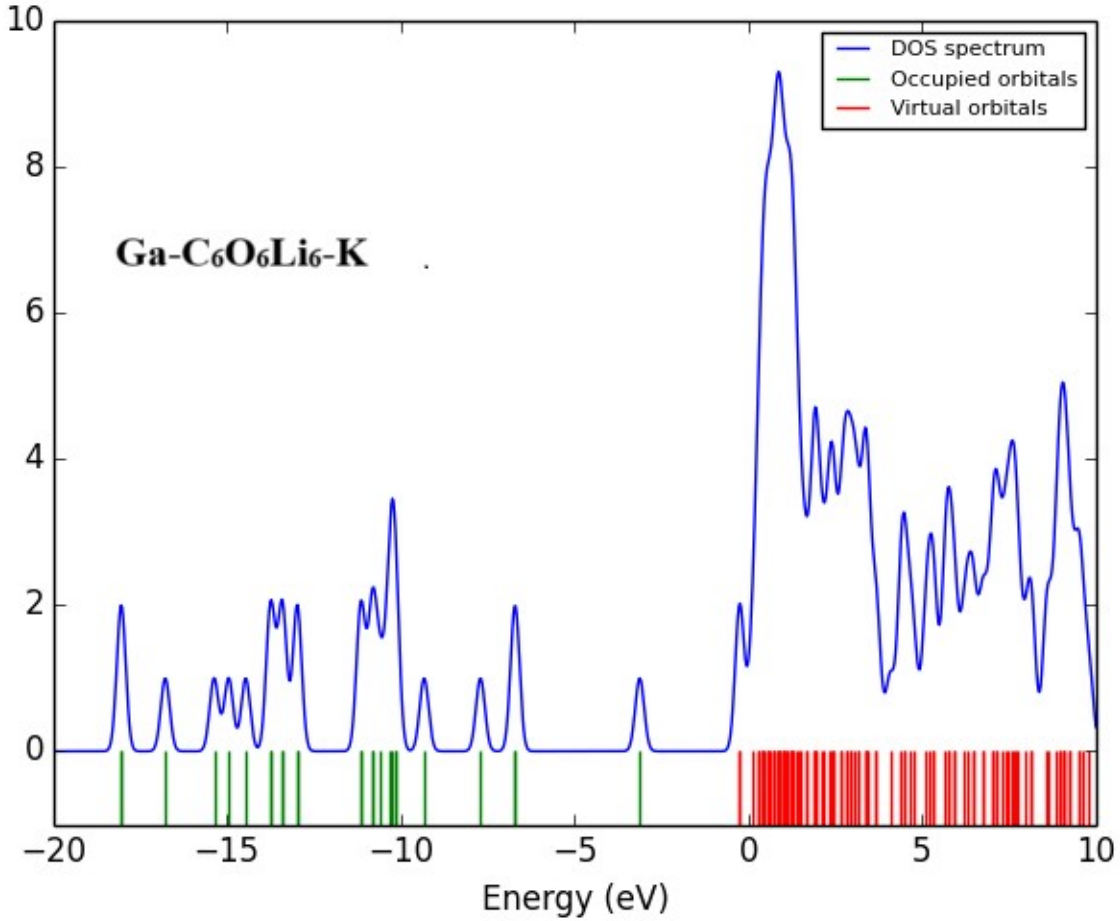

B-C6O6Li6-Li
DOS spectrum
Occupied orbitals
Virtual orbitals
10
8
6
4
2
0
−20
−15
−10
−5
0
5
10
Energy (eV)


B-C6O6Li6-Na
DOS spectrum
Occupied orbitals
Virtual orbitals
8
7
6
5
4
3
2
1
0
−1
−20
−15
−10
−5
0
5
10
Energy (eV)


DOS spectrum
Occupied orbitals
Virtual orbitals
Al-C6O6Li6-Li
10
8
6
4
2
0
−20
−15
−10
−5
0
5
10
Energy (eV)


DOS spectrum
Occupied orbitals
Virtual orbitals
Al-C6O6Li6-Na
8
7
6
5
4
3
2
1
0
−1
−20
−15
−10
−5
0
5
10
Energy (eV)


DOS spectrum
Occupied orbitals
Virtual orbitals
Al-C6O6Li6-K
10
8
6
4
2
0
−20
−15
−10
−5
0
5
10
Energy (eV)



SI. Fig. 1: DOS spectra of Group-III/IA metals doped C6O6Li alkalides.