Supplementary Information for :

Improving Excited-state Dynamic Properties with the Help of Metalide Character and Excess Electrons: Earlier Transition-metal Pairing with Superalkali Clusters

Atazaz Ahsin,[1,3] Aamna Qamar,[2,3] Sadegh Kaviani,[4] Safi Ullah Majid,[5] Jianwei Cao[1], Wensheng Bian[1,3*]*

[1]Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[2]Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Polymer Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[3]School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

[4] Institute of Physics, Kazan Federal University, 420008 Kazan, Russia

[5]Department of Chemistry, Abbottabad Campus, COMSATS University Islamabad, Abbottabad 22060, KPK, Pakistan

*E-mail: caojw@iccas.ac.cn; bian@iccas.ac.cn

Contents

Optimized geometric analysis	S3
Figure S1	S3
Figure S2	S4
Figure S3	S5
Figure S4	S5
Figure S5	S6
Figure S6	S6
Figure S7	S7
Table S1	S7
Table S2	S8
Table S3	S10
Table S4	S11
Table S5	S13
Table S6	S14

S1: Optimized geometric analysis

The average Li-O bond distance (BD_{Li-O}) and average Li-O-Li bond angle ($BA_{Li-O-Li}$) obtained are found to be 1.678 Å and 120°, respectively. The optimized molecular geometries of complexes are provided in Figure S1. The doped alkali metals on the other side of the complexant exhibit higher BD_{Li-O} and lower $BA_{Li-O-Li}$ values. The most significant changes in BD_{Li-O} and $BA_{Li-O-Li}$ are associated with Sc and Ti complexes. Moreover, the C-O bond length in 12-crown-4 increases slightly after transition metal doping. The complex's geometry is also slightly distorted for Sc, Ti, and V complexes. The highest C-O bond elongation occurs in the Ti complex, while the least distortion is seen in the Mn complex.

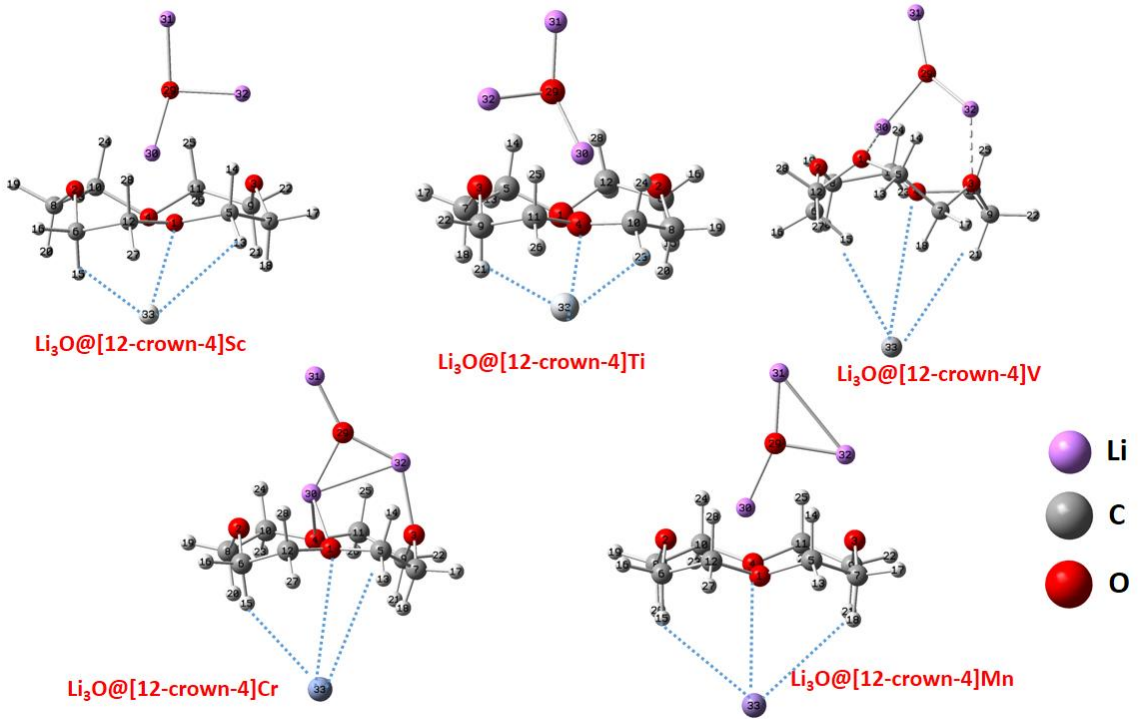

Figure S1: Optimized molecualr geometries of the Li_3O@[12-crown-4]M (where M = Sc, Ti, V, Cr, and Mn) complexes at the ωB97xd/def2tzvp level.

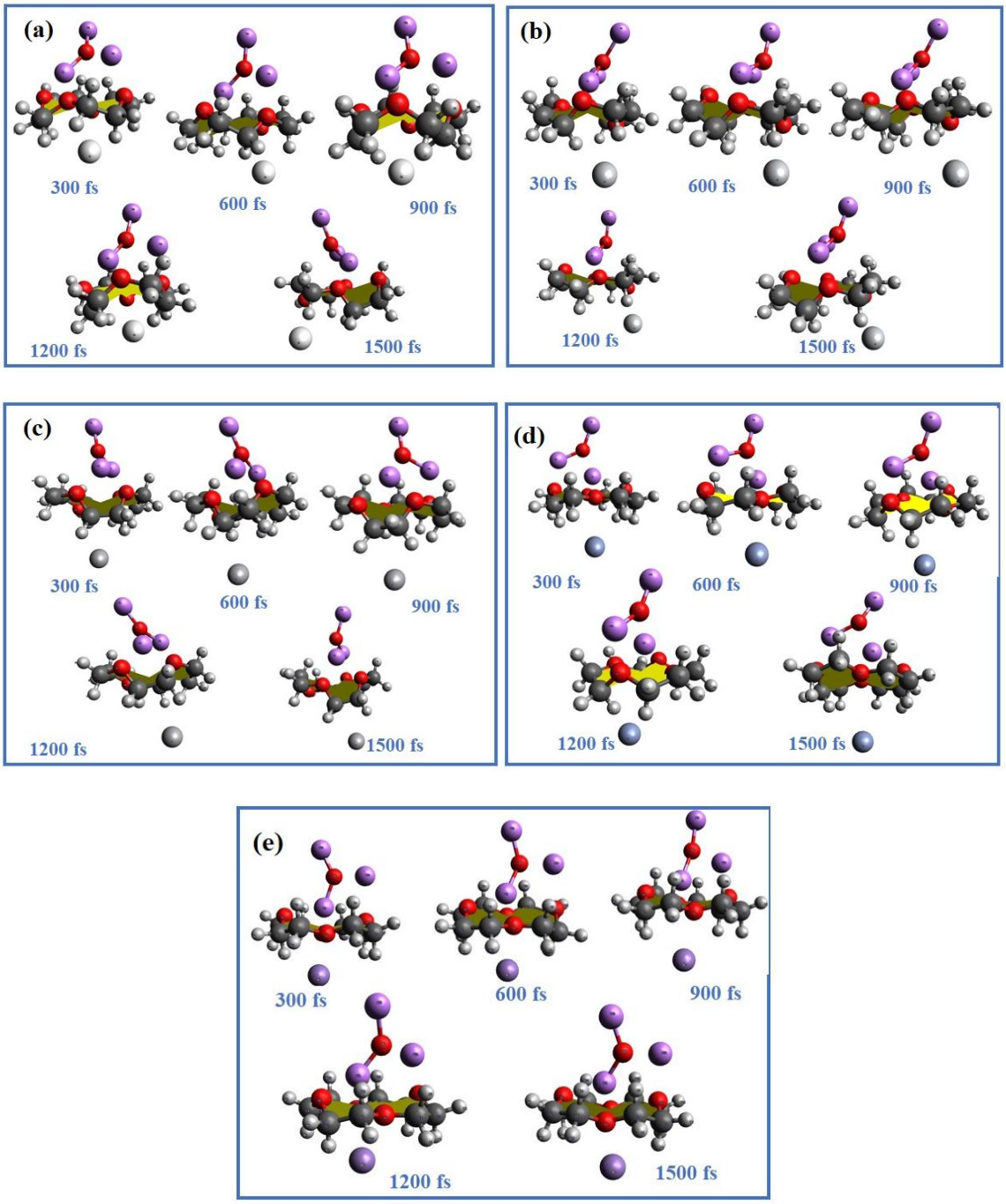

Figure S2: Snapshot of geometries for the Li_3O@[12-crown-4]M complex at 300 K, where (a) M=Sc, (b) M=Ti, (c) M=V, (d) M=Cr, and (e) M=Mn.

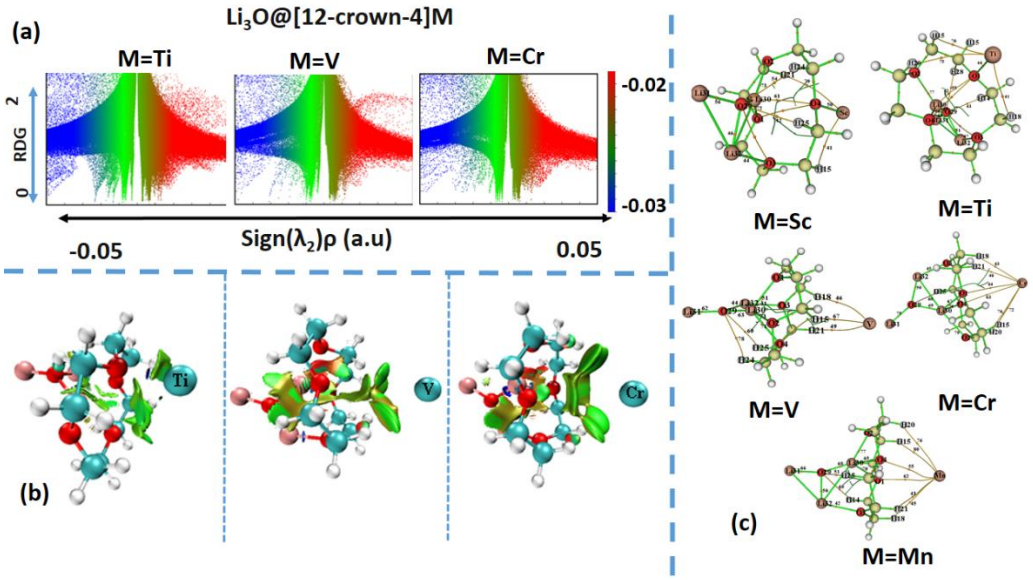

Figure S3: (a) Reduced density gradient scattered plots and (b) representation of isosurface from the non-covalent interaction study, and (c) generated bond critical points from the quantum theory of atoms in molecule analysis at the ωB97xd/def2tzvp method.

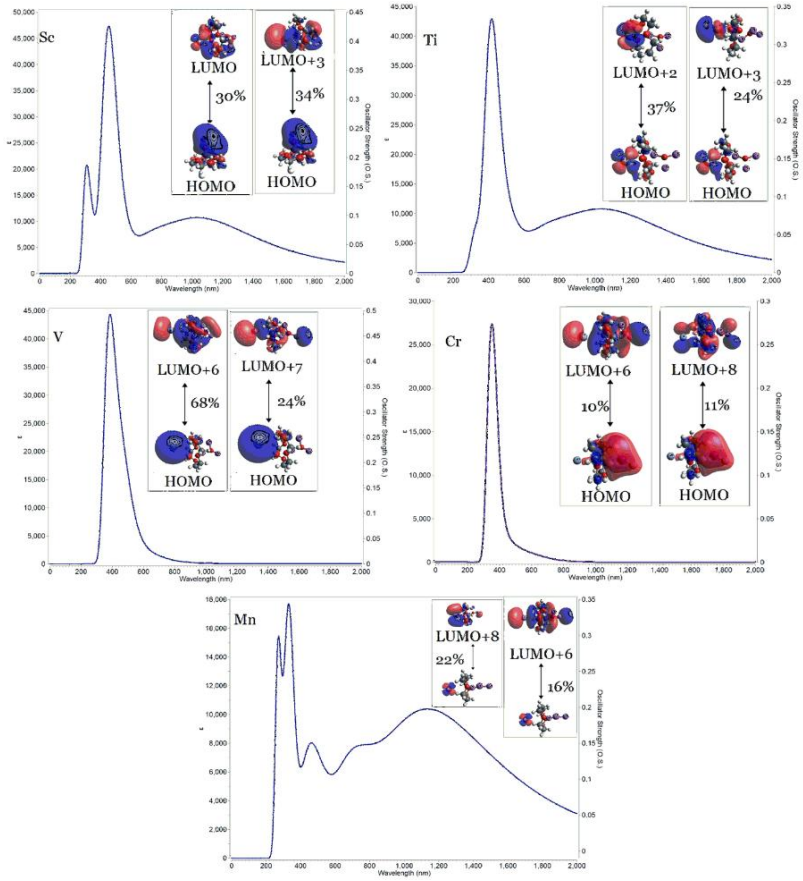

Figure S4: Absorption spectra of the Li_3O@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn) complexes.

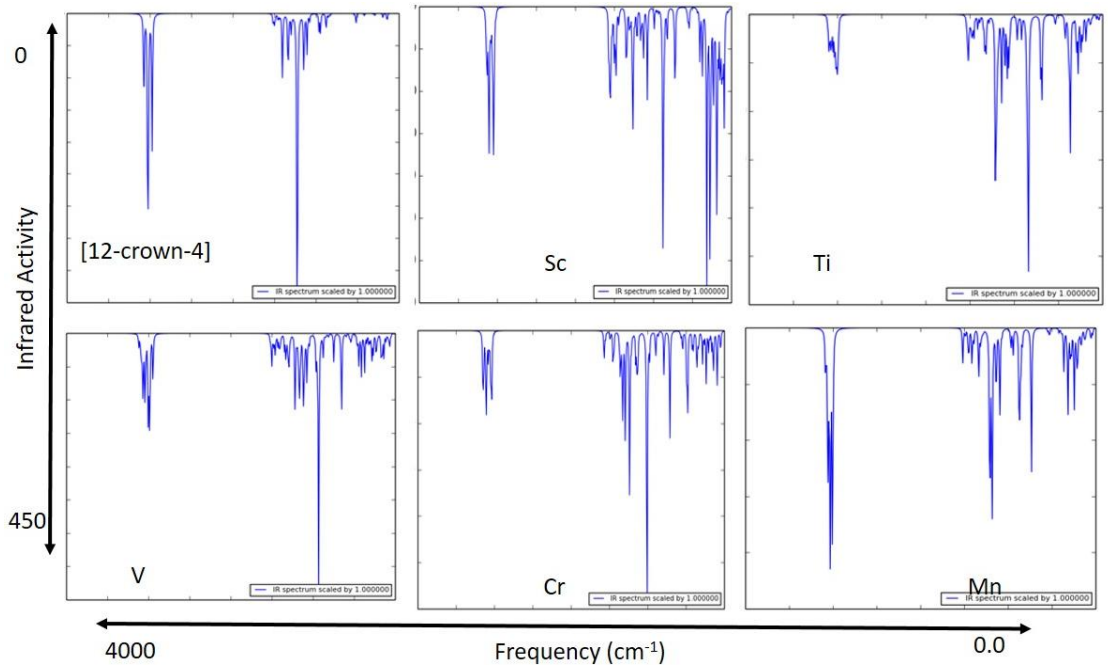

Figure S5: IR spectra of the [12-crown-4] and Li_3O@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn) complexes in the gas phase.

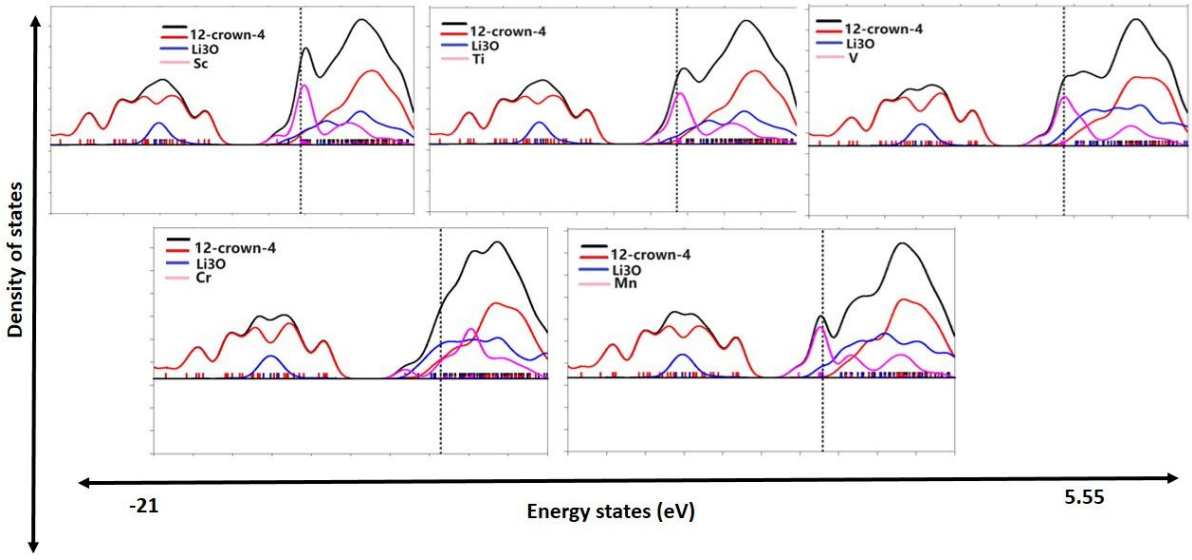

Figure S6: The plotted projected density of states (PDOS) spectra for the Li_3O@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn) complexes.

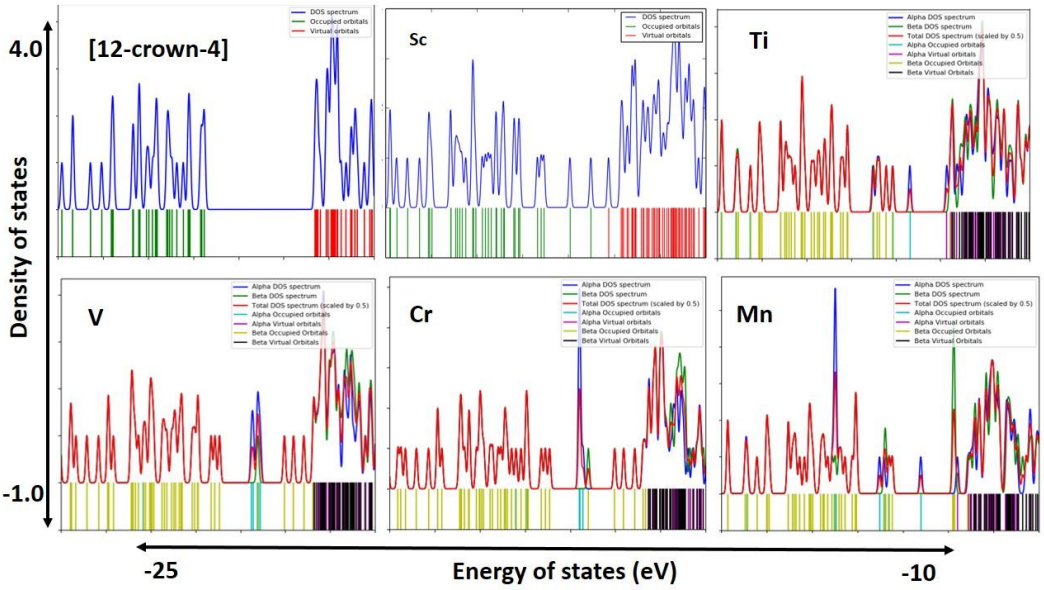

Figure S7: Plotted total density of state spectra of the [12-crown-4] and Li_3O@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn) complexes.

Table S1: The computed interaction energies (kcal/mol) at various double hybrid DFT methods for Li_3O@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn).

	Interaction energies (kcal/mol)	
	UDSD-PBEP86-D3BJ	UB2PLYP-D3BJ
Li_3O@[12-crown-4]Sc	-33.70	-34.64
Li_3O@[12-crown-4]Ti	-81.55	-79.45
Li_3O@[12-crown-4]V	-90.02	-125.67
Li_3O@[12-crown-4]Cr	-171.29	-166.50
Li_3O@[12-crown-4]Mn	-194.91	-225.71

Table S2: The optimized geometric coordinates of present complexes at the wb97xd/def2tzvp method.

Li_3O@[12-crown-4]S			
O	0.69318300	1.04535500	1.26363800
O	-0.75936100	2.01341000	-0.72647500
O	1.81667800	-1.25179200	0.38038500
O	-0.89283400	-0.83991400	-0.70819100
C	1.91001000	0.63083600	1.84238200
C	-0.93846700	2.55630900	0.56950000
C	1.93520600	-0.87872600	1.74260400
C	-1.84058700	1.30497500	-1.30803300
C	0.90732600	-2.29205100	0.04744000
C	-1.35828400	-0.03531500	-1.82013900
C	0.02376100	-1.89055500	-1.11159100
C	0.37688800	2.41996500	1.30640500
H	1.96886100	0.92783400	2.89570700
H	2.75864100	1.07498100	1.30455500
H	-1.70928100	1.99645400	1.11030600
H	-1.23520200	3.60766000	0.50998800
H	2.86955100	-1.26545100	2.15951700
H	1.09607400	-1.28599800	2.31347500
H	-2.23592500	1.87108700	-2.15646600
H	-2.64927300	1.18074400	-0.57918000
H	0.31441400	-2.56427900	0.92716600
H	1.47035100	-3.18014400	-0.25809800
H	-2.17178300	-0.55470700	-2.33385600
H	-0.50025800	0.10778400	-2.48969200
H	0.64962700	-1.46967600	-1.91093100
H	-0.55168600	-2.75744600	-1.44858300
H	0.26836000	2.77119400	2.33821200
H	1.16428600	3.00736900	0.81585600
O	1.78177500	0.28574500	-2.15169800
Li	0.88024900	0.82909200	-0.79782800
Li	2.89030400	0.84337700	-3.30663100
Li	2.97938900	-0.61418200	-1.28750900
Sc	-2.33177300	-1.31225300	0.99548800

Li_3O@[12-crown-4]Ti			
O	0.95230800	-0.76072400	-0.65658200
O	0.61058400	2.07391300	-0.71898500
O	-1.76774500	-1.37314400	0.35819000
O	-0.83343600	1.01017700	1.23413800
C	0.12587400	-1.88173700	-1.06429300
C	1.74616700	1.44227800	-1.28717600
C	-0.76136100	-2.33588500	0.07223700
C	0.73207600	2.60684000	0.58728900
C	-1.95715700	-0.98533300	1.70727900
C	-0.59290200	2.39903800	1.28911700
C	-2.03740000	0.52412500	1.78175900
C	1.37709900	0.05711400	-1.77494600
H	0.77264900	-2.70899100	-1.37150400
H	-0.50450800	-1.52234000	-1.88928400
H	2.56044600	1.39935500	-0.55727400
H	2.09056500	2.02254500	-2.14798600
H	-1.23850000	-3.27166600	-0.23731500
H	-0.17581000	-2.54132000	0.97297100
H	0.98018800	3.67181500	0.54845500
H	1.51459500	2.07653000	1.14044700
H	-1.11395000	-1.32630300	2.31386000
H	-2.87732900	-1.42752600	2.10008900
H	-0.53032100	2.75116600	2.32449300
H	-1.39647100	2.94683000	0.77935300
H	-2.89658200	0.90112000	1.21051000
H	-2.15011100	0.83223800	2.82757700
H	2.23825500	-0.40815800	-2.26309900
H	0.52496700	0.12048800	-2.46403300
O	-1.76567600	0.14890100	-2.18938900
Li	-0.93978700	0.78211300	-0.82677600
Li	-2.88532200	0.61013700	-3.37579600
Li	-2.90708700	-0.83553400	-1.34313200
Ti	2.41072000	-1.13352600	0.96651300

Li_3O@[12-crown-4]V			
O	0.69828300	-0.44123600	1.91103800
O	0.87107700	2.08357300	0.83463300
O	0.42800800	-2.07511800	-0.50524400
O	0.55192700	0.56963200	-1.28071700
C	0.21003200	-1.76660600	1.86819800
C	-0.39524100	1.62457300	1.32320500
C	-0.50202700	-2.10118800	0.58018700
C	0.76973900	2.73358300	-0.42512200
C	-0.09300300	-1.62680800	-1.76060700
C	1.20076200	1.78942500	-1.53729800
C	0.70150100	-0.43721100	-2.24538700
C	-0.17346300	0.58264800	2.38845300
H	-0.47304600	-1.95219300	2.70241600
H	1.08425000	-2.41150500	2.00797200
H	-0.99160400	1.19199600	0.51084900
H	-0.95861700	2.46277000	1.74597000
H	-0.94699300	-3.09865100	0.65670300
H	-1.31691000	-1.38377400	0.39614700
H	1.41588100	3.61353900	-0.41077000
H	-0.25952800	3.05863400	-0.59175000
H	-1.14175900	-1.33300200	-1.63986800
H	-0.03161600	-2.44471200	-2.48349500
H	0.91377100	2.20135100	-2.51195200
H	2.28911300	1.62911800	-1.52593500
H	1.76923200	-0.67518200	-2.36645100
H	0.29966600	-0.11583100	-3.21424100
H	-1.15276100	0.17348300	2.65413700
H	0.29198300	1.01267900	3.27892400
O	3.30064100	-0.61331000	-0.05739100
Li	1.86341300	0.27184300	0.49027300
Li	4.87983800	-0.19958300	0.11311300
Li	2.33141400	-1.97327800	-0.34608300
V	-3.70105900	0.12154400	-0.36299500

Li_3O@[12-crown-4]Cr				Li_3O@[12-crown-4]Mn			
O	0.31220000	0.05734800	1.46377300	O	0.01960400	0.09317800	1.49874700
O	0.53508400	2.32996400	0.09975700	O	0.11245000	2.38025400	-0.00844100
O	0.86369800	-2.22324700	-0.01492500	O	1.34342600	-1.97462100	-0.00439200
O	0.42785400	0.14584600	-1.42580400	O	0.02103900	0.08962900	-1.50475400
C	0.42200100	-1.17129700	2.12669900	C	0.76792500	-0.94403300	2.10148200
C	-0.33243900	2.28607100	1.23107200	C	-0.60146300	2.33912600	1.21268700
C	0.02071300	-2.24777500	1.14201000	C	0.65784500	-2.16904700	1.22042700
C	-0.11471800	2.39544800	-1.16716300	C	-0.61120100	2.33242700	-1.22315400
C	0.20515000	-2.18199100	-1.28569500	C	0.65723100	-2.17253900	-1.22781800
C	0.50148800	1.37566700	-2.10405300	C	0.07157300	1.34703600	-2.14864500
C	0.71955900	-1.03245100	-2.12431100	C	0.76486800	-0.94852100	-2.11068400
C	0.16167500	1.24099100	2.21051200	C	0.08401700	1.35357600	2.13595400
H	-0.26930900	-1.22266700	2.97584800	H	0.36816100	-1.18158900	3.09530600
H	1.44686600	-1.31114800	2.50285300	H	1.81694000	-0.63418100	2.19310600
H	-1.34005800	1.99425600	0.91541800	H	-1.63324700	2.01573100	1.03927400
H	-0.36938400	3.26784200	1.71289800	H	-0.61902300	3.33168200	1.67232900
H	0.09187500	-3.23190700	1.61398600	H	1.09806300	-3.02424700	1.74156100
H	-1.01657000	-2.06034000	0.84356900	H	-0.39689000	-2.38791400	1.02930800
H	-0.01534500	3.40161500	-1.58517000	H	-0.63751300	3.32333200	-1.68606200
H	-1.17514000	2.15006800	-1.05376300	H	-1.63995100	2.00431800	-1.04064100
H	-0.86973100	-2.03909200	-1.13560300	H	-0.39718300	-2.39201500	-1.03567400
H	0.37742600	-3.12920600	-1.80452900	H	1.09798800	-3.02796400	-1.74813400
H	-0.07572200	1.34955600	-3.03524500	H	-0.44463700	1.31856500	-3.11543200
H	1.54808200	1.61629800	-2.34059100	H	1.11692400	1.64062600	-2.31157600
H	1.80211300	-1.10523500	-2.30950200	H	1.81399600	-0.64085100	-2.20895300
H	0.19742900	-1.05777000	-3.08838100	H	0.36033600	-1.18619200	-3.10252200
H	-0.59003200	1.11547000	2.99763700	H	-0.42305500	1.33303400	3.10779100
H	1.11831000	1.52454100	2.67073300	H	1.13296400	1.64085800	2.28666200
O	3.28993300	-0.07437200	0.11293600	O	3.04655300	0.51737100	0.02026900
Li	1.63704000	0.56412700	0.10548100	Li	1.37295300	0.75891700	-0.00551700
Li	4.66050900	0.82594500	0.16855900	Li	4.69087500	0.90166500	0.01086200
Li	2.68630000	-1.65296400	0.10754000	Li	3.25282700	-1.17689400	0.00031500
Cr	-3.36429500	-0.26441200	-0.12855100	Mn	-3.10612800	-0.77035600	0.01175000

Table S3: Static polarizabilities α_0 (in au), static first hyperpolarizabilities β_o (in au), and dipole moment μ_o (in D) of the Li_3@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn) complexes in gas and aqueous phases of Li_3@[12-crown-4]M complexes.

Complex	water			ethanol			DMF		
	α_o	β_o	μ_o	α_o	β_o	μ_o	μ_o	α_o	β_o
Li_3O@[12-crown-4]Sc	1792.97	2142703.17	10.32	1601.76	2057246.62	9.88	11.04	1663.89	1783948.77
Li_3O@[12-crown-4]Ti	2440.92	3560120.23	45.92	2034.90	2334454.36	45.16	46.67	2027.79	3369274.33
Li_3O@[12-crown-4]V	823.99	40099.11	19.02	729.07	14036.91	19.6	19.12	789.08	25982.52
Li_3O@[12-crown-4]Cr	991.43	2465115.200	23.308	7630.34	2656120.23	15.56	23.55	948.91	1109719.44
Li_3O@[12-crown-4]Mn	1057.10	1070094.99	16.45	1011.58	1090460.63	16.01	17.37	1017.32	1109719.44

Table S4: Calculated topological parameters, including electron densities (ρ_b) and its Laplacian ($\nabla^2\rho_b$), kinetic energy density (G_b), potential energy density (V_b), total electron energy densities (H_b), and negative ratio of density ($G_b/|-V_b|$), in a.u. at the bond critical points (BCPs).

Complex	Bond	BCP	ρ_b	$\nabla^2\rho_b$	G_b	V_b	H_b	$G_b/\|V_b\|$
Li_3O@[12-	Sc−O4	50	0.042	0.206	0.489	-0.463	0.026	1.056
crown-4]Sc	Sc−H21	79	0.083	0.100	0.298	-0.345	-0.047	0.863
	Sc−H15	41	0.082	0.700	0.197	-0.220	-0.023	0.895
	O29−H24	54	0.016	0.510	0.429	-0.283	0.146	1.515
	O29−H25	42	0.023	0.180	0.286	-0.171	0.115	1.672
	Li30−O1	72	0.019	0.142	0.290	-0.226	0.064	1.283
	Li30−O2	73	0.022	0.166	0.343	-0.269	0.074	1.275
	Li30−O4	61	0.016	0.121	0.239	-0.176	0.063	1.357
	Li32−O3	44	0.074	0.534	0.231	-0.173	0.058	1.335
	Li30−O29	62	0.056	0.436	0.986	-0.880	0.106	1.120
	Li31−O29	56	0.060	0.471	0.906	-0.859	0.047	1.054
	Li32−O29	46	0.055	0.422	0.961	-0.867	0.094	1.108
Li_3O@[12-	Ti−O1	44	0.049	0.222	0.553	-0.551	0.002	1.003
crown-4]Ti	Ti−H18	41	0.083	0.120	0.329	-0.356	-0.027	0.924
	Ti−H15	70	0.078	0.120	0.325	-0.349	-0.024	0.931
	Ti−H20	75	0.063	0.845	0.222	-0.233	-0.011	0.952
	O29−H14	43	0.023	0.170	0.180	-0.168	0.012	1.071
	O29−H28	55	0.016	0.121	0.115	-0.100	0.015	1.150
	Li30−O1	62	0.071	0.515	0.981	-0.674	0.307	1.455
	Li30−O2	77	0.023	0.168	0.348	-0.275	0.073	1.265
	Li30−O4	74	0.020	0.144	0.296	-0.231	0.065	1.281
	Li32−O3	47	0.017	0.126	0.253	-0.190	0.063	1.331
	Li30−O29	69	0.056	0.436	0.980	-0.869	0.111	1.127
	Li31−O29	60	0.060	0.471	0.907	-0.874	0.033	1.037
	Li32−O29	51	0.056	0.424	0.973	-0.885	0.088	1.099
Li_3O@[12-	V−H18	46	0.078	0.965	0.285	-0.330	-0.045	0.863
crown-4]V	V−H15	67	0.070	0.930	0.297	-0.361	-0.064	0.822
	V−H21	49	0.074	0.731	0.221	-0.260	0.039	0.850
	O29−H25	60	0.042	0.239	0.525	-0.452	0.073	1.161
	O29−H24	78	0.069	0.202	0.439	-0.371	0.068	1.183

	Li30−O1	51	0.041	0.167	0.330	-0.242	0.088	1.363
	Li30−O2	73	0.019	0.136	0.280	-0.218	0.062	1.284
	Li30−O4	71	0.077	0.965	0.189	-0.136	0.053	1.389
	Li32−O3	41	0.030	0.230	0.486	-0.396	0.090	1.227
	Li30−O29	63	0.048	0.359	0.804	-0.709	0.095	1.133
	Li31−O29	62	0.0689	0.559	0.127	-0.115	0.012	1.104
	Li32−O29	44	0.060	0.468	0.906	-0.854	0.052	1.060
Li_3O@[12-crown-4]Cr	Cr−O1	44	0.0383	0.649	0.147	-0.132	0.015	1.113
	Cr−O4	63	0.0370	0.622	0.141	-0.126	0.015	1.119
	Cr−H18	43	0.0724	0.716	0.213	-0.247	-0.034	0.862
	Cr−H21	46	0.0634	0.664	0.189	-0.212	-0.023	0.891
	Cr−H15	72	0.0629	0.658	0.211	-0.232	-0.021	0.909
	Cr−H20	76	0.0511	0.599	0.157	-0.165	-0.008	0.951
	Li30−O1	67	0.026	0.200	0.416	-0.330	0.086	1.260
	Li30−O2	79	0.019	0.141	0.290	-0.226	0.064	1.283
	Li30−O4	70	0.024	0.184	0.380	-0.299	0.081	1.270
	Li32−O3	45	0.030	0.230	0.485	-0.395	0.090	1.227
	Li30−O29	69	0.048	0.363	0.811	-0.714	0.097	1.135
	Li31−O29	75	0.069	0.560	0.128	-0.115	0.027	1.113
	Li32−O29	50	0.060	0.476	0.908	-0.870	0.038	1.043
Li_3O@[12-crown-4]Mn	Mn−O1	62	0.052	0.102	0.239	-0.222	0.171	1.076
	Mn−O4	55	0.051	0.100	0.234	-0.217	0.172	1.078
	Mn−H20	76	0.058	0.836	0.205	-0.207	0.172	0.990
	Mn−H15	80	0.058	0.834	0.204	-0.206	0.218	0.900
	Mn−H21	43	0.056	0.761	0.182	-0.186	0.388	0.978
	Mn−H18	45	0.057	0.769	0.186	-0.189	0.311	0.984
	O29−H25	51	0.080	0.224	0.491	-0.422	0.690	1.163
	Li30−O1	70	0.017	0.126	0.253	-0.191	0.062	1.324
	Li30−O2	77	0.021	0.15	0.315	-0.247	0.068	1.275
	Li30−O4	65	0.017	0.127	0.255	-0.193	0.062	1.321
	Li32−O3	42	0.020	0.145	0.296	-0.228	0.068	1.298
	Li30−O29	68	0.058	0.468	0.904	-0.818	0.086	1.105
	Li31−O29	66	0.062	0.481	0.11	-0.10	0.010	1.100
	Li32−O29	50	0.059	0.452	0.903	-0.839	0.064	1.076

Table S5: Donor orbital (i), acceptor orbital (j), second-order perturbation energy (E^2), orbital energies (E_i and E_j), off-diagonal NBO Fock matrix element ($F_{i,j}$), donation (d), back donation (b), total charge transfer (d-b), and repulsive polarization (r) of the Li_3@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn) complexes.

Complex	LP(O) → LP*(M)			CDA analysis			
	E^2 (kcal/mol)	$E_j - E_i$	F(i,j)	d	b	d-b	r
Li_3O@[12-crown-4]Sc	31.45	0.93	0.097	-0.007	-0.45	0.44	-0.07
Li_3O@[12-crown-4]Ti	12.78	0.76	0.139	-0.018	-0.42	0.40	-0.08
Li_3O@[12-crown-4]V	0.79	0.84	0.023	-0.001	-0.06	0.06	-0.007
Li_3O@[12-crown-4]Cr	0.08	0.48	0.006	-0.006	-0.07	0.06	-0.02
Li_3O@[12-crown-4]Mn	0.06	0.91	0.007	-0.004	-0.25	0.24	-0.03

Table S6: Vibrational frequencies of the [12-crown-4] and Li_3O@[12-crown-4]M (M = Sc, Ti, V, Cr, and Mn) complexes in the gas phase.

Vibrational modes of complexes			
Compound	Vibrational frequency (cm^{-1})	Group	Vibrational mode
[12-crown-4]	3330.21	C-H	C-H stretching
	1221.17	C-O	C-O stretching
Li_3O@[12-crown-4]Sc	2981-3093	C-H	C-H stretching
	1505-1312	C-H	C-H bending
	1203	C-O	C-O-C (1120-1250)
	1068	C-C	C-C stretching
Li_3O@[12-crown-4]Ti	2987-3105	C-H	C-H stretching
	1500-1316	C-H	C-H bending
	1207	C-O	C-O-C (1120-1250)
	1069	C-C	C-C stretching
Li_3O@[12-crown-4]V	2947-3119	C-H	C-H stretching
	1521-1270	C-H	C-H bending
	1216	C-O	C-O-C (1120-1250)
	1072	C-C	C-C stretching
Li_3O@[12-crown-4]Cr	3029-3150	C-H	C-H stretching
	1521-1270	C-H	C-H bending
	1232	C-O	C-O-C (1120-1250)
	1093	C-C	C-C stretching
Li_3O@[12-crown-4]Mn	2997-3083	C-H	C-H stretching
	1513-1312	C-H	C-H bending
	1206	C-O	C-O-C (1120-1250)
	1067	C-O	C-O-C (1120-1250)