Where to bind in buckybowls? The dilemma of a metal ion

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Supporting Information
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Figure S1: Correlation between the cation–π distance and the interaction energy of the (a) Li^+ and (b) Na^+ (c) K^+ and (d) Cu^+ complexes.

Figure S2: The correlation between the interaction energies of the a)Li^+, b)Na^+, c)K^+ , and d)Cu^+ complexes of sumanene at various levels of theories.

Figure S3: The correlation between the interaction energies of the a)Li^+, b)Na^+, c)K^+ , and d)Cu^+ complexes of corannulene at various levels of theories.

Table S1: The geometrical parameters (in Å) of the buckybowl complexes of sumanene (**1**) and corannulene (**2**) with Na^+ and K^+ ions evaluated at the M05-2X level in conjugation with the cc-pVDZ and 6-31G* basis sets.

Table S2: The inversion barriers ($\Delta E^{\#}$ in kcal/mol) of various complexes considered in the study evaluated at the M05-2X/cc-pVDZ level. The 6-31G* basis set was used for the K^+ complexes alone.

Table S3: The charge on the cation calculated using different schemes viz. Mulliken (q1 in a.u.), NPA (q2 in a.u.) and CHelpG (q3 in a.u.), charge density ($\rho*10^2$), Laplacian of the charge density ($\nabla\ ^2\rho*10^2$) at the (3,+3) cage critical point of the complexes of sumanene (**1**) and corannulene (**2**) with different ions. The calculations were performed at the M05-2X-cc-pVDZ level. The 6-31G* basis set was employed for $\mathbf{K^+}$ complexes.

Table S4: Summary of the factors contributing to the total bonding interaction in the metal complexes of sumanene (**1**). Calculations were carried out at M05-2X /6-31G(d,p) level using localized molecular orbital energy decomposition analysis (LMO-EDA) as implemented in GAMESS program. All values are provided in kcal/mol.

Table S5: Summary of the factors contributing to the total bonding interaction in the metal complexes of corannulene (**2**). Calculations were carried out at M05-2X/6-31G(d,p) level using localized molecular orbital energy decomposition analysis

(LMO-EDA) as implemented in GAMESS program. All values are provided in kcal/mol.

Table S6: The M05-2X/cc-pVDZ optimized coordinates of the Li^+ complexes of sumanene (**1**) and corannulene (**2**).

Table S7: The M05-2X/cc-pVDZ optimized coordinates of the Cu^+ complexes of sumanene (**1**) and corannulene (**2**).

Table S8: The geometrical parameters (in Å) of the bucky bowl complexes of sumanene (**1**) and corannulene (**2**) with Li^+ ion evaluated at the B3LYP (in plain) and B3LYP-D (in italics) level in conjugation with the cc-pVDZ basis set.

Table S9: Summary of the factors contributing to the total bonding interaction in the Li+ and Cu+ complexes of sumanene (1) and corannulene (2). Calculations were carried out at BLYP-D/ATZP level using ADF program. All values are provided in kcal/mol.

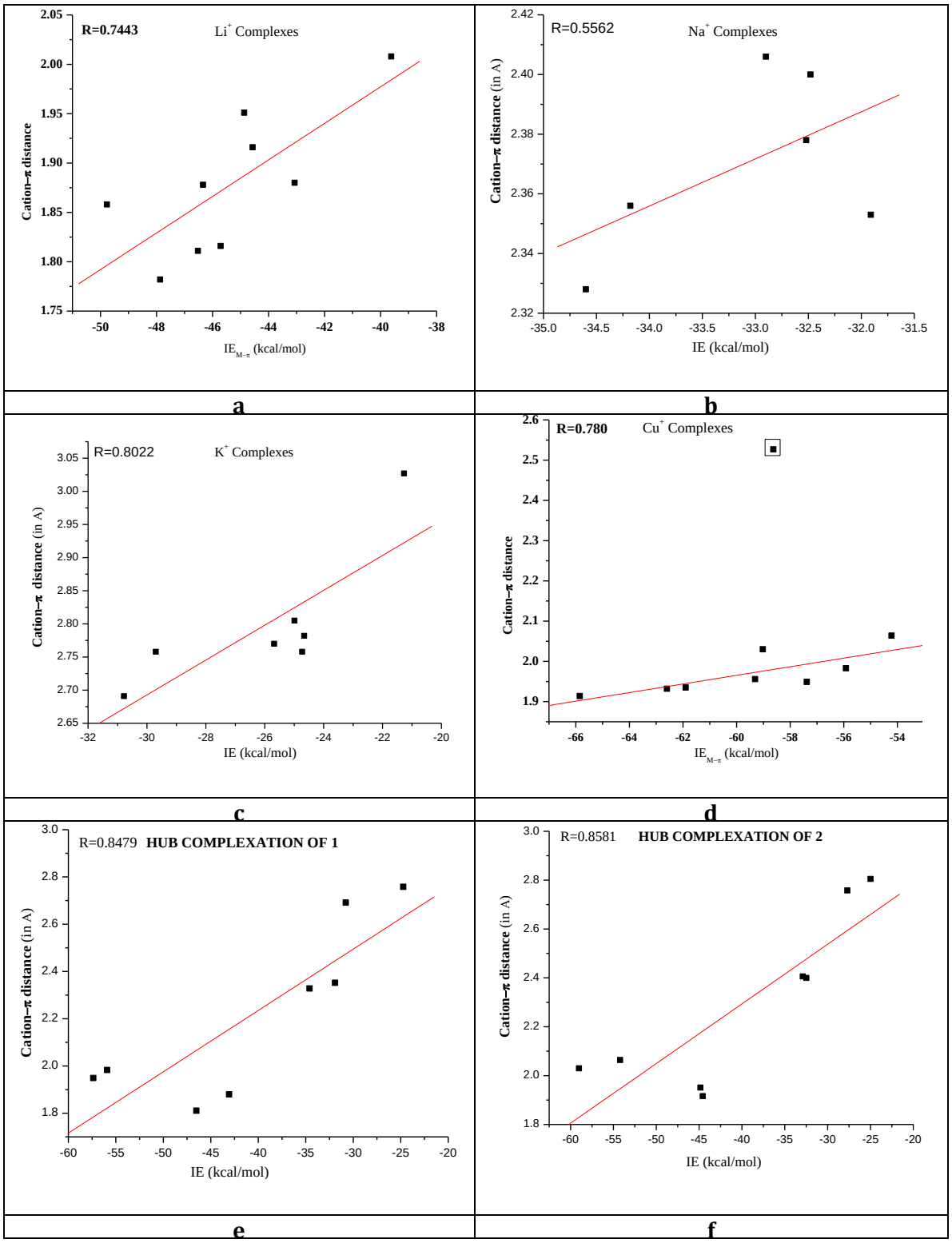

Figure S1: Correlation between the cation–π distance and the interaction energy of the (a) Li^+ and (b) Na^+ (c) K^+ and (d) Cu^+ complexes.

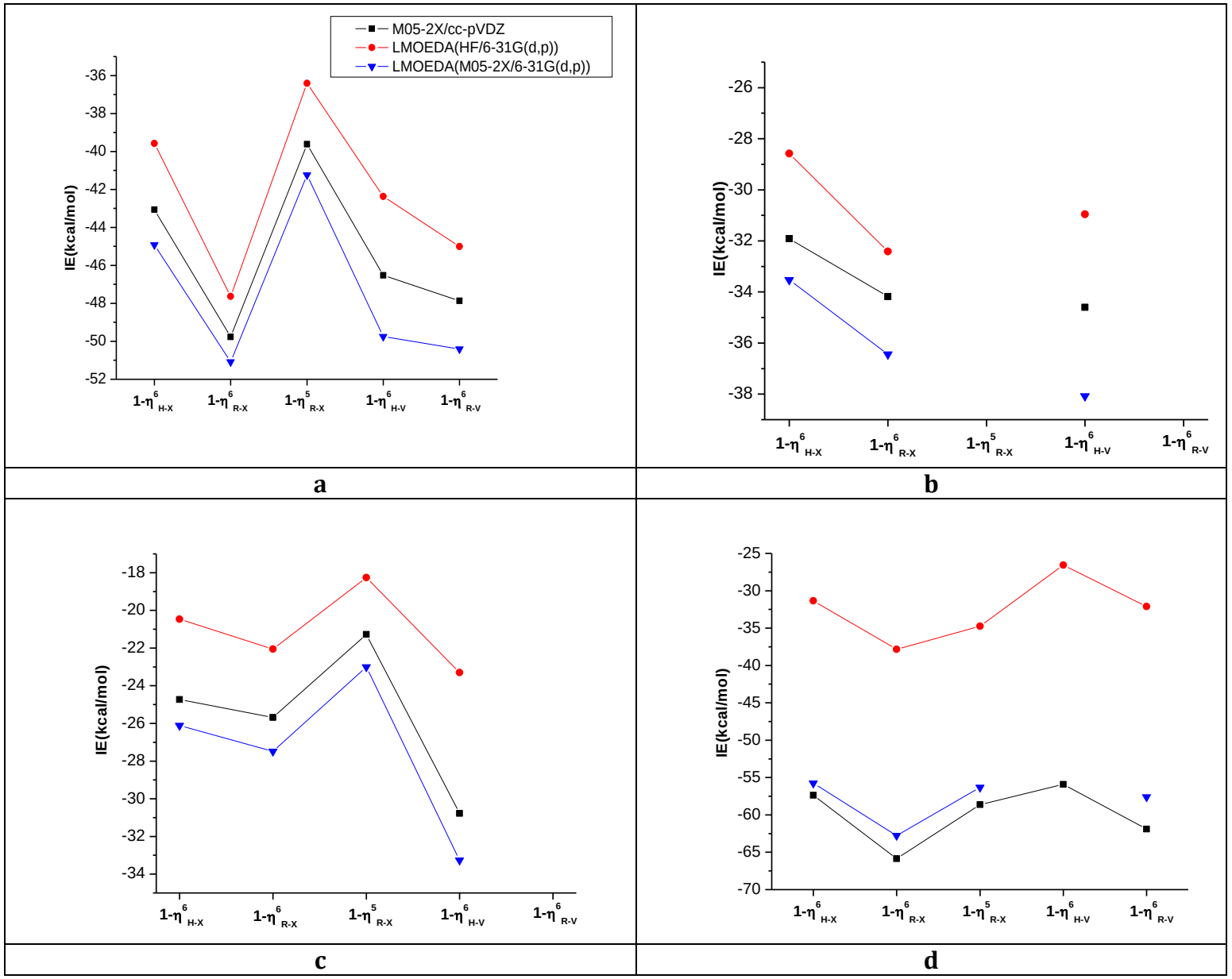

Figure S2: The correlation between the interaction energies of the a)Li^+, b)Na^+, c)K^+ , and d)Cu^+ complexes of sumanene at various levels of theories.

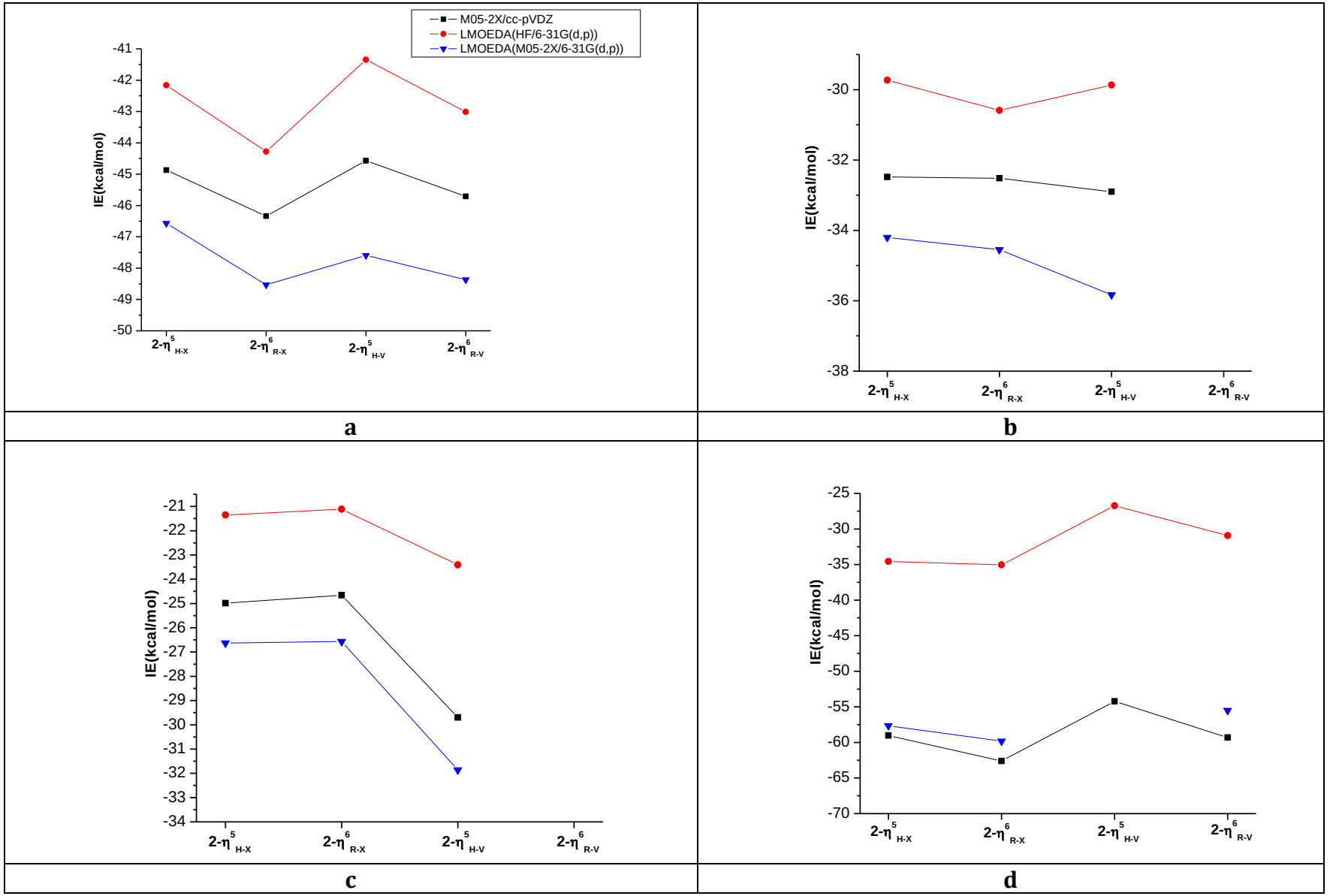

Figure S3: The correlation between the interaction energies of the a)Li^+, b)Na^+, c)K^+ , and d)Cu^+ complexes of corannulene at various levels of theories.

Table S1: The geometrical parameters (in Å) of the bucky bowl complexes of sumanene (1) and corannulene (2) with Na^+ and K^+ ions evaluated at the M05-2X level in conjugation with the cc-pVDZ basis set and 6-31G* bais set respectively.

	Na^+							K^+						
	r_1	r_2	r_3	r_4	r_5	r_6	cation–π	r_1	r_2	r_3	r_4	r_5	r_6	cation–π
1$-\eta^6_{H-X}$	1.387	1.398	1.396	1.429	1.442	1.547	2.353	1.384	1.395	1.395	1.427	1.439	1.549	2.758
1$-\eta^6_{R-X}$	1.390	1.404	1.404	1.437	1.433	1.547	2.356	1.386	1.400	1.400	1.433	1.433	1.549	2.770
1$-\eta^5_{R-X}$	collapsed to **1**$-\eta^6_{R-X}$							1.382	1.393	1.397	1.425	1.440	1.554	3.027
1$-\eta^6_{H-V}$	1.386	1.403	1.397	1.430	1.443	1.546	2.328	1.383	1.401	1.394	1.429	1.440	1.547	2.691
1$-\eta^6_{R-V}$	collapsed to **1**$-\eta^6_{H-V}$							collapsed to **1**$-\eta^6_{H-V}$						
2$-\eta^5_{H-X}$	1.422	1.384	1.444	1.386			2.400	1.418	1.381	1.444	1.384			2.805
2$-\eta^6_{R-X}$	1.425	1.386	1.451	1.395			2.378	1.421	1.382	1.448	1.391			2.782
2$-\eta^5_{H-V}$	1.423	1.384	1.448	1.385			2.406	1.420	1.382	1.446	1.383			2.758
2$-\eta^6_{R-V}$	collapsed to **2**$-\eta^5_{H-V}$							collapsed to **2**$-\eta^5_{H-V}$						

Table S2. The inversion barriers ($\Delta E^{\#}$ in kcal/mol) of various complexes considered in the study evaluated at the M05-2X/cc-pVDZ level. The 6-31G* basis set was used for the K^+ complexes alone.

	Li^+	Na^+	K^+	Cu^+
1$-\eta^6_{H-X}$	17.72	19.29	17.46	18.64
1$-\eta^6_{R-X}$	18.99	20.17	18.42	20.95
1$-\eta^5_{R-X}$	17.48			-b-
1$-\eta^6_{H-V}$	20.01	21.33	22.79	16.99
1$-\eta^6_{R-V}$	17.11			16.43
2$-\eta^5_{H-X}$	11.63	11.12	9.28	11.85
2$-\eta^6_{R-X}$	9.20	10.23	8.87	10.51
2$-\eta^5_{H-V}$	11.21	11.41	13.71	7.02
2$-\eta^6_{R-V}$	9.26			7.13

Table S3: The charge on the cation calculated using different schemes viz. Mulliken (q1 in a.u.), NPA (q2 in a.u.) and CHelpG (q3 in a.u.), charge density ($\rho*10^2$), Laplacian of the charge density ($\nabla^2\rho*10^2$) at the (3,+3) cage critical point of the complexes of sumanene (**1**) and corannulene (**2**) with different ions. The calculations were performed at the M05-2X-cc-pVDZ level. The 6-31G* basis set was employed for $\mathbf{K}^+$ complexes.

Li^+	q1	q2	q3	ρ	$\nabla^2\rho$	$\mathbf{Na}^+$	q1	q2	q3	ρ	$\nabla^2\rho$
1$-\eta^6_{H-X}$	0.564	0.948	0.653	1.154	1.519	**1**$-\eta^6_{H-X}$	0.842	0.985	0.758	0.811	1.016
1$-\eta^6_{R-X}$	0.433	0.914	0.624	1.307	1.728	**1**$-\eta^6_{R-X}$	0.762	0.975	0.748	0.893	1.106
1$-\eta^5_{R-X}$	0.564	0.957	0.696	-a-	-a-	**1**$-\eta^5_{R-X}$	Collapsed to 1$-\eta^6_{H-X}$				
1$-\eta^6_{H-V}$	0.441	0.920	0.603	1.465	1.904	**1**$-\eta^6_{H-V}$	0.729	0.954	0.681	0.944	1.144
1$-\eta^6_{R-V}$	0.380	0.914	0.593	1.549	2.101	**1**$-\eta^6_{R-V}$	Collapsed to **1**$-\eta^6_{H-V}$				
2$-\eta^5_{H-X}$	0.575	0.947	0.612	1.477	2.290	**2**$-\eta^5_{H-X}$	0.852	0.986	0.712	1.054	1.444
2$-\eta^6_{R-X}$	0.482	0.927	0.594	1.301	1.650	**2**$-\eta^6_{R-X}$	0.791	0.979	0.706	0.880	1.042
2$-\eta^5_{H-V}$	0.496	0.935	0.577	1.713	2.652	**2**$-\eta^5_{H-V}$	0.765	0.969	0.673	1.091	1.487
2$-\eta^6_{R-V}$	0.437	0.929	0.580	1.456	1.873	**2**$-\eta^6_{R-V}$	Collapsed to **2**$-\eta^5_{H-V}$				
$\mathbf{K}^+$	q1	q2	q3	ρ	$\nabla^2\rho$	$\mathbf{Cu}^+$	q1	q2	q3	ρ	$\nabla^2\rho$
1$-\eta^6_{H-X}$	0.880	0.979	0.727	0.729	0.880	**1**$-\eta^6_{H-X}$	0.581	0.936	0.597	2.005	3.012
1$-\eta^6_{R-X}$	0.855	0.976	0.749	0.787	0.960	**1**$-\eta^6_{R-X}$	0.476	0.895	0.555	2.126	3.418
1$-\eta^5_{R-X}$	0.889	0.986	0.767			**1**$-\eta^5_{R-X}$	0.654	0.934	0.644	-a-	-a-
1$-\eta^6_{H-V}$	0.803	0.931	0.621	0.890	1.067	**1**$-\eta^6_{H-V}$	0.575	0.887	0.601	2.154	3.050
1$-\eta^6_{R-V}$	Collapsed to **1**$-\eta^6_{H-V}$					**1**$-\eta^6_{R-V}$	0.491	0.931	0.565	2.186	3.560
2$-\eta^5_{H-X}$	0.891	0.983	0.688	0.939	1.147	**2**$-\eta^5_{H-X}$	0.604	0.938	0.570	2.917	4.035
2$-\eta^6_{R-X}$	0.871	0.979	0.716	0.785	0.918	**2**$-\eta^6_{R-X}$	0.510	0.906	0.531	2.127	3.344
2$-\eta^5_{H-V}$	0.824	0.946	0.594	1.060	1.311	**2**$-\eta^5_{H-V}$	0.612	0.922	0.587	3.045	3.684
2$-\eta^6_{R-V}$	Collapsed to **2**$-\eta^5_{H-V}$					**2**$-\eta^6_{R-V}$	0.521	0.939	0.558	2.112	3.245

Table S4: Summary of the factors contributing to the total bonding interaction in the metal complexes of sumanene (**1**). Calculations were carried out at M05-2X /6-31G(d,p) level using localized molecular orbital energy decomposition analysis (LMO-EDA) as implemented in GAMESS program. All values are provided in kcal/mol.

		$1-\eta^6_{H-X}$	$1-\eta^6_{R-X}$	$1-\eta^5_{R-X}$	$1-\eta^6_{H-V}$	$1-\eta^6_{R-V}$
	Electrostatic	-13.61	-22.89	-13.2	-17.79	-22.3
	Exchange	-2.58	-3.21	-2.89	-3.05	-3.55
Li^+	Repulsion	13.03	16.64	14.37	15.76	19.84
	Polarization	-35.70	-35.38	-34.18	-33.1	-34.35
	Dispersion	-6.06	-6.24	-5.34	-11.57	-10.04
	IE	-44.92	-51.08	-41.24	-49.75	-50.41
	Electrostatic	-15.61	-21.4		-18.94	
	Exchange	-2.11	-2.71		-1.66	
Na^+	Repulsion	11.93	14.70	a	12.99	a
	Polarization	-20.4	-19.44		-17.17	
	Dispersion	-7.34	-7.59		-13.31	
	IE	-33.53	-36.44		-38.08	
	Electrostatic	-15.51	-18.83	-14.51	-18.93	
K^+	Exchange	-2.83	-3.94	-3.32	-3.04	
	Repulsion	16.17	18.99	15.38	21.51	
	Polarization	-14.59	-14.32	-13.09	-14.29	a
	Dispersion	-9.34	-9.38	-7.45	-18.52	
	IE	-26.11	-27.48	-23.00	-33.26	
	Electrostatic	-46.10	-63.00	-53.87		-65.21
Cu^+	Exchange	-28.39	-35.58	-30.04		-36.49
	Repulsion	92.83	115.13	95.89	b	121.09
	Polarization	-46.09	-49.96	-46.72		-45.35
	Dispersion	-28.02	-29.35	-21.59		-31.63
	IE	-55.77	-62.77	-56.32		-57.59

a) Stationary point not obtained
b) Convergence failure

Table S5: Summary of the factors contributing to the total bonding interaction in the metal complexes of corannulene (**2**). Calculations were carried out at M05-2X/6-31G(d,p) level using localized molecular orbital energy decomposition analysis (LMO-EDA) as implemented in GAMESS program. All values are provided in kcal/mol.

		2–η^5_{H-X}	**2**–η^6_{R-X}	**2**–η^5_{H-V}	**2**–η^6_{R-V}
Li$^+$	Electrostatic	-16.08	-18.9	-17.13	-19.54
	Exchange	-2.94	-3.43	-2.65	-3.46
	Repulsion	14.85	15.51	15.26	17.21
	Polarization	-37.18	-35.72	-32.54	-33.66
	Dispersion	-5.22	-5.99	-10.53	-8.92
	IE	-46.57	-48.53	-47.59	-48.37
Na$^+$	Electrostatic	-17.32	-18.7	-18.33	
	Exchange	-2.55	-2.5	-1.68	
	Repulsion	13.2	13.6	12.4	
	Polarization	-20.6	-19.74	-16.59	**a**
	Dispersion	-6.92	-7.21	-11.63	
	IE	-34.2	-34.55	-35.83	
K$^+$	Electrostatic	-16.68	-17.14	-18.67	
	Exchange	-3.34	-3.66	-2.95	
	Repulsion	16.62	17.82	19.82	
	Polarization	-14.46	-14.45	-13.9	**a**
	Dispersion	-8.76	-9.15	-16.16	
	IE	-26.63	-26.57	-31.86	
Cu$^+$	Electrostatic	-50.14	-57.35		-60.63
	Exchange	-29.25	-33.65	b	-34.21
	Repulsion	94.37	109.15		114.19
	Polarization	-47.18	-49.54		-44.79
	Dispersion	-25.45	-28.45		-30.06
	IE	-57.65	-59.83		-55.5

a) Stationary point not obtained.
b) Convergence failure

Table S6: The M05-2X/cc-pVDZ optimized coordinates of the sumanene (**1**) and corannulene (**2**) dimers.

SUMANENE (**1**)

6	0.000000	3.291688	0.186461
6	2.850685	-1.645844	0.186461
6	-2.850685	-1.645844	0.186461
1	0.000000	4.152786	-0.496742
1	0.000000	3.679724	1.211857
1	3.596418	-2.076393	-0.496742
1	3.186734	-1.839862	1.211857
1	-3.596418	-2.076393	-0.496742
1	-3.186734	-1.839862	1.211857
6	0.717506	1.212322	-0.696722
6	1.408655	0.015218	-0.696722
6	-1.408655	0.015218	-0.696722
6	-0.717506	1.212322	-0.696722
6	-0.691148	-1.227540	-0.696722
6	0.691148	-1.227540	-0.696722
6	1.208103	2.357832	-0.067368
6	2.645994	-0.132668	-0.067368
6	-2.645994	-0.132668	-0.067368
6	-1.208103	2.357832	-0.067368
6	-1.437891	-2.225164	-0.067368
6	1.437891	-2.225164	-0.067368
6	2.503357	2.269212	0.447688
6	3.216873	1.033364	0.447688
6	-3.216873	1.033364	0.447688
6	-2.503357	2.269212	0.447688
6	-0.713517	-3.302576	0.447688
6	0.713517	-3.302576	0.447688
1	2.949419	3.108211	0.981469
1	4.166499	1.000166	0.981469
1	-4.166499	1.000166	0.981469
1	-2.949419	3.108211	0.981469
1	-1.217080	-4.108377	0.981469
1	1.217080	-4.108377	0.981469

CORANNULENE (**2**)

6	0.000000	1.206004	0.625048
6	-1.146978	0.372676	0.625048
6	-0.708871	-0.975678	0.625048
6	0.708871	-0.975678	0.625048
6	1.146978	0.372676	0.625048
6	0.000000	2.479242	0.096638
6	-2.357899	0.766128	0.096638
6	-1.457262	-2.005749	0.096638
6	1.457262	-2.005749	0.096638
6	2.357899	0.766128	0.096638
6	-1.310212	2.980282	-0.257114
6	-2.429539	2.167043	-0.257114
6	-3.239294	-0.325128	-0.257114
6	-2.811749	-1.640975	-0.257114
6	-0.691782	-3.181222	-0.257114
6	0.691782	-3.181222	-0.257114
6	2.811749	-1.640975	-0.257114
6	3.239294	-0.325128	-0.257114
6	2.429539	2.167043	-0.257114
6	1.310212	2.980282	-0.257114
1	-1.411647	4.002030	-0.622375
1	-3.369933	2.579252	-0.622375
1	-4.242379	-0.105861	-0.622375
1	-3.494381	-2.407964	-0.622375
1	-1.210287	-4.067455	-0.622375
1	1.210287	-4.067455	-0.622375
1	3.494381	-2.407964	-0.622375
1	4.242379	-0.105861	-0.622375
1	3.369933	2.579252	-0.622375
1	1.411647	4.002030	-0.622375

1–η^6_{H-X}

6	0.720655	1.216483	0.629784
6	0.693178	-1.232347	0.629784
6	1.413833	0.015863	0.629784
6	-0.693178	-1.232347	0.629784
6	-0.720655	1.216483	0.629784
6	-1.413833	0.015863	0.629784
6	1.210770	2.372672	0.014094
6	1.449409	-2.234894	0.014094
6	2.660179	-0.137778	0.014094
6	-1.449409	-2.234894	0.014094
6	-1.210770	2.372672	0.014094
6	-2.660179	-0.137778	0.014094
6	0.000000	3.304927	-0.235619
6	2.862151	-1.652464	-0.235619
6	-2.862151	-1.652464	-0.235619
6	-3.221365	1.033178	-0.495356
6	2.505441	2.273195	-0.495356
6	-0.715924	-3.306373	-0.495356
6	-2.505441	2.273195	-0.495356
6	3.221365	1.033178	-0.495356
6	0.715924	-3.306373	-0.495356
1	-4.169829	1.006787	-1.030394
1	2.956818	3.107784	-1.030394
1	-1.213011	-4.114571	-1.030394
1	-2.956818	3.107784	-1.030394
1	4.169829	1.006787	-1.030394

1	1.213011	-4.114571	-1.030394
1	0.000000	3.692122	-1.260839
1	3.197472	-1.846061	-1.260839
1	-3.197472	-1.846061	-1.260839
1	0.000000	4.169224	0.443038
1	3.610654	-2.084612	0.443038
1	-3.610654	-2.084612	0.443038
3	0.000000	0.000000	2.510037

1$-\eta^{6}_{R-X}$

6	-0.671599	-0.071371	1.421297
6	-0.696724	-1.262167	-0.717358
6	-0.696724	-1.262167	0.717358
6	-0.671599	-0.071371	-1.421297
6	-0.604790	1.160223	0.695367
6	-0.604790	1.160223	-0.695367
6	-0.032384	0.066103	2.653363
6	-0.098347	-2.422934	-1.205486
6	-0.098347	-2.422934	1.205486
6	-0.032384	0.066103	-2.653363
6	0.040456	2.156398	1.447531
6	0.040456	2.156398	-1.447531
6	0.268033	1.569589	2.861300
6	0.131903	-3.362890	0.000000
6	0.268033	1.569589	-2.861300
6	0.564209	3.240031	-0.719983
6	0.451294	-1.114689	3.223349
6	0.451294	-1.114689	-3.223349
6	0.564209	3.240031	0.719983
6	0.414011	-2.345566	2.504979
6	0.414011	-2.345566	-2.504979
1	1.092244	4.050075	-1.221408
1	0.984016	-1.100950	4.173032
1	0.984016	-1.100950	-4.173032
1	1.092244	4.050075	1.221408
1	0.920361	-3.199928	2.952741
1	0.920361	-3.199928	-2.952741
1	1.300421	1.738641	3.188026
1	1.146088	-3.778135	0.000000
1	1.300421	1.738641	-3.188026
1	-0.394046	2.028949	3.608308
1	-0.572493	-4.206323	0.000000
1	-0.394046	2.028949	-3.608308
3	-1.593642	3.140276	0.000000

1$-\eta^{5}_{R-X}$

6	0.599124	-1.170485	0.722250
6	0.690247	1.272138	0.691829
6	0.645713	0.031904	1.408861
6	0.690247	1.272138	-0.691829
6	0.599124	-1.170485	-0.722250
6	0.645713	0.031904	-1.408861
6	-0.047593	-2.308465	1.221988
6	0.088517	2.281528	1.441089
6	0.031685	0.192894	2.648950
6	0.088517	2.281528	-1.441089
6	-0.047593	-2.308465	-1.221988
6	0.031685	0.192894	-2.648950
6	-0.392308	-3.213997	0.000000
6	-0.183983	1.709787	2.852218
6	-0.183983	1.709787	-2.852218
6	-0.488360	-0.969149	-3.235584
6	-0.529418	-2.207671	2.535558
6	-0.394772	3.373980	-0.712335
6	-0.529418	-2.207671	-2.535558
6	-0.488360	-0.969149	3.235584
6	-0.394772	3.373980	0.712335
1	-0.996211	-0.924176	-4.198374
1	-1.067047	-3.033318	2.999761
1	-0.902572	4.196817	-1.213738
1	-1.067047	-3.033318	-2.999761
1	-0.996211	-0.924176	4.198374
1	-0.902572	4.196817	1.213738
1	-1.463102	-3.449441	0.000000
1	-1.205171	1.925399	3.187256
1	-1.205171	1.925399	-3.187256
1	0.112013	-4.198372	0.000000
1	0.504693	2.119988	3.603873
1	0.504693	2.119988	-3.603873
3	2.034543	-2.705056	0.000000

1$-\eta^{6}_{H-V}$

6	-0.722135	1.218327	-0.738308
6	-0.694034	-1.234551	-0.738308
6	-1.416170	0.016224	-0.738308
6	0.694034	-1.234551	-0.738308
6	0.722135	1.218327	-0.738308
6	1.416170	0.016224	-0.738308
6	-1.205126	2.361475	-0.083146
6	-1.442534	-2.224407	-0.083146
6	-2.647660	-0.137068	-0.083146
6	1.442534	-2.224407	-0.083146
6	1.205126	2.361475	-0.083146
6	2.647660	-0.137068	-0.083146
6	0.000000	3.305813	0.137577
6	-2.862918	-1.652907	0.137577
6	2.862918	-1.652907	0.137577
6	3.206432	1.025476	0.452970
6	-2.491304	2.264114	0.452970
6	0.715128	-3.289590	0.452970

6	2.491304	2.264114	0.452970
6	-3.206432	1.025476	0.452970
6	-0.715128	-3.289590	0.452970
1	4.151370	0.990669	0.993881
1	-2.933630	3.099858	0.993881
1	1.217741	-4.090527	0.993881
1	2.933630	3.099858	0.993881
1	-4.151370	0.990669	0.993881
1	-1.217741	-4.090527	0.993881
1	0.000000	3.761069	1.134211
1	-3.257181	-1.880534	1.134211
1	3.257181	-1.880534	1.134211
1	0.000000	4.122851	-0.597943
1	-3.570494	-2.061426	-0.597943
1	3.570494	-2.061426	-0.597943
3	0.000000	0.000000	1.072315

1$-\eta^{6}_{R-V}$

6	-0.730288	-0.057342	1.417651
6	-0.706484	-1.249930	-0.717311
6	-0.706484	-1.249930	0.717311
6	-0.730288	-0.057342	-1.417651
6	-0.734623	1.185077	0.694719
6	-0.734623	1.185077	-0.694719
6	-0.104395	0.103979	2.656772
6	-0.060765	-2.387381	-1.206198
6	-0.060765	-2.387381	1.206198
6	-0.104395	0.103979	-2.656772
6	-0.110145	2.195467	1.450169
6	-0.110145	2.195467	-1.450169
6	0.097365	1.623817	2.876333
6	0.192583	-3.322095	0.000000
6	0.097365	1.623817	-2.876333
6	0.414316	3.275698	-0.720448
6	0.430981	-1.055411	3.224342
6	0.430981	-1.055411	-3.224342
6	0.414316	3.275698	0.720448
6	0.448887	-2.288949	2.504305
6	0.448887	-2.288949	-2.504305
1	0.933808	4.091242	-1.222542
1	0.951681	-1.021893	4.180472
1	0.951681	-1.021893	-4.180472
1	0.933808	4.091242	1.222542
1	0.986140	-3.122507	2.955414
1	0.986140	-3.122507	-2.955414
1	1.081377	1.870090	3.291391
1	1.211180	-3.726162	0.000000
1	1.081377	1.870090	-3.291391
1	-0.657532	2.032871	3.562972
1	-0.500438	-4.175099	0.000000
1	-0.657532	2.032871	-3.562972
3	1.401540	1.331311	0.000000

2$-\eta^{5}_{H-X}$

6	0.000000	1.208834	0.565163
6	-1.149670	0.373550	0.565163
6	-0.710535	-0.977968	0.565163
6	0.710535	-0.977968	0.565163
6	1.149670	0.373550	0.565163
6	0.000000	2.490317	0.039540
6	-2.368432	0.769550	0.039540
6	-1.463771	-2.014709	0.039540
6	1.463771	-2.014709	0.039540
6	2.368432	0.769550	0.039540
6	-1.309505	2.983264	-0.313548
6	-2.432594	2.167293	-0.313548
6	-3.241912	-0.323534	-0.313548
6	-2.812931	-1.643804	-0.313548
6	-0.694107	-3.183220	-0.313548
6	0.694107	-3.183220	-0.313548
6	2.812931	-1.643804	-0.313548
6	3.241912	-0.323534	-0.313548
6	2.432594	2.167293	-0.313548
6	1.309505	2.983264	-0.313548
1	-1.413674	4.000891	-0.687742
1	-3.368224	2.580827	-0.687742
1	-4.241923	-0.108141	-0.687742
1	-3.495351	-2.405852	-0.687742
1	-1.207978	-4.067726	-0.687742
1	1.207978	-4.067726	-0.687742
1	3.495351	-2.405852	-0.687742
1	4.241923	-0.108141	-0.687742
1	3.368224	2.580827	-0.687742
1	1.413674	4.000891	-0.687742
3	0.000000	0.000000	2.516391

2$-\eta^{6}_{R-X}$

6	0.600972	0.424526	1.147667
6	0.531203	-0.921523	0.712453
6	0.531203	-0.921523	-0.712453
6	0.600972	0.424526	-1.147667
6	0.629352	1.251507	0.000000
6	0.078552	0.827545	2.358139
6	-0.015841	-1.946653	1.471273
6	-0.015841	-1.946653	-1.471273
6	0.078552	0.827545	-2.358139
6	0.127395	2.536968	0.000000
6	-0.296248	-0.256326	3.244792
6	-0.334374	-1.576285	2.834464
6	-0.390402	-3.116809	0.699729

6	-0.390402	-3.116809	-0.699729
6	-0.334374	-1.576285	-2.834464
6	-0.296248	-0.256326	-3.244792
6	-0.237874	2.235108	-2.432241
6	-0.214875	3.045879	-1.309484
6	-0.214875	3.045879	1.309484
6	-0.237874	2.235108	2.432241
1	-0.646435	-0.022994	4.249900
1	-0.706327	-2.330348	3.526109
1	-0.773033	-4.000378	1.210357
1	-0.773033	-4.000378	-1.210357
1	-0.706327	-2.330348	-3.526109
1	-0.646435	-0.022994	-4.249900
1	-0.594038	2.657335	-3.370839
1	-0.556240	4.075452	-1.410074
1	-0.556240	4.075452	1.410074
1	-0.594038	2.657335	3.370839
3	1.786101	-2.691511	0.000000

2$-\eta^5_{H-V}$

6	0.000000	1.210850	-0.675296
6	1.151587	0.374173	-0.675296
6	0.711720	-0.979598	-0.675296
6	-0.711720	-0.979598	-0.675296
6	-1.151587	0.374173	-0.675296
6	0.000000	2.482205	-0.122006
6	2.360718	0.767044	-0.122006
6	1.459004	-2.008146	-0.122006
6	-1.459004	-2.008146	-0.122006
6	-2.360718	0.767044	-0.122006
6	1.309955	2.981928	0.236124
6	2.431183	2.167308	0.236124
6	3.240780	-0.324375	0.236124
6	2.812509	-1.642458	0.236124
6	0.692957	-3.182402	0.236124
6	-0.692957	-3.182402	0.236124
6	-2.812509	-1.642458	0.236124
6	-3.240780	-0.324375	0.236124
6	-2.431183	2.167308	0.236124
6	-1.309955	2.981928	0.236124
1	1.410878	4.002603	0.602983
1	3.370716	2.578697	0.602983
1	4.242687	-0.104953	0.602983
1	3.494095	-2.408880	0.602983
1	1.211246	-4.067467	0.602983
1	-1.211246	-4.067467	0.602983
1	-3.494095	-2.408880	0.602983
1	-4.242687	-0.104953	0.602983
1	-3.370716	2.578697	0.602983
1	-1.410878	4.002603	0.602983
3	0.000000	0.000000	1.240603

2$-\eta^6_{R-V}$

6	0.653040	0.416066	1.147741
6	0.666967	-0.935830	0.712153
6	0.666967	-0.935830	-0.712153
6	0.653040	0.416066	-1.147741
6	0.647166	1.246188	0.000000
6	0.116179	0.801483	2.359070
6	0.157536	-1.980183	1.470720
6	0.157536	-1.980183	-1.470720
6	0.116179	0.801483	-2.359070
6	0.097610	2.511940	0.000000
6	-0.217658	-0.295401	3.245598
6	-0.202830	-1.615721	2.829469
6	-0.187932	-3.161542	0.698455
6	-0.187932	-3.161542	-0.698455
6	-0.202830	-1.615721	-2.829469
6	-0.217658	-0.295401	-3.245598
6	-0.250521	2.198319	-2.433141
6	-0.258920	3.009837	-1.310782
6	-0.258920	3.009837	1.310782
6	-0.250521	2.198319	2.433141
1	-0.571676	-0.078929	4.253165
1	-0.535375	-2.387458	3.522553
1	-0.538006	-4.056757	1.212340
1	-0.538006	-4.056757	-1.212340
1	-0.535375	-2.387458	-3.522553
1	-0.571676	-0.078929	-4.253165
1	-0.611065	2.609796	-3.374956
1	-0.628691	4.029314	-1.413694
1	-0.628691	4.029314	1.413694
1	-0.611065	2.609796	3.374956
3	-1.469789	-1.341679	0.000000

***Table S7*:** The M05-2X/cc-pVDZ optimized coordinates of the Cu^+ complexes of sumanene (**1**) and corannulene (**2**).

1–η^6_{H-X}

6	-0.714782	-1.222583	0.224746
6	-0.701256	1.229631	0.224270
6	-1.416111	-0.023885	0.224731
6	0.687499	1.237373	0.224258
6	0.728371	-1.214539	0.224746
6	1.416292	-0.008096	0.224733
6	-1.198582	-2.383235	-0.388150
6	-1.464488	2.229394	-0.388182
6	-2.665153	0.123807	-0.388064
6	1.439524	2.245593	-0.388200
6	1.225088	-2.369722	-0.388156
6	2.663605	0.153531	-0.388066
6	0.018454	-3.309390	-0.634082
6	-2.875313	1.638663	-0.633788
6	2.856842	1.670635	-0.633809
6	3.228625	-1.014679	-0.897518
6	-2.492997	-2.288370	-0.897327
6	0.698474	3.310706	-0.897651
6	2.518375	-2.260420	-0.897312
6	-3.217099	-1.050630	-0.897538
6	-0.735376	3.302709	-0.897639
1	4.175607	-0.984356	-1.435005
1	-2.940565	-3.123917	-1.434275
1	1.189400	4.121379	-1.434637
1	2.975249	-3.090922	-1.434244
1	-4.164348	-1.030876	-1.435045
1	-1.235313	4.107864	-1.434613
1	0.020652	-3.703422	-1.656541
1	-3.218144	1.833823	-1.656171
1	3.197466	1.869593	-1.656198
1	0.023256	-4.169295	0.050253
1	-3.621833	2.064503	0.051092
1	3.598571	2.104784	0.051061
29	0.000002	0.000754	2.173528

1–η^6_{R-X}

6	0.505006	0.500901	1.422398
6	0.709268	1.673854	-0.717532
6	0.709268	1.673854	0.717532
6	0.505006	0.500901	-1.422398
6	0.253255	-0.706240	0.697356
6	0.253255	-0.706240	-0.697356
6	-0.149413	0.463359	2.653664
6	0.293674	2.912099	-1.205311
6	0.293674	2.912099	1.205311
6	-0.149413	0.463359	-2.653664
6	-0.540525	-1.593106	1.452706
6	-0.540525	-1.593106	-1.452706
6	-0.675432	-0.976356	2.864512
6	0.206734	3.875691	0.000000
6	-0.675432	-0.976356	-2.864512
6	-1.235622	-2.582614	-0.723399
6	-0.449289	1.703692	3.222868
6	-0.449289	1.703692	-3.222868
6	-1.235622	-2.582614	0.723399
6	-0.225478	2.914143	2.504388
6	-0.225478	2.914143	-2.504388
1	-1.888286	-3.295343	-1.225111
1	-0.978567	1.771055	4.172249
1	-0.978567	1.771055	-4.172249
1	-1.888286	-3.295343	1.225111
1	-0.597404	3.835692	2.950805
1	-0.597404	3.835692	-2.950805
1	-1.721450	-0.986036	3.191054
1	-0.734670	4.436785	0.000000
1	-1.721450	-0.986036	-3.191054
1	-0.090291	-1.530835	3.610990
1	1.028752	4.604979	0.000000
1	-0.090291	-1.530835	-3.610990
29	0.937662	-2.882819	0.000000

1–η^5_{R-X}

6	0.017907	-0.986715	0.730923
6	0.552600	1.405887	0.692713
6	0.278589	0.197156	1.413328
6	0.552600	1.405887	-0.692713
6	0.017907	-0.986715	-0.730923
6	0.278589	0.197156	-1.413328
6	-0.861959	-1.972074	1.214538
6	0.152857	2.513082	1.441782
6	-0.304650	0.477991	2.652184
6	0.152857	2.513082	-1.441782
6	-0.861959	-1.972074	-1.214538
6	-0.304650	0.477991	-2.652184
6	-1.328054	-2.814267	0.000000
6	-0.223347	2.008299	2.853720
6	-0.223347	2.008299	-2.853720
6	-1.066630	-0.548157	-3.212742
6	-1.346889	-1.759357	2.502927
6	-0.112245	3.676277	-0.712770
6	-1.346889	-1.759357	-2.502927
6	-1.066630	-0.548157	3.212742
6	-0.112245	3.676277	0.712770

1	-1.587816	-0.395374	-4.157262
1	-2.065782	-2.446165	2.947607
1	-0.455354	4.580501	-1.214072
1	-2.065782	-2.446165	-2.947607
1	-1.587816	-0.395374	4.157262
1	-0.455354	4.580501	1.214072
1	-2.418971	-2.922947	0.000000
1	-1.184035	2.418110	3.185419
1	-1.184035	2.418110	-3.185419
1	-0.906247	-3.829679	0.000000
1	0.531005	2.282345	3.604580
1	0.531005	2.282345	-3.604580
29	1.923542	-1.703078	0.000000

1$-\eta^6_{H-V}$

6	0.099459	-1.415040	-0.926522
6	1.177045	0.794179	-0.925368
6	1.261169	-0.651258	-0.925772
6	-0.065184	1.418371	-0.925811
6	-1.194588	-0.764985	-0.926317
6	-1.275143	0.622989	-0.925811
6	0.017928	-2.656780	-0.281343
6	2.293349	1.344596	-0.280214
6	2.433726	-1.069007	-0.280711
6	-0.289802	2.642317	-0.280335
6	-2.142645	-1.571764	-0.281457
6	-2.310141	1.314496	-0.280657
6	-1.485411	-2.956779	-0.059801
6	3.304501	0.192440	-0.058123
6	-1.817612	2.766069	-0.058079
6	-3.338766	0.522636	0.242701
6	1.217427	-3.151455	0.243152
6	0.844448	3.272332	0.244190
6	-3.255769	-0.904416	0.242392
6	2.412061	-2.366460	0.243556
6	2.121680	2.630763	0.244140
1	-4.175512	0.976216	0.772675
1	1.242249	-4.103004	0.772762
1	0.758926	4.219982	0.774387
1	-4.034266	-1.452156	0.772042
1	3.275263	-2.766222	0.774310
1	2.932928	3.127565	0.774834
1	-1.689551	-3.363094	0.936950
1	3.758263	0.218684	0.938793
1	-2.066994	3.145199	0.939149
1	-1.852614	-3.688314	-0.793993
1	4.121818	0.240281	-0.791866
1	-2.267355	3.450741	-0.791422
29	-0.001709	-0.002943	1.057190

1$-\eta^6_{R-V}$

6	0.953806	0.415519	1.419646
6	0.797735	1.596230	-0.716946
6	0.797735	1.596230	0.716946
6	0.953806	0.415519	-1.419646
6	1.069626	-0.816584	0.694811
6	1.069626	-0.816584	-0.694811
6	0.361847	0.188127	2.664577
6	0.030687	2.655272	-1.206619
6	0.030687	2.655272	1.206619
6	0.361847	0.188127	-2.664577
6	0.574984	-1.892712	1.457415
6	0.574984	-1.892712	-1.457415
6	0.332956	-1.344901	2.888906
6	-0.329064	3.554018	0.000000
6	0.332956	-1.344901	-2.888906
6	0.204923	-3.045382	-0.727588
6	-0.298201	1.280914	3.231037
6	-0.298201	1.280914	-3.231037
6	0.204923	-3.045382	0.727588
6	-0.460407	2.501953	2.506358
6	-0.460407	2.501953	-2.506358
1	-0.165704	-3.938387	-1.229676
1	-0.806767	1.193113	4.190296
1	-0.806767	1.193113	-4.190296
1	-0.165704	-3.938387	1.229676
1	-1.087921	3.269916	2.957444
1	-1.087921	3.269916	-2.957444
1	-0.607807	-1.698186	3.325170
1	-1.388189	3.835357	0.000000
1	-0.607807	-1.698186	-3.325170
1	1.145526	-1.665016	3.556891
1	0.259419	4.482107	0.000000
1	1.145526	-1.665016	-3.556891
29	-1.264378	-1.462955	0.000000

2$-\eta^5_{H-X}$

6	-0.001936	-1.211480	0.135947
6	1.152173	-0.375658	0.137436
6	0.713626	0.979986	0.138253
6	-0.710493	0.982264	0.138254
6	-1.153364	-0.371971	0.137448
6	-0.003989	-2.492714	-0.390085
6	2.370880	-0.772895	-0.387080
6	1.468973	2.016563	-0.384813
6	-1.462523	2.021248	-0.384815
6	-2.373336	-0.765314	-0.387065
6	1.306027	-2.985562	-0.741390
6	2.430846	-2.171008	-0.739802
6	3.244978	0.320801	-0.736392

6	2.817662	1.642120	-0.735437
6	0.699442	3.185786	-0.735547
6	-0.689261	3.188007	-0.735552
6	-2.812406	1.651115	-0.735432
6	-3.243939	0.331166	-0.736384
6	-2.437779	-2.163223	-0.739792
6	-1.315573	-2.981371	-0.741384
1	1.410328	-4.003173	-1.115510
1	3.366020	-2.586986	-1.112577
1	4.245783	0.105618	-1.108920
1	3.502916	2.402921	-1.107146
1	1.213959	4.070921	-1.107774
1	-1.200941	4.074782	-1.107783
1	-3.495228	2.414103	-1.107137
1	-4.245423	0.119180	-1.108919
1	-3.374276	-2.576203	-1.112576
1	-1.423126	-3.998639	-1.115515
29	-0.000002	-0.006541	2.167092

2–η^6_{R-X}

6	0.448673	0.815032	1.147502
6	0.152105	-0.499940	0.714918
6	0.152105	-0.499940	-0.714918
6	0.448673	0.815032	-1.147502
6	0.616707	1.623586	0.000000
6	0.003979	1.302886	2.357831
6	-0.566423	-1.415702	1.477111
6	-0.566423	-1.415702	-1.477111
6	0.003979	1.302886	-2.357831
6	0.347312	2.977827	0.000000
6	-0.555204	0.302060	3.244497
6	-0.821467	-0.992885	2.836416
6	-1.125547	-2.516880	0.703385
6	-1.125547	-2.516880	-0.703385
6	-0.821467	-0.992885	-2.836416
6	-0.555204	0.302060	-3.244497
6	-0.063693	2.743798	-2.432074
6	0.100224	3.538613	-1.309436
6	0.100224	3.538613	1.309436
6	-0.063693	2.743798	2.432074
1	-0.861933	0.594491	4.248271
1	-1.318889	-1.670279	3.528525
1	-1.650026	-3.324275	1.212925
1	-1.650026	-3.324275	-1.212925
1	-1.318889	-1.670279	-3.528525
1	-0.861933	0.594491	-4.248271
1	-0.341624	3.221396	-3.370567
1	-0.056588	4.611973	-1.410542
1	-0.056588	4.611973	1.410542
1	-0.341624	3.221396	3.370567
29	1.096630	-2.544788	0.000000

2–η^5_{H-V}

6	-0.712719	0.981837	-0.881477
6	0.712712	0.981842	-0.881477
6	1.153700	-0.374312	-0.882041
6	0.000004	-1.212679	-0.882649
6	-1.153697	-0.374320	-0.882041
6	-1.465361	2.017605	-0.351470
6	1.465347	2.017615	-0.351470
6	2.371251	-0.769617	-0.352145
6	0.000009	-2.492516	-0.351822
6	-2.371246	-0.769633	-0.352145
6	-0.693556	3.195059	-0.008781
6	0.693534	3.195064	-0.008781
6	2.824528	1.647716	-0.011357
6	3.253291	0.328625	-0.011680
6	2.439222	-2.176570	-0.011104
6	1.317051	-2.991914	-0.010737
6	-1.317031	-2.991923	-0.010737
6	-2.439207	-2.176587	-0.011104
6	-3.253294	0.328602	-0.011680
6	-2.824539	1.647697	-0.011357
1	-1.209149	4.088913	0.340443
1	1.209121	4.088922	0.340443
1	3.515697	2.414309	0.336838
1	4.263226	0.114687	0.336060
1	3.381908	-2.596779	0.337326
1	1.425599	-4.018038	0.338128
1	-1.425572	-4.018048	0.338128
1	-3.381890	-2.596802	0.337326
1	-4.263227	0.114658	0.336060
1	-3.515713	2.414285	0.336838
29	0.000000	-0.002609	1.182026

2–η^6_{R-V}

6	0.828579	0.805335	1.147534
6	0.992410	-0.532489	0.712633
6	0.992410	-0.532489	-0.712633
6	0.828579	0.805335	-1.147534
6	0.723926	1.627202	0.000000
6	0.264005	1.125767	2.364250
6	0.638730	-1.633816	1.479404
6	0.638730	-1.633816	-1.479404
6	0.264005	1.125767	-2.364250
6	0.031399	2.819266	0.000000
6	0.079546	-0.001977	3.255568
6	0.254679	-1.313081	2.843896
6	0.476848	-2.863971	0.704619
6	0.476848	-2.863971	-0.704619

6	0.254679	-1.313081	-2.843896
6	0.079546	-0.001977	-3.255568
6	-0.266520	2.469243	-2.437418
6	-0.378547	3.270681	-1.313014
6	-0.378547	3.270681	1.313014
6	-0.266520	2.469243	2.437418
1	-0.284368	0.171132	4.267907
1	0.036209	-2.116916	3.545605
1	0.301525	-3.809835	1.216672
1	0.301525	-3.809835	-1.216672
1	0.036209	-2.116916	-3.545605
1	-0.284368	0.171132	-4.267907
1	-0.667805	2.838727	-3.380107
1	-0.866478	4.239170	-1.417456
1	-0.866478	4.239170	1.417456
1	-0.667805	2.838727	3.380107
29	-1.249892	-1.559713	0.000000

Table S8: The geometrical parameters (in Å) of the bucky bowl complexes of sumanene (**1**) and corannulene (**2**) with Li^+ ion evaluated at the B3LYP (in plain) and B3LYP-D (in italics) level in conjugation with the cc-pVDZ basis set.

	r1	r2	r3	r4	r5	r6	cation-p
1– η^6_{H-X}	1.394	1.404	1.400	1.437	1.442	1.554	1.882
	1.395	*1.404*	*1.400*	*1.437*	*1.442*	*1.553*	*1.890*
1– η^6_{R-X}	1.399	1.411	1.412	1.447	1.432	1.553	1.865
	1.399	*1.411*	*1.411*	*1.447*	*1.431*	*1.551*	*1.885*
1– η^5_{R-X}	1.393	1.408	1.407	1.429	1.445	1.566	1.984
	1.393	*1.408*	*1.406*	*1.430*	*1.444*	*1.565*	*1.973*
1– η^6_{H-V}	1.395	1.408	1.403	1.436	1.444	1.553	1.815
	1.397	*1.409*	*1.400*	*1.434*	*1.447*	*1.548*	*1.844*
1– η^6_{R-V}	1.396	1.411	1.412	1.448	1.436	1.558	1.787
	1.399	*1.415*	*1.407*	*1.445*	*1.440*	*1.551*	*1.847*

	r1	r2	r3	r4	cation-p
2– η^5_{H-X}	1.424	1.394	1.446	1.396	1.951
	1.424	*1.395*	*1.445*	*1.396*	*1.992*
2– η^6_{R-X}	1.429	1.397	1.454	1.407	1.883
	1.428	*1.398*	*1.454*	*1.408*	*1.896*
2– η^5_{H-V}	1.425	1.395	1.451	1.395	1.917
	1.427	*1.397*	*1.448*	*1.392*	*1.955*
2– η^6_{R-V}	1.426	1.395	1.456	1.406	1.818
	1.429	*1.398*	*1.455*	*1.403*	*1.855*

Table S9: Summary of the factors contributing to the total bonding interaction in the Li^+ and Cu^+ complexes of sumanene (**1**) and corannulene (**2**). Calculations were carried out at BLYP-D/ATZP level using ADF program. All values are provided in kcal/mol.

Li^+	**1**$-\eta^6_{H-X}$	**1**$-\eta^6_{R-X}$	**1**$-\eta^5_{R-X}$	**1**$-\eta^6_{H-V}$	**1**$-\eta^6_{R-V}$	**2**$-\eta^5_{H-X}$	**2**$-\eta^6_{R-X}$	**2**$-\eta^5_{H-X}$	**2**$-\eta^6_{R-V}$
Electrostatic:	-6.76	-14.11	-7.30	-6.94	-11.78	-10.76	-10.79	-6.23	-9.18
Pauli Repulsion:	8.68	11.03	9.73	10.76	13.36	10.18	10.37	10.44	11.53
Orbital Interaction:	-44.10	-44.90	-41.84	-43.37	-44.40	-44.27	-44.28	-42.77	-43.19
Dispersion Energy:	-13.12	-12.39	-10.82	-18.64	-15.27	-10.98	-12.44	-16.39	-15.12
Total Bonding	-55.30	-60.37	-50.22	-58.19	-58.09	-55.82	-57.14	-54.95	-55.96
Cu^+									
Electrostatic:	-39.76	-55.30	-46.86	-39.81	-56.63	-45.10	-49.94	-38.49	-51.56
Pauli Repulsion:	51.70	63.40	53.44	54.86	67.34	53.20	60.12	53.80	63.28
Orbital Interaction:	-68.86	-73.91	-71.34	-59.41	-68.16	-69.31	-72.89	-59.13	-67.39
Dispersion Energy:	-5.17	-4.22	-7.25	-12.33	-8.86	-5.36	-4.44	-11.33	-7.85
Total Bonding	-62.09	-70.03	-72.01	-56.70	-66.32	-66.56	-67.15	-55.15	-63.52

In order to analyze the various factors which contribute to the total binding strength of the cationic complexes of bowls, the Morokuma–Ziegler decomposition scheme as implemented in the program ADF was carried out. In this energy decomposition analysis scheme, the interaction energy (ΔE_{int}) is expressed as the sum of the electrostatic interaction (ΔV_{elst}), Pauli repulsion (ΔE_{Pauli}) and orbital (ΔE_{oi}) interaction.

$\Delta E_{int} = \Delta V_{elst} + \Delta E_{Pauli} + \Delta E_{oi}$

The calculations were carried out using the BLYP-D (BLYP augmented with an empirical dispersion term) functional. Hence, an empirical dispersion correction (ΔE_{disp}) with a S6 scaling factor of 1.20 (the default), evaluated by the scheme proposed by Grimme is also added to ΔE_{int}. The ATZVP basis set which is a valence-triple-ζ quality basis set with polarization functions and augmented with one additional diffuse function for each angular momentum is used in the EDA analysis.