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Supplementary information for;

Stacking interactions in stabilizing supramolecular assembly of $M[9C]_2M$ complexes: Dynamic stability with remarkable nonlinear optical features.

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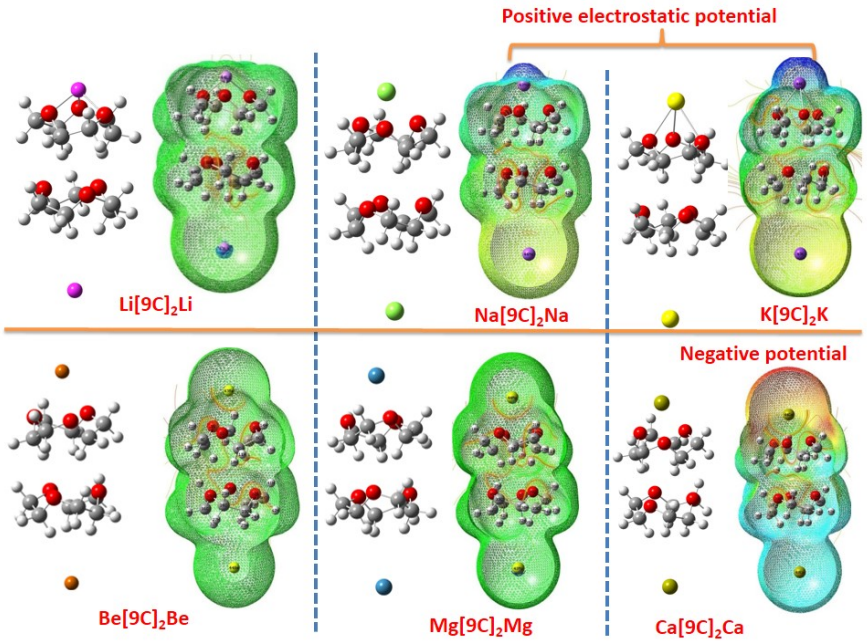

Figure S1: Optimized molecular geometries of [9C], dimer $[9C]_2$, and their2M$[9C]_2$M (M=Li, Na, K, Be, Mg, and Ca) complexes along with their molecular electrostatic potential maps at the m062x/def2qzvpp level.

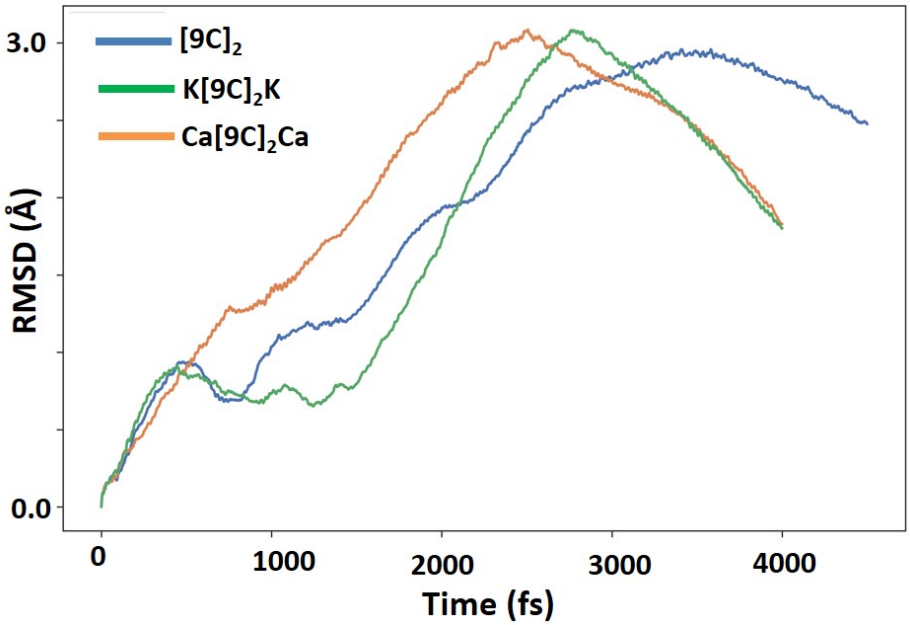

Figure S2**:** The plotted RMSD curve of $[9C]_2$, and $M[9C]_2M$ (where M=Kand Ca) complexes.

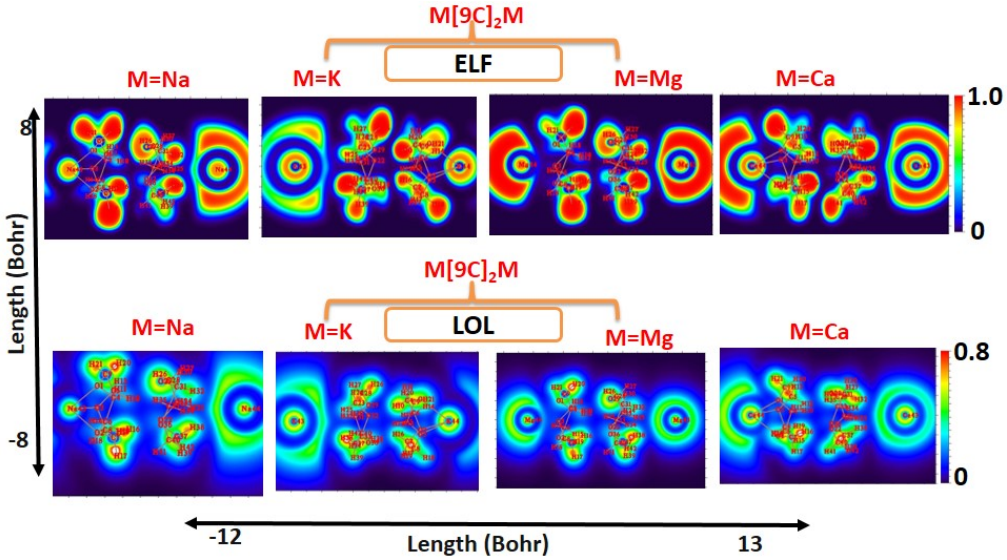

Figure S3: Electron localization function (upper panel) and localized orbital locator (lower panel) of $M[9C]_2M$ complexes at the m062X/def2tqzvpp level.

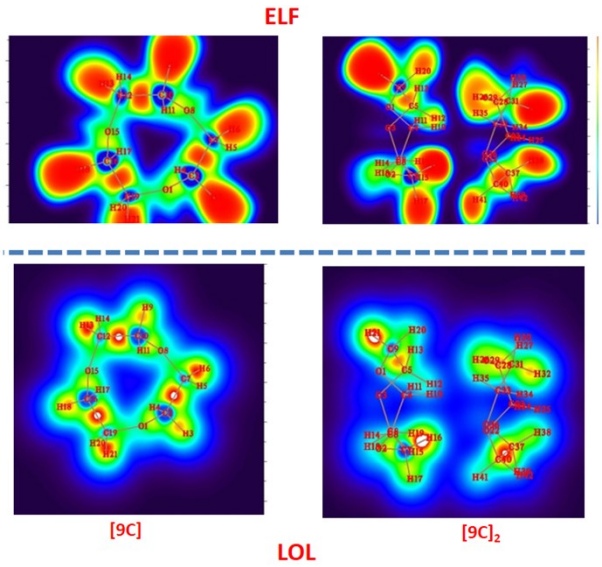

Figure S4: The ELF (upper pannel) and LOL pictures (lower pannel) of pure [9C] and its dimer $[9C]_2$

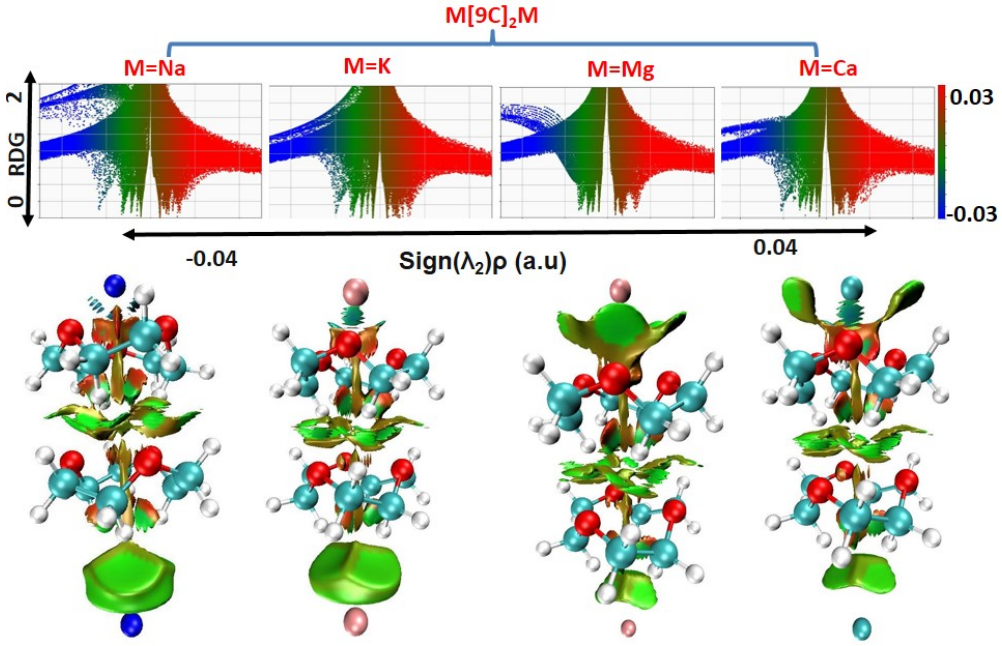

Figure S5: The molecular isosurface from noncovalent interaction analysis and radiant density gradient (RDG) 2D spectra of $[9C]_2$ and $M[9C]_2M$ (M=Li and Be) complexes at the m062X/def2qzvpp level.

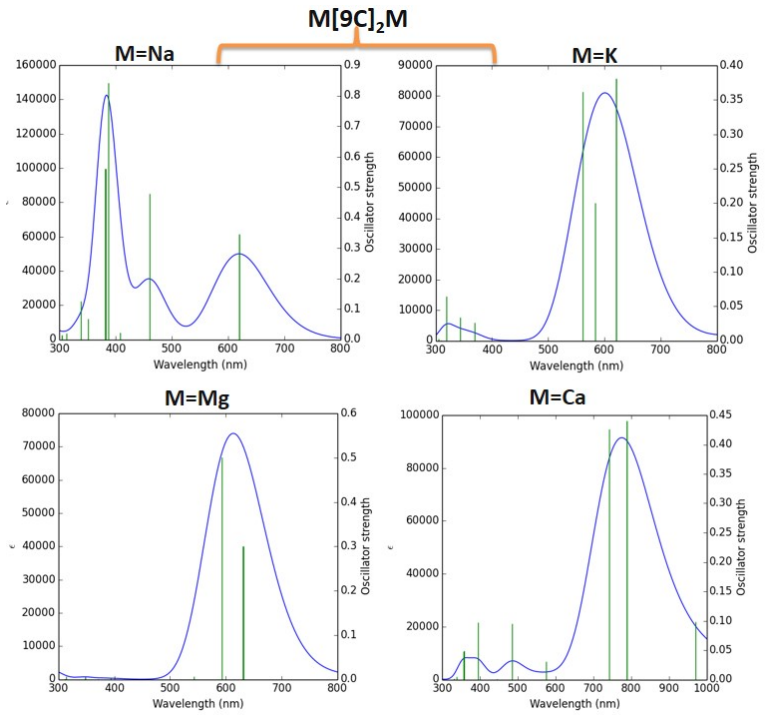

Figure S6: The obtained UV-visible spectra of $M[9C]_2M$ (where M= Na, K, Mg, and Ca) complexes at the m062X/def2qzvpp level.

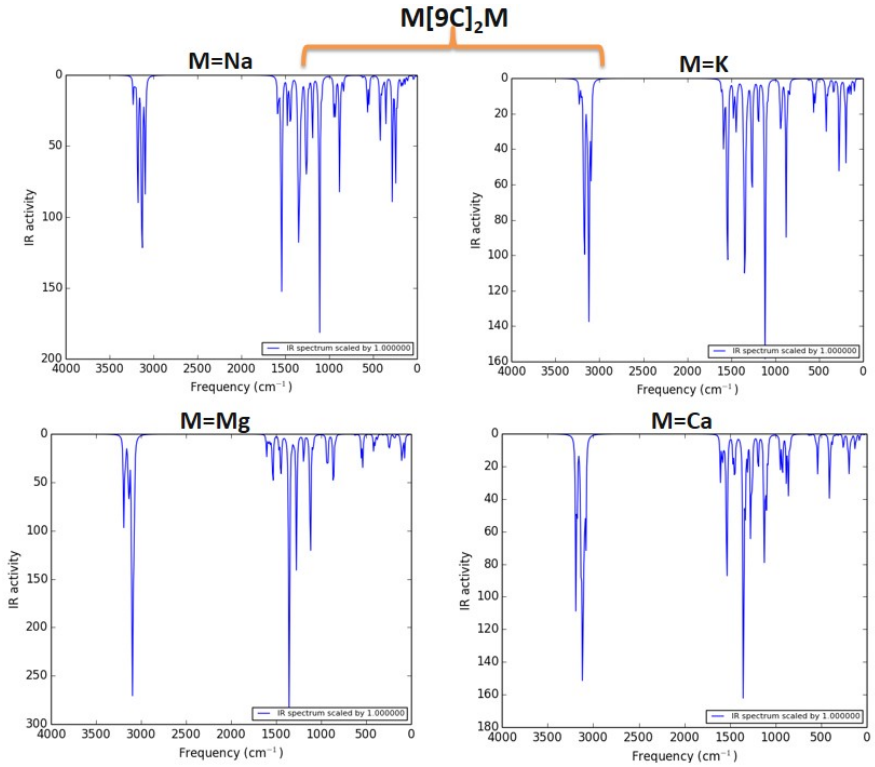

Figure S7: The obtained FT-IR spectra of $M[9C]_2M$ (where M= Na, K, Mg, and Ca) complexes at the m062X/def2qzvpp level.

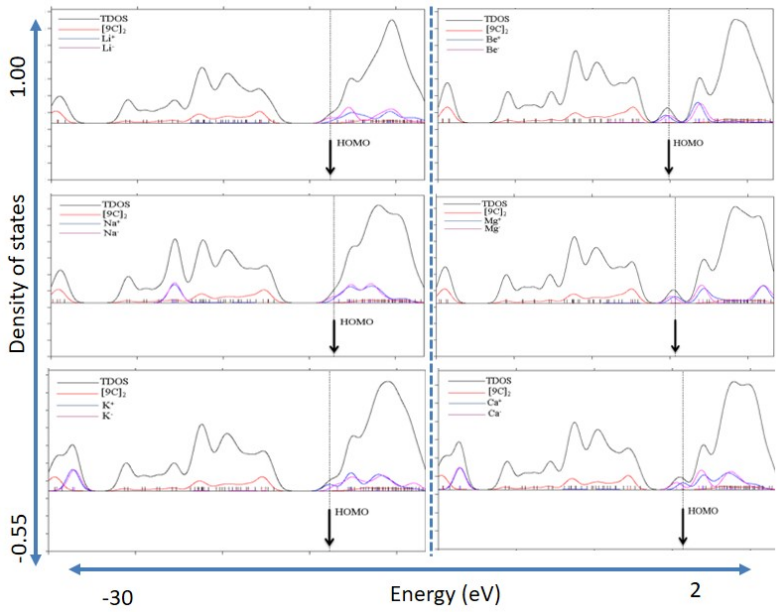

Fig. S8: Partial density of states (PDOS) spectra for M[9C]$_2$M complexes (upper series for alkalide complexes) and lower panel for alkaline earth metal-based complexes.

Table S1: The geometric parameters, interaction energies (ΔE), and thermodynamic parameters of M[9C]$_2$M complexes were calculated at different levels.

Complex	**Level**	**d_{AM-O} (Å)**	**d_{AM-H} (Å)**	**d_{AM-AM} (Å)**	**ΔE (kcal/mol)**	**ΔH (kcal/mol)**	**ΔG (kcal/mol)**	**ΔS (kcal/mol K)**
Li[9C]$_2$Li	**B3LYP-D3**	1.93	3.15	9.81	-47.62	-48.31	-30.74	-0.058
	MN-15	1.94	2.88	9.57	-55.84	-57.60	-39.72	-0.060
	WB97XD	1.92	3.19	9.81	-43.48	-44.61	-27.10	-0.058
Na[9C]$_2$Na	**B3LYP-D3**	2.77	3.66	11.53	-27.42	-25.53	-11.29	-0.047
	MN-15	2.65	3.68	11.38	-26.04	-27.17	-11.48	-0.052
	WB97XD	2.62	3.95	11.57	-12.70	-19.31	-2.69	-0.055
K[9C]$_2$K	**B3LYP-D3**	2.67	2.97	10.77	-17.19	-15.93	-3.20	-0.042
	MN-15	2.56	3.38	11.07	-15.06	-16.25	-3.45	-0.043
	WB97XD	2.55	3.47	11.17	-12.36	-13.49	-2.39	-0.037

Be[9C]$_2$Be	**B3LYP-D3**	2.31	3.15	10.54	-30.68	-31.81	-15.12	-0.056
	MN-15	2.29	3.20	10.37	-31.18	-32.31	-18.69	-0.045
	WB97XD	2.25	3.38	10.47	-27.35	-28.61	-11.48	-0.057
Mg[9C]$_2$Mg	**B3LYP-D3**	2.76	2.77	11.17	-22.08	-20.83	-2.60	-0.061
	MN-15	2.54	3.00	11.68	-19.70	-21.02	-8.03	-0.043
	WB97XD	2.64	3.14	12.04	-18.69	-17.82	-7.71	-0.033
Ca[9C]$_2$Ca	**B3LYP-D3**	2.67	3.27	10.63	-13.49	-13.05	-1.19	-0.039
	MN-15	2.68	3.80	10.64	-11.79	-15.43	-1.44	-0.046
	WB97XD	2.65	4.17	10.89	-7.21	-8.47	-1.82	-0.022

Table S2: The performed charge decomposition analysis. The units are in |e|.

System	**Donation (d)**	**Back-donation (b)**	**Residual (d–b)**	**Repulsion (r)**
Li[9C]$_2$Li	0.20	-0.05	0.25	0.04
Na[9C]$_2$Na	0.11	-0.02	0.13	0.06
K[9C]$_2$K	0.06	-0.02	0.08	0.007
Be[9C]$_2$Be	0.09	0.03	0.06	0.11
Mg[9C]$_2$Mg	0.11	0.01	0.10	-0.20
Ca[9C]$_2$Ca	0.19	0.01	0.18	-0.54

Table S3: Second order perturbation theory of fock matrix theory in NBO basis of isolated [9C]$_2$ and dual metal-doped [9C]$_2$ complexes.

System	**Donor(i)**	**Type**	**Acceptor(j)**	**Type**	**E(2)[a] (kJmol^{-1})**	**E(i)-E(j)[b] (a.u.)**	**F(i,j)[c] (a.u.)**
[9C]$_2$	22O	LP (1)	C7 - H16	σ*	0.25	1.11	0.015
	29O	LP (1)	C4 - H10	σ*	0.19	0.85	0.012

	36O	LP (1)	C5-H12	σ*	0.27	1.11	0.015
$Li[9C]_2Li$	O1	LP (1)	Li44	RY(1)	1.76	1.15	0.042
	O1	LP (1)	Li43-Li44	σ*	5.03	0.71	0.054
	O2	LP (1)	Li44	RY(1)	1.76	1.15	0.040
	O2	LP (1)	Li43-Li44	σ*	5.06	0.72	0.054
	O3	LP (1)	Li44	RY(1)	1.76	1.15	0.040
	O3	LP (1)	Li43-Li44	σ*	5.06	0.72	0.054
	Li43-Li44	σ	C23-H25	σ*	2.43	0.50	0.032
	Li43-Li44	σ	C31-H32	σ*	2.43	0.50	0.032
	Li43-Li44	σ	C37-H38	σ*	2.46	0.50	0.032
$Na[9C]_2Na$	O1	LP (1)	Na43	RY*(1)	0.28	1.75	0.02
	O1	LP (1)	Na43-Na44	σ	2.99	0.67	0.04
	O2	LP (1)	Na43	RY*(1)	0.29	1.75	0.02
	O2	LP (1)	Na43-Na44	σ	2.99	0.67	0.04
	O3	LP (1)	Na43	RY*(1)	0.29	1.75	0.02
	O3	LP (1)	Na43-Na44	σ	2.99	0.67	0.04
	Na43-Na44	σ*	C23-H25	σ*	1.83	0.5	0.027
	Na43-Na44	σ*	C31-H32	σ*	1.83	0.5	0.027
	Na43-Na44	σ*	C37-H38	σ*	1.82	0.5	0.027
$K[9C]_2K$	O1	LP (1)	K44	RY*(1)	0.53	1.5	0.025
	O1	LP (1)	K44-K43	σ	1.53	0.66	0.028
	O2	LP (1)	K44	RY*(1)	0.14	1.5	0.013
	O2	LP (1)	K44-K43	σ	1.53	0.66	0.028
	O3	LP (1)	K44	RY*(1)	0.13	1.5	0.012
	O3	LP (1)	K44-K43	σ	1.53	0.66	0.028

	K44-K43	σ*	C23-H25	σ*	1.25	0.49	0.022
	K44-K43	σ*	C31-H32	σ*	1.24	0.49	0.022
	K44-K43	σ*	C37-H38	σ*	1.25	0.49	0.023
Be[9C]$_2$Be	O1	LP (1)	Be43	RY*(1)	0.05	1.51	0.008
	O2	LP (1)	Be43	RY*(1)	0.07	1.26	0.008
	O3	LP (1)	Be43	RY*(1)	0.13	1.24	0.012
	Be44	LP (1)	C23-H25	σ*	0.91	0.68	0.022
	Be44	LP (1)	C31-H32	σ*	0.92	0.68	0.022
	Be44	LP (1)	C37-H38	σ*	0.93	0.68	0.023
Mg[9C]$_2$Mg	O1	LP (2)	Mg44	RY*(1)	0.05	1.58	0.008
	O2	LP (2)	Mg44	RY*(1)	0.05	1.58	0.008
	O3	LP (2)	Mg44	RY*(1)	0.05	1.58	0.008
	Mg43	LP (1)	C23-H25	σ*	0.8	0.64	0.02
	Mg43	LP (1)	C31-H32	σ*	0.82	0.64	0.021
	Mg43	LP (1)	C37-H38	σ*	0.83	0.64	0.021
Ca[9C]$_2$Ca	O1	LP (1)	Ca44	RY*(1)	0.47	1.73	0.026
	O2	LP (1)	Ca44	RY*(1)	0.47	1.73	0.026
	O3	LP (1)	Ca44	RY*(1)	0.47	1.73	0.026
	Ca43	LP (1)	C23-H25	σ*	0.69	0.59	0.018
	Ca43	LP (1)	C31-H32	σ*	0.69	0.59	0.018
	Ca43	LP (1)	C37-H38	σ*	0.69	0.59	0.018

E_D means electron density.

[a] E(2) means energy of hyper conjugative interactions.

[b] Energy difference between donor and acceptor i and j NBO orbitals.

Table S4: Calculated polarizability (α_o au) hyperpolarizability (β_o au), and total dipole moment (μ_o D) using the various solvent in SDM model.

		9C	**[9C]2**	**$Li(9C)_2Li$**	**$Na(9C)_2Na$**	**$K(9C)_2K$**	**$Be(9C)_2Be$**	**$Mg(9C)_2Mg$**	**$Ca(9C)_2Ca$**
DMSO	α_o	89.38	182.96	696.77	954.90	1242.47	375.41	511.29	1394.93
	β_o	361.96	697.04	396189.89	196888.13	332758.22	9972.95	6345.56	275200.15
	μ_o	2.19	4.91	11.18	13.68	15.87	6.46	7.22	10.38
Acetone	α_o	241.54	180.84	639.76	860.59	1128.43	360.39	488.94	1271.87
	β_o	355.80	684.42	255050.77	355.79	172577.83	7995.63	5339.43	355.79
	μ_o	2.18	4.89	11.15	13.55	15.70	6.43	7.20	10.24
Methanol	α_o	89.54	183.17	695.19	913.20	1196.36	381.07	508.44	1248.70
	β_o	429.61	763.13	447675.76	195914.78	234053.69	6.71	7034.79	213963.95
	μ_o	2.48	5.33	10.96	13.42	15.56	9745.37	7.42	10.65
n-hexane	α_o	76.36	153.73	412.96	476.04	711.07	250.51	332.74	645.68
	β_o	246.77	516.78	30653.14	33908.45	50387.44	1118.93	847.51	21867.27
	μ_o	1.83	4.35	10.21	12.23	14.09	5.78	6.59	9.06
water	α_o	90.27	184.89	746.44	984.76	1284.40	394.59	526.02	1311.61
	β_o	442.13	777.96	650587.02	211119.97	391328.07	11561.46	8220.09	257231.28
	μ_o	2.52	5.38	10.97	13.49	15.68	6.74	7.45	10.76

Table S5: QTAIM topological parameters for electron density ρ(r), Laplacian of electron density $\nabla^2\rho(r)$, kinetic electron density G(r), potential electron density V(r), eigenvalues of Hessian matrix (λ), and bond ellipticity index (ε) at the BCPs of the [9C], $[9C]_2$ and $M[9C]_2M$ (where M can be Li, K, Na, Be, Mg, and Ca).

System	Bond	ρ(r)	$\nabla^2\rho(r)$	G (r)	V(r)	G(r)/ |-V(r)|	λ1	λ2	λ3	ε	E_{nt} (kj/mol)
[9C]	1O-2C	0.2913	- 1.199	0.043	-0.386	0.111	0.452	-0.843	-0.808	0.0424	-506.7
	1O-19C	0.265	-0.575	0.249	-0.643	0.387	0.450	-0.510	-0.515	0.0089	-844.1
	8O-7C	0.265	-0.575	0.249	-0.643	0.387	-0.510	0.450	-0.515	0.0089	-844.1
	8O-10C	0.268	-0.611	0.244	-0.641	0.381	-0.533	-0.518	0.440	0.0271	-841.5
	15O-16C	0.268	-0.611	0.244	-0.642	0.380	-0.518	0.441	-0.533	0.0272	-842.8
	15O-12C	0.265	-0.575	0.249	-0.643	0.387	-0.510	0.450	-0.515	0.0089	-844.1
$[9C]_2$	22O-16H	0.0066	0.024	0.0050	-0.0039	1.282	0.0321	-0.0028	-0.0047	0.673	-5.1
	29O-12H	0.0065	0.0241	0.0049	-0.0038	1.289	0.0314	-0.0026	-0.0046	0.729	-5.0
	36O-10H	0.0065	0.0242	0.0049	-0.0038	1.289	0.0316	-0.0046	-0.0027	0.711	-5.0
$Li[9C]_2Li$	22O-16H	0.0094	0.0357	0.0076	-0.0062	1.226	0.0490	-0.0056	-0.0075	0.345	-8.1
	29O-12H	0.0134	0.0516	0.0111	-0.0094	1.181	0.0774	-0.0133	-0.0123	0.080	-12.3
	36O-10H	0.0093	0.0351	0.0074	-0.0061	1.213	0.0479	-0.0073	-0.0054	0.366	-8.0
	1O-44Li	0.0346	0.243	0.0531	-0.0454	1.170	-0.0608	-0.0637	0.367	0.0466	-59.6
	2O-44Li	0.0346	0.243	0.0532	-0.0454	1.172	-0.0609	0.368	-0.0638	0.0472	-59.6
	3O-44Li	0.0340	0.238	0.0520	-0.0443	1.174	-0.0594	0.360	-0.0621	0.0464	-58.2
	25H-43Li	0.293	1.222	0.0404	-0.386	0.105	0.460	-0.826	-0.855	0.0355	-506.7
	30H-43Li	0.0051	0.0027	0.0008	-0.0010	0.800	0.0049	-0.0010	-0.0012	0.259	-1.3
	32H-43Li	0.0051	0.0026	0.0008	-0.0010	0.800	0.0049	-0.0012	-0.0010	0.256	-1.3
$Na[9C]_2Na$	22O-16H	0.0124	0.0472	0.0101	-0.0084	1.202	0.0702	-0.0118	-0.011	0.0721	-11.0
	29O-12H	0.0070	0.0307	0.0063	-0.005	1.260	0.0218	0.0096	-0.0007	-1.081	-6.6
	36O-10H	0.0089	0.0334	0.007	-0.0057	1.228	0.0455	-0.0070	-0.005	0.377	-7.5
	1O-44Na	0.0234	0.153	0.0323	-0.0263	1.228	0.215	-0.0321	-0.0299	0.0735	-34.5
	2O-44 Na	0.0235	0.153	0.0324	-0.0264	1.227	0.216	-0.0300	-0.0323	0.0736	-34.7

	3O-44 Na	0.0234	0.153	0.0323	-0.0263	1.228	0.215	-0.0299	-0.0322	0.0738	-34.5
	25H-43 Na	0.0043	0.002	0.0007	-0.0009	0.778	0.0036	-0.0006	-0.0009	0.373	-1.2
	30H-43 Na	0.0043	0.002	0.0007	-0.0009	0.778	0.0036	-0.0006	-0.0009	0.378	-1.2
	32H-43 Na	0.0043	0.002	0.0007	-0.0009	0.778	0.0036	-0.0006	-0.0009	0.378	-1.2
K[9C]$_2$K	22O-16H	0.012	0.045	0.0097	-0.0081	1.198	0.0678	-0.0106	-0.0114	0.067	-10.6
	29O-12H	0.260	0.562	0.242	-0.624	0.388	-0.503	0.491	0.432	0.0232	-819.2
	36O-10H	0.0085	0.0321	0.0067	-0.0055	1.218	0.0435	-0.0066	-0.0047	0.401	-7.2
	1O-44K	0.020	0.097	0.020	-0.017	1.176	0.138	-0.021	-0.020	0.079	-22.3
	2O-44K	0.020	0.097	0.020	-0.017	1.176	0.138	-0.021	-0.020	0.079	-22.3
	3O-44K	0.020	0.097	0.020	-0.017	1.176	0.138	-0.021	-0.020	0.079	-22.3
	25H-43K	0.003	0.001	0.0004	-0.0006	0.667	0.001	-0.0003	-0.0001	2.034	-0.8
	30H-43K	0.003	0.001	0.0004	-0.0006	0.667	0.001	-0.0001	-0.0003	1.796	-0.8
	32H-43K	0.003	0.001	0.0004	-0.0006	0.667	0.001	-0.0003	-0.0001	2.470	-0.8
Be[9C]$_2$Be	22O-16H	0.006	0.024	0.005	-0.004	1.250	0.033	-0.0029	-0.0047	0.651	-5.3
	29O-12H	0.009	0.034	0.007	-0.005	1.400	0.049	-0.007	-0.0078	0.032	-6.6
	36O-10H	0.006	0.024	0.005	-0.004	1.250	0.032	-0.0047	-0.0028	0.663	-5.3
	1O-44Be	0.009	0.016	0.004	-0.004	1.000	0.028	-0.0059	-0.0055	0.074	-5.3
	2O-44 Be	0.009	0.016	0.004	-0.004	1.000	0.028	-0.0059	-0.0055	0.075	-5.3
	3O-44 Be	0.009	0.016	0.004	-0.004	1.000	0.028	-0.0059	-0.0055	-0.005	-5.3
	25H-43 Be	0.004	0.008	0.002	-0.001	2.000	0.012	-0.0019	-0.0023	0.192	-1.3
	30H-43 Be	0.290	1.190	0.0429	-0.383	0.112	0.450	-0.804	-0.836	0.039	-502.8
	32H-43 Be	0.004	0.008	0.001	-0.001	1.000	0.013	-0.0024	-0.002	0.182	-1.3
Mg[9C]$_2$Mg	22O-16H	0.261	0.561	0.244	-0.629	0.388	-0.502	-0.497	0.438	0.010	-825.7
	29O-12H	0.009	0.034	0.007	-0.005	1.400	0.050	-0.008	-0.007	0.036	-6.6
	36O-10H	0.297	1.247	0.042	-0.396	0.106	0.460	-0.838	-0.869	0.035	-519.8
	1O-44Mg	0.009	0.013	0.003	-0.004	0.750	0.022	-0.004	-0.004	0.068	-5.3
	2O-44 Mg	0.009	0.013	0.003	-0.004	0.750	0.022	-0.004	-0.004	0.068	-5.3
	3O-44 Mg	0.009	0.013	0.003	-0.004	0.750	0.022	-0.004	-0.004	0.067	-5.3
	25H-43 Mg	0.004	0.005	0.001	-0.001	1.000	0.008	-0.001	-0.001	0.221	-1.3
	30H-43 Mg	0.004	0.005	0.001	-0.001	1.000	0.008	-0.001	-0.001	0.215	-1.3

	32H-43 Mg	0.004	0.005	0.001	-0.001	1.000	0.008	-0.001	-0.001	0.235	-1.3
Ca[9C]$_2$Ca	22O-16H	0.007	0.026	0.005	-0.004	1.250	0.034	-0.005	-0.003	0.641	-5.3
	29O-12H	0.297	1.256	0.041	-0.395	0.104	0.459	-0.873	-0.842	0.038	-518.5
	36O-10H	0.007	0.026	0.005	-0.004	1.250	0.035	-0.003	-0.005	0.609	-5.3
	1O-44Ca	0.021	0.101	0.022	-0.018	1.222	0.144	-0.022	-0.021	0.118	-23.6
	2O-44 Ca	0.021	0.101	0.022	-0.018	1.222	0.144	-0.022	-0.023	0.118	-23.6
	3O-44 Ca	0.021	0.101	0.022	-0.018	1.222	0.144	-0.022	-0.021	0.118	-23.6
	25H-43 Ca	0.003	0.003	0.0007	-0.0007	1.000	0.004	-0.0009	-0.0007	0.308	-0.9
	30H-43 Ca	0.290	1.196	0.042	-0.384	0.109	0.452	-0.808	-0.840	0.038	-504.1
	32H-43 Ca	0.262	0.564	0.246	-0.634	0.388	-0.506	0.442	-0.500	0.012	-832.3

Table S6: Vibrational stretching frequencies of isolated $[9C]_2$ and dual metal-doped $[9C]_2$ complexes.

Complex	υ_{C-O}	υ_{C-H}	υ_{M-O}
$[9C]_2$	1368.54	3076.32	-
$Li[9C]_2Li$	1265.08	3079.08	525.16
$Na[9C]_2Na$	1107.45	3127.26	242.89
$K[9C]_2K$	1120.71	3124.33	242.89
$Be[9C]_2Be$	1361.21	3093.56	135.15
$Mg[9C]_2Mg$	1348.41	3104.45	70.50
$Ca[9C]_2Ca$	1336.59	3124.33	192.59