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Supporting Information

Gas Storage Potential of $ExBox^{4+}$ and its Li-decorated derivative

Ranjita Das and Pratim Kumar Chattaraj*

Department of Chemistry and Center for Theoretical Studies, Indian Institute of Technology

Kharagpur, Kharagpur – 721302, West Bengal, India

*Author for correspondence: Email: pkc@chem.iitkgp.ernet.in

Table S1: Geometrical parameters of hydrogen adsorbed complexes

System	C-H bond length range(Å)	N-H bond length (Å)	Distance between hydrogen and centroid of ring (Å)			Geometrical parameter for ExBox			
			Pyridinium ring	Phenyl ring (T)	Phenyl ring (S)	C-C bond length (Å)	C-N bond length (Å)	<C-C-C-C (deg)	<N-C-C (deg)
$(2H_2)_{endo}$@$ExBox^{4+}$	2.872-3.090	-	-	-	2.788	1.481	1.495	146.455	110.639
$(3H_2)_{endo}$@$ExBox^{4+}$	2.873-3.023	-		2.671	2.814	1.481	1.495	146.768	110.645
$(8H_2)_{exo}$@$ExBox^{4+}$	2.978-3.148	2.967	2.690	2.691	2.669	1.481	1.494	146.007	110.585
$(8H_2)_{exo}$ +$(2H_2)_{endo}$@$ExBox^{4+}$	2.945(2.878)[a]-3.114(3.103)[a]	2.974	2.670	2.684	2.685 (2.790)[a]	1.480	1.494	145.586	110.470
$(8H_2)_{exo}$ +$(3H_2)_{endo}$@$ExBox^{4+}$	2.974(2.876)[a]-3.113(3.011)[a]	2.971	2.683	2.716 (3.457)[a]	2.686 (2.764)[a]	1.480	1.495	146.068	110.517
$(12H_2)_{exo}$@$ExBox^{4+}$	2.975-3.183	3.044	2.689	2.689	2.679	1.481	1.494	146.817	110.603
$(12H_2)_{exo}$ +$(2H_2)_{endo}$@$ExBox^{4+}$	2.970(2.876)[a]-3.290(3.117)[a]	3.045	2.686	2.690	2.654 (2.790)[a]	1.481	1.494	145.157	110.112
$(12H_2)_{exo}$ +$(3H_2)_{endo}$@$ExBox^{4+}$	2.980(2.880)[a]-3.301(3.004)[a]	3.046	2.699	2.695 (2.678)[a]	2.654 (2.775)[a]	1.480	1.495	145.442	110.465

a the values in parenthesis indicate the endohedral hydrogen

Table S2: Bond critical point data (a.u.) calculated at wB97x-D/6-311G (d, p) level for hydrogen bound $ExBox^{4+}$ complexes

System	bond type	ρ	$\nabla^2\rho$	G_{bcp}	V_{bcp}	H_{bcp}
$(2H_2)_{endo}$@$ExBox^{4+}$	N-H	0.00375	0.01304	0.00243	-0.00161	0.00083
	C-H	0.00608	0.01661	0.00335	-0.00255	0.00080
$(3H_2)_{endo}$@$ExBox^{4+}$	N-H	0.00385	0.01348	0.00252	-0.00167	0.00085
	C-H	0.00586	0.01620	0.00325	-0.00244	0.00080
	H-H	0.00025	0.00095	0.00016	-0.00008	0.00008
$3H_2$@model	N-H	0.00468	0.01601	0.00305	-0.00209	0.00096
	C-H	0.00468	0.01526	0.00292	-0.00202	0.00090
$5H_2$@model	C-H	0.004055	0.01473	0.00275	-0.00182	0.00093
	H-H	0.003183	0.01031	0.00192	-0.00125	0.00066

Table S3: Energy decomposition analysis (kcal/mol) of $(nM)_{endo/exo}$@$ExBox^{4+}$ (M= H_2, CO; n=2, 8) complexes at B3LYP-D/DZP level

Energy terms		**$(2H_2)_{endo}$@$ExBox^{4+}$**		**$(8H_2)_{exo}$@$ExBox^{4+}$**		**$(2CO)_{endo}$@$ExBox^{4+}$**	
		Without counter ions	With counter ions	Without counter ions	With counter ions	Without counter ions	With counter ions
ΔV_{elstat}		-4.61(29.6%)	-2.74(18.4%)	-8.87(20.4%)	-9.79(29.1%)	-18.26(44.8%)	-12.33(37.5%)
ΔE_{pauli}		7.48	8.04	17.67	15.83	24.36	18.53
ΔE_{oi}		-5.19(33.2%)	-5.91(39.8%)	-20.5(47.1%)	-11.64(34.6%)	-9.08(22.2%)	-8.22(25%)
ΔE_{disp}		-5.81(37.2%)	-6.19(41.7%)	-14.12(32.5%)	-12.21(36.3%)	-13.41(33%)	-12.34(37.5%)
ΔE_{int}		-8.14	-6.8	-25.82	-17.8	-16.39	-14.36

Table S4: CDA data for gas adsorbed complexes

	d	**b**	**d-b**	**r**
$(2H_2)_{endo}$@$ExBox^{4+}$	-0.005	0.005	-0.001	-0.070
$(3H_2)_{endo}$@$ExBox^{4+}$	-0.002	0.005	-0.004	-0.094
$(8H_2)_{exo}$@$ExBox^{4+}$	-0.070	0.008	-0.078	-0.188
$(8H_2)_{exo}$ +$(2H_2)_{endo}$@$ExBox^{4+}$	-0.062	0.012	-0.074	-0.254
$(8H_2)_{exo}$ +$(3H_2)_{endo}$@$ExBox^{4+}$	-0.066	0.011	-0.076	-0.279
$(12H_2)_{exo}$@$ExBox^{4+}$	-0.069	0.062	-0.130	-0.244
$(12H_2)_{exo}$ +$(2H_2)_{endo}$@$ExBox^{4+}$	-0.063	0.074	-0.137	-0.316
$(12H_2)_{exo}$ +$(3H_2)_{endo}$@$ExBox^{4+}$	-0.069	0.073	-0.136	-0.339
$(CO)_{endo}$@$ExBox^{4+}$	0.005	0.013	-0.008	-0.025
$(2CO)_{endo}$@$ExBox^{4+}$	0.015	0.034	-0.019	-0.100
$(3CO)_{endo}$@$ExBox^{4+}$	0.019	0.043	-0.024	-0.127

Table S5: Geometrical parameters of CO adsorbed complexes

System	**Shortest C-C bond length (Å)**	**Shortest C-O bond length (Å)**	**Shortest N-C bond length (Å)**	**Shortest N-O bond length (Å)**	**Distance between CO and centroid of pyridinium ring (Å)**	**Geometrical parameter for ExBox**			
						C-C bond length (Å)	**C-N bond length (Å)**	**<C-C-C-C (deg)**	**<N-C-C (deg)**
$(CO)_{endo}$@$ExBox^{4+}$	3.493	3.374	3.469	3.387	3.151(3.307)[a]	1.481	1.495	145.558	110.530
$(2CO)_{endo}$@$ExBox^{4+}$	3.393	3.471	3.463	3.383	3.142(3.293)[a]	1.481	1.495	145.895	110.661
$(3CO)_{endo}$@$ExBox^{4+}$	3.397	3.476	3.443	3.388	3.145(3.269)[a]	1.481	1.495	144.083	110.588

a the values in parenthesis indicate the bonding distance of C center of CO from centroid of ring

Table S6: Bond critical point data (a.u.) calculated at wB97x-D/6-311G (d, p) level for CO bound $ExBox^{4+}$ complexes

System	bond type	ρ	$\nabla^2\rho$	G_{bcp}	V_{bcp}	H_{bcp}
$(CO)_{endo}$@$ExBox^{4+}$	C-O	0.00421	0.01337	0.00254	-0.00174	0.00080
	C-O(pyridinium ring)	0.00429	0.01595	0.00298	-0.00198	0.00100
	C-C	0.00569	0.01604	0.00319	-0.00238	0.00082
	C-C(pyridinium ring)	0.00493	0.01560	0.00301	-0.00212	0.00089
$(2CO)_{endo}$@$ExBox^{4+}$	C-O	0.00417	0.01322	0.00251	-0.00172	0.00079
	C-O(pyridinium ring)	0.00425	0.01535	0.00288	-0.00192	0.00096
	N-C	0.00485	0.01597	0.00306	-0.00213	0.00093
	C-C	0.00566	0.01591	0.00317	-0.00236	0.00081
	C-C(pyridinium ring)	0.00489	0.01520	0.00294	-0.00208	0.00086
$(3CO)_{endo}$@$ExBox^{4+}$	C-O	0.00409	0.01306	0.00248	-0.00169	0.00079
	C-C	0.01646	0.14705	0.02757	-0.01837	0.00920
	third CO molecule					
	C-O	0.00398	0.01292	0.00244	-0.00165	0.00079
	C-C	0.00539	0.01545	0.00305	-0.00224	0.00081
	H-C	0.00041	0.00164	0.00028	-0.00015	0.00013
	Interaction between 2CO-3CO					
	C-C	0.00377	0.01241	0.00233	-0.00156	0.00077
	C-O	0.00185	0.00799	0.00141	-0.00083	0.00059

Table S7: Adsorption energy (E_{ads}, kcal/mol), reaction enthalpy (ΔH, kcal/mol), HOMO-LUMO gap (HLG, eV) for gas adsorbed ExBox.4Cl calculated at wB97x-D/6-311G (d, p) basis set

System	E_{ads}	ΔH	HLG
$(2H_2)_{endo}$@ ExBox.4Cl	-3.4	-2.2	5.477
$(3H_2)_{endo}$@ ExBox.4Cl	-2.5	-1.3	5.419
$(8H_2)_{exo}$@ ExBox.4Cl	-1.5	-0.3	5.492
$(12H_2)_{exo}$@ ExBox.4Cl	-1.7	-0.4	5.551
$(2CO)_{endo}$@ ExBox.4Cl	-5.5	-4.6	5.488

Table S8: Energy decomposition analysis (kcal/mol) of Li_3model and its gas bound complexes at B3LYP-D/DZP level

Energy terms	Li_3model		$3H_2$@Li_3model	3CO@Li_3model
	Without counter ions	With counter ions		
ΔV_{elstat}	-257.59(40.8%)	-293.99(47.4%)	-15.21(39.3%)	-22.05(37.7%)
ΔE_{pauli}	455.06	491.85	8.07	15.09
ΔE_{oi}	-343.03(54.4%)	-294.98(47.6%)	-14.11(36.5%)	-28.94(49.5%)
ΔE_{disp}	-30.41(4.8%)	-30.25(~5%)	-9.35(24.1%)	-7.44(12.73%)
ΔE_{int}	-175.97	-127.37	-15.21(39.3%)	-43.34

Table S9: CDA data for gas adsorbed Li_8ExBox^{4+}complexes

CDA analysis	**$8CO@Li_8ExBox^{4+}$**			**$8H_2@Li_8ExBox^{4+}$**		
	ExBox to Li	ExBox to CO	Li-CO	ExBox to Li	ExBox to H_2	Li-H_2
d	1.29721	0.00350	-0.00927	1.44325	0.00267	-0.00719
b	0.00300	-0.00529	0.29693	0.01338	-0.00548	0.57090
d-b	1.29830	0.00880	-0.30620	1.42987	0.00815	-0.58628
r	-0.16241	-0.03195	-0.18178	-0.16292	-0.07131	-0.18322

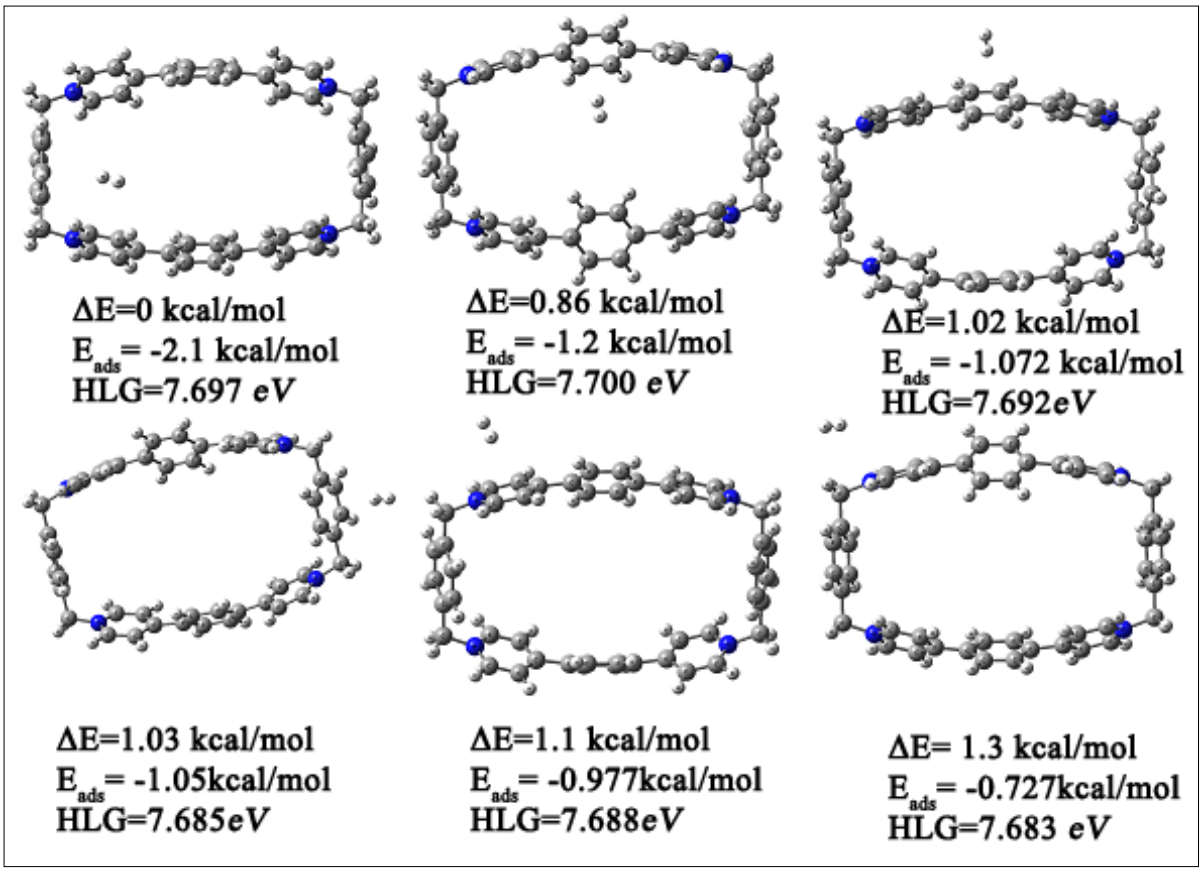


Fig. S1: Optimized geometries of different isomers of H_2@ExBox^{4+}

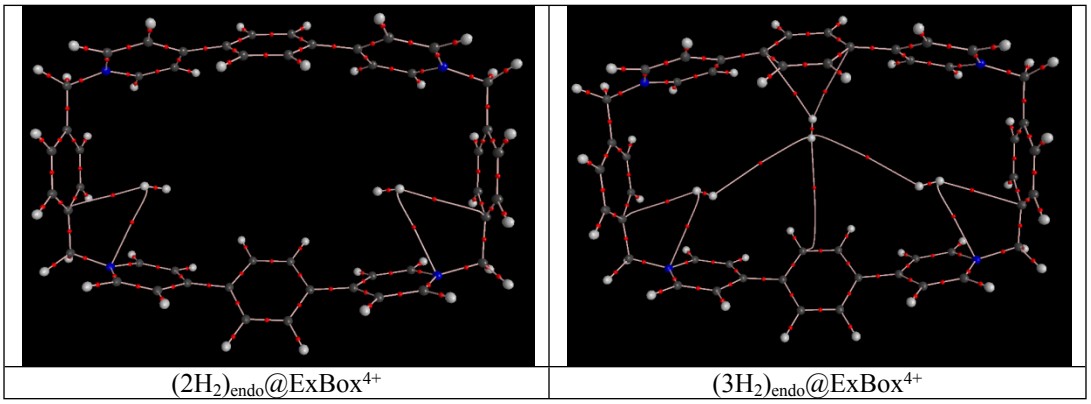


Fig. S2: Molecular graphs showing bond paths, bond critical points (BCP, red dots) of nH_2@ExBox^{4+}

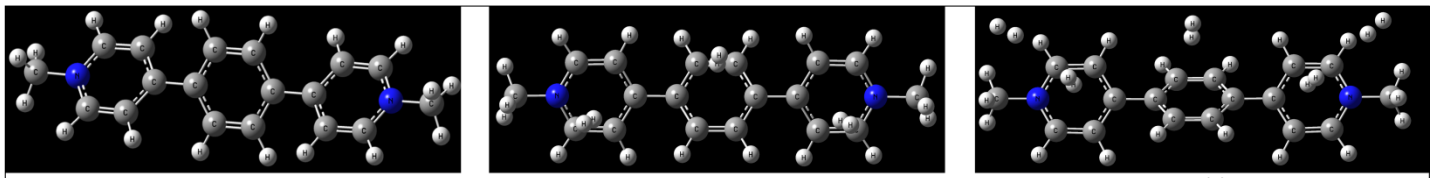


Fig. S3: Structures of model and nH_2@model (n=3,5)

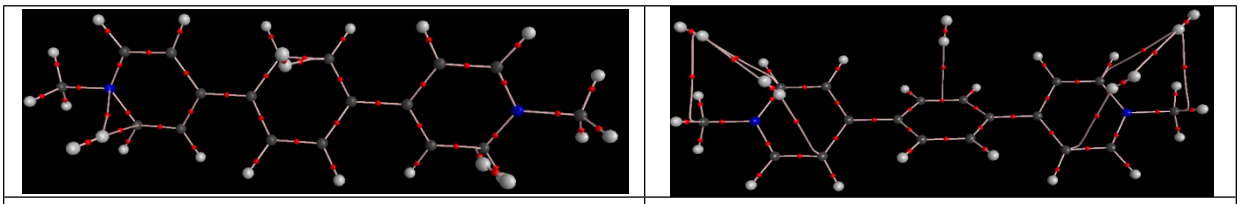


Fig. S4: Molecular graphs showing bond paths, bond critical points (BCP, red dots) of nH_2@model (n=3,5)

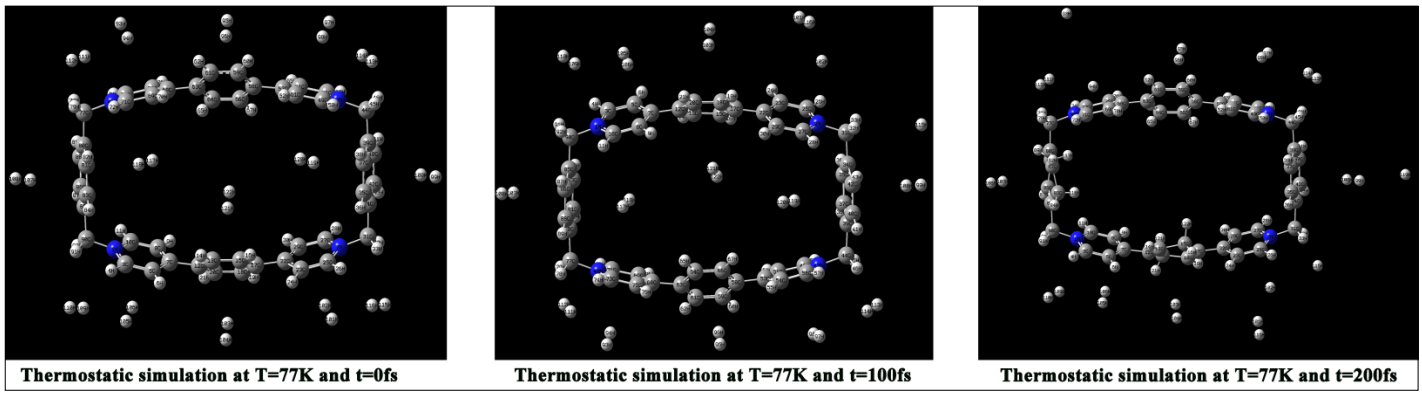
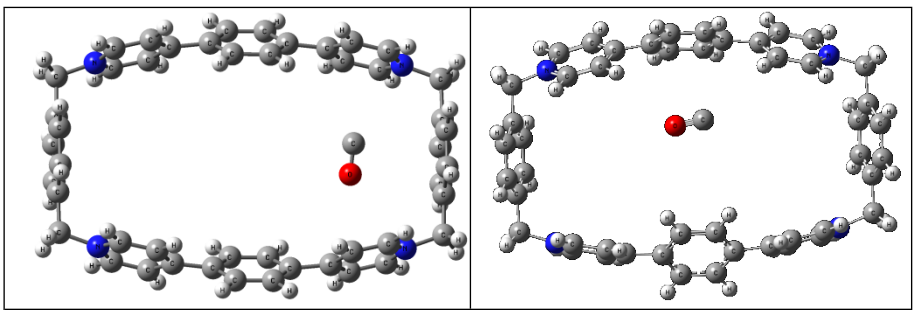


Fig. S5: Snap shots of $(12H_2)_{exo}$ +$(3H_2)_{endo}$@$ExBox^{4+}$ thermostatic simulation at 77K temperature at different time steps



ΔE=0.0 kcal/mol, E_{ads}= -5.6 kcal/mol HOMO-LUMO gap = 7.708 *eV*	ΔE=2.0 kcal/mol, E_{ads}= -3.5 kcal/mol HOMO-LUMO gap = 7.697*eV*

Fig. S6: Optimized geometries of different isomers of $(CO)_{endo}$@$ExBox^{4+}$

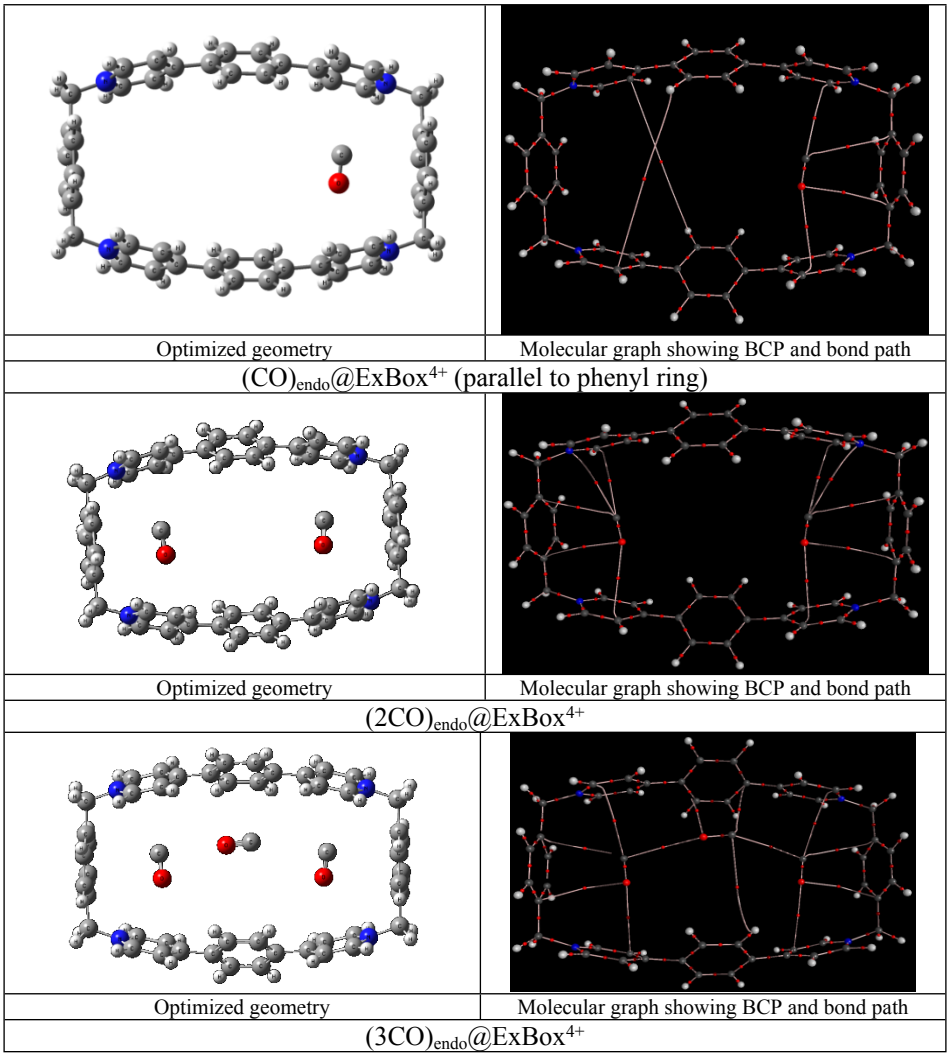


Fig. S7: Optimized geometries and molecular graphs showing bond paths, bond critical points (BCP, red dots) of $(nCO)_{endo}@ExBox^{4+}$; n=1,2,3

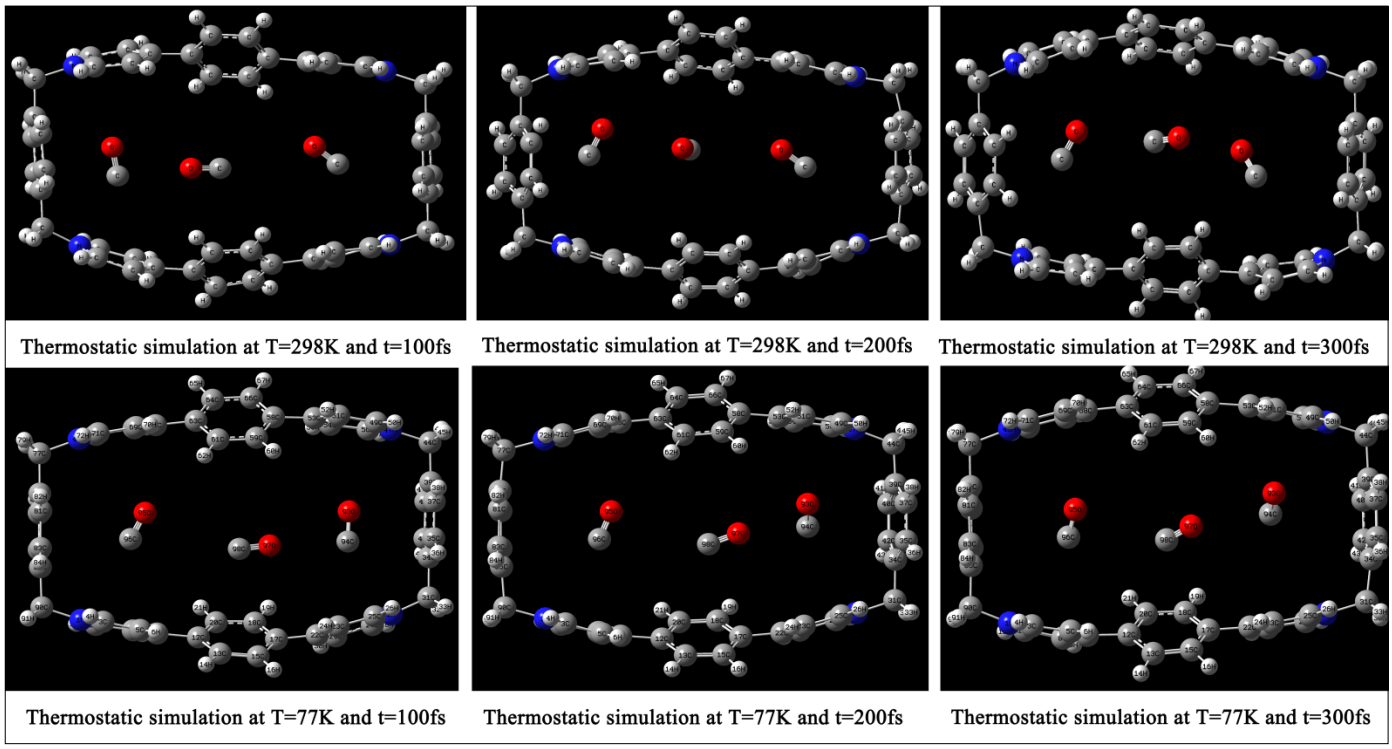


Fig. S8: Snap shots of $(3CO)_{endo}$@ExBox^{4+} under different simulation conditions at different time steps

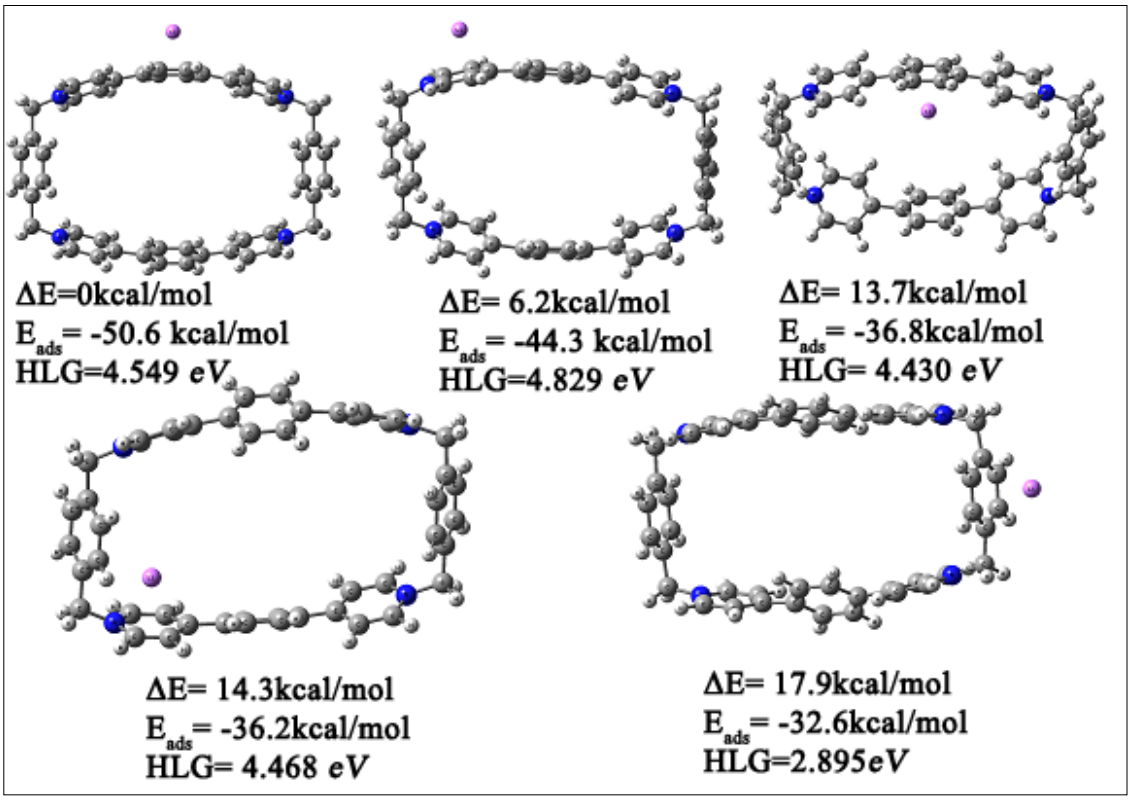


Fig. S9: Optimized geometries of different isomers of Li@ExBox^{4+}

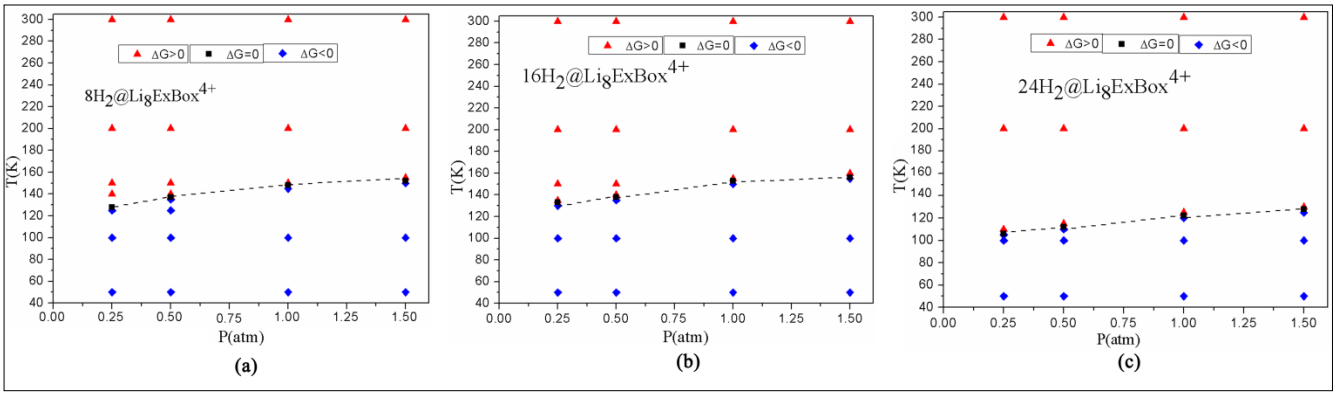


Fig. S10: T-P phase diagrams showing variation of ΔG for (a) $8H_2$@ Li_8ExBox^{4+} (b) $16H_2$@ Li_8ExBox^{4+} and (c) $24H_2$@ Li_8ExBox^{4+}

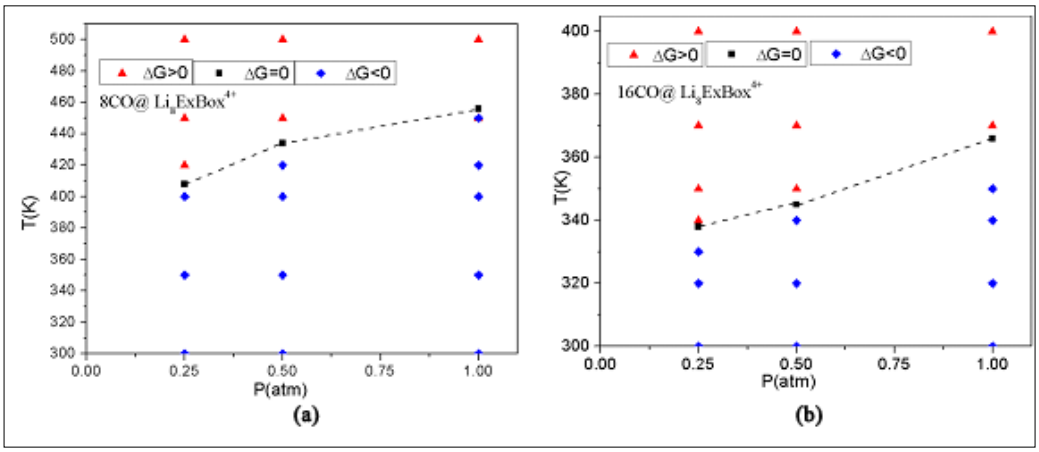
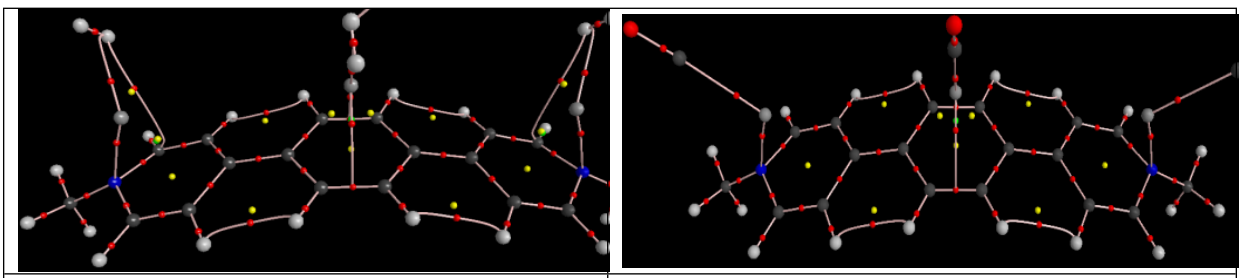


Fig. S11: T-P phase diagrams showing variation of ΔG for (a) 8CO@ Li_8ExBox^{4+} and (b) 16CO@ Li_8ExBox^{4+}



$3H_2$@Li_3model	3CO@Li_3model

Fig. S12: Molecular graphs showing bond paths, bond critical points (BCP, red dots)