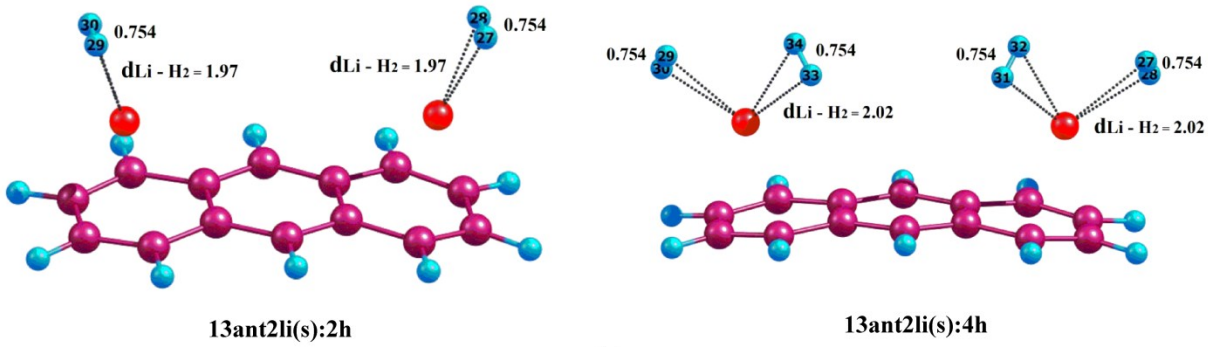
Electronic Supplementary Material (ESI) for RSC Advances.

Multiple Li^{+} and Mg^{2+} Decorated PAHs: Potential Systems for Reversible Hydrogen Storage

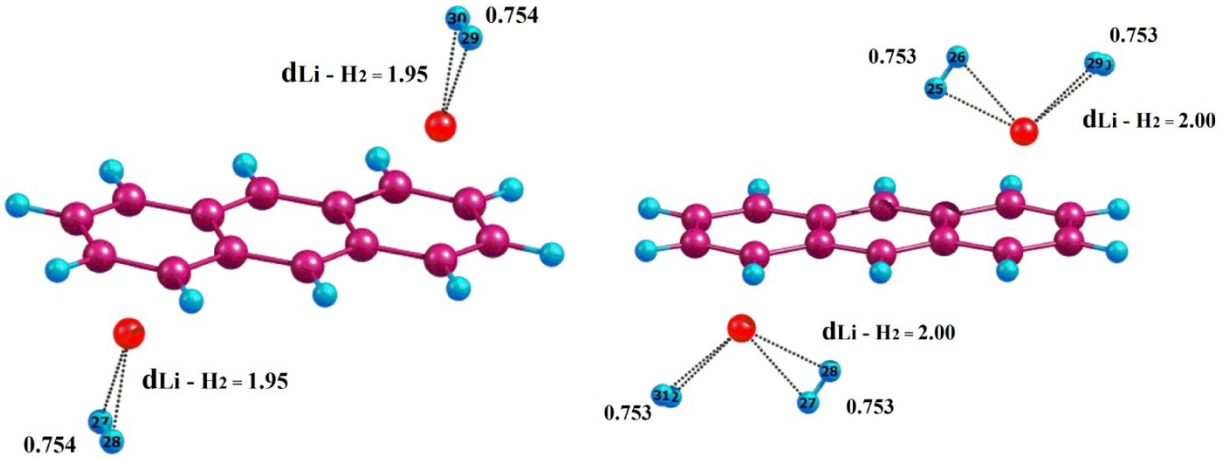
Avik Ghosh, Tanay Debnath, Tamalika Ash, Abhijit K. Das*

Supporting Information



13ant2li(s):2h 13ant2li(s):4h

(a)



13ant2li(o):2h 13ant2li(o):4h

(b)

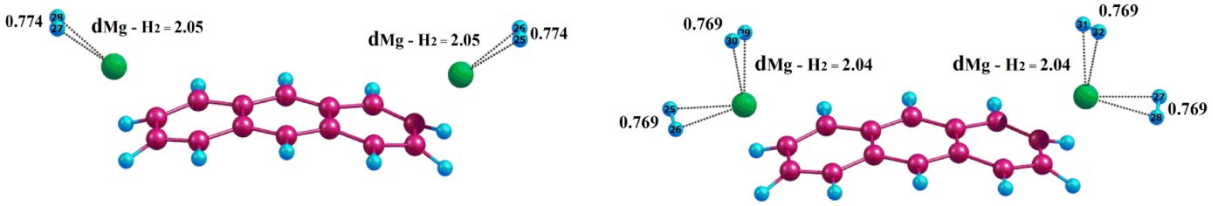
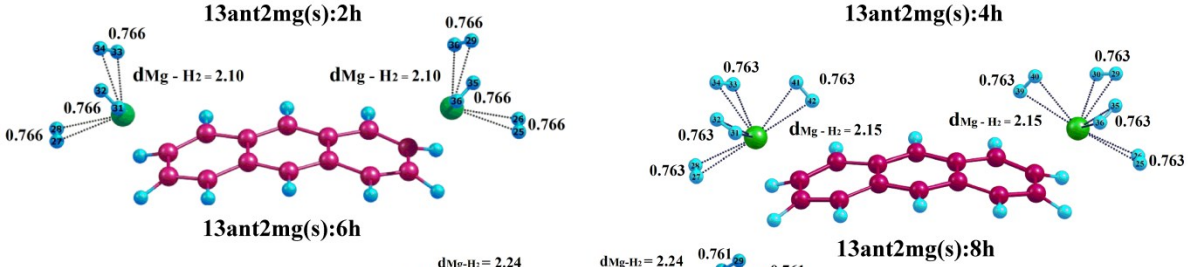
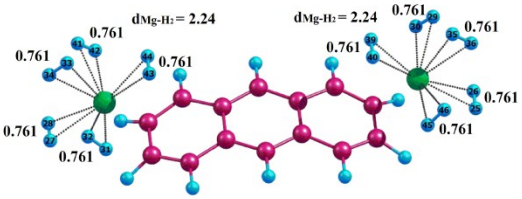
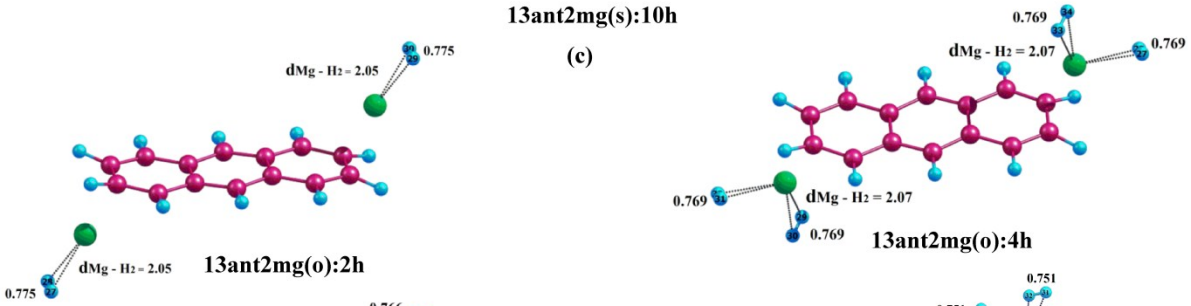


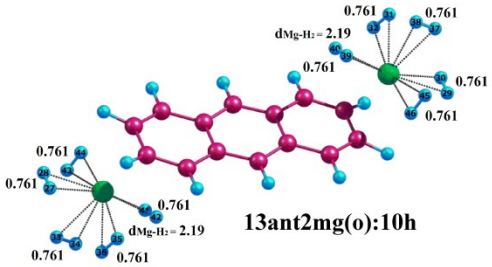
Fig. S1 2,4; (c) 13ant2r evel in conjunc etween Li+/Mg





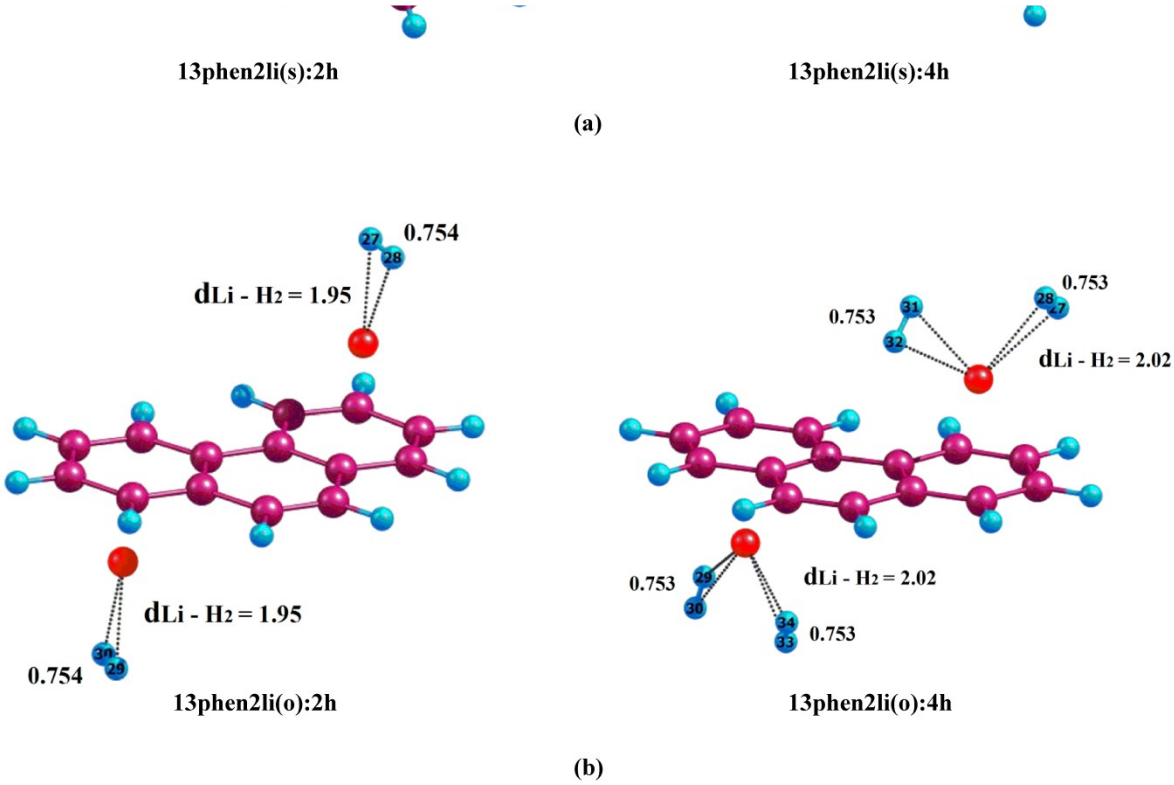
(c)

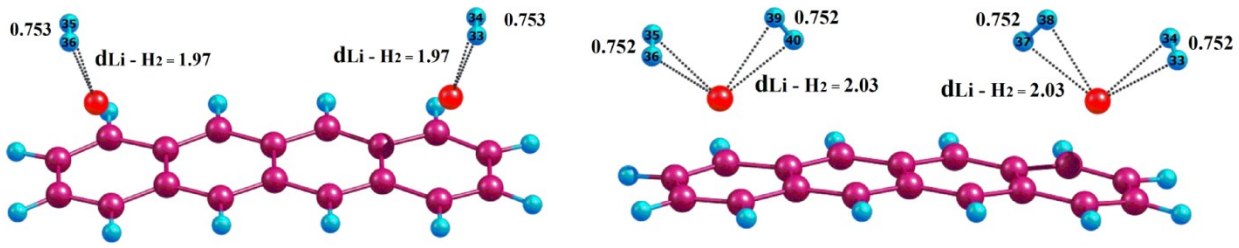




(d)

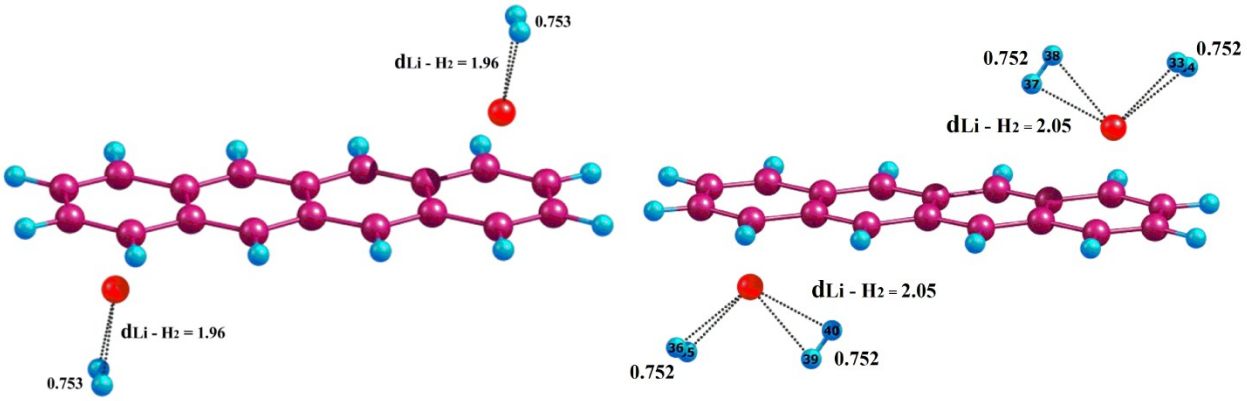
Fig. S2. Optimized geometries of (a) 13phen2li(s):nH_2, for n = 2,4; (b) 13phen2li(o):nH_2 , for n = 2,4 at CAM-B3LYP level in conjunction with 6-311+G(d,p) basis set. $d_{Li\text{-}H_2}$ represents the average bond length between Li^+ and H_2 molecules. All the bond lengths are given in angstrom (Å).





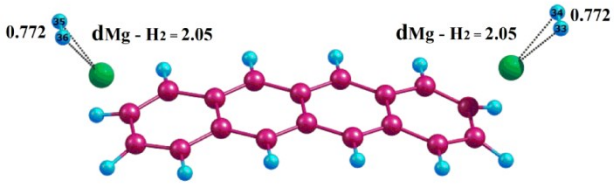
14napc2li(s):2h **14napc2li(s):4h**

(a)

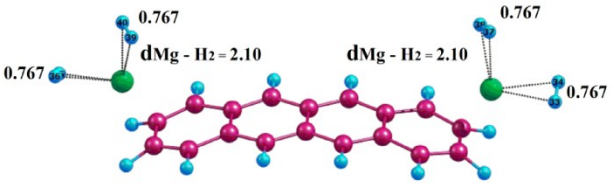


14napc2li(o):2h **14napc2li(o):4h**

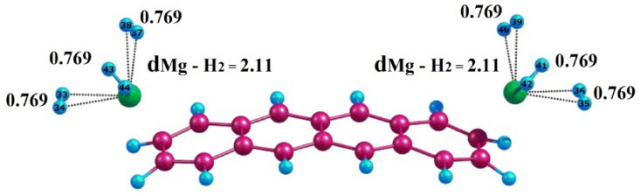
(b)



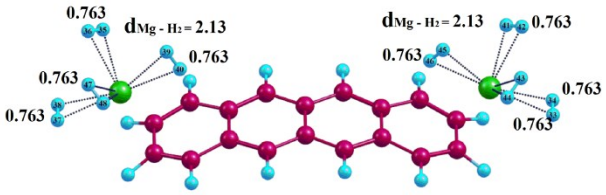
14napc2mg(s):2h



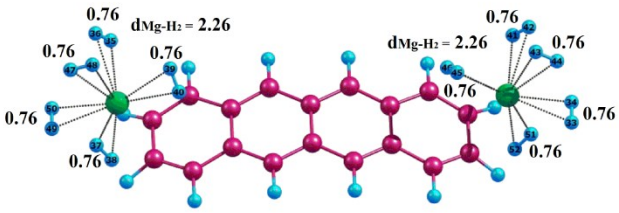
14napc2mg(s):4h



14napc2mg(s):6h

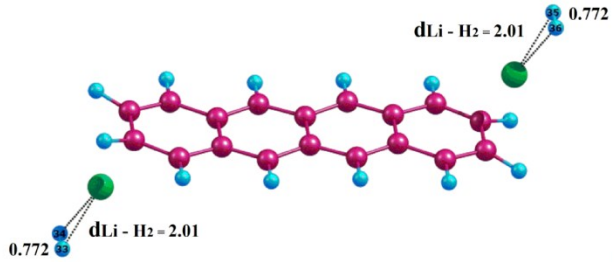


14napc2mg(s):6h

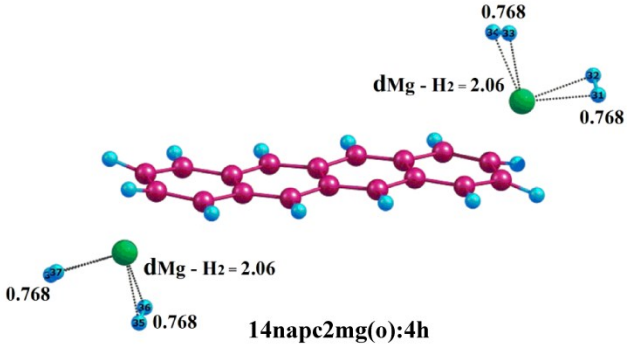


14napc2mg(s):10h

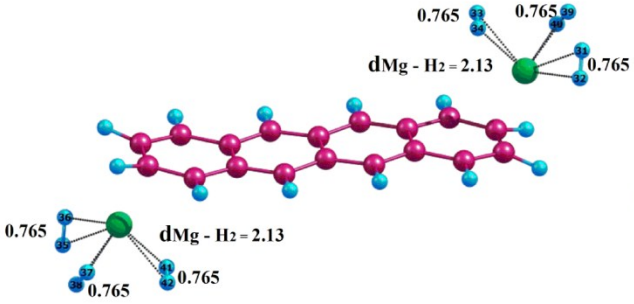
(c)



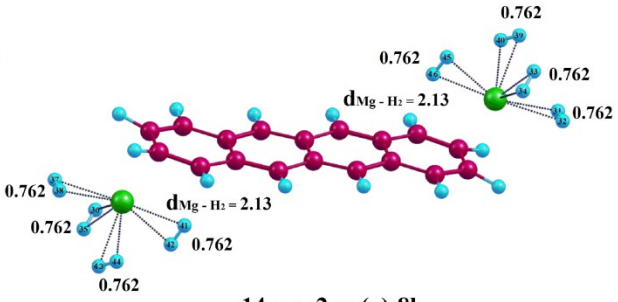
14napc2mg(o):2h



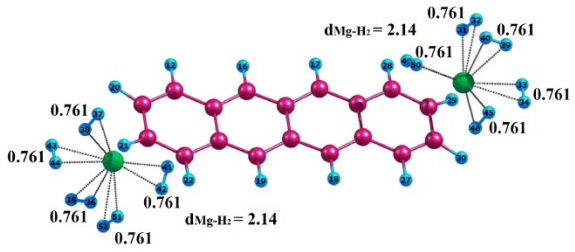
14napc2mg(o):4h



14napc2mg(o):6h



14napc2mg(o):8h



14napc2mg(o):8h

(d)

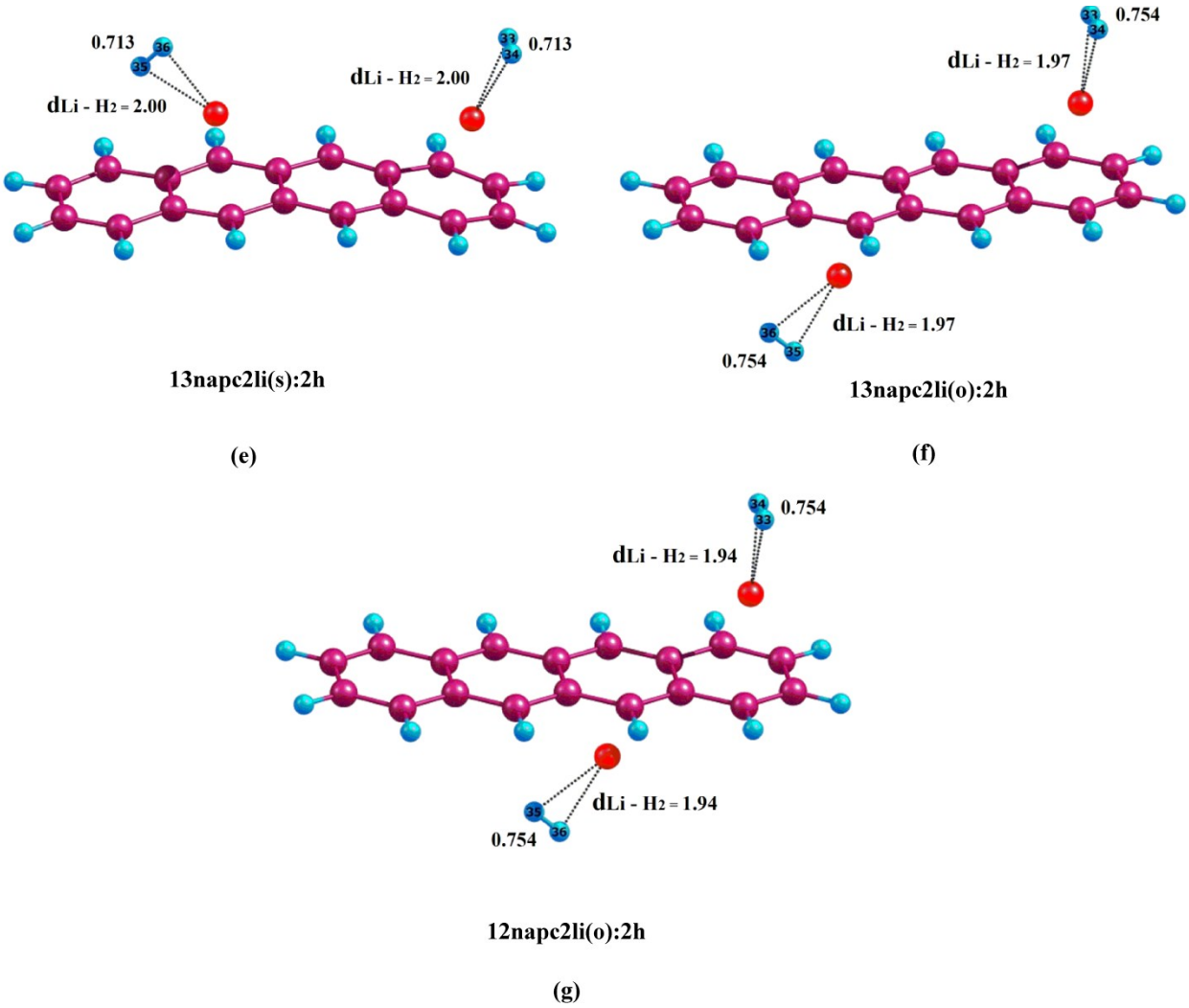


Fig. S3. Optimized geometries of (a) 14napc2li(s):nH_2, for n = 2,4; (b) 14napc2li(o):nH_2 , for n = 2,4; (c) 14napc2mg(s):nH_2, for n = 2,4,6,8,10; (d) 14napc2mg(o):nH_2, for n = 2,4,6,8,10; (e) 13napc2li(s):nH_2, for n = 2; (f) 13napc2li(o):nH_2, for n = 2; (g) 12napc2li(o):nH_2, for n = 2 at CAM-B3LYP level in conjunction with 6-311+G(d,p) basis set. $dLi\text{-}H_2$/$dMg\text{-}H_2$ represents the average bond length between Li^+/Mg^{2+} and H_2 molecules. All the bond lengths are given in angstrom (Å).

Table S1 : BSSE corrected Successive H_2 binding energy (ΔBE(n)) (kJ mol^{-1}) of Li^{+}/Mg^{2+}- decorated anthracene, phenanthrene and naphthacene at CAM-B3LYP level.

System	$\Delta BE(n)$	**System**	$\Delta BE(n)$
13ant2li(s) : 2h	-	12napc2li(o) : 2h	-
13ant2li(s) : 4h	-20.7	12napc2li(o) : 4h	-25.8
13ant2li(s) : 6h	-16.4	13napc2li(s) : 2h	-
13ant2li(o) : 2h	-	13napc2li(s) : 4h	34.7
13ant2li(o) : 4h	-22.9	13napc2li(o) : 2h	-
13ant2li(o) : 6h	-14.0	13napc2li(o) : 4h	-22.8
13ant2mg(s) : 2h	-	14napc2li(s) : 2h	-
13ant2mg(s) : 4h	-101.0	14napc2li(s) : 4h	-18.0
13ant2mg(s) : 6h	-83.4	14napc2li(s) : 6h	-10.5
13ant2mg(s) : 8h	-55.8	14napc2li(o) : 2h	-
13ant2mg(s) : 10h	-30.4	14napc2li(o) : 4h	-19.3
13ant2mg(s) : 12h	-15.5	14napc2li(o) : 6h	-10.7
13ant2mg(o) : 2h	-	14napc2mg(s) : 2h	-
13ant2mg(o) : 4h	-103.2	14napc2mg(s) : 4h	-93.6
13ant2mg(o) : 6h	-82.9	14napc2mg(s) : 6h	-73.0
13ant2mg(o) : 8h	-58.3	14napc2mg(s) : 8h	-55.1
13ant2mg(o) : 10h	-31.5	14napc2mg(s) : 10h	-22.8
13ant2mg(o) : 12h	-15.8	14napc2mg(s) : 12h	-11.6
13phen2li(s) : 2h	-	14napc2mg(o) : 2h	-
13phen2li(s) : 4h	-19.2	14napc2mg(o) : 4h	-94.4
13phen2li(s) : 6h	-15.8	14napc2mg(o) : 6h	-73.8
13phen2li(o) : 2h	-	14napc2mg(o) : 8h	-55.2
13phen2li(o) : 4h	-21.2	14napc2mg(o) : 10h	-22.8
13phen2li(o) : 6h	-12.9	14napc2mg(o) : 12h	-11.6

Table S2 : AIM analysis of H_2 adsorbed-Li^+/Mg^{2+}-decorated anthracene at CAM-B3LYP method in conjunction with 6-311+G(d,p) basis set.

System	BCP	ρ(r)	$\nabla^2\rho$	G	V	H	- G/V
13ant2li(s):6h	Li25-H27	0.012	0.063	0.013	-0.010	0.003	1.290
	Li25-H31	0.012	0.061	0.012	-0.010	0.003	1.282
	Li25-H37	0.012	0.061	0.012	-0.010	0.003	1.282
	Li26-H29	0.012	0.063	0.013	-0.010	0.003	1.290
	Li26-H33	0.012	0.061	0.012	-0.010	0.003	1.282
	Li26-H35	0.012	0.061	0.012	-0.010	0.003	1.282
13ant2li(o):6h	Li37-H25	0.012	0.062	0.013	-0.010	0.003	1.280
	Li37-H31	0.011	0.058	0.012	-0.009	0.003	1.282
	Li37-H33	0.011	0.058	0.012	-0.009	0.003	1.285
	Li38-H27	0.012	0.062	0.013	-0.010	0.003	1.280
	Li38-H29	0.011	0.058	0.012	-0.009	0.003	1.285
	Li38-H35	0.011	0.058	0.012	-0.009	0.003	1.282
13ant2mg(s):12h	Mg37-H25	0.015	0.065	0.014	-0.012	0.002	1.156
	Mg37-H29	0.013	0.051	0.011	-0.010	0.001	1.149
	Mg37-H35	0.018	0.076	0.017	-0.015	0.002	1.135
	Mg37-H39	0.014	0.061	0.013	-0.012	0.002	1.158
	Mg37-H45	0.013	0.052	0.011	-0.010	0.002	1.158
	Mg37-H49	0.013	0.053	0.012	-0.010	0.002	1.154
	Mg38-H27	0.015	0.066	0.014	-0.013	0.002	1.156
	Mg38-H31	0.013	0.051	0.011	-0.010	0.001	1.149
	Mg38-H33	0.018	0.076	0.017	-0.015	0.002	1.135
	Mg38-H41	0.013	0.052	0.011	-0.010	0.002	1.158
	Mg38-H43	0.013	0.053	0.012	-0.010	0.002	1.154
	Mg38-H47	0.014	0.061	0.013	-0.012	0.002	1.158
13ant2mg(o):12h	Mg25-H29	0.015	0.063	0.014	-0.012	0.002	1.158
	Mg25-H31	0.013	0.056	0.012	-0.011	0.002	1.157
	Mg25-H37	0.018	0.076	0.017	-0.015	0.002	1.135
	Mg25-H39	0.013	0.056	0.012	-0.011	0.002	1.154
	Mg25-H45	0.013	0.054	0.012	-0.010	0.002	1.150
	Mg25-H49	0.015	0.064	0.014	-0.012	0.002	1.155
	Mg26-H27	0.013	0.056	0.012	-0.011	0.002	1.157
	Mg26-H33	0.018	0.076	0.017	-0.015	0.002	1.135
	Mg26-H35	0.013	0.056	0.012	-0.011	0.002	1.157
	Mg26-H41	0.015	0.063	0.014	-0.012	0.002	1.158
	Mg26-H43	0.013	0.054	0.012	-0.010	0.002	1.150
	Mg26-H47	0.013	0.056	0.012	-0.011	0.002	1.154

Table S3 : AIM analysis of H_2 adsorbed-Li^+ and Mg^{2+}-decorated phenanthrene at CAM-B3LYP conjunction with 6-311+G(d,p) basis set.

System	BCP	ρ(r)	$\nabla^2\rho$	G	V	H	- G/V
13phen2li(s)6H	Li25-H29	0.011	0.054	0.011	-0.009	0.002	1.285
	Li25-H33	0.010	0.050	0.010	-0.008	0.002	1.297
	Li25-H37	0.010	0.051	0.010	-0.008	0.002	1.297
	Li26-H27	0.013	0.067	0.014	-0.011	0.003	1.272
	Li26-H31	0.013	0.067	0.014	-0.011	0.003	1.272
	Li26-H35	0.013	0.069	0.014	-0.003	0.011	4.301
13phen2li(o)6h	Li25-H27	0.012	0.058	0.012	-0.009	0.003	1.276
	Li25-H31	0.010	0.053	0.011	-0.008	0.002	1.294
	Li25-H35	0.011	0.055	0.011	-0.009	0.002	1.286
	Li26-H29	0.011	0.058	0.012	-0.009	0.003	1.278
	Li26-H33	0.011	0.054	0.011	-0.008	0.002	1.289
	Li26-H37	0.011	0.054	0.011	-0.009	0.002	1.287

Table S4 : AIM analysis of H_2 adsorbed-Li^+ and Mg^{2+}-decorated naphthacene at CAM-B3LYP method in conjunction with 6-311+G(d,p) basis set.

System	BCP	ρ(r)	$\nabla^2\rho$	G	V	H	- G/V
14napc2li(s)6h	Li31-H33	0.011	0.058	0.012	-0.009	0.003	1.283
	Li31-H37	0.011	0.054	0.011	-0.008	0.002	1.289
	Li31-H41	0.011	0.054	0.011	-0.008	0.002	1.293
	Li32-H35	0.011	0.058	0.012	-0.009	0.003	1.283
	Li32-H39	0.011	0.054	0.011	-0.008	0.002	1.292
	Li32-H43	0.011	0.053	0.011	-0.008	0.002	1.290
14napc2li(o)6h	Li31-H33	0.011	0.059	0.012	-0.009	0.003	1.282
	Li31-H38	0.011	0.054	0.011	-0.009	0.002	1.290
	Li31-H41	0.011	0.054	0.011	-0.009	0.002	1.288
	Li32-H35	0.011	0.059	0.012	-0.009	0.003	1.282
	Li32-H39	0.011	0.054	0.011	-0.009	0.002	1.290
	Li32-H43	0.011	0.054	0.011	-0.009	0.002	1.288

14napc2mg(s):12h	Mg31-H33	0.015	0.066	0.014	-0.012	0.002	1.158
	Mg31-H41	0.012	0.048	0.011	-0.009	0.001	1.156
	Mg31-H43	0.017	0.075	0.017	-0.015	0.002	1.140
	Mg31-H45	0.016	0.071	0.016	-0.013	0.002	1.162
	Mg31-H51	0.012	0.046	0.010	-0.009	0.001	1.148
	Mg31-H55	0.010	0.038	0.008	-0.007	0.001	1.150
	Mg32-H35	0.015	0.064	0.014	-0.012	0.002	1.157
	Mg32-H37	0.016	0.074	0.016	-0.014	0.002	1.162
	Mg32-H39	0.008	0.028	0.006	-0.005	0.001	1.143
	Mg32-H47	0.013	0.052	0.011	-0.010	0.002	1.155
	Mg32-H49	0.015	0.064	0.014	-0.012	0.002	1.157
	Mg32-H53	0.018	0.076	0.017	-0.015	0.002	1.139
14napc2mg(o):12h	Mg47-H31	0.012	0.048	0.011	-0.009	0.001	1.156
	Mg47-H33	0.015	0.066	0.015	-0.013	0.002	1.157
	Mg47-H39	0.017	0.075	0.017	-0.015	0.002	1.140
	Mg47-H45	0.012	0.048	0.011	-0.009	0.001	1.148
	Mg47-H49	0.009	0.034	0.008	-0.007	0.001	1.150
	Mg47-H53	0.016	0.073	0.016	-0.014	0.002	1.162
	Mg48-H35	0.012	0.049	0.011	-0.009	0.001	1.156
	Mg48-H37	0.012	0.048	0.011	-0.009	0.001	1.148
	Mg48-H41	0.016	0.073	0.016	-0.014	0.002	1.162
	Mg48-H43	0.015	0.066	0.015	-0.013	0.002	1.157
	Mg48-H51	0.012	0.049	0.011	-0.009	0.001	1.156
	Mg48-H55	0.009	0.034	0.007	-0.006	0.001	1.150
13napc2li(s):4h	Li31-H33	0.009	0.044	0.009	-0.007	0.002	1.332
	Li31-H35	0.009	0.045	0.009	-0.007	0.002	1.312
	Li32-H37	0.009	0.045	0.009	-0.007	0.002	1.315
	Li32-H39	0.009	0.044	0.009	-0.007	0.002	1.324
13napc2li(o):4h	Li31-H37	0.013	0.065	0.014	-0.011	0.003	1.263
	Li31-H39	0.013	0.064	0.013	-0.010	0.003	1.268
	Li32-H33	0.013	0.064	0.013	-0.011	0.003	1.262
	Li32-H35	0.013	0.065	0.013	-0.011	0.003	1.261
12napc2li(o):4h	Li31-H33	0.010	0.047	0.009	-0.007	0.002	1.301
	Li31-H35	0.010	0.047	0.009	-0.007	0.002	1.301
	Li32-H37	0.010	0.046	0.009	-0.007	0.002	1.304
	Li32-H39	0.009	0.045	0.009	-0.007	0.002	1.320