Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Role of aromaticity and charge of a system in its hydrogen trapping potential and vice-versa

Santanab Giri, Sateesh Bandaru, Arindam Chakraborty and Pratim K Chattaraj*

Department of Chemistry and Center for Theoretical Studies
Indian Institute of Technology, Kharagpur - 721302, India
E-mail- pkc@chem.iitkgp.ernet.in

Table S1: Total energy (au) of different C_nH_n (n = 4-6) and H_2 trapped C_nLi_n (n = 4-6) systems computed at different levels of theory and basis sets.

Systems	Energy (au)					
	B3LYP		**M05-2X**		**MPW1K**	
	6-311+G(d,p)	***aug-cc-pvdz***	***6-311+G(d,p)***	***aug-cc-pvdz***	***6-311+G(d,p)***	***aug-cc-pvdz***
C_4H_4	-154.72116	-154.69533	-154.69134	-154.67269	-154.66702	-154.64721
C_4Li_4	-182.39114	-182.36900	-182.36773	-182.35121	-182.28826	-182.26906
$4H_2@C_4Li_4$	-187.12064	-187.08285	-187.05777	-187.02033	-187.00024	*
$8H_2@C_4Li_4$	-191.84598	-191.79338	-191.75172	-191.69453	-191.71124	-191.67080
$C_5H_5^-$	-193.58078	-193.55065	-193.55230	-193.52929	-193.51847	-193.49485
$C_5Li_5^-$	-228.09749	-228.07162	-228.07460	-228.05623	-227.96914	-227.94694
$5H_2@C_5Li_5^-$	-234.00354	-233.95852	-233.93357	-@-	*	*
C_6H_6	-232.31125	-232.27461	-232.27526	-232.24827	-232.23809	-232.20942
C_6Li_6	-273.77263	-273.74093	-273.74214	-273.72080	-273.62834	-273.60121
$6H_2@C_6Li_6$	-280.87235	-280.81733	-280.77844	-280.73071	-280.69961	-280.65531
$12H_2@C_6Li_6$	-287.96195	-287.88444	*	*	-@-	-@-

* Convergence at some saddle point (NIMAG > 0). So, values not reported
-@- no convergence achieved

Table S2: The total energy (E, au) and the enthalpies (E_H, Kcal mol^{-1}) of the Li^+/F^- bound annular hydrocarbon rings and their associated H_2-bound complexes computed at MP2 level of theory using 6-31+G(d) basis set.

	Systems	E	E_H		Systems	E	E_H
1	C_3H_3Li	-123.0503945	-123.000220	50	*Anthra-m*-$C_{14}H_{10}Li_2^{2+}$	-552.2698703	-552.060425
2	$1H_2@C_3H_3Li$	-124.1986325	-124.132550	51	$2H_2@$ *m*-$C_{14}H_{10}Li_2^{2+}$	-554.5742495	-554.332920
3	$2H_2@C_3H_3Li$	-125.3453170	-125.263640	52	$4H_2@$ *m*-$C_{14}H_{10}Li_2^{2+}$	-556.8775413	-556.604772
4	$3H_2@C_3H_3Li$	-126.4900227	-126.393190	53	$6H_2@$ *m*-$C_{14}H_{10}Li_2^{2+}$	-559.1757792	-558.871207
5	$4H_2@C_3H_3Li$	-127.6347506	-127.522775	54	$8H_2@$ *m*-$C_{14}H_{10}Li_2^{2+}$	-561.4673621	-561.133133
6	$C_4H_4Li^+$	-161.4395824	-161.370164	55	*Anthra-t*-$C_{14}H_{10}Li_2^{2+}$	-552.2967414	-552.086382
7	$1H_2@C_4H_4Li^+$	-162.5903638	-162.505130	56	$4H_2@$ *t*-$C_{14}H_{10}Li_2^{2+}$	-556.8990673	-556.625835
8	$2H_2@C_4H_4Li^+$	-163.7398564	-163.638906	57	$6H_2@$ *t*-$C_{14}H_{10}Li_2^{2+}$	-559.1953094	-558.890858
9	$3H_2@C_4H_4Li^+$	-164.8869800	-164.770495	58	$8H_2@$ *t*-$C_{14}H_{10}Li_2^{2+}$	-561.4880447	-561.153329
10	$4H_2@C_4H_4Li^+$	-166.0329439	-165.901058				
11	C_5H_5Li	-200.3738976	-200.284035	59	*Anthra-st*-$C_{14}H_{10}Li_2^{2+}$	-552.2812479	-552.071418
12	$1H_2@C_5H_5Li$	-201.5223528	-201.416719	60	$2H_2@$ *st*-$C_{14}H_{10}Li_2^{2+}$	-554.5847937	-554.343290
13	$2H_2@C_5H_5Li$	-202.6674837	-202.546435	61	$4H_2@$ *st*-$C_{14}H_{10}Li_2^{2+}$	-556.8863964	-556.613492
14	$3H_2@C_5H_5Li$	-203.8122636	-203.676105	62	$6H_2@$ *st*-$C_{14}H_{10}Li_2^{2+}$	-559.183608	-558.879168
15	$4H_2@C_5H_5Li$	-204.957005	-204.805742				
16	$C_5H_5Li_2^+$	-207.7023829	-207.608312	63	*Phenan*-$C_{14}H_{10}Li^+$	-545.110115	-544.901450
17	$4H_2@C_5H_5Li_2^+$	-212.2972074	-212.140193	64	$1H_2@C_{14}H_{10}Li^+$	-546.2609465	-546.036396
18	$6H_2@C_5H_5Li_2^+$	-214.5889014	-214.401161	65	$2H_2@C_{14}H_{10}Li^+$	-547.4109375	-547.170545
19	$8H_2@C_5H_5Li_2^+$	-216.878113	-216.660499	66	$3H_2@C_{14}H_{10}Li^+$	-548.5583951	-548.302612
20	$C_6H_6Li^+$	-238.7692623	-238.658866	67	*Phenan-r1*-$C_{14}H_{10}Li^+$	-545.1114417	-544.902305
21	$1H_2@$ $C_6H_6Li^+$	-239.9195616	-239.793424	68	$2H_2@$ *r1*-$C_{14}H_{10}Li^+$	-547.4107241	-547.170028
22	$2H_2@$ $C_6H_6Li^+$	-241.143542	-241.002538	69	$3H_2@$ *r1*-$C_{14}H_{10}Li^+$	-548.5580808	-548.302093
23	$3H_2@$ $C_6H_6Li^+$	-242.214249	-242.057052				
24	$4H_2@$ $C_6H_6Li^+$	-243.3591543	-243.186883				
25	$C_6H_6Li_2^{2+}$	-245.9150026	-245.801923	70	*Phenan-m*-$C_{14}H_{10}Li_2^{2+}$	-552.2813458	-552.070054
26	$2H_2@C_6H_6Li_2^{2+}$	-248.2193707	-248.074788	71	$6H_2@$ *m*-$C_{14}H_{10}Li_2^{2+}$	-559.187252	-558.881520
27	$4H_2@C_6H_6Li_2^{2+}$	-250.5206404	-250.344677	72	$8H_2@$ *m*-$C_{14}H_{10}Li_2^{2+}$	-561.4779842	-561.141672
28	$6H_2@C_6H_6Li_2^{2+}$	-252.8192048	-252.612081	73			
29	$8H_2@C_6H_6Li_2^{2+}$	-255.1127663	-254.875153				
30	$C_{10}H_8Li^+$	-391.9382825	-391.779043	74	*Phenan-r1*-$C_{14}H_{10}Li_2^{2+}$	-552.2796358	-552.068213
31	$1H_2@C_{10}H_8Li^+$	-393.0889221	-392.914402	75	$4H_2@$ *r1*-$C_{14}H_{10}Li_2^{2+}$	-556.8860348	-556.611141
32	$2H_2@C_{10}H_8Li^+$	-394.2378836	-394.047686	76	$6H_2@$ *r1*-$C_{14}H_{10}Li_2^{2+}$	-559.1842857	-558.878321
33	$3H_2@C_{10}H_8Li^+$	-395.3846105	-395.179216	77	$8H_2@$ *r1*-$C_{14}H_{10}Li_2^{2+}$	-561.4746547	-561.138369
34	$4H_2@C_{10}H_8Li^+$	-396.5297162	-396.308980				
35	$C_{10}H_8Li_2^{2+}$	-399.1096521	-398.947768	78	*Phenan-t*-$C_{14}H_{10}Li_2^{2+}$	-552.3056535	-552.094224
36	$2H_2@C_{10}H_8Li_2^{2+}$	-401.4133682	-401.219921	79	$4H_2@$ *t*-$C_{14}H_{10}Li_2^{2+}$	-556.9083448	-556.633470
37	$4H_2@C_{10}H_8Li_2^{2+}$	-403.71412	-403.489341	80	$6H_2@$ *t*-$C_{14}H_{10}Li_2^{2+}$	-559.204734	-558.898801
38	$6H_2@C_{10}H_8Li_2^{2+}$	-406.0116225	-405.755734	81	$8H_2@$ *t*-$C_{14}H_{10}Li_2^{2+}$	-561.4971229	-561.161216
39	$8H_2@C_{10}H_8Li_2^{2+}$	-408.303282	-408.016991				

40	*Anthra*-$C_{14}H_{10}Li^+$	-545.0998894	-544.892549	82	*Phenan-cis*-$C_{14}H_{10}Li_2^{2+}$	-552.2994747	-552.088649
41	$1H_2$@ $C_{14}H_{10}Li^+$	-546.2506985	-546.027391	83	$2H_2$@ *cis*-$C_{14}H_{10}Li_2^{2+}$	-554.6021393	-554.359779
42	$2H_2$@ $C_{14}H_{10}Li^+$	-547.400848	-547.161816	84	$4H_2$@ *cis*-$C_{14}H_{10}Li_2^{2+}$	-556.9013845	-556.627518
43	$3H_2$@ $C_{14}H_{10}Li^+$	-548.547978	-548.293257	85	$6H_2$@ *cis*-$C_{14}H_{10}Li_2^{2+}$	-559.1968724	-558.891950
44	$4H_2$@ $C_{14}H_{10}Li^+$	-549.6920701	-549.422796	86	$8H_2$@ *cis*-$C_{14}H_{10}Li_2^{2+}$	-561.4881316	-561.151847
45	*Anthra-r1*-$C_{14}H_{10}Li^+$	-545.1008472	-544.892598	87	C_7H_7F	-369.6187953	-369.489799
46	$1H_2$@ *r1*-$C_{14}H_{10}Li^+$	-546.2514629	-546.027355	88	$1H_2$@ C_7H_7F	-370.7640706	-370.619853
47	$2H_2$@ *r1*-$C_{14}H_{10}Li^+$	-547.4004233	-547.160596	89	$2H_2$@ C_7H_7F	-371.9091408	-371.749664
48	$3H_2$@ *r1*-$C_{14}H_{10}Li^+$	-548.5472765	-548.291983	90	$3H_2$@ C_7H_7F	-373.0541931	-372.879539
49	$4H_2$@ *r1*-$C_{14}H_{10}Li^+$	-549.6923478	-549.422023	91	$4H_2$@ C_7H_7F	-374.1994528	-374.009591

m- Metals placed on the middle ring (above and below), *t*- metal placed on the trans positions, *st* – metal placed on the trans to adjacent rings, *cis*- metal placed in the *cis* positions (1 and 3 rings).

Table S3: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0), charge on the metal ion (q_M, NPA charge) of cyclobutadiene-Li^+($C_4H_4Li^+$) and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
$C_4H_4Li^+$	9.387	8.566	5.144	27.01	28.05	16.91	0.919
$1H_2@C_4H_4Li^+$	9.314	8.525	5.088	27.25	28.04	16.91	0.852
$2H_2@C_4H_4Li^+$	9.182	8.592	4.906	26.18	26.81	16.23	0.753
$3H_2@C_4H_4Li^+$	9.033	8.568	4.762	26.25	26.82	16.19	0.688
$4H_2@C_4H_4Li^+$	8.895	8.625	4.587	24.712	25.08	15.16	0.616

Table S4: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0), charge on the metal ion (q_M, NPA charge) of C_5H_5Li**,** $C_5H_5Li_2^+$ and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
C_5H_5Li	4.028	7.877	1.030	-14.88	-13.77	-10.82	0.730
$1H_2@C_5H_5Li$	3.937	8.270	0.937	-15.46	-14.21	-10.94	0.620
$2H_2@C_5H_5Li$	3.788	8.061	0.890	-15.14	-13.91	-10.75	0.580
$3H_2@C_5H_5Li$	3.766	8.089	0.877	-15.12	-13.91	-10.78	0.579
$4H_2@C_5H_5Li$	3.731	8.146	0.855	-15.11	-13.85	-10.72	0.579
$C_5H_5Li_2^+$	8.470	10.311	3.479	-15.46	-16.41	-15.76	0.887,0.887
$4H_2@C_5H_5Li_2^+$	7.392	11.471	2.382	-15.55	-16.43	-15.62	0.718,0.718
$6H_2@C_5H_5Li_2^+$	7.331	11.505	2.336	-15.15	-15.94	-15.12	0.648,0.648
$8H_2@C_5H_5Li_2^+$	7.450	11.012	2.520	-15.32	-16.24	-15.58	0.689,0.689

Table S5: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0), charge on the metal ion (q_M, NPA charge) of $C_6H_6Li^+$, $C_6H_6Li_2^{2+}$ and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
$C_6H_6Li^+$	9.351	11.201	3.904	-7.83	-9.93	-10.17	0.889
$1H_2@C_6H_6Li^+$	8.907	11.926	3.326	-8.00	-10.06	-10.24	0.802
$3H_2@ C_6H_6Li^+$	8.739	11.781	3.242	-7.778	-9.94	-10.19	0.648
$4H_2@ C_6H_6Li^+$	8.729	11.738	3.246	-7.761	-9.92	-10.18	0.645
$C_6H_6Li_2^{2+}$	13.385	11.897	7.529	-6.49	-8.99	-11.01	0.963,0.963
$2H_2@C_6H_6Li_2^{2+}$	13.300	12.001	7.369	-6.75	-9.28	-11.30	0.911,0.910
$4H_2@C_6H_6Li_2^{2+}$	13.120	11.876	7.247	-6.77	-9.27	-11.22	0.835,0.835
$6H_2@C_6H_6Li_2^{2+}$	13.562	13.096	7.022	-6.59	-8.98	-10.86	0.751,0.751
$8H_2@C_6H_6Li_2^{2+}$	11.836	11.026	6.353	-7.29	-9.55	-10.73	0.737,0.737

Table S6: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0), charge on the metal ion (q_M, NPA charge) of $C_{10}H_8Li^+$, t-$C_{10}H_8Li_2^{2+}$ and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
$C_{10}H_8Li^+$	8.137	9.043	3.661	-8.33	-10.25	-10.19	0.897
$1H_2@C_{10}H_8Li^+$	8.033	9.159	3.523	-8.494	-10.25	-10.28	0.816
$2H_2@C_{10}H_8Li^+$	7.990	9.127	3.497	-8.472	-10.23	-10.26	0.729
$3H_2@C_{10}H_8Li^+$	7.928	9.115	3.448	-8.437	-10.27	-10.15	0.653
$4H_2@C_{10}H_8Li^+$	7.912	9.129	3.429	-8.358	-10.27	-10.20	0.644
$C_{10}H_8Li_2^{2+}$	12.137	9.229	7.981	-7.56, -7.55	-9.81, -9.81	-10.26, -10.26	0.949,0.949
$2H_2@C_{10}H_8Li_2^{2+}$	12.032	9.219	7.852	-7.74 -7.74	-9.98, -10.39	-9.98, -10.39	0.885,0.885
$4H_2@C_{10}H_8Li_2^{2+}$	11.940	9.203	7.746	-7.89, -7.88	-10.12, -10.12	-10.53, -10.53	0.802,0.802
$6H_2@C_{10}H_8Li_2^{2+}$	11.693	9.158	7.464	-7.72, -7.52	-9.83, -10.35	-10.53, -10.41	0.725,0.725
$8H_2@C_{10}H_8Li_2^{2+}$	11.037	9.074	6.712	-7.97, -7.97	-10.23, -10.23	-10.66, -10.66	0.698,0.698

t- Metal placed at the *trans* positions

Table S7: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0), and charge on the metal ion (q_M, NPA charge) of *m-Anthracene* ($C_{14}H_{10}Li^+$), *r1*-$C_{14}H_{10}Li^+$ and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
m-$C_{14}H_{10}Li^+$	7.806	7.841	3.886	-10.956	-12.62	-12.15	0.906
$1H_2@C_{14}H_{10}Li^+$	7.778	7.837	3.860	-11.094	-12.68	-12.16	0.829
$2H_2@C_{14}H_{10}Li^+$	7.756	7.823	3.845	-11.099	-11.82	-11.77	0.731
$3H_2@C_{14}H_{10}Li^+$	7.713	7.833	3.798	-11.064	-11.86	-11.83	0.649
$4H_2@C_{14}H_{10}Li^+$	7.670	7.822	3.761	-11.075	-12.83	-12.28	0.622
r1- $C_{14}H_{10}Li^+$	7.526	7.572	3.740	-7.143	-8.92	-9.19	0.893
$1H_2@C_{14}H_{10}Li^+$	7.502	7.565	3.719	-7.296	-8.99	-9.21	0.812
$2H_2@C_{14}H_{10}Li^+$	7.462	7.553	3.686	-7.300	-8.99	-9.20	0.725

$3H_2@C_{14}H_{10}Li^+$	7.417	7.552	3.642	-7.198	-8.95	-9.18	0.641
$4H_2@C_{14}H_{10}Li^+$	7.410	7.535	3.643	-7.346	-9.10	-9.30	0.647

m- Metal placed on the middle ring *r1*- metal placed on the first ring

Table S8: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0) and charge on the metal ion (q_M, NPA charge) of *m-Anthracene* (*m*-$C_{14}H_{10}Li_2^{2+}$), *t*-$C_{14}H_{10}Li_2^{2+}$, *st*-$C_{14}H_{10}Li_2^{2+}$ and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
m-$C_{14}H_{10}Li_2^{2+}$	11.671	7.713	8.830	-9.786	-11.96	-13.10	0.948,0.949
$2H_2@C_{14}H_{10}Li_2^{2+}$	11.592	7.685	8.743	-10.084	-12.31	-13.46	0.897,0.897
$4H_2@C_{14}H_{10}Li_2^{2+}$	11.505	7.644	8.658	-9.9637	-12.22	-13.44	0.813,0.813
$6H_2@C_{14}H_{10}Li_2^{2+}$	11.351	7.640	8.433	-10.157	-12.30	-13.33	0.718,0.718
$8H_2@C_{14}H_{10}Li_2^{2+}$	11.197	7.588	8.261	-10.044	-12.033	-12.96	0.680,0.680
t-$C_{14}H_{10}Li_2^{2+}$	11.178	7.607	8.213	-7.22, -7.24	-9.61, -10.14	-9.44, -10.05	0.925,0.925
$2H_2@C_{14}H_{10}Li_2^{2+}$	11.081	7.728	7.944	-7.36, -7.37	-9.50, -9.64	-9.99, -10.08	0.879,0.861
$4H_2@C_{14}H_{10}Li_2^{2+}$	10.939	7.725	7.746	-7.36, -7.37	-9.63, -9.63	-9.98, -9.98	0.767,0.767
$6H_2@C_{14}H_{10}Li_2^{2+}$	11.157	8.111	7.673	-8.28, -8.28	-10.24, -10.24	-10.32, 10.33	0.681,0.758
$8H_2@C_{14}H_{10}Li_2^{2+}$	11.139	8.090	7.668	-7.33, -7.33	-9.69, -9.68	-10.08, -10.09	0.680,0.756
st-$C_{14}H_{10}Li_2^{2+}$	11.378	7.485	8.647	-10.25, -6.11	-12.12, -11.94	-8.17, -8.76	0.941,0.941
$1H_2@C_{14}H_{10}Li_2^{2+}$	11.302	7.482	8.535	-10.48, -6.28	-12.35, -8.32	-8.89, -12.07	0.875,0.875
$2H_2@C_{14}H_{10}Li_2^{2+}$	11.221	7.474	8.423	-10.66, -6.49	-12.51, -8.58	-9.14, -12.29	0.789,0.789
$3H_2@C_{14}H_{10}Li_2^{2+}$	11.068	7.489	8.178	-10.53, -12.39	-8.56, -6.48	-9.12, -12.18	0.703,0.703
$4H_2@C_{14}H_{10}Li_2^{2+}$	10.739	7.476	7.713	-10.78, -6.43	-8.61, -12.82	-9.35, -12.51	0.775,0.658

m- Metals placed on the middle ring (above and below), *t*- metal placed on the trans positions, *st* – metal placed on the trans to adjacent rings

Table S9: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0) and charge on the metal ion (q_M, NPA charge) of *m*- Phenanthrene-Li^+(*m*-$C_{14}H_{10}Li^+$), *r1*-$C_{14}H_{10}Li^+$ and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
m-$C_{14}H_{10}Li^+$	8.097	9.183	3.570	-5.88	-7.56	-8.14	0.908
$1H_2@C_{14}H_{10}Li^+$	7.402	10.519	2.605	-6.00	-7.59	-8.13	0.831
$2H_2@C_{14}H_{10}Li^+$	7.386	10.523	2.592	-6.03	-7.58	-8.08	0.736
$3H_2@C_{14}H_{10}Li^+$	7.350	10.491	2.574	-5.98	-7.57	-8.08	0.657
$4H_2@C_{14}H_{10}Li^+$	7.209	10.558	2.461	-5.53	-7.16	-7.74	0.690
r1-$C_{14}H_{10}Li^+$	8.322	9.608	3.604	-8.31	-10.07	-10.12	0.893
$1H_2@C_{14}H_{10}Li^+$	8.210	9.799	3.439	-8.44	-10.14	-10.16	0.823
$2H_2@C_{14}H_{10}Li^+$	8.173	9.815	3.402	-8.42	-10.14	-10.15	0.725
$3H_2@C_{14}H_{10}Li^+$	8.141	9.850	3.364	-8.27	-10.02	-10.06	0.644

m- Metals placed on the middle ring *r1*- metal placed on the first ring

Table S10: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0), and charge on the metal ion (q_M, NPA charge) of *m*- Phenanthrene –Li_2^{2+}(*m*-$C_{14}H_{10}Li_2^{2+}$), *r1*-$C_{14}H_{10}Li_2^{2+}$, *t*-$C_{14}H_{10}Li_2^{2+}$, *cis*-$C_{14}H_{10}Li_2^{2+}$ and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

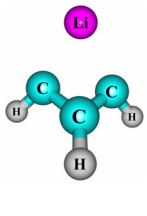
System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_M
m-$C_{14}H_{10}Li_2^{2+}$	11.161	10.264	6.068	-4.837	-6.91	-8.73	0.949,0.949
$6H_2@C_{14}H_{10}Li_2^{2+}$	10.882	10.199	5.806	-5.17	-7.19	-8.93	0.722,0.722
$8H_2@C_{14}H_{10}Li_2^{2+}$	10.739	10.237	5.633	-5.04	-6.96	-8.68	0.684,0.684
r1-$C_{14}H_{10}Li_2^{2+}$	11.964	9.202	7.778	-7.15	-9.55	-11.31	0.950,0.950
$4H_2@C_{14}H_{10}Li_2^{2+}$	11.828	9.275	7.542	-7.44	-9.84	-11.53	0.810,0.810
$6H_2@C_{14}H_{10}Li_2^{2+}$	11.721	9.379	7.324	-7.25	-9.56	-11.23	0.719,0.719
$8H_2@C_{14}H_{10}Li_2^{2+}$	11.580	9.509	7.051	-7.17	-9.34	-10.85	0.684,0.684
t-$C_{14}H_{10}Li_2^{2+}$	11.336	10.352	6.207	-8.34, -8.33	-10.48, -10.49	-10.63, -10.63	0.924,0.923
$4H_2@C_{14}H_{10}Li_2^{2+}$	11.175	10.344	6.036	-8.48, -8.42	-10.49, -10.51	-10.64, -10.62	0.765,0.765
$6H_2@C_{14}H_{10}Li_2^{2+}$	11.052	10.362	5.893	-8.25, -8.28	-10.35, -10.38	-10.53, -10.54	0.680,0.680
$8H_2@C_{14}H_{10}Li_2^{2+}$	11.043	10.315	5.911	-8.55, -8.51	-10.28, -10.79	-11.22, -10.95	0.680,0.680
cis-$C_{14}H_{10}Li_2^{2+}$	11.629	9.844	6.869	-8.365, -8.368	-10.94, -10.94	-11.09, -11.09	0.915,0.915
$2H_2@C_{14}H_{10}Li_2^{2+}$	11.305	10.337	6.181	-8.561, -8.565	-11.11, -11.10	-11.19, -11.20	0.835,0.835
$4H_2@C_{14}H_{10}Li_2^{2+}$	11.206	10.343	6.071	-8.523, -8.526	-11.08, -11.07	-11.18, -11.19	0.751,0.751
$6H_2@C_{14}H_{10}Li_2^{2+}$	11.084	10.377	5.919	-8.345, -8.345	-10.97, -10.97	-11.13, -11.14	0.671,0.671
$8H_2@C_{14}H_{10}Li_2^{2+}$	10.377	10.842	4.966	-8.268, -8.394	-11.07, -10.82	-11.35, -10.96	0.660,0.660

m- Metals placed on the middle ring (above and below), *t*- metal placed in the *trans* positions, *r1*- metals placed on the first ring (above and below) *cis*- metal placed in the *cis* positions (1 and 3 rings)

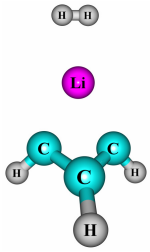
Table S11: The electronegativity (χ), hardness (η) and electrophilicity (ω) NICS(0), NICS(0.5) and NICS(1.0), and charge on the fluorine atom (q_F, NPA charge) of C_7H_7F and their H_2-bound analogues computed at MP2 level of theory using 6-31+G(d) basis set.

System	χ	η	ω	NICS(0)	NICS(0.5)	NICS(1.0)	q_F
C_7H_7F	4.108	10.307	0.819	--@--	--@--	--@--	-0.404
$1H_2@C_7H_7F$	4.126	10.291	0.827	--@--	--@--	--@--	-0.405
$2H_2@C_7H_7F$	4.142	10.276	0.835	--@--	--@--	--@--	-0.406
$3H_2@C_7H_7F$	4.147	10.269	0.837	--@--	--@--	--@--	-0.408
$4H_2@C_7H_7F$	4.158	10.267	0.842	--@--	--@--	--@--	-0.410

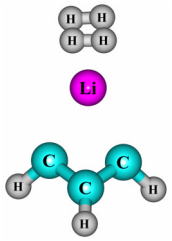
--@-- NICS not performed due to non planarity of C_7H_7 ring



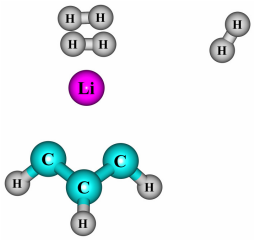
C_3H_3Li



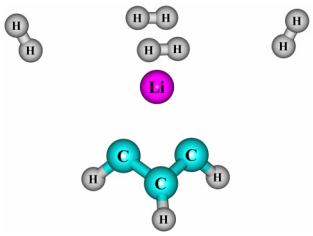
$1H_2@C_3H_3Li$



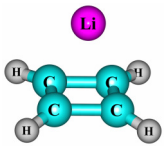
$2H_2@C_3H_3Li$



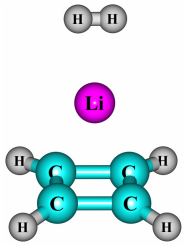
$3H_2@C_3H_3Li$



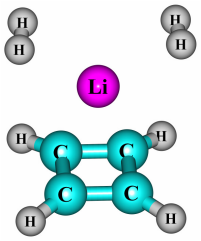
$4H_2@C_3H_3Li$



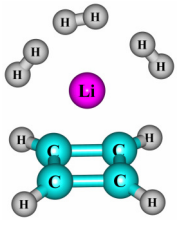
$C_4H_4Li^+$



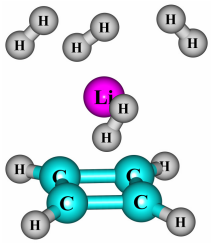
$1H_2@C_4H_4Li^+$



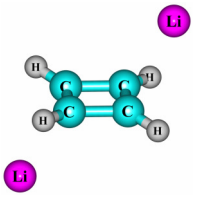
$2H_2@C_4H_4Li^+$



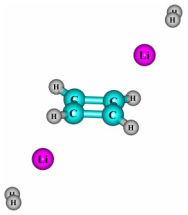
$3H_2@C_4H_4Li^+$



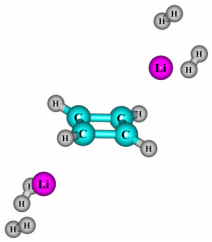
$4H_2@C_4H_4Li^+$



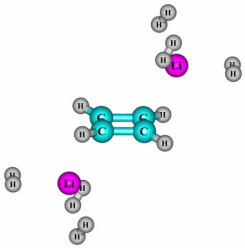
$C_4H_4Li_2^{2+}$



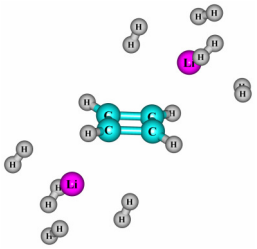
$2H_2@C_4H_4Li_2^{2+}$



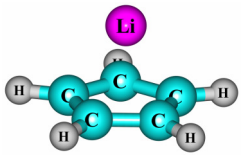
$4H_2@C_4H_4Li_2^{2+}$



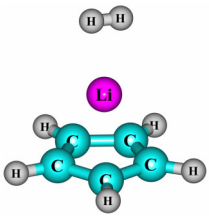
$6H_2@C_4H_4Li_2^{2+}$



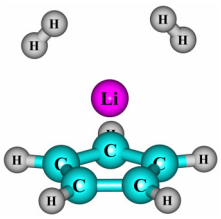
$8H_2@C_4H_4Li_2^{2+}$



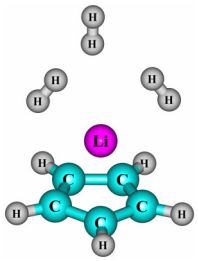
C_5H_5Li



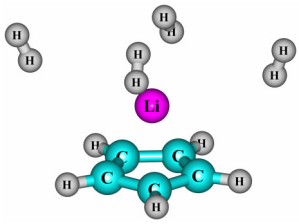
$1H_2@C_5H_5Li$



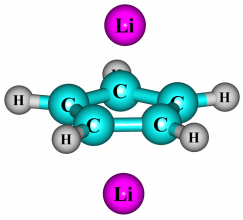
$2H_2@C_5H_5Li$



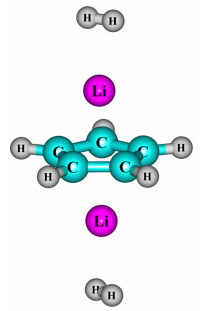
$3H_2@C_5H_5Li$



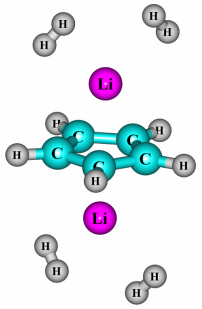
$4H_2@C_5H_5Li$



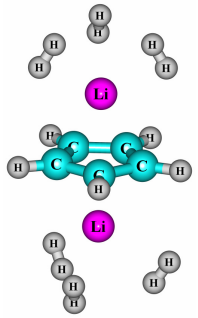
$C_5H_5Li_2^+$



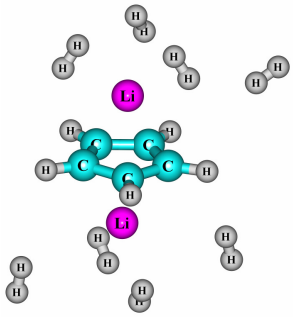
$2H_2@C_5H_5Li_2^+$



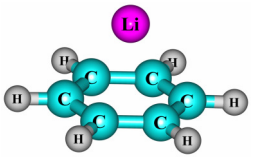
$4H_2@C_5H_5Li_2^+$



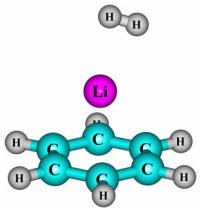
$6H_2@C_5H_5Li_2^+$



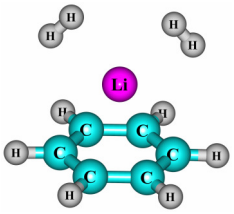
$8H_2@C_5H_5Li_2^+$



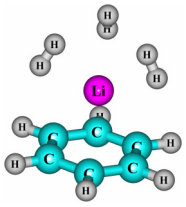
$C_6H_6Li^+$



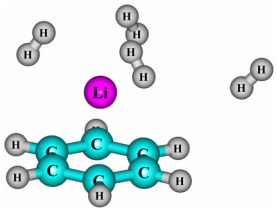
$1H_2@C_6H_6Li^+$



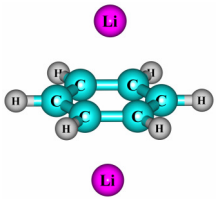
$2H_2@C_6H_6Li^+$



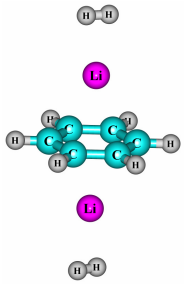
$3H_2@C_6H_6Li^+$



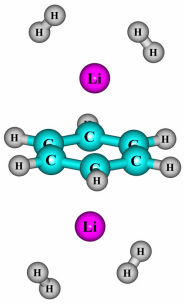
$4H_2@C_6H_6Li^+$



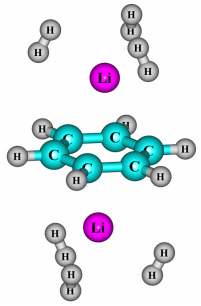
$C_6H_6Li_2^{2+}$



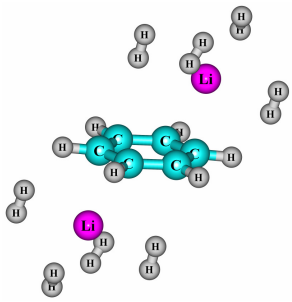
$2H_2@C_6H_6Li_2^{2+}$



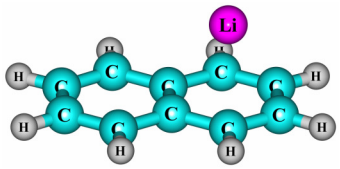
$4H_2@C_6H_6Li_2^{2+}$



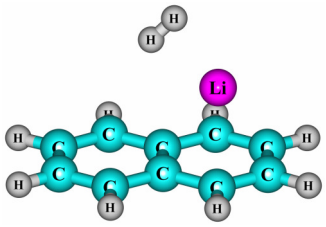
$6H_2@C_6H_6Li_2^{2+}$



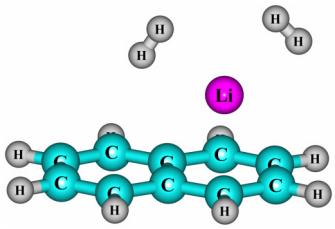
$8H_2@C_6H_6Li_2^{2+}$



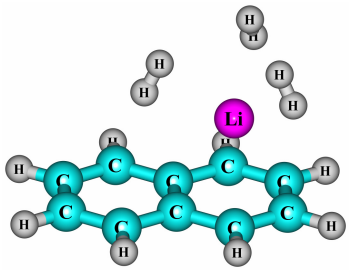
$C_{10}H_8Li^+$



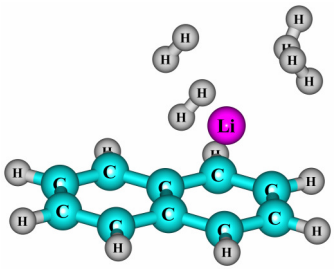
$1H_2@C_{10}H_8Li^+$



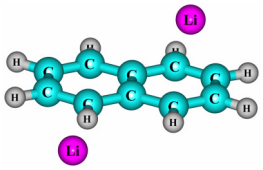
$2H_2@C_{10}H_8Li^+$



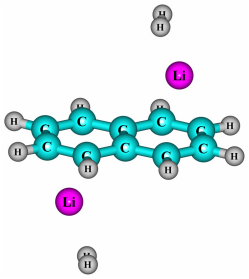
$3H_2@C_{10}H_8Li^+$



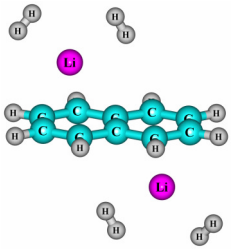
$4H_2@C_{10}H_8Li^+$



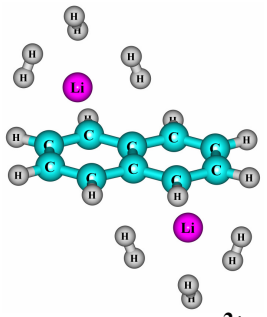
$C_{10}H_8Li_2^{2+}$



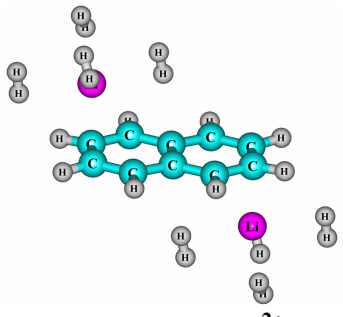
$2H_2@C_{10}H_8Li_2^{2+}$



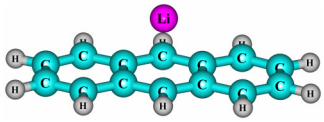
$4H_2@C_{10}H_8Li_2^{2+}$



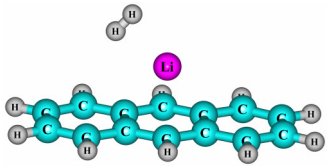
$6H_2@C_{10}H_8Li_2^{2+}$



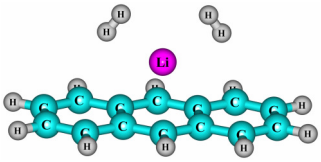
$8H_2@C_{10}H_8Li_2^{2+}$



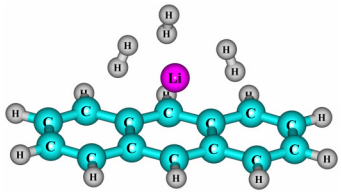
$C_{14}H_{10}Li^+$



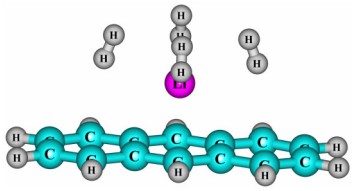
$1H_2@C_{14}H_{10}Li^+$



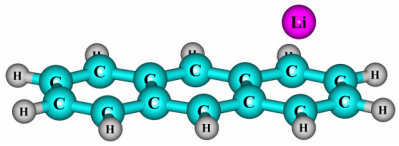
$2H_2@C_{14}H_{10}Li^+$



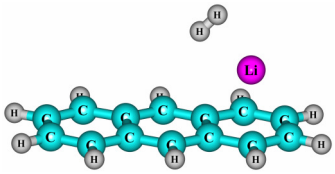
$3H_2@C_{14}H_{10}Li^+$



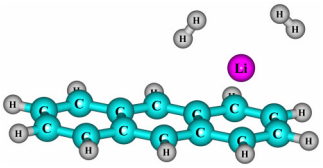
$4H_2@C_{14}H_{10}Li^+$



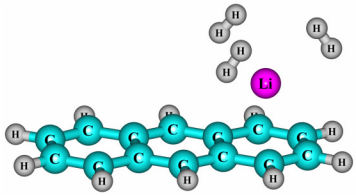
$C_{14}H_{10}Li^+$



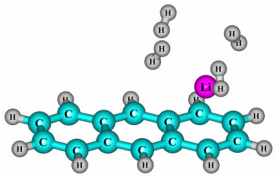
$1H_2@C_{14}H_{10}Li^+$



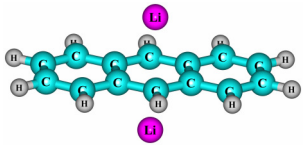
$2H_2@C_{14}H_{10}Li^+$



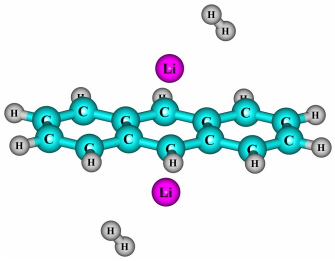
$3H_2@C_{14}H_{10}Li^+$



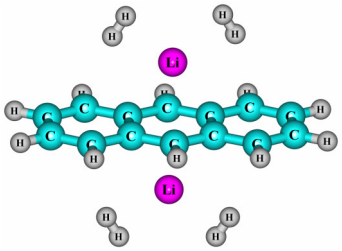
$4H_2@C_{14}H_{10}Li^+$



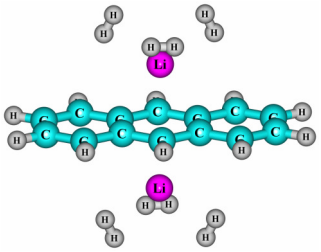
$C_{14}H_{10}Li_2^{2+}$



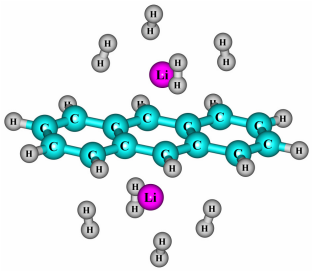
$2H_2@C_{14}H_{10}Li_2^{2+}$



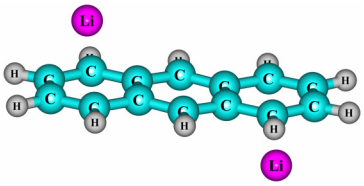
$4H_2@C_{14}H_{10}Li_2^{2+}$



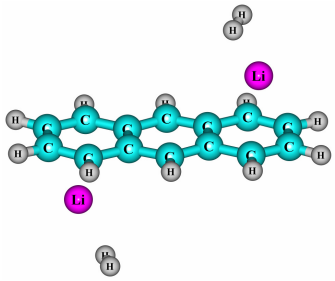
$6H_2@C_{14}H_{10}Li_2^{2+}$



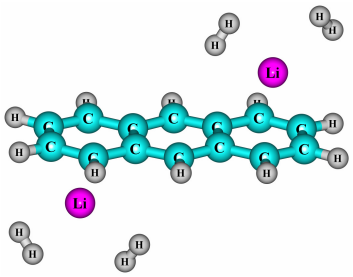
$8H_2@C_{14}H_{10}Li_2^{2+}$



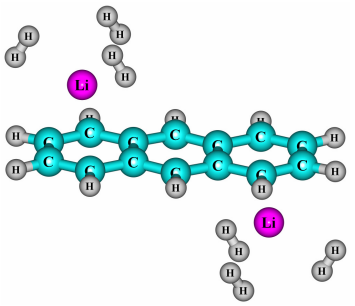
$C_{14}H_{10}Li_2^{2+}$



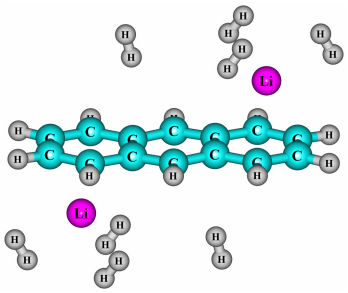
$2H_2@C_{14}H_{10}Li_2^{2+}$



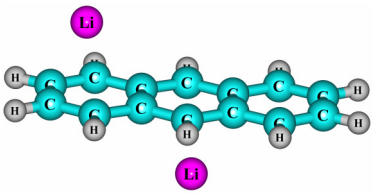
$4H_2@C_{14}H_{10}Li_2^{2+}$



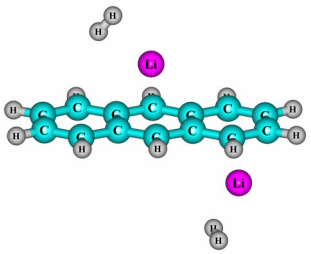
$6H_2@C_{14}H_{10}Li_2^{2+}$



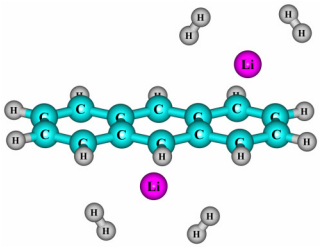
$8H_2@C_{14}H_{10}Li_2^{2+}$



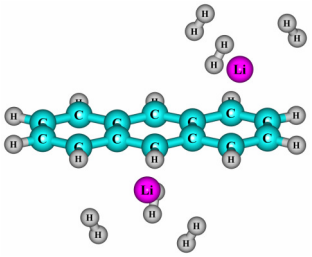
$C_{14}H_{10}Li_2^{2+}$



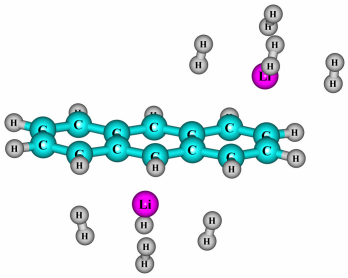
$2H_2@C_{14}H_{10}Li_2^{2+}$



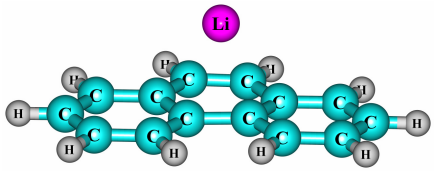
$4H_2@C_{14}H_{10}Li_2^{2+}$



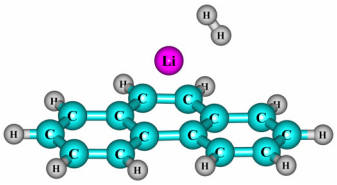
$6H_2@C_{14}H_{10}Li_2^{2+}$



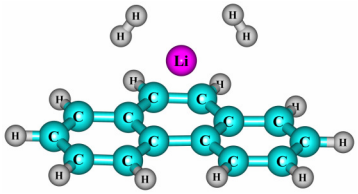
$8H_2@C_{14}H_{10}Li_2^{2+}$



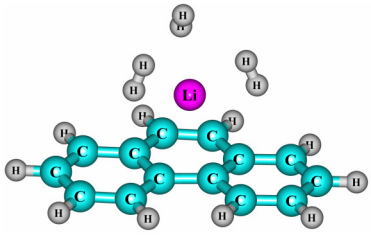
$C_{14}H_{10}Li^{+}$



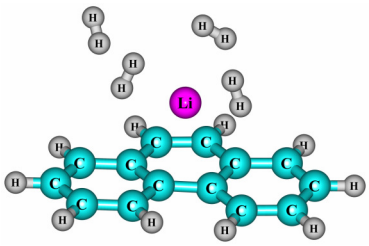
$1H_2@C_{14}H_{10}Li^{+}$



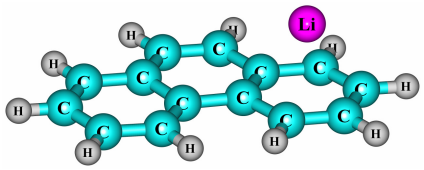
$2H_2@C_{14}H_{10}Li^{+}$



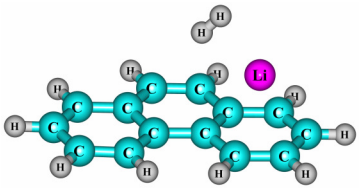
$3H_2@C_{14}H_{10}Li^{+}$



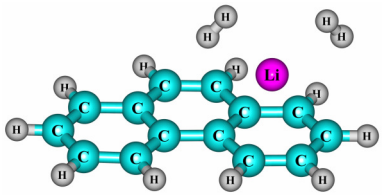
$4H_2@C_{14}H_{10}Li^{+}$



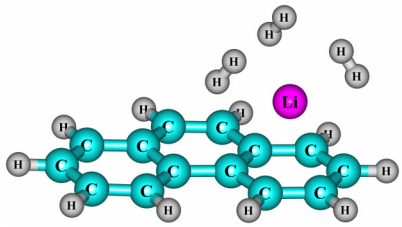
$C_{14}H_{10}Li^{+}$



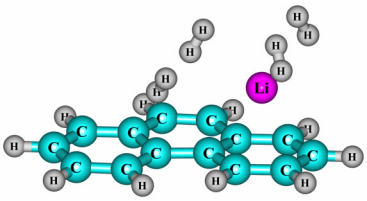
$1H_2@C_{14}H_{10}Li^{+}$



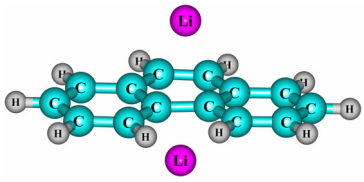
$2H_2@C_{14}H_{10}Li^{+}$



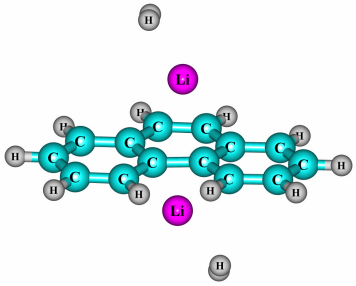
$3H_2@C_{14}H_{10}Li^{+}$



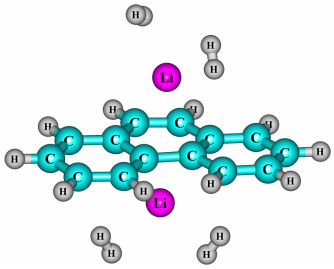
$4H_2@C_{14}H_{10}Li^{+}$



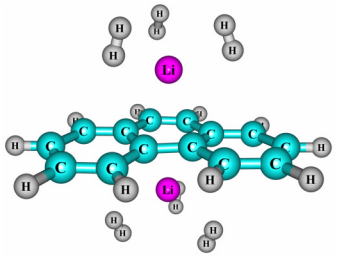
$C_{14}H_{10}Li_2^{2+}$



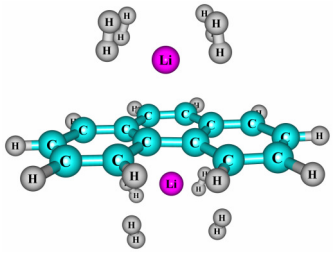
$2H_2@C_{14}H_{10}Li_2^{2+}$



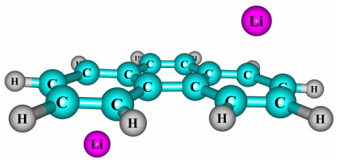
$4H_2@C_{14}H_{10}Li_2^{2+}$



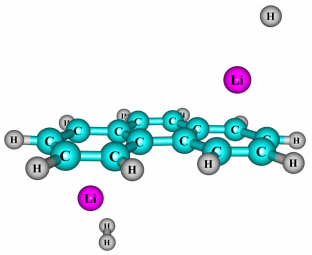
$6H_2@C_{14}H_{10}Li_2^{2+}$



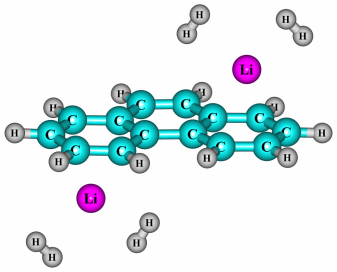
$8H_2@C_{14}H_{10}Li_2^{2+}$



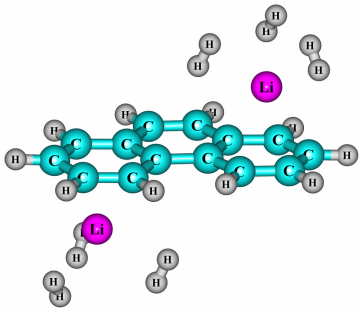
$C_{14}H_{10}Li_2^{2+}$



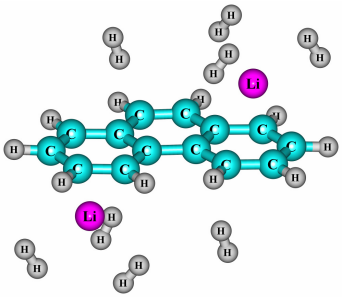
$2H_2@C_{14}H_{10}Li_2^{2+}$



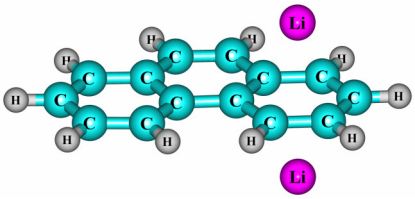
$4H_2@C_{14}H_{10}Li_2^{2+}$



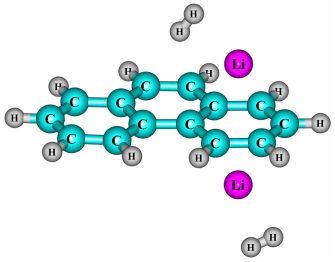
$6H_2@C_{14}H_{10}Li_2^{2+}$



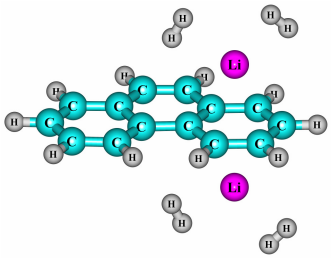
$8H_2@C_{14}H_{10}Li_2^{2+}$



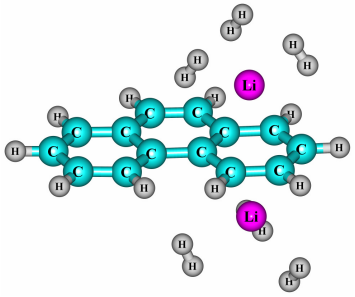
$C_{14}H_{10}Li_2^{2+}$



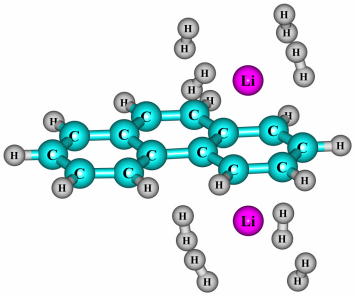
$2H_2@C_{14}H_{10}Li_2^{2+}$



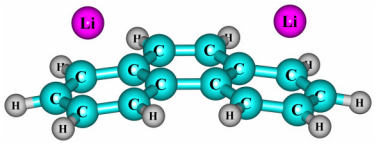
$4H_2@C_{14}H_{10}Li_2^{2+}$



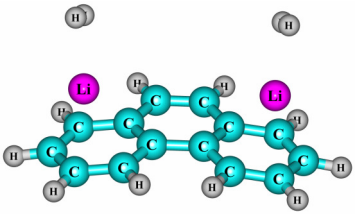
$6H_2@C_{14}H_{10}Li_2^{2+}$



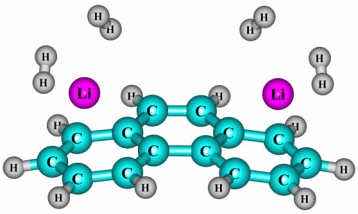
$8H_2@C_{14}H_{10}Li_2^{2+}$



$C_{14}H_{10}Li_2^{2+}$



$2H_2@C_{14}H_{10}Li_2^{2+}$



$4H_2@C_{14}H_{10}Li_2^{2+}$

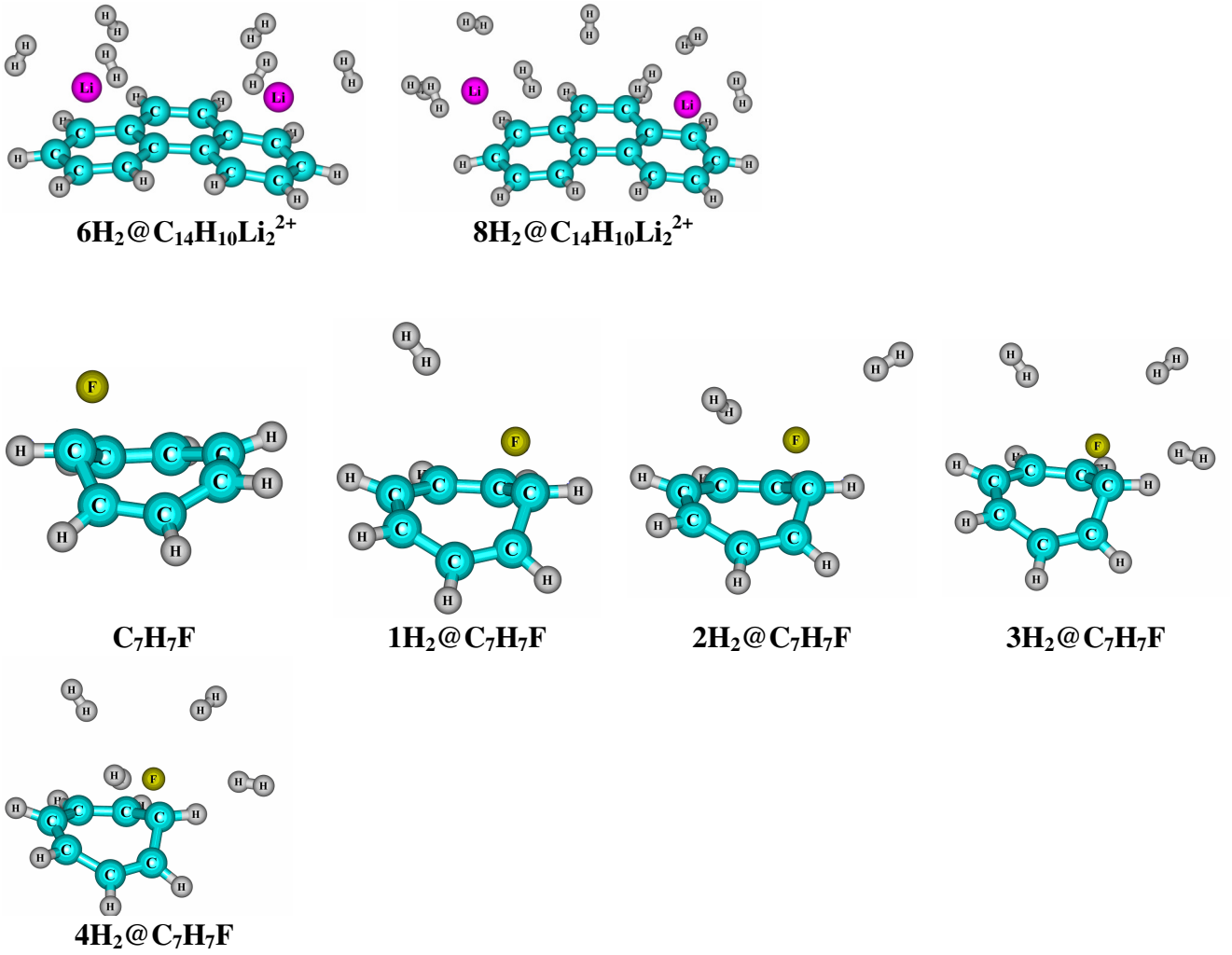
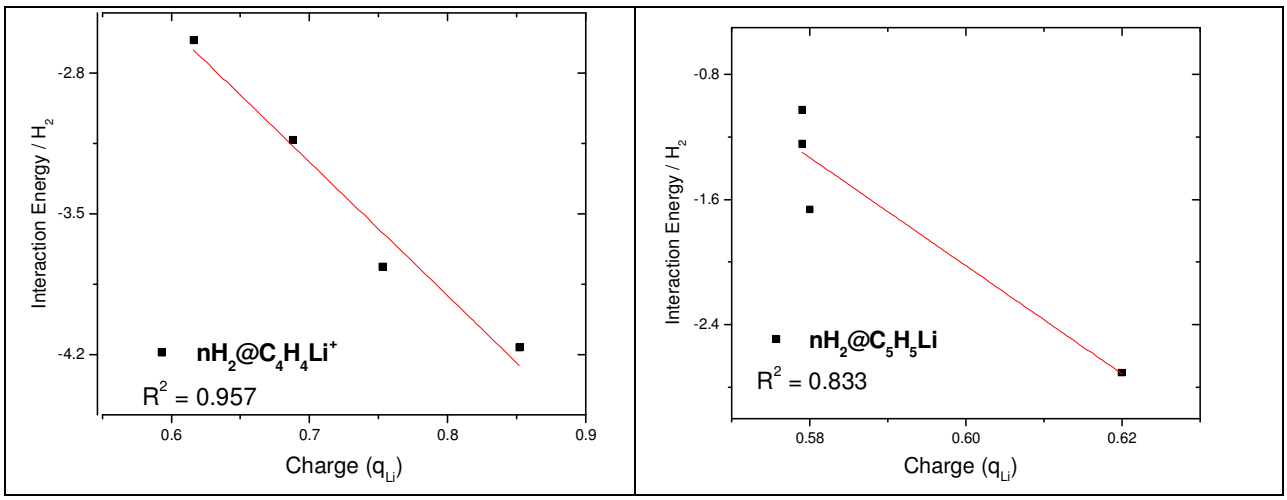


Figure S1: Structures considered in the present study



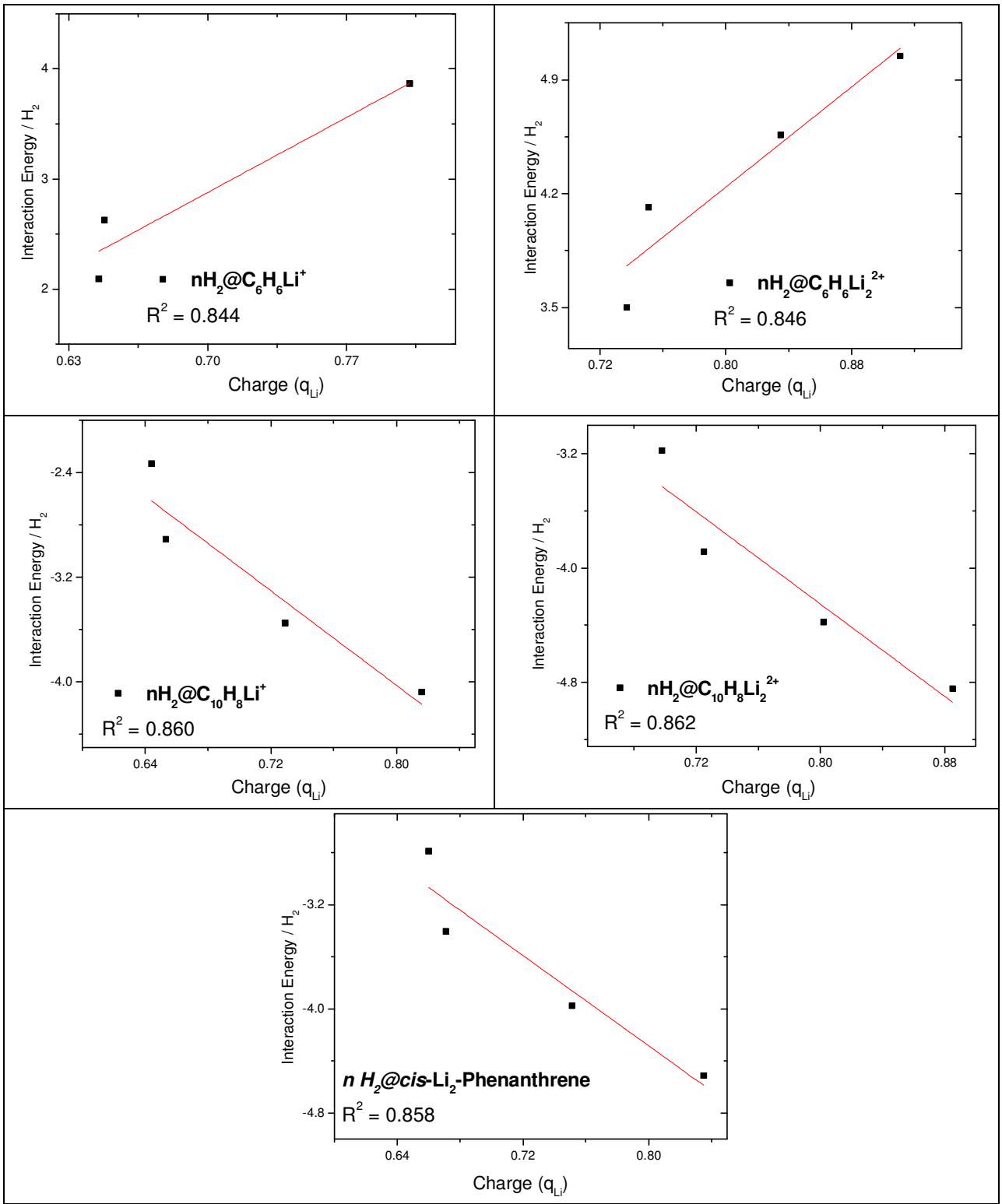


Figure S2. Variation of the interaction energy per H_2 molecules as a function of the atomic charge on the Li-center of the H_2-trapped annular complexes of the associated reactions.

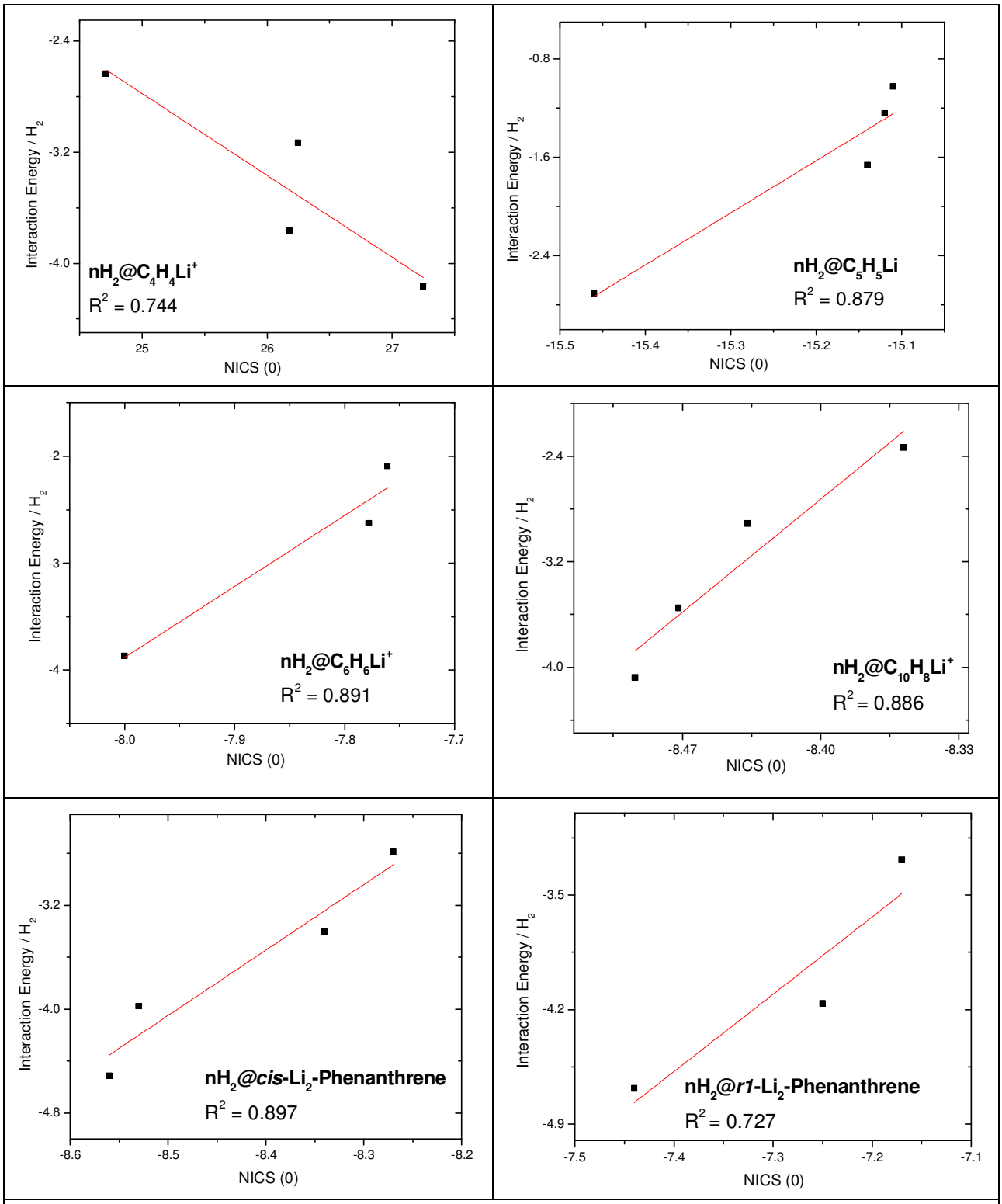


Figure S3. Variation of the interaction energy per H_2 molecules as a function of the NICS(0) values of the H_2-trapped annular complexes of the associated reactions.

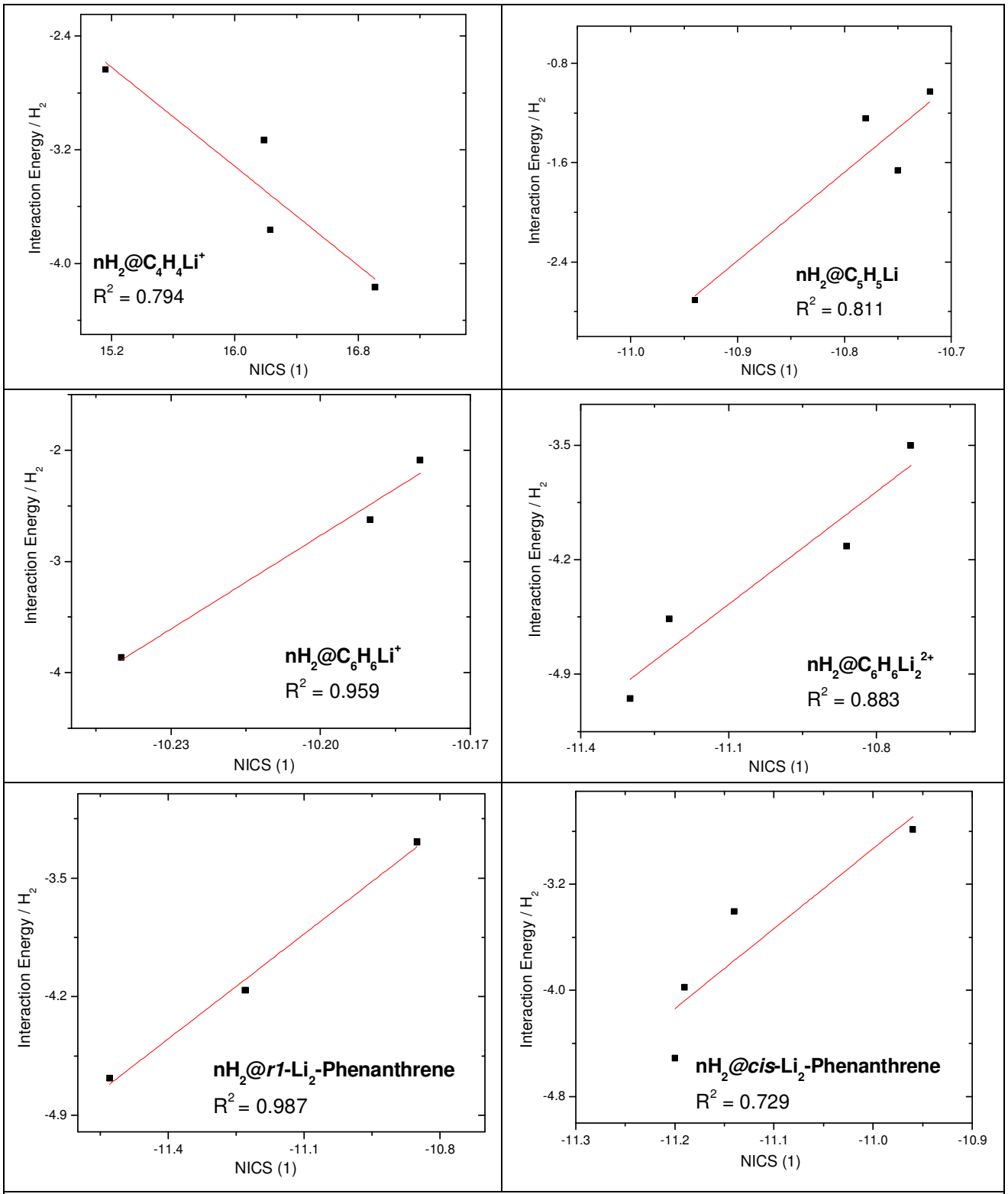
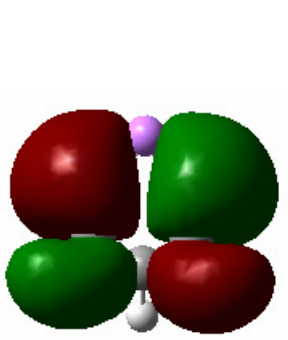
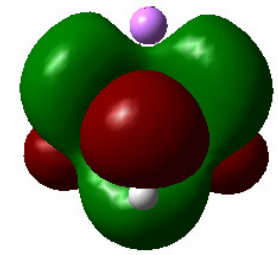
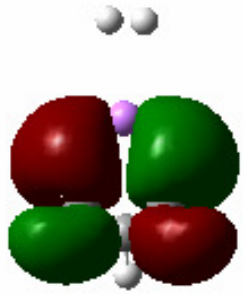
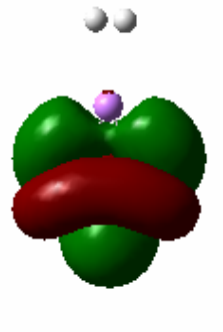


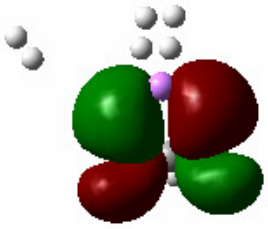
Figure S4. Variation of the interaction energy per H_2 molecule as a function of the NICS(1) values of the H_2-trapped annular complexes of the associated reactions.

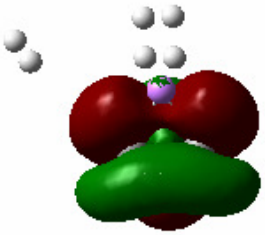

Cypro-Li HOMO

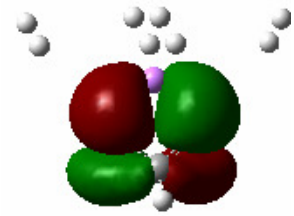

Cypro-Li LUMO

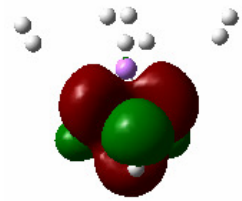

Cypro-Li-H_2 HOMO

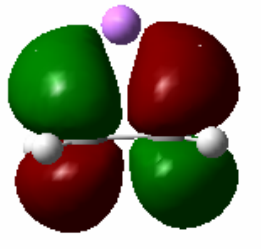

Cypro-Li-H_2 LUMO

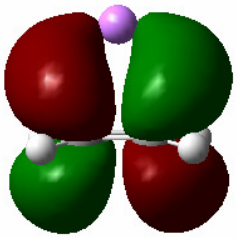

Cypro-Li-$3H_2$ HOMO

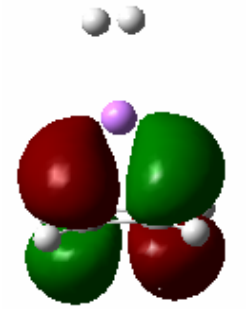

Cypro-Li-$3H_2$ LUMO

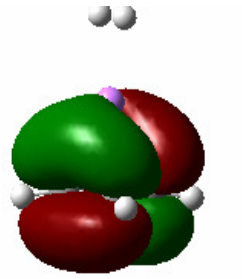

Cypro-Li-$4H_2$ HOMO

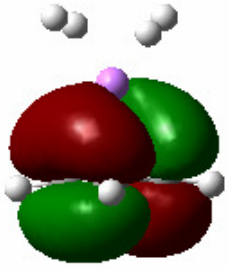

Cypro-Li-$4H_2$ LUMO

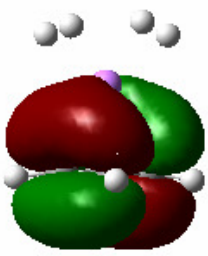

Cybut-Li HOMO

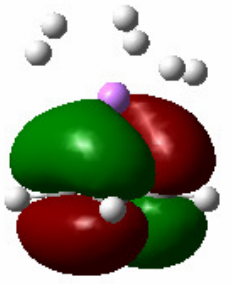

Cybut-Li LUMO

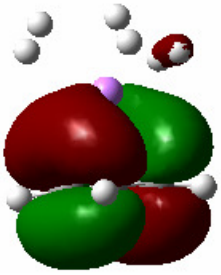

Cybut-Li-H_2 HOMO

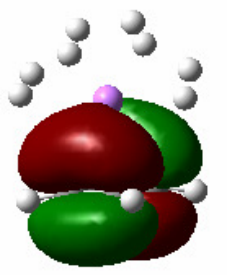

Cybut-Li-H_2 LUMO

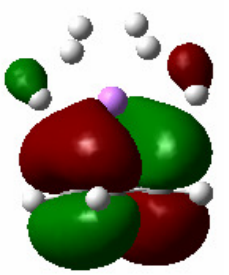

Cybut-Li-$2H_2$ HOMO

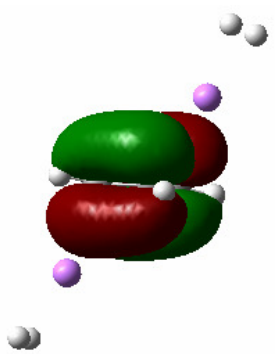

Cybut-Li-$2H_2$ LUMO

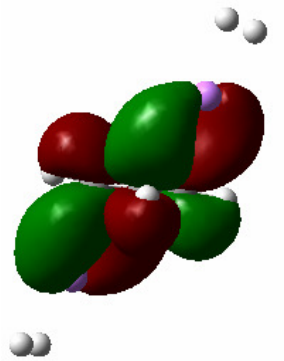

Cybut-Li-$3H_2$ HOMO

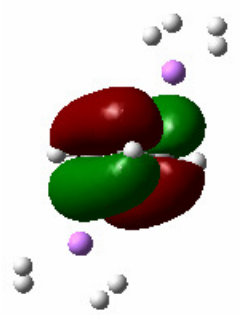

Cybut-Li-$3H_2$ LUMO

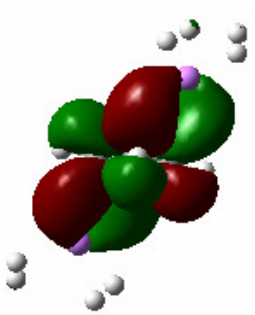

Cybut-Li-4H_2 HOMO

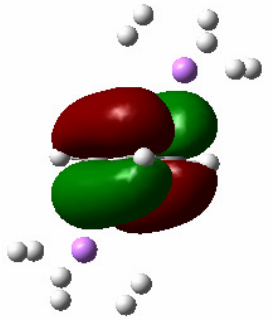

Cybut-Li-4H_2 LUMO

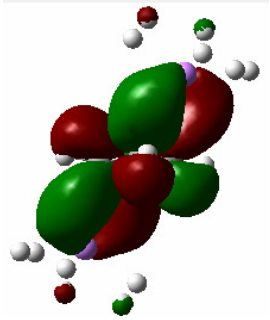

Cybut-Li_2-2H_2 HOMO

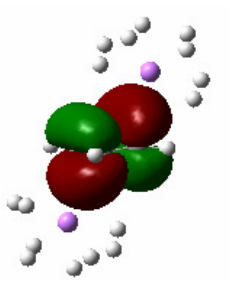

Cybut-Li_2-2H_2 LUMO

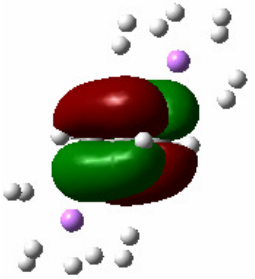

Cybut-Li_2-4H_2 HOMO

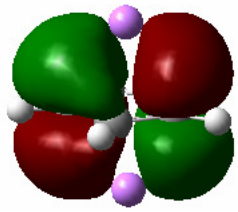

Cybut-Li_2-4H_2 LUMO

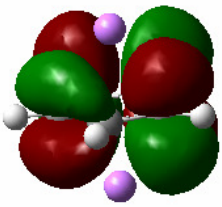

Cybut-Li_2-6H_2 HOMO

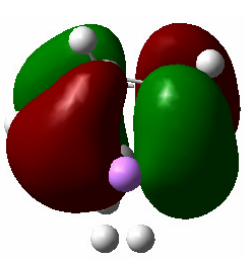

Cybut-Li_2-6H_2 LUMO

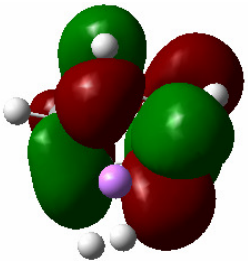

Cybut-Li_2-8H_2 HOMO

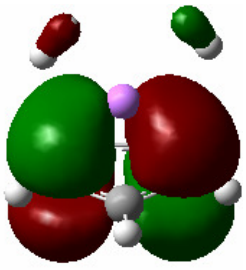

Cybut-Li_2-8H_2 LUMO

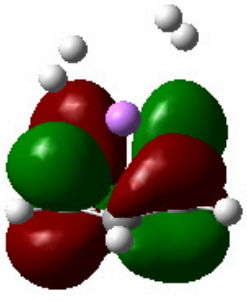

Cypent-Li HOMO

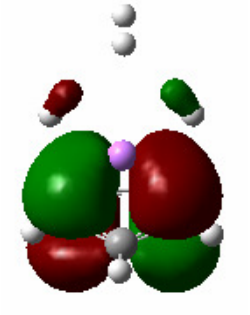

Cypent-Li LUMO

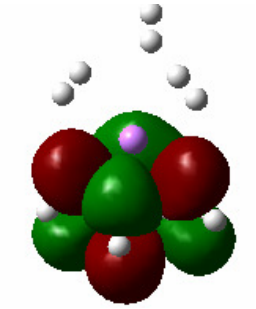

Cypent-Li-H_2 HOMO

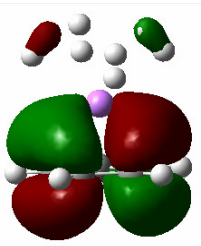

Cypent-Li-H_2 LUMO

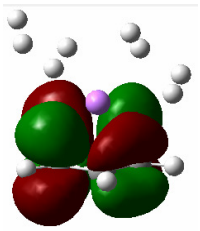

Cypent-Li-2H_2 HOMO

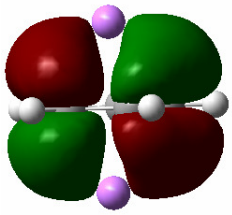

Cypent-Li-2H_2 LUMO

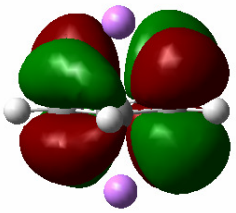

Cypent-Li-3H_2 HOMO

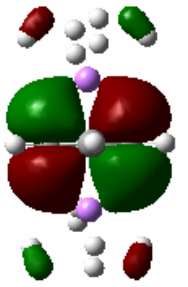

Cypent-Li-3H_2 LUMO

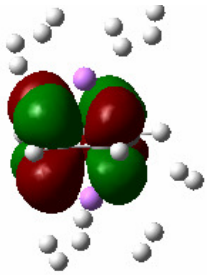

Cypent-Li-4H_2 HOMO

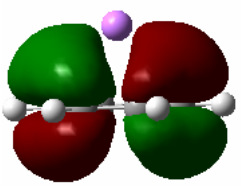

Cypent-Li-4H_2 LUMO

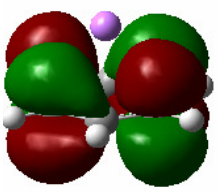

Cypent-Li_2 HOMO

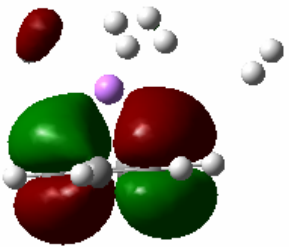

Cypent-Li_2 LUMO

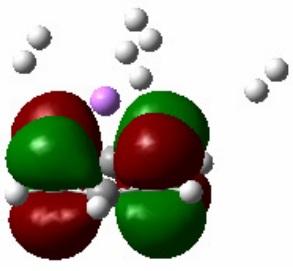

Cypent-Li_2-8H_2 HOMO

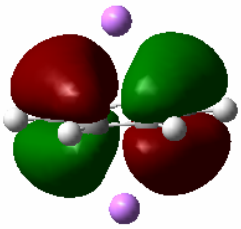

Cypent-Li_2-8H_2 LUMO

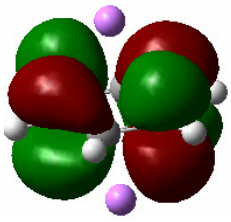

Benz-Li HOMO

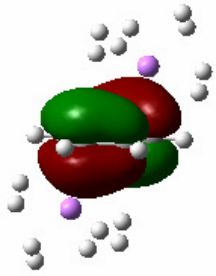

Benz-Li LUMO

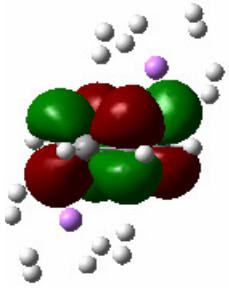

Benz-Li-4H_2 HOMO

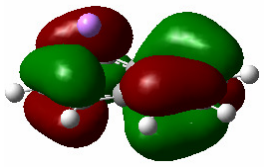

Benz-Li-4H_2 LUMO

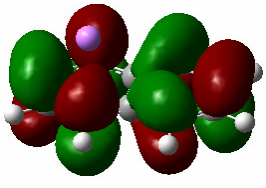

Benz-Li_2 HOMO

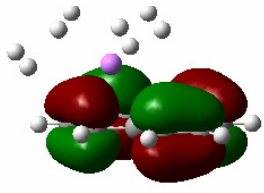

Benz-Li_2 LUMO

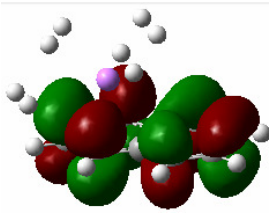

Benz-Li_2-8H_2 HOMO


Benz-Li_2-8H_2 LUMO


Naphth-Li HOMO


Naphth-Li LUMO


Naphth-Li-4H_2 HOMO


Naphth-Li-4H_2 LUMO

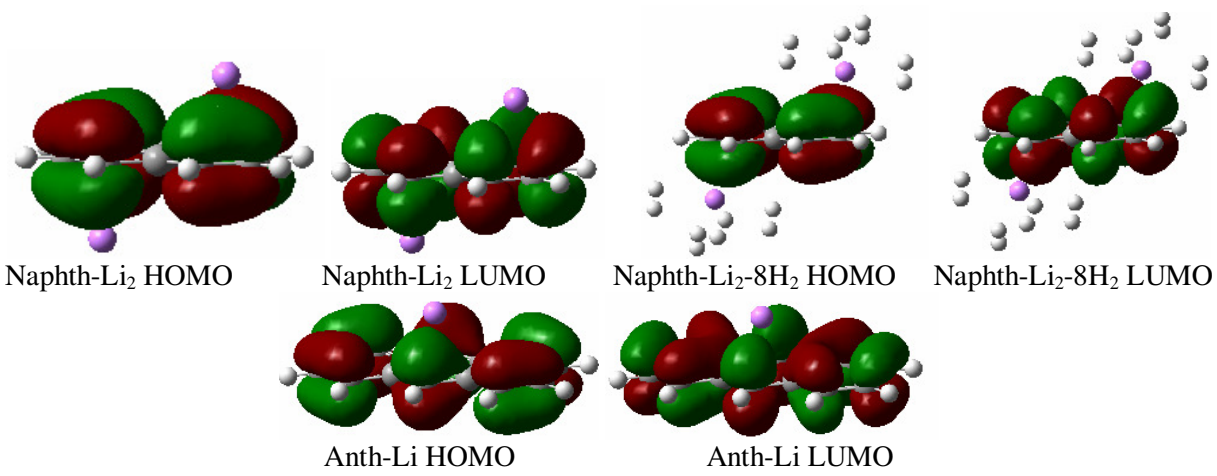


Figure S5. Some important frontier molecular orbitals of polynuclear hydrocarbons with and without H_2 trapping.