Supplementary Information (SI) for Physical Chemistry Chemical Physics.

From Loose to Tight: Unveiling Bond Stretch Isomerism in π-Complexes of Li, Na and K

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Supporting Information

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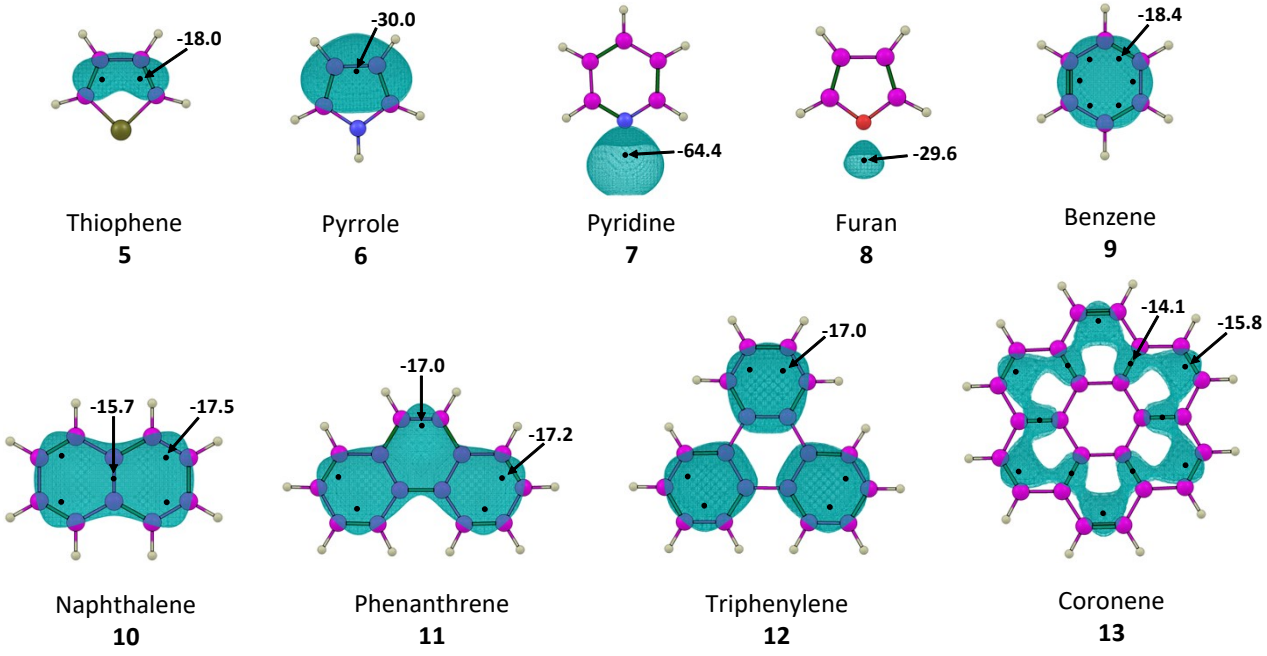

Figure S1. MESP isosurface plots of all HASs and AHs at -13.8 kcal/mol. The black dots represent V_{min} positions.

Table S1. Interaction energy (E_{ts}, kcal/mol), binding distance (d_{ts}, Å), reaction barrier (kcal/mol), spin density ($\delta_{M\text{-}ts}$), Mulliken charge ($q_{M\text{-}ts}$) and MESP minima (V_{min}, kcal/mol).

ts-bi	M	E_{ts}	d_{ts}	Activation barrier		$\delta_{M\text{-}ts}$	$q_{M\text{-}ts}$	V_{min} (Rich centers)
				Forward	Backward			
(**1**···Li)$_{ts}$	Li	4.5	2.19	5.1	12.3	0.728	0.096	-26.2 (Li)
(**3**···Li)$_{ts}$	Li	2.5	2.26	3.1	4.1	0.718	0.075	-25.8 (Li)
(**4**···K)$_{ts}$	K	-1.2	3.11	0.2	2.4	0.815	0.105	-15.3 (**4**)
(**5**···Li)$_{ts}$	Li	-0.6	2.34	1.6	8.8	0.799	0.017	-23.1 (Li)
(**7**···Li)$_{ts}$	Li	2.0	2.55	2.3	10.6	0.807	0.009	-22.1 (Li) -52.8 (N of **7**)
(**9**···Li)$_{ts}$	Li	-0.8	2.36	3.2	2.5	0.595	0.128	-13.4 (Li)
(**10**···Li)$_{ts}$	Li	-3.2	2.66	0.1	10.8	0.941	-0.056	-32.9 (Li)

(**10**···Na)$_{ts}$	Na	1.1	2.75	4.7	2.4	0.510	0.355	-23.4 (**10**)
(**10**···K)$_{ts}$	K	-1.6	3.17	1.7	5.4	0.707	0.223	-16.8 (**10**)
(**11**$_{R1}$···Li)$_{ts}$	Li	-3.3	2.60	0.2	8.3	0.893	-0.020	-30.6 (Li)
(**11**$_{R1\text{-}R2}$···Li)$_{ts}$	Li	-5.0	2.06	6.6	6.4	0.015	0.644	-31.3 (**11**)
(**11**$_{R2}$···Li)$_{ts}$	Li	-2.6	2.59	8.8	-0.2	0.916	-0.011	-32.7 (Li)
(**11**$_{R1}$···K)$_{ts}$	K	-1.3	3.09	2.1	3.9	0.634	0.294	-19.1 (**11**)
(**11**$_{R1\text{-}R2}$···K)$_{ts}$	K	-2.8	2.70	2.5	4.9	0.077	0.793	-37.5 (**11**)
(**12**$_{R1}$···Li)$_{ts}$	Li	-1.9	2.48	1.6	8.8	0.757	0.083	-23.3 (Li)
(**12**$_{R1}$···K)$_{ts}$	K	-3.7	2.88	-0.6	2.5	0.044	0.808	-39.3 (**12**)
(**13**$_{R1\text{-}R2}$···Li)$_{ts}$	Li	-3.3	2.12	8.3	-1.2	0.037	0.734	-26.0 (**13**)

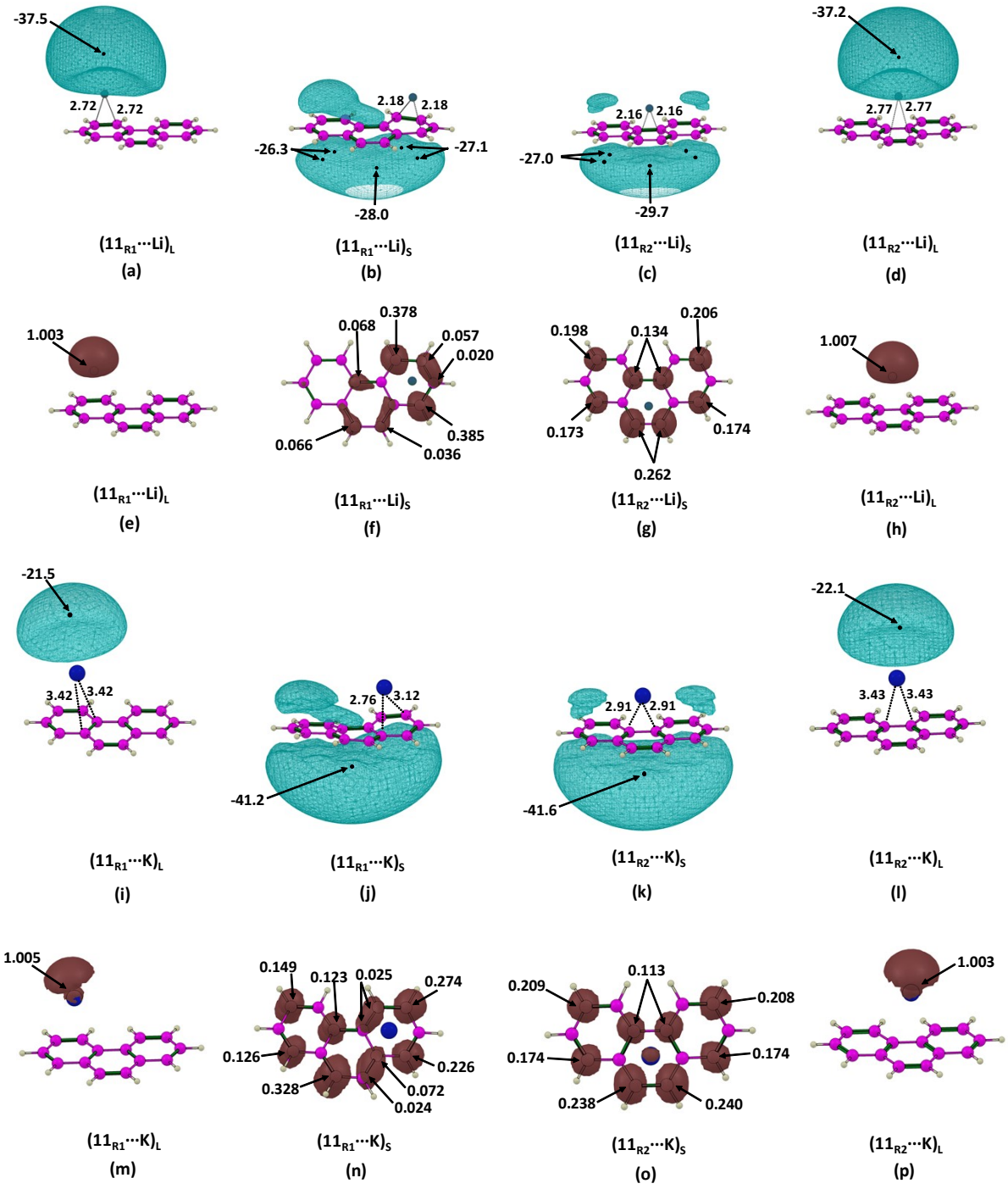

Figure S2. (a), (b), (c), (d), (i), (j), (k) and (l) represent MESP isosurface plots at -13.8 kcal/mol, and (e), (f), (g), (h), (m), (n), (o) and (p) represent spin density plots at 1.9 kcal/mol of phenanthrene···M complexes (M = Li, K).

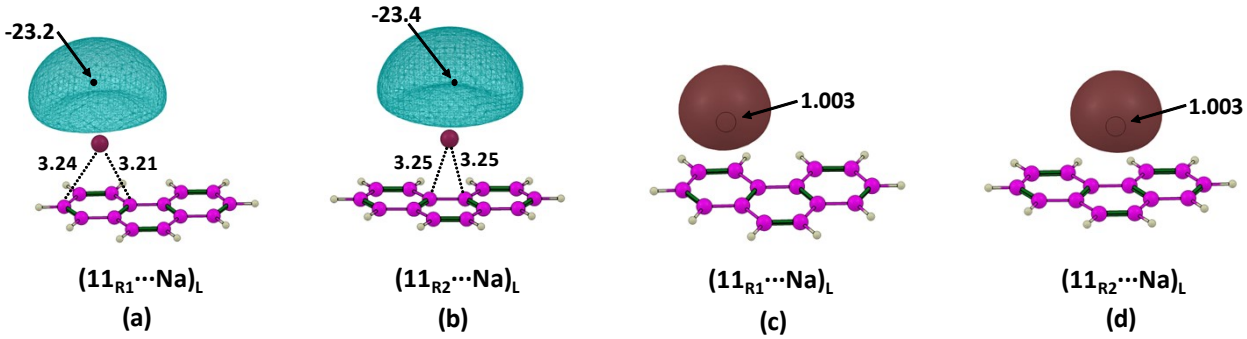

Figure S3. (a) and (b) represent MESP isosurface plots at -13.8 kcal/mol, (c) and (d) represent spin density plots at 1.9 kcal/mol of phenanthrene···Na complexes.

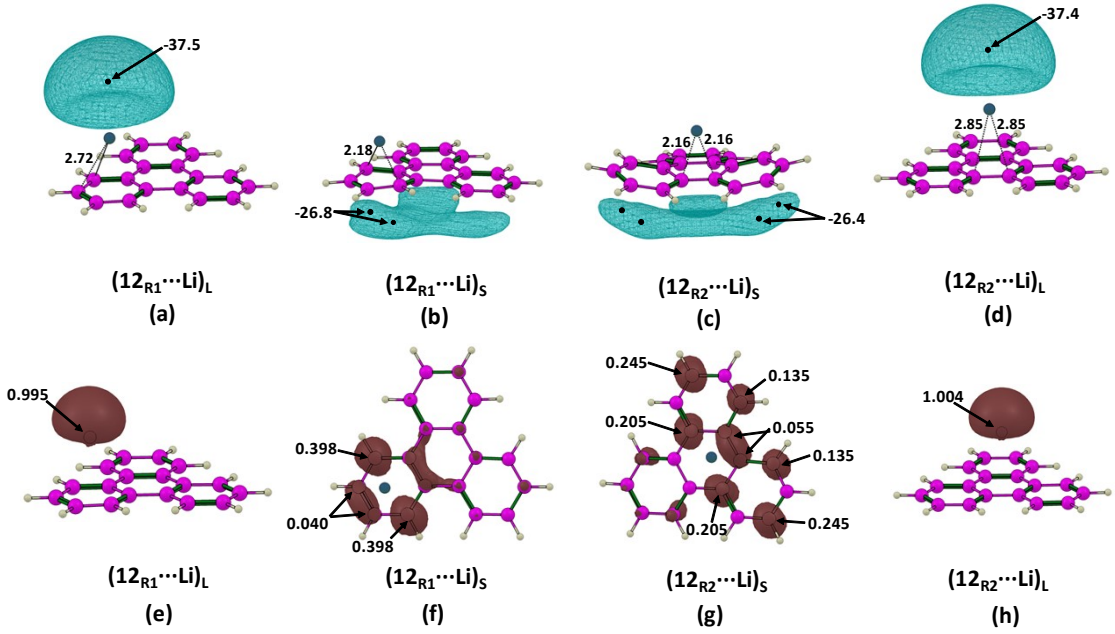

Figure S4. (a), (b), (c) and (d) represent MESP an isosurface plots at -21.3 kcal/mol, and (e), (f), (g), and (h) represent spin density plots at 1.9 kcal/mol of triphenylene···Li complexes.

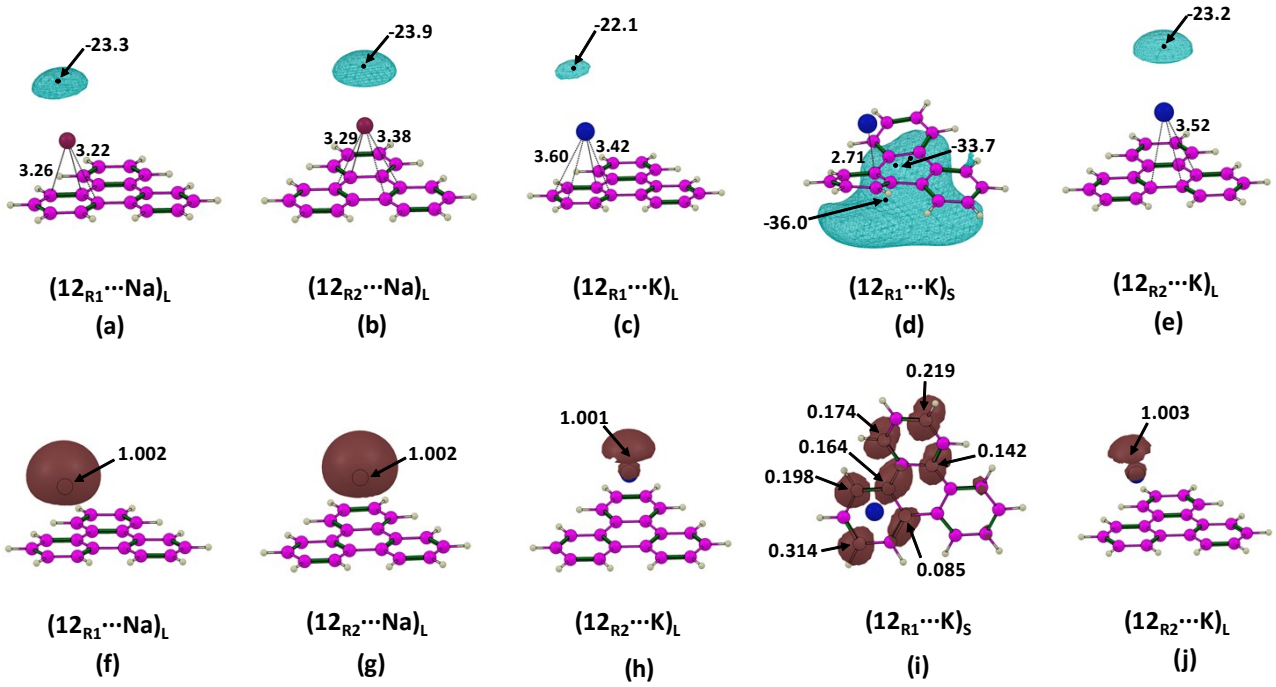

Figure S5. (a), (b), (c), (d), and (e) represent MESP isosurface plots at -21.3 kcal/mol, and (f), (g), (h), (i), and (j) represent spin density plots at 1.3 kcal/mol of triphenylene···M complexes (M = Na, K).

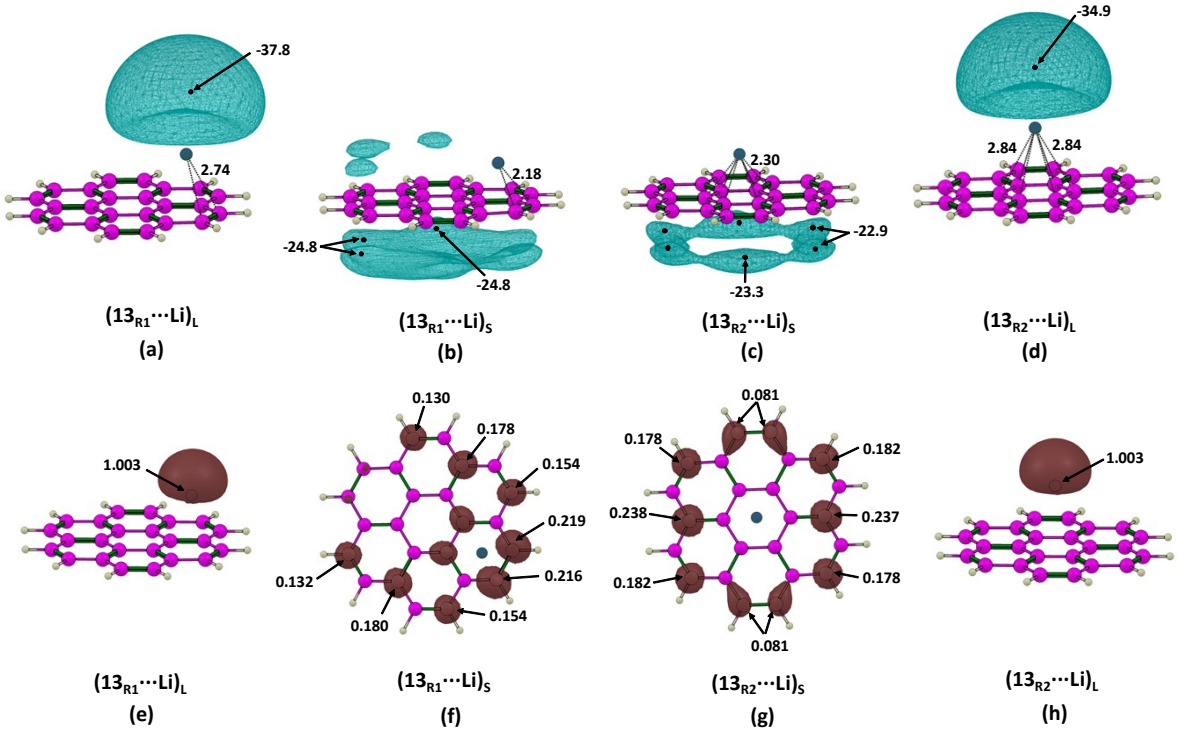

Figure S6. (a), (b), (c) and (d) represent MESP isosurface plots at -18.8 kcal/mol, and (e), (f), (g), and (h) represent spin density plots of BSIs at 1.9 kcal/mol of coronene···Li complexes.

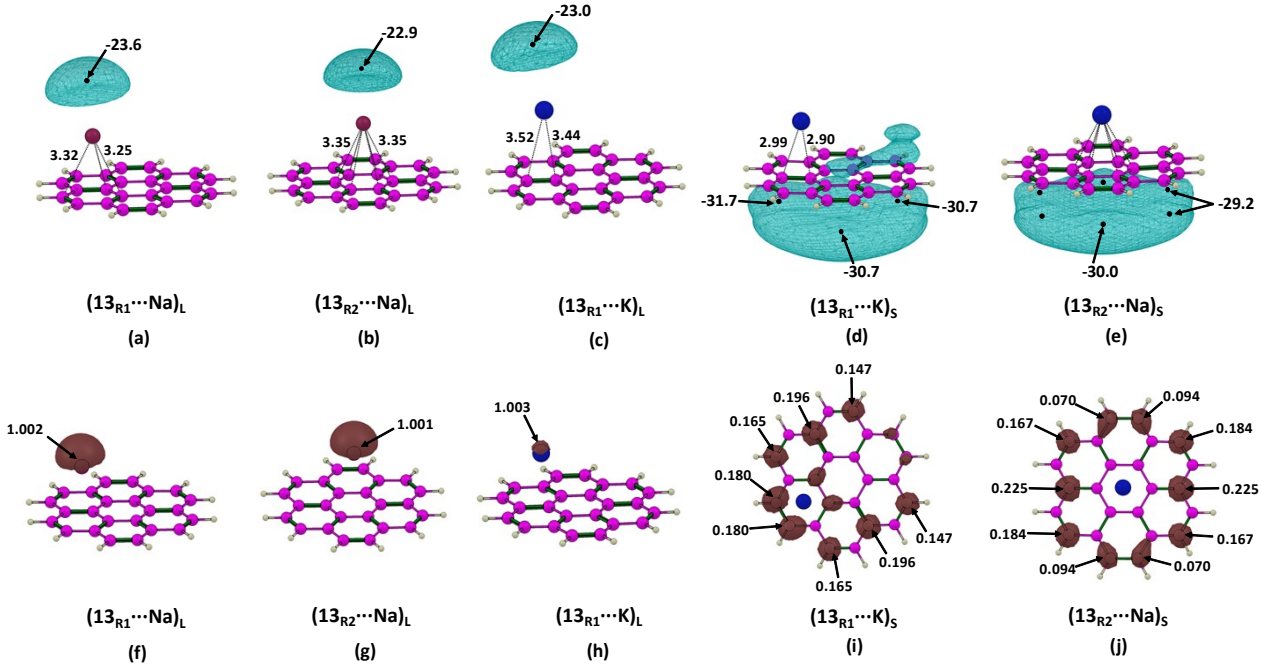

Figure S7. (a), (b), (c), (d), and (e) represent MESP isosurface plots at -18.8 kcal/mol, and (f), (g), (h), (i), and (j) represent spin density plots at 1.3 kcal/mol of coronene···M complexes (M=Na, K).

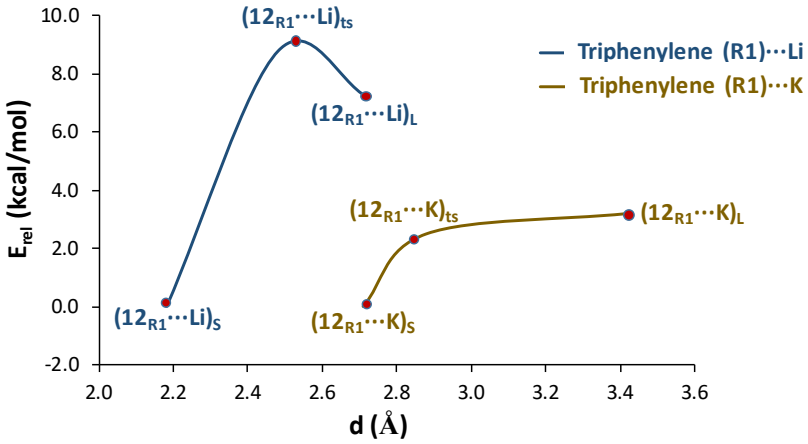

Figure S8. Relative energy (E_{rel}) level diagram plotted against nearest C···M distances (d) for *lbi* ↔ *sbi* of triphenylene···M (M = Li/K) complexes *via* corresponding *ts-bi*.

Table S2. Natural population analysis, Mulliken charge and Hirshfeld charges of all *sbi* and *lbi* complexes.

π-systems	M	NPA (S)	NPA (L)	Mulliken (S)	Mulliken (L)	Hirshfeld (S)	Hirshfeld (L)
Acetylene (**1**)	Li	0.782	-0.014	0.423	-0.076	0.427	-0.110
	Na	-	-0.008	-	-0.041	-	-0.048
	K	-	-0.007	-	-0.035	-	-0.051
Diacetylene (**2**)	Li	0.816	-	0.499	-	0.421	-
	Na	0.844	-0.004	0.636	-0.028	0.532	-0.046
	K	0.884	-	0.746	-	0.552	-
Ethylene (**3**)	Li	0.751	-0.019	0.362	-0.092	0.413	-0.103
	Na	-	-0.012	-	-0.053	-	-0.044
	K	-	-0.010	-	-0.045	-	-0.047
Butadiene (**4**)	Li	0.808	-	0.427	-	0.424	-
	Na	-	-0.008	-	-0.062	-	-0.066
	K	0.830	0.022	0.661	-0.028	0.516	-0.058
Thiophene (**5**)	Li	0.776	-0.041	0.459	-0.114	0.374	-0.176
	Na	-	-0.015	-	-0.058	-	-0.088
	K	-	-0.015	-	-0.045	-	-0.100
Pyrrole (**6**)	Li	-	-0.036	-	-0.140	-	-0.199
	Na	-	-0.013	-	-0.079	-	-0.112
	K	-	-0.013	-	-0.063	-	-0.121
Pyridine (**7**)	Li	0.848	-0.008	0.465	-0.097	0.426	-0.137
	Na	-	-	-	-	-	-
	K	0.932	-	0.770	-	0.562	-
Furan (**8**)	Li	-	-0.019	-	-0.095	-	-0.153
	Na	-	-0.007	-	-0.054	-	-0.076
	K	-	-0.007	-	-0.042	-	-0.087
Benzene (**9**)	Li	0.804	-0.032	0.456	-0.130	0.374	-0.188
	Na	-	-0.070	-	-0.070	-	-0.096

	K	-	-0.012	-	-0.057	-	-0.109
Naphthalene (**10**)	Li	0.858	0.918	0.519	-0.014	0.416	0.574
	Na	0.904	0.960	0.708	-0.055	0.553	0.722
	K	0.953	0.969	0.827	-0.046	0.568	0.724

Table S3. Natural population analysis, Mulliken charge and Hirshfeld charges of all *sbi* and *lbi* complexes of AHs with multiple rings.

AHs	Ring	M	NPA (S)	NPA (L)	Mulliken (S)	Mulliken (L)	Hirshfeld (S)	Hirshfeld (L)
Phenanthrene (**11**)	R1	Li	0.851	0.911	0.527	-0.097	0.411	-0.177
		Na	-	-0.008	-	-0.050	-	-0.092
		K	0.952	-0.011	0.840	-0.041	0.574	-0.121
	R2	Li	0.902	0.939	0.585	-0.077	0.438	0.602
		Na	-	0.972	-	-0.042	-	0.738
		K	0.961	0.977	0.853	-0.035	0.567	0.726
Triphenylene (**12**)	R1	Li	0.846	0.903	0.536	-0.086	0.406	-0.171
		Na	-	-0.007	-	-0.045	-	-0.089
		K	0.935	-0.010	0.828	-0.036	0.543	-0.121
	R2	Li	0.905	-0.012	0.647	-0.053	0.436	-0.151
		Na	-	-0.007	-	-0.032	-	-0.079
		K	-	-0.009	-	-0.027	-	-0.126
Coronene (**13**)	R1	Li	0.908	0.950	0.615	-0.065	0.447	0.610
		Na	-	0.979	-	-0.031	-	0.749
		K	0.966	0.982	0.886	-0.024	0.584	0.734
	R2	Li	0.941	0.970	0.693	-0.031	0.469	0.662
		Na	-	0.984	-	-0.016	-	0.768
		K	0.973	-	0.915	-	0.592	-

Table S4. The electrostatics (E_{elst}), exchange (E_{exch}), induction (E_{ind}), dispersion (E_{disp}) and total SAPT0 interaction energies (E_{SAPT0}) at HF/6-311G (d,p) level of theory. All values in kcal/mol.

BSIs	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{SAPT0}
(**1**···Li)$_L$	-19.9	29.1	-8.3	-4.4	-3.5
(**1**···Li)$_S$	-61.0	102.1	-75.2	-14.5	-48.6
(**1**···Na)$_L$	-8.9	13.1	-2.8	-2.3	-0.8
(**1**···K)$_L$	-9.6	13.4	-2.9	-2.4	-1.5
(**2**···Li)$_S$	-72.4	110.7	-78.2	-17.9	-57.8
(**2**···Na)$_L$	-10.8	15.7	-3.0	-3.2	-1.3
(**2**···Na)$_S$	-50.7	75.5	-46.4	-12.3	-33.9
(**2**···K)$_S$	-46.0	69.6	-50.8	-12.7	-40.0
(**3**···Li)$_L$	-20.8	30.9	-9.1	-4.9	-3.9
(**3**···Li)$_S$	-66.0	105.9	-41.6	-13.9	-15.6
(**3**···Na)$_L$	-9.3	14.0	-3.1	-2.5	-1.0
(**3**···K)$_L$	-10.5	14.8	-3.3	-2.8	-1.7
(**4**···Li)$_S$	-77.6	123.8	-54.3	-19.6	-27.6
(**4**···Na)$_L$	-16.1	23.3	-5.2	-4.8	-2.7
(**4**···K)$_L$	-22.3	30.8	-7.2	-6.4	-5.0
(**4**···K)$_S$	-51.1	77.7	-20.4	-13.7	-7.5
(**5**···Li)$_L$	-44.5	60.3	-14.9	-10.9	-10.0
(**5**···Li)$_S$	-103.0	150.3	-59.4	-25.1	-37.3
(**5**···Na)$_L$	-23.5	31.2	-5.9	-6.3	-4.5
(**5**···K)$_L$	-26.0	33.1	-6.3	-6.9	-6.2
(**6**···Li)$_L$	-54.2	70.4	-20.4	-12.5	-16.7
(**6**···Na)$_L$	-29.9	37.9	-8.8	-7.3	-8.1
(**6**···K)$_L$	-32.7	40.1	-9.2	-8.3	-10.0
(**7**···Li)$_L$	-36.9	52.6	-12.4	-10.3	-7.0
(**7**···Li)$_S$	-103.3	157.9	-61.3	-26.9	-33.6
(**7**···K)$_S$	-63.4	95.8	-26.7	-17.7	-12.0
(**8**···Li)$_L$	-38.5	53.1	-13.5	-9.3	-8.2
(**8**···Na)$_L$	-20.9	28.3	-5.6	-5.5	-3.6
(**8**···K)$_L$	-23.4	30.6	-6.3	-6.2	-5.3
(**9**···Li)$_L$	-48.0	65.3	-17.6	-12.9	-13.2
(**9**···Li)$_S$	-105.0	154.5	-48.6	-28.1	-27.2
(**9**···Na)$_L$	-25.2	33.4	-7.0	-7.3	-6.1
(**9**···K)$_L$	-28.1	35.6	-7.6	-8.1	-8.2
(**10**···Li)$_L$	-48.4	66.7	-17.4	-14.2	-13.4
(**10**···Li)$_S$	-104.9	155.4	-52.9	-29.3	-31.7
(**10**···Na)$_L$	-26.7	35.8	-7.2	-8.6	-6.7
(**10**···Na)$_S$	-70.3	101.4	-16.7	-19.1	-4.7
(**10**···K)$_L$	-32.5	41.7	-8.7	-10.4	-9.8
(**10**···K)$_S$	-68.9	98.2	-17.8	-20.9	-9.3
(**11**$_{R1}$···Li)$_L$	-50.4	69.2	-18.1	-14.9	-14.3
(**11**$_{R1}$···Li)$_S$	-105.3	154.9	-50.1	-29.8	-30.3

(**11**$_{R2}$···Li)$_L$	-45.6	63.7	-15.8	-14.5	-12.2
(**11**$_{R2}$···Li)$_S$	-106.2	159.5	-56.7	-31.6	-35.1
(**11**$_{R1}$···Na)$_L$	-27.7	37.1	-7.4	-9.1	-7.1
(**11**$_{R2}$···Na)$_L$	-27.1	36.8	-7.0	-9.5	-6.8
(**11**$_{R1}$···K)$_L$	-33.4	42.8	-8.8	-11.0	-10.4
(**11**$_{R1}$···K)$_S$	-70.9	100.1	-24.7	-22.4	-17.7
(**11**$_{R2}$···K)$_L$	-34.8	44.9	-9.1	-11.9	-10.9
(**11**$_{R2}$···K)$_S$	-72.6	103.5	-25.7	-23.4	-18.2
(**12**$_{R1}$···Li)$_L$	-51.7	70.9	-18.4	-15.5	-14.8
(**12**$_{R1}$···Li)$_S$	-105.4	154.4	-50.6	-30.1	-31.7
(**12**$_{R2}$···Li)$_L$	-43.8	62.1	-14.4	-15.1	-11.3
(**12**$_{R2}$···Li)$_S$	-104.0	157.8	-50.3	-32.9	-29.4
(**12**$_{R1}$···Na)$_L$	-27.7	36.9	-7.3	-9.3	-7.3
(**12**$_{R2}$···Na)$_L$	-26.6	36.4	-6.6	-9.9	-6.8
(**12**$_{R1}$···K)$_L$	-33.9	43.5	-8.9	-11.5	-10.7
(**12**$_{R1}$···K)$_S$	-76.2	108.1	-27.8	-25.3	-21.3
(**12**$_{R2}$···K)$_L$	-35.9	46.4	-9.2	-12.8	-11.4
(**13**$_{R1}$···Li)$_L$	-47.9	66.5	-16.3	-15.7	-13.4
(**13**$_{R1}$···Li)$_S$	-107.5	159.4	-52.7	-32.7	-33.6
(**13**$_{R2}$···Li)$_L$	-40.8	57.3	-12.2	-15.1	-10.8
(**13**$_{R2}$···Li)$_S$	-106.2	159.2	-45.4	-34.8	-27.2
(**13**$_{R1}$···Na)$_L$	-27.9	37.7	-6.9	-10.3	-7.4
(**13**$_{R2}$···Na)$_L$	-26.7	36.2	-6.1	-10.7	-7.2
(**13**$_{R1}$···K)$_L$	-35.9	46.2	-8.9	-13.0	-11.7
(**13**$_{R1}$···K)$_S$	-72.6	101.8	-23.2	-24.6	-18.7
(**13**$_{R2}$···K)$_S$	-74.2	103.1	-20.6	-26.3	-18.1

Table S5. The energy corresponds to basis set super position error (E_{BSSE}, kcal/mol) of all complexes at ωB97XD/6-311G (d,p) level of theory.

BSIs	E_{BSSE}	BSIs	E_{BSSE}	BSIs	E_{BSSE}
(**1**···Li)$_L$	0.44	(**7**···Li)$_L$	0.86	(**11**$_{R1}$···K)$_L$	0.50
(**1**···Li)$_S$	0.82	(**7**···Li)$_S$	1.53	(**11**$_{R1}$···K)$_S$	0.87
(**1**···Na)$_L$	0.40	(**7**···K)$_S$	1.14	(**11**$_{R2}$···K)$_L$	0.51
(**1**···K)$_L$	0.33	(**8**···Li)$_L$	1.36	(**11**$_{R2}$···K)$_S$	0.87
(**2**···Li)$_S$	0.61	(**8**···Na)$_L$	0.81	(**12**$_{R1}$···Li)$_L$	0.81
(**2**···Na)$_L$	0.36	(**8**···K)$_L$	0.60	(**12**$_{R1}$···Li)$_S$	1.05
(**2**···Na)$_S$	0.60	(**9**···Li)$_L$	0.77	(**12**$_{R2}$···Li)$_L$	0.89
(**2**···K)$_S$	0.50	(**9**···Li)$_S$	1.10	(**12**$_{R2}$···Li)$_S$	1.20
(**3**···Li)$_L$	0.42	(**9**···Na)$_L$	0.71	(**12**$_{R1}$···Na)$_L$	0.77
(**3**···Li)$_S$	0.70	(**9**···K)$_L$	0.49	(**12**$_{R2}$···Na)$_L$	0.79

(**3**···Na)$_L$	0.43	(**10**···Li)$_L$	0.74	(**12**$_{R1}$···K)$_L$	0.54
(**3**···K)$_L$	0.38	(**10**···Li)$_S$	1.01	(**12**$_{R1}$···K)$_S$	0.99
(**4**···Li)$_S$	0.78	(**10**···Na)$_L$	0.71	(**12**$_{R2}$···K)$_L$	0.58
(**4**···Na)$_L$	0.56	(**10**···Na)$_S$	1.13	(**13**$_{R1}$···Li)$_L$	0.79
(**4**···K)$_L$	0.46	(**10**···K)$_L$	0.47	(**13**$_{R1}$···Li)$_S$	1.09
(**4**···K)$_S$	0.74	(**10**···K)$_S$	0.82	(**13**$_{R2}$···Li)$_L$	0.85
(**5**···Li)$_L$	1.13	(**11**$_{R1}$···Li)$_L$	0.78	(**13**$_{R2}$···Li)$_S$	1.21
(**5**···Li)$_S$	1.66	(**11**$_{R1}$···Li)$_S$	1.05	(**13**$_{R1}$···Na)$_L$	0.76
(**5**···Na)$_L$	0.96	(**11**$_{R2}$···Li)$_L$	0.76	(**13**$_{R2}$···Na)$_L$	0.78
(**5**···K)$_L$	0.73	(**11**$_{R2}$···Li)$_S$	1.05	(**13**$_{R1}$···K)$_L$	0.55
(**6**···Li)$_L$	1.03	(**11**$_{R1}$···Na)$_L$	0.74	(**13**$_{R1}$···K)$_S$	0.90
(**6**···Na)$_L$	0.92	(**11**$_{R2}$···Na)$_L$	0.75	(**13**$_{R2}$···K)$_S$	0.92
(**6**···K)$_L$	0.72				