Supporting Information

Impact of Surface Modification on the Li, Na, and K Intercalation Efficiency and Capacity of Few-Layer Graphene Electrodes

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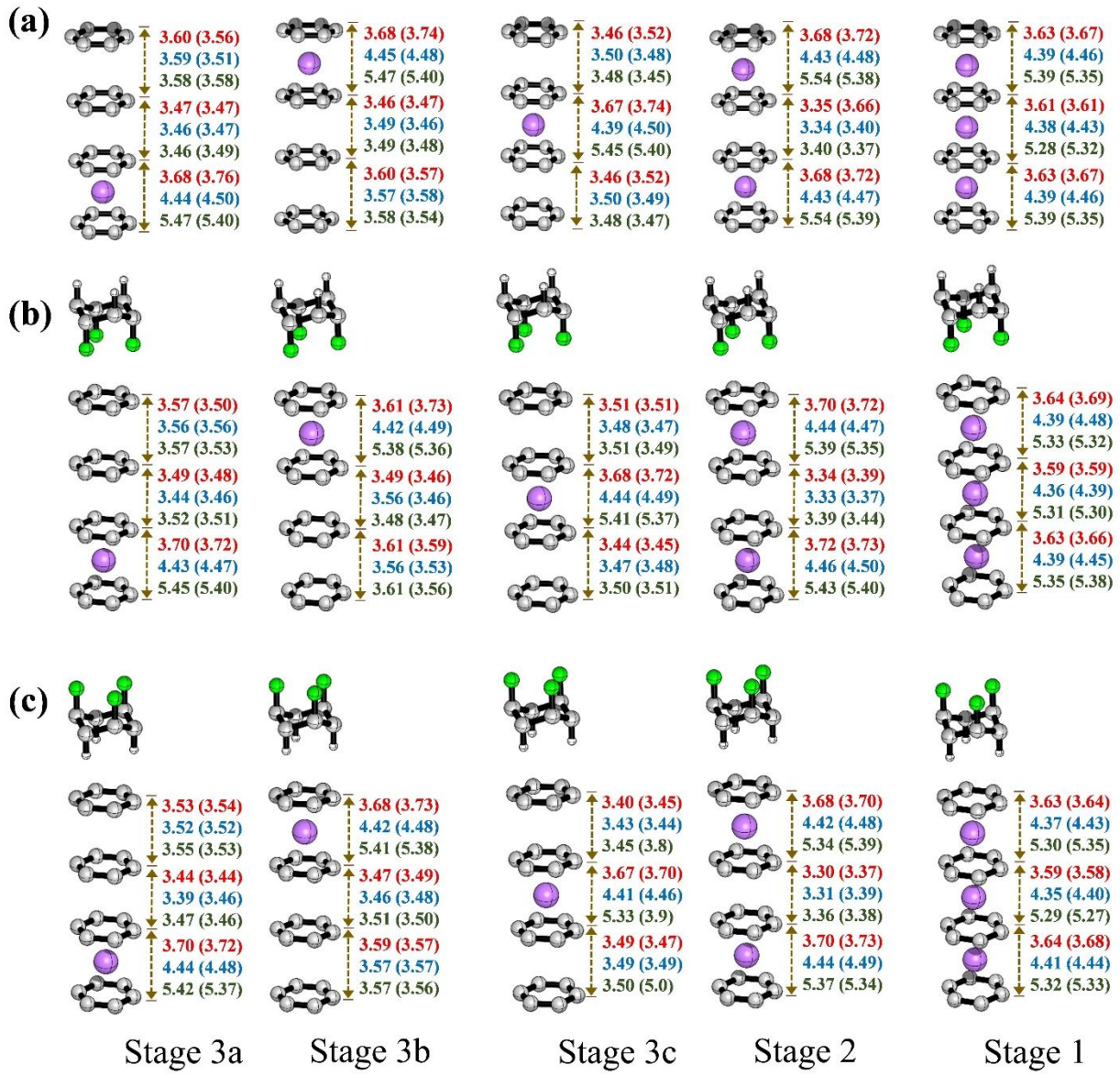

Figure S1. Interlayer stacking distances (in Å) in metal intercalated 4LG during different stages: (a) no surface modifier, and in the presence of (b) negative and (c) positive surface modifiers. The values outside parenthesis correspond to C_6M models, whereas the values inside parenthesis represent those obtained for C_8M models described in Figure 1c: C_6M values (C_8M values). Different label color codes represent the intercalated metals distance: **red, Li**; **blue, Na**; and **green, K**.

Table S1. Thermodynamics for M intercalation within a 4LG either in the presence or absence of a 2D-C_2HF SM. Binding energy with respect to the intercalation of different metals while using C_6M-type models are presented. The values presented outside and inside of parenthesis represent the BE for M intercalation in the presence or absence of a SM, respectively.

System	**Binding energy (BE) per metal atom (in eV)**					
	Positive modifier, 2D-C_2HF (no SM = pristine 4LG)			Negative modifier, 2D-C_2HF (no SM = pristine 4LG)		
Intercalated metal	Li	Na	K	Li	Na	K
Stage 3a	-0.17 (-0.09)	0.11 (0.20)	-0.04 (0.04)	-0.14 (-0.09)	0.14 (0.20)	-0.01 (0.04)
Stage 3b	-0.11 (-0.09)	0.16 (0.20)	0.02 (0.04)	-0.23 (0.09)	0.04 (0.20)	-0.10 (0.04)
Stage 3c	-0.16 (-0.11)	0.11 (0.19)	-0.02 (0.04)	-0.18 (-0.11)	0.09 (0.19)	-0.04 (0.04)
Stage 2	-0.14 (-0.09)	0.12 (0.18)	-0.02 (0.03)	-0.19 (-0.09)	0.08 (0.18)	-0.06 (0.03)
Stage 1	-0.25 (-0.20)	0.06 (0.11)	-0.18 (-0.08)	-0.28 (-0.20)	0.03 (0.11)	-0.15 (-0.08)

Table S2. Thermodynamics for M intercalation within a 4LG either in the presence or absence of a 2D-C_2HF SM. Binding energy with respect to the intercalation of different metals while using C_8M-type models are presented. The values presented outside and inside of parenthesis represent the BE for M intercalation in the presence or absence of a SM, respectively.

System	**Binding energy (BE) per metal atom (in eV)**					
	Positive modifier, 2D-C_2HF (no modifier)			Negative modifier, 2D-C_2HF (no modifier)		
Intercalated metal	Li	Na	K	Li	Na	K
Stage 3a	-0.24 (-0.17)	-0.03 (0.07)	-0.20 (-0.10)	-0.19 (-0.17)	0.02 (0.07)	-0.14 (-0.10)
Stage 3b	-0.17 (-0.17)	0.05 (0.06)	-0.11 (-0.10)	-0.32 (-0.17)	-0.11 (0.06)	-0.28 (-0.10)
Stage 3c	-0.23 (-0.18)	-0.01 (0.05)	-0.17 (-0.10)	-0.24 (-0.18)	-0.03 (0.05)	-0.19 (-0.10)
Stage 2	-0.19 (-0.15)	0.02 (0.07)	-0.16 (-0.10)	-0.24 (-0.15)	-0.04 (0.07)	-0.22 (-0.10)
Stage 1	-0.26 (-0.22)	-0.01 (0.06)	-0.33 (-0.17)	-0.29 (-0.22)	-0.06 (0.06)	-0.26 (-0.17)

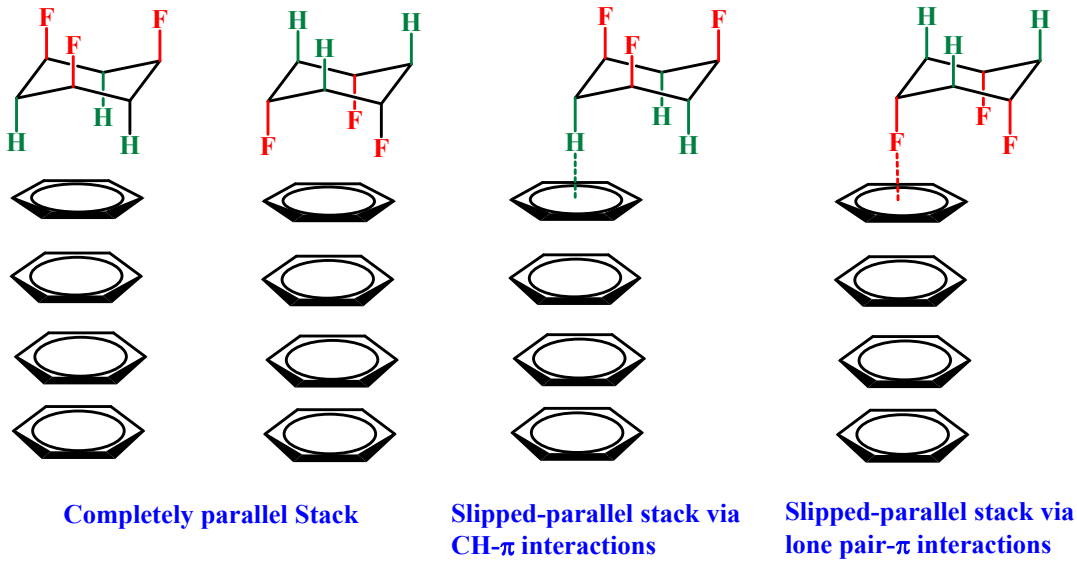

Figure S2. Schematic representation of different stacking arrangements of 4LG with the 2D SM layers.

Table S3. Thermodynamics for metal intercalation in 4LG modified by SM via different stacking arrangements shown in Figure S2. Binding energies calculated for M-4LG (both C_6M and C_8M type models), in which SM is stacked in either a complete-parallel (value outside parenthesis) or slipped-parallel (value inside parenthesis) stack conformation with M-4LG.

System	**Binding energy (BE) per *M* atom (in eV)**					
	Positive modifier, SM = 2D-C_2HF			Negative modifier, SM = 2D-C_2HF		
Intercalated metal	Li	Na	K	Li	Na	K
Stage 1 of C_6M model	-0.25 (-0.24)	0.06 (0.05)	-0.18 (-0.18)	-0.28 (-0.28)	0.03 (0.03)	-0.15 (-0.15)
Stage 1 of C_8M model	-0.26 (-0.27)	-0.01 (-0.02)	-0.33 (-0.33)	-0.29 (-0.30)	-0.06 (-0.06)	-0.26 (-0.26)

Table S4. Calculated binding energies for the *M* intercalation in 4LG either in the presence or absence of a 2D-C_2F surface modifier. The values presented outside and inside of parenthesis represent the BE for *M* intercalation in the presence or absence of a SM, respectively.

System	**Binding energy (BE) per metal atom (in eV)**					
	C_6M-type models			**C_8M-type models**		
	with SM, 2D-C_2F (no SM = pristine 4LG)			with SM, 2D-C_2F (no SM = pristine 4LG)		
Intercalated metal	Li	Na	K	Li	Na	K
Stage 3a	-0.17 (-0.09)	0.10 (0.20)	-0.05 (0.04)	-0.25 (-0.17)	-0.04 (0.07)	-0.21 (-0.10)
Stage 3b	-0.27 (-0.09)	-0.09 (0.20)	-0.14 (0.04)	-0.34 (-0.17)	-0.15 (0.06)	-0.31 (-0.10)
Stage 3c	-0.18 (-0.11)	0.10 (0.19)	-0.04 (0.04)	-0.25 (-0.18)	-0.04 (0.05)	-0.20 (-0.10)
Stage 2	-0.22 (-0.09)	0.03 (0.18)	-0.10 (0.03)	-0.27 (-0.15)	-0.08 (0.07)	-0.24 (-0.10)
Stage 1	-0.29 (-0.20)	0.0 (0.11)	-0.18 (-0.08)	-0.31 (-0.22)	-0.07 (0.06)	-0.42 (-0.17)

Table S5. Energy decomposition analyses of stage 1 structures of *M*-4LG and SM-*M*-4LG based on a distortion-interaction model (SM = 2D-C_2F). BE, E_{coh}, E_{dis}, and E_{int} represent the binding energy/atom, cohesive energy, distortion energy, and interaction energy, respectively.

System	BE (eV)	E_{coh} (eV)	E_{dis} (eV)	E_{int} (eV)
C_6Li	-0.20	1.63	0.03	-1.86
C_8Li	-0.22	1.63	0.04	-1.88
2D-C_2F…C_6Li	-0.29	1.63	0.03	-1.96
2D-C_2F…C_8Li	-0.31	1.63	0.04	-1.98
C_6Na	0.11	1.113	0.13	-1.14
C_8Na	0.06	1.113	0.17	-1.24
2D-C_2F…C_6Na	0.00	1.113	0.14	-1.25
2D-C_2F…C_8Na	-0.07	1.113	0.17	-1.36
C_6K	-0.08	0.93	0.21	-1.22
C_8K	-0.17	0.93	0.27	-1.36
2D-C_2F…C_6K	-0.18	0.93	0.22	-1.33
2D-C_2F…C_8K	-0.42	0.93	0.28	-1.62

Table S6. Energy decomposition analyses of stage 0 structures of *M*-4LG and SM-*M*-4LG based on a distortion-interaction model (SM = 2D-C_2F). BE, E_{coh}, E_{dis}, and E_{int} represent the binding energy/atom, cohesive energy, distortion energy, and interaction energy, respectively. **Stage 0 structures**

System	BE (eV)	E_{coh} (eV)	E_{dist} (eV)	E_{int} (eV)
C_6Li	0.05	1.63	0.03	-1.61
C_8Li	0.10	1.63	0.04	-1.57
2D-C_2F…C_6Li	-0.35	1.63	0.05	-2.04
2D-C_2F…C_8Li	-0.33	1.63	0.07	-2.03
C_6Na	0.12	1.113	0.09	-1.08
C_8Na	0.18	1.113	0.11	-1.04
2D-C_2F…C_6Na	-0.17	1.113	1.69	-2.97
2D-C_2F…C_8Na	-0.20	1.113	0.17	-1.48
C_6K	-0.09	0.93	0.14	-1.16
C_8K	-0.15	0.93	0.17	-1.24
2D-C_2F…C_6K	-0.38	0.93	0.19	-1.50
2D-C_2F…C_8K	-0.42	0.93	2.26	-3.61

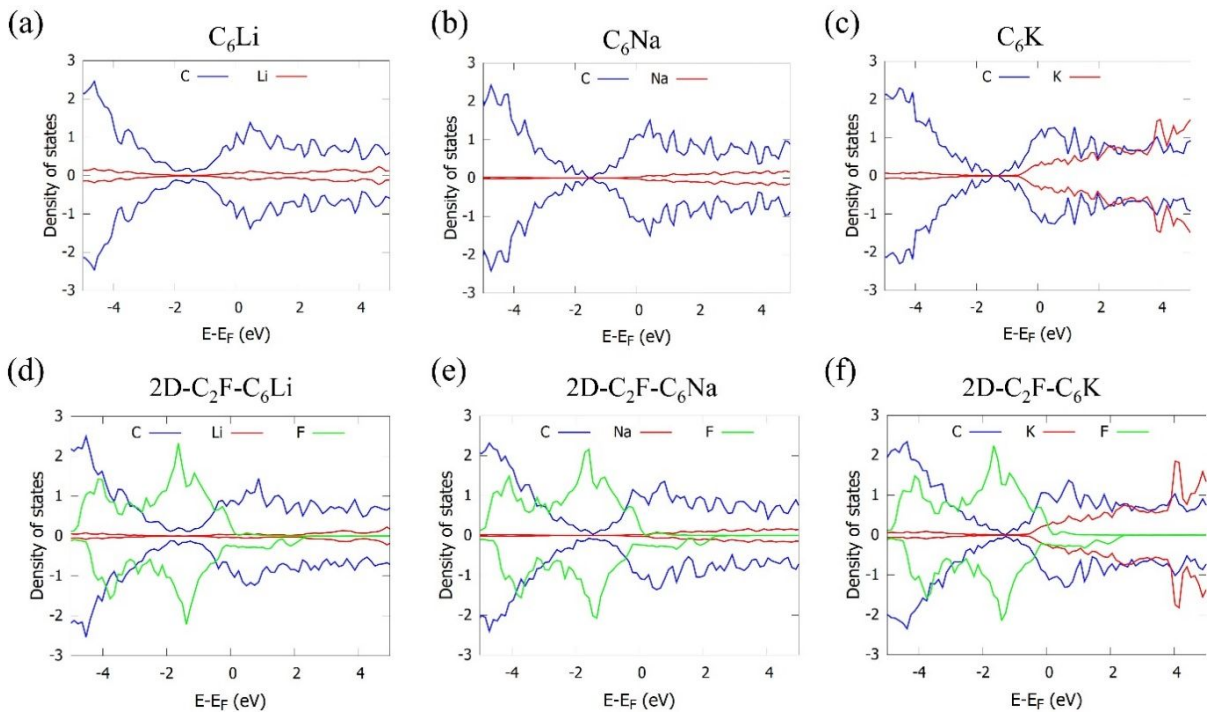

Figure S3. Calculated density of states for the stage 1 of different *M* intercalated 4LG and SM-4LG (SM = 2D-C_2F) systems.; (a) C_6Li, (b) C_6Na, (c) C_6K, (d) 2D-C_2F-Li, (e) 2D-C_2F-Na, and (f) 2D-C_2F-K. DOSs for C_6M-type configurations are presented.