Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Physisorption of benzene derivatives on graphene: critical roles of steric and stereoelectronic effects of the substituent

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Table S1 The minimal distance (d_m, Å) for the interaction between benzene derivative and the graphene surface at the three sites (H, B, O).

		a	b	c	d	e	f	g
1	**H**	3.647	3.647	3.647	3.647	3.647	3.647	3.647
	B	3.644	3.644	3.644	3.644	3.644	3.644	3.644
	O	3.646	3.646	3.646	3.646	3.646	3.646	3.646
2	**H**	3.604	3.615	3.634	3.611	3.629	3.593	3.631
	B	3.538	3.615	3.626	3.607	3.633	3.606	3.620
	O	3.599	3.614	3.629	3.615	3.597	3.591	3.623
3	**H**	3.144	2.934	2.783	3.337	2.997	2.592	2.956
	B	3.170	2.948	2.790	3.333	3.029	2.593	2.955
	O	3.272	2.959	2.779	3.335	3.010	2.587	2.750
4	**H**	2.624	3.039	2.901	2.718	3.066	2.816	3.056
	B	2.621	3.017	2.905	2.624	3.066	2.821	3.057
	O	2.618	3.045	2.904	2.618	3.062	2.815	3.052
5	**H**	2.733	2.961	2.859	2.835	2.918	2.876	3.220
	B	2.712	2.957	2.766	2.841	2.892	2.892	3.212
	O	2.769	2.953	2.853	2.818	2.994	2.698	3.102
6	**H**	3.395	3.175	3.437	3.658	3.145	3.436	3.510
	B	3.317	3.168	3.135	3.542	3.104	3.082	3.442
	O	3.307	3.128	3.331	3.466	3.071	3.202	3.260
7	**H**	3.621	3.611	3.564	3.609	3.622	3.623	3.645
	B	3.657	3.610	3.566	3.433	3.632	3.619	3.644
	O	3.612	3.607	3.545	3.435	3.621	3.618	3.636
8	**H**	3.503	2.777	3.544	3.574	2.776	3.542	2.864
	B	3.338	2.862	3.538	3.562	2.845	3.399	2.822
	O	3.498	2.810	3.546	3.558	2.796	3.334	2.836
9	**H**	3.402	3.578	3.521	3.555	3.281	3.551	3.577
	B	3.391	3.104	3.449	3.550	3.185	3.527	3.572
	O	3.384	3.109	3.280	3.536	3.189	3.479	3.503
10	**H**	3.159	3.163	3.589	3.546	2.847	3.566	3.107
	B	3.228	3.150	3.517	3.178	2.809	3.565	3.260
	O	3.163	3.105	3.538	3.559	2.789	3.580	3.214
11	**H**	3.594	3.622	3.614	3.634	2.742	3.621	3.503
	B	3.605	3.623	3.617	3.624	2.667	3.609	3.506
	O	3.597	3.617	3.615	3.639	2.756	3.587	3.528
12	**H**	3.495	3.043	3.537	3.648	2.694	3.663	2.855
	B	3.496	3.166	3.482	3.657	2.702	3.522	2.801
	O	3.497	3.009	3.511	3.666	2.709	3.672	2.810
13	**H**	2.786	2.817	2.766	2.929	2.689	2.835	2.894
	B	2.789	2.776	2.678	2.936	2.699	2.746	2.891
	O	2.814	2.812	2.757	2.928	2.719	2.838	2.918

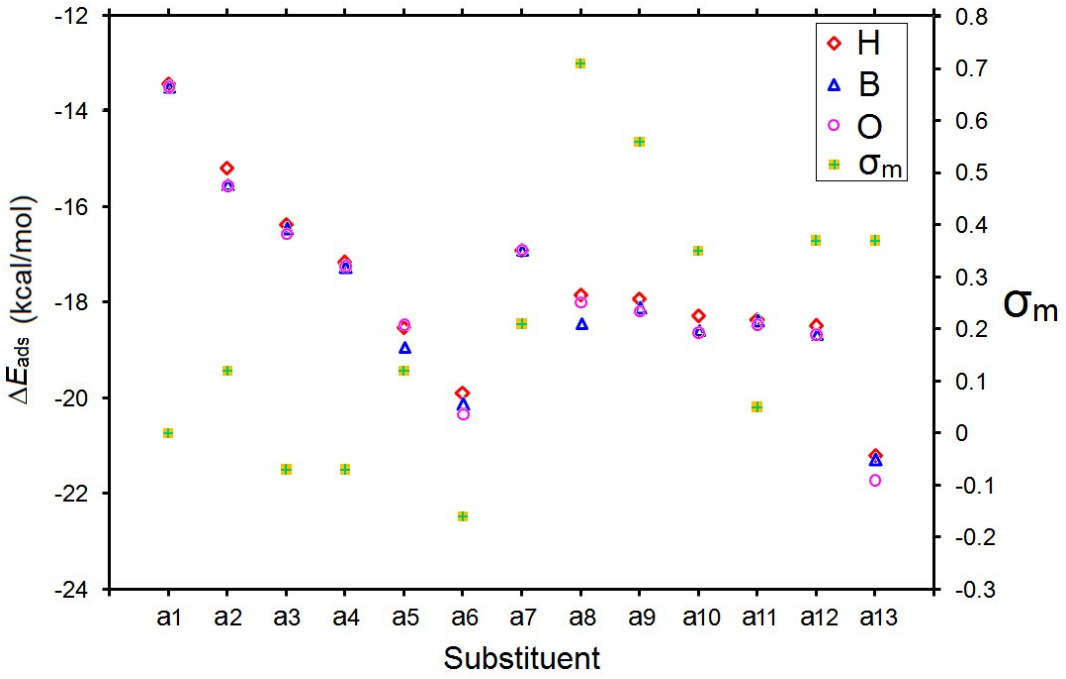

Fig. S1 The relationship between the Hammett sigma *meta* constant (σ_m) and the interaction energies.

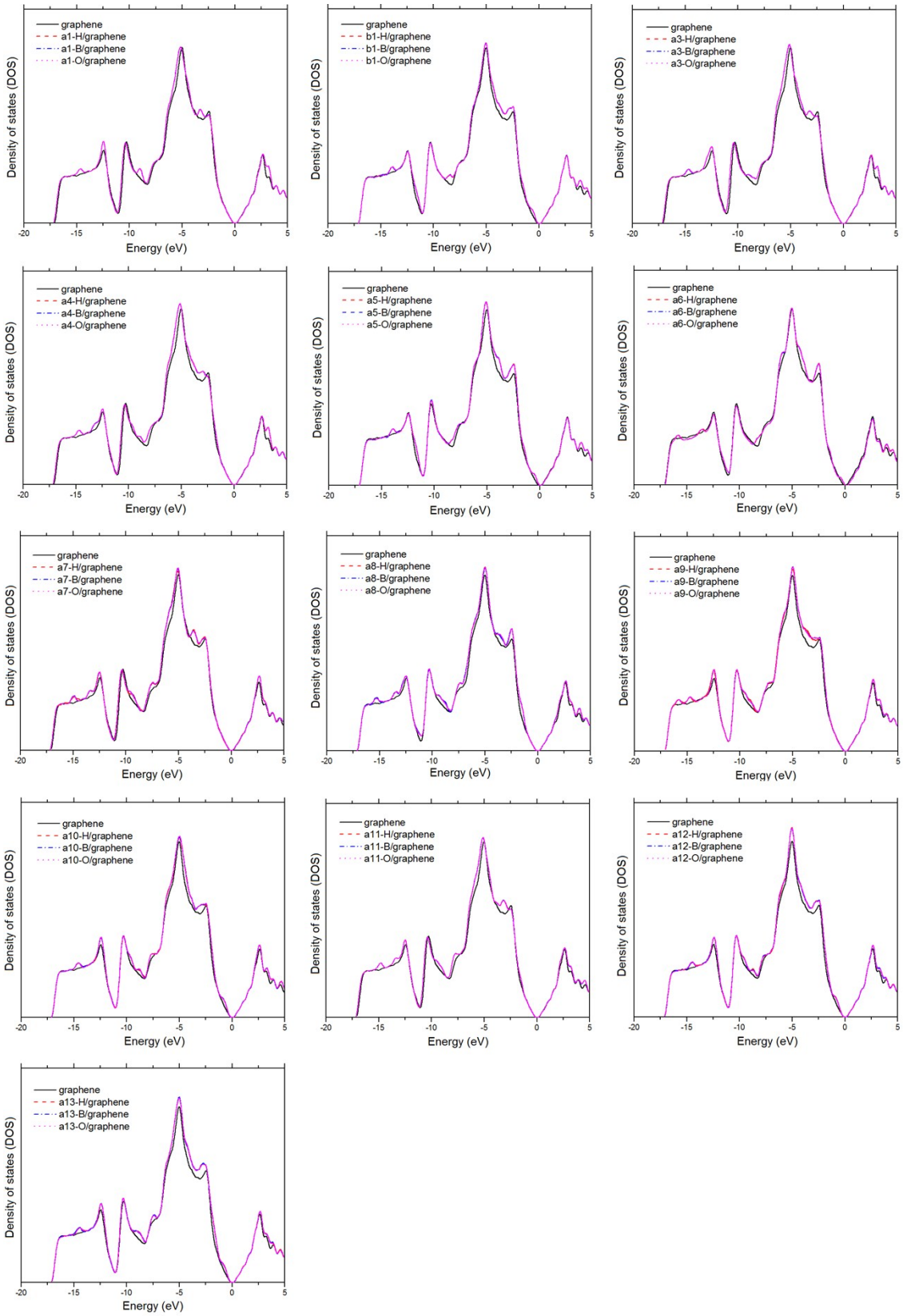

Fig. S2 Total electronic DOSs for graphene and molecule/graphene systems with three different adsorption (H, B, O) sites. The Fermi level is set to zero.

Table S2 The HOMO and LUMO orbital energies (in eV) for molecules (**a1-13**).

Orbital	**a1**	**a2**	**a3**	**a4**	**a5**	**a6**	**a7**	**a8**	**a9**	**a10**	**a11**	**a12**	**a13**
HOMO	–8.37	–7.67	–8.02	–8.00	–7.53	–6.79	–7.94	–9.26	–8.90	–8.81	–7.63	–8.75	–8.65
LUMO	0.52	0.35	0.54	0.50	0.51	0.41	–0.30	–1.67	–0.80	–1.05	–0.38	–0.72	–0.57