Electronic Supplementary Material (ESI) for Nanoscale

Signatures in vibrational and UV-visible absorption spectra for identifying cyclic hydrocarbons by graphene fragments

Yan Meng,[a,b] Qi Wu,[b, c] Lei Chen,[a, d] Sonam Wangmo,[a] Yang Gao,[a] Zhigang Wang,*[a, c]
Rui-Qin Zhang,*[b, c] Dajun Ding,[a] Thomas Niehaus[e] and Thomas Frauenheim[f]

Supporting Information

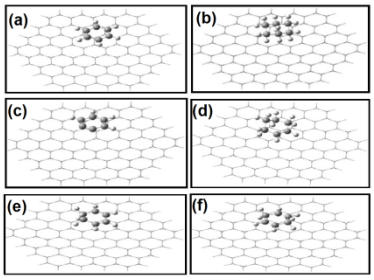

Fig. S1 The neutral systems of C_6H_6, C_6H_{12}, C_6H_4, C_6H_{10}, C_6H_8(1) and C_6H_8(2) adsorbed on the graphene fragment, respectively. a–f severally represent the corresponding adsorption systems.

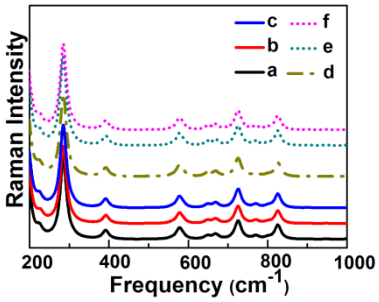

Fig. S2 The Raman spectra between 200 and 1000 cm^{-1} of the six neutral adsorption systems.

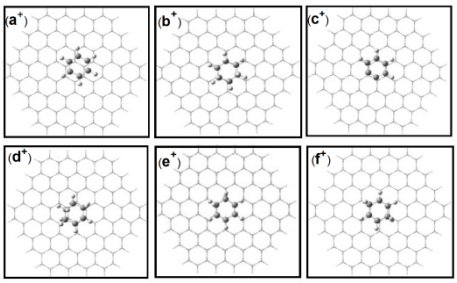

Fig. S3 a^+- f^+ represent the six adsorption systems carrying +1e charge, respectively.

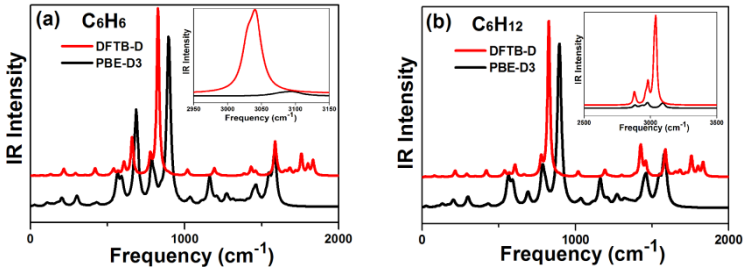

Fig. S4 IR spectra of the two approaches (1) entirely based on the DFTB-D method, 2) entirely based on the PBE-D3 method), the scaling factor of PBE-D3 is 0.986 cm^{-1}. (a) IR spectra of the Gra-C_6H_6 complex, the inset explains the spectra between 2950 and 3150 cm^{-1}. (b) IR spectra of the Gra-C_6H_{12} complex, and the inset shows the spectra changing from 2500 to 3500 cm^{-1}.

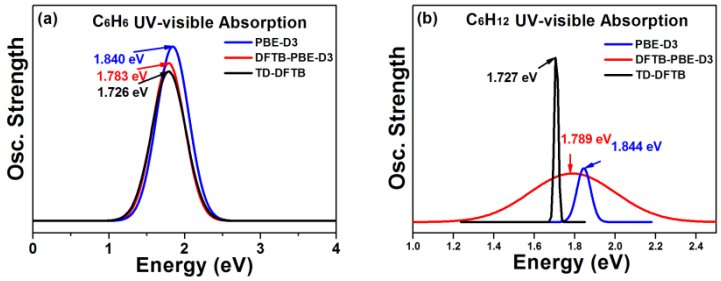

Fig. S5 UV-visible absorption spectra of the three approaches (1) DFTB-D optimizations with further TD-DFTB calculations at the same level, 2) DFTB-D optimizations with further PBE-D3 calculations, denoted as the DFTB-PBE-D3, 3) PBE-D3 optimizations with further PBE-D3 calculations at the same level) (a) UV-visible absorption spectra of the Gra-C_6H_6 complex. (b) UV-visible absorption spectra of the Gra-C_6H_{12} complex.

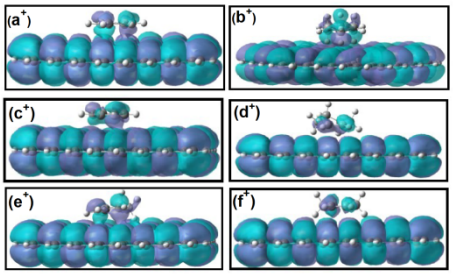

Fig. S6 The highest occupied molecular orbitals (HOMOs) for the ionic adsorption systems between six hydrocarbons and the graphene.

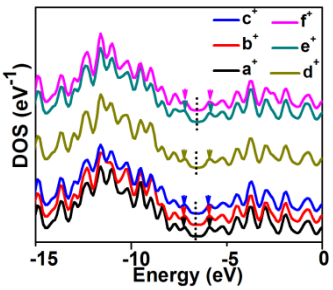

Fig. S7 The density of states (DOS) for the ionic adsorption systems. The arrows represent HOMO and LUMO, respectively, and the dotted line refers to place of the Fermi energy.

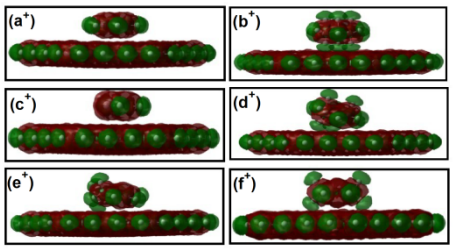

Fig. S8 The differential charge isosurface of the ionic adsorption systems.

Table S1 The absorption transition energies, oscillator strength, and transition orbital of the six ionic adsorption systems.

Ionic geometry	E (eV)	Oscillator strength	Orbital Transition
a^+	1.713	0.676	HOMO-1 → LUMO+1
b^+	1.715	0.684	HOMO-1 → LUMO+1
c^+	1.408	0.008	HOMO → LUMO
	1.702	0.227	HOMO → LUMO+2
d^+	1.407	0.008	HOMO → LUMO
	1.705	0.039	HOMO → LUMO+2
e^+	1.403	0.009	HOMO → LUMO
	1.633	0.057	HOMO-2 → LUMO+1
f^+	1.404	0.009	HOMO → LUMO

Table S2 The largest oscillator strengths, the corresponding absorbed energies (E) and the orbital transitions in the neutral systems of the Gra-C_6H_6 and the Gra-C_6H_{12} complex, based on three methods.

TD-DFTB (DFTB-PBE-D3) {PBE-D3}	E (eV)	Oscillator strength	Obital Transiton
a	1.726	0.675	HOMO-1 → LUMO+1
	(1.783)	(0.543)	(HOMO-1 → LUMO+1)
	{1.840}	{0.719}	{HOMO → LUMO+1, HOMO-1 → LUMO}
b	1.727	0.682	HOMO-1 → LUMO+1
	(1.789)	(0.672)	(HOMO-1 → LUMO+1)
	{1.844}	{0.744}	{HOMO-1 → LUMO}