ELECTRONIC SUPPORTING INFORMATION (ESI)

Pentacene on Ni(111): room-temperature molecular packing and temperature-activated conversion to graphene

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Supporting Table

Surface	Precursor	T [°C]	Ref.	Observations about quality
Ni(111)	CO	> 300	[1]	ILS, ELS, (graphitic)
	ethylene (C_2H_4)	475	[2]	Auger (carbon peak - graphitic line shape)
	ethylene (C_2H_4)	400-500	[3]	STM
	propylene (C_3H_6)	500	[4-9]	-
	ethylene (C_2H_4)	425-525	[10]	STM (small graphitic domains)
	ethylene (C_2H_4)	~550	[11]	LEEM
	toluene (C_7H_8)	400-650	[12, 13]	STM,
	ethylene (C_2H_4)	460-650	[14, 15]	STM, Auger
	ethylene (C_2H_4)	675	[16]	STM
	graphite, thermal doping	725-825	[17]	Auger, LEED
	benzene (C_6H_6)	800-900	[18, 19]	-
	graphite, thermal doping	730-1015	[20]	STM
Ni(111)/ W(110)	propylene (C_3H_6)	400	[21]	ARPES
Ni(111) /MgO(111)	propylene	600-680	[22]	STM, LEEM
Ni(111) /Al_2O_3(0001)	methane (CH_4)	900-980	[23]	STM
Ni-poly.	C_{60}	760-825	[24]	-
Ni/SiO_2	graphite powder; specialized preparation, by diffusion of carbon in a carbon-nickel/substrate sandwich	25–260	[25]	Raman
Ni/SiO_2	methane (CH_4)	800	[26]	-
Ni/SiO_2	methane (CH_4)	900-1000	[27]	-
Ni/SiO_2	methane (CH_4)	1000	[28]	-
Ni/SiO_2	methane (CH_4), poly(methyl methacrylate) (PMMA), high impact polystyrene (HIPS) or acrylonitrile butadiene styrene (ABS)	1000	[29]	-
Ni/plastic, glass	graphite powder; by diffusion of carbon in a carbon-nickel/substrate sandwich	< 160	[25]	Raman, (nanocrystalline graphene)

Table S1. Graphene growth on the Ni(111) as well as plastic/glass surfaces coated with a Ni film (the Ni films in Ref. 25 had a strong (111) texture);[25] reported precursors and thermal conditions. (ILS – ionization loss spectroscopy, ELS – energy-loss spectroscopy, LEED – low-energy electron diffraction, STM – scanning tunnelling microscopy, LEEM – micro LEED, ARPES – angle-resolved photoemission spectroscopy.)

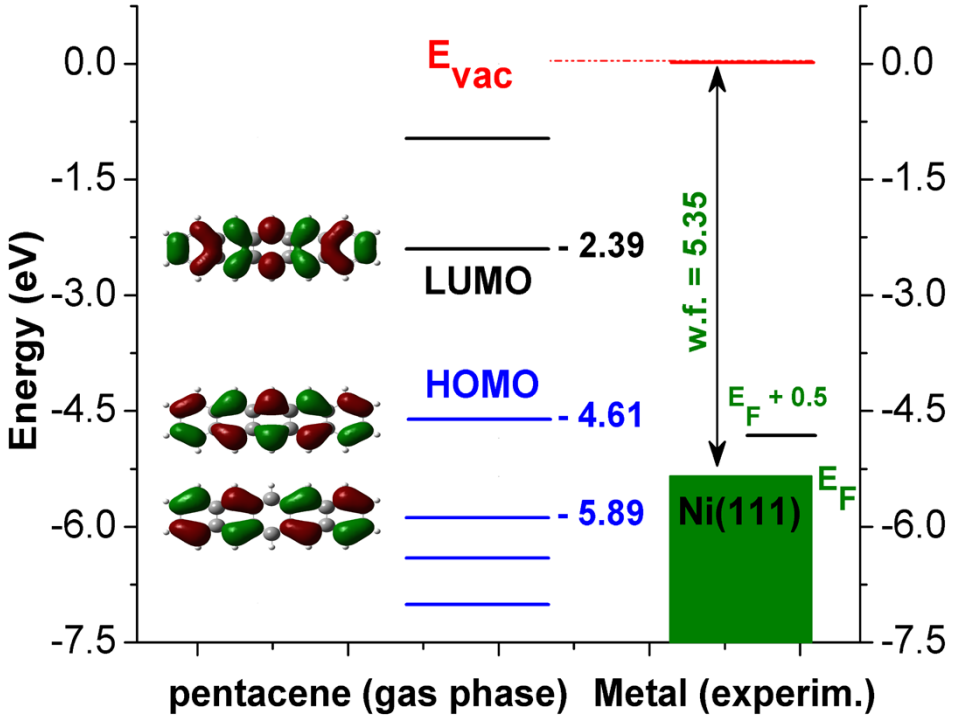

Fig. S1. Basic energetics of pentacene and Ni(111), as separate systems. The calculated molecular orbitals of a single pentacene molecule (iso value = 0.02 electrons/Bohr^3) are visually represented alongside the corresponding energies for the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). The calculations were performed using DFT at the B3LYP/6-31G(d) level. A representation of the nickel Fermi energy (E_F) is schematized as well, using the literature reported value of 5.35 eV (experimental) for the work function (w.f.) of its (111) facet.[30] Since the Fermi level of Ni(111) is about 5.35 eV below the vacuum level and 0.74 V below the HOMO,[30] a first order approximation suggests that the HOMO is emptied upon adsorption on Ni(111). At either positive (+0.5 V) or negative (-0.5 V) bias voltages commonly used to image the pentacene on the Ni(111) surface, HOMO-1 is the only accessible molecular state. However, systematic sub-molecularly resolved STM images at biases close to the Fermi level of Ni(111) (Fig. 1(a) from the main article; Fig. S2) show a remarkable similarity with the calculated HOMO orbitals of pentacene, which should normally be revealed at a much higher bias voltage. This suggests that pentacene adsorbed on Ni(111) is chemisorbed, and that the presence of the metallic surface lowers and broadens the pentacene molecular orbitals,[31] by direct coupling of the surface electronic states with the molecular states.[32, 33] The Ni(111) surface possesses indeed three surface states. The first two, close to the Fermi level, are at 20 and 250 meV. Originating in the *d* bands of the outermost Ni(111) atomic layer, a third surface state is placed 1.19 eV away of the Fermi level.[34]

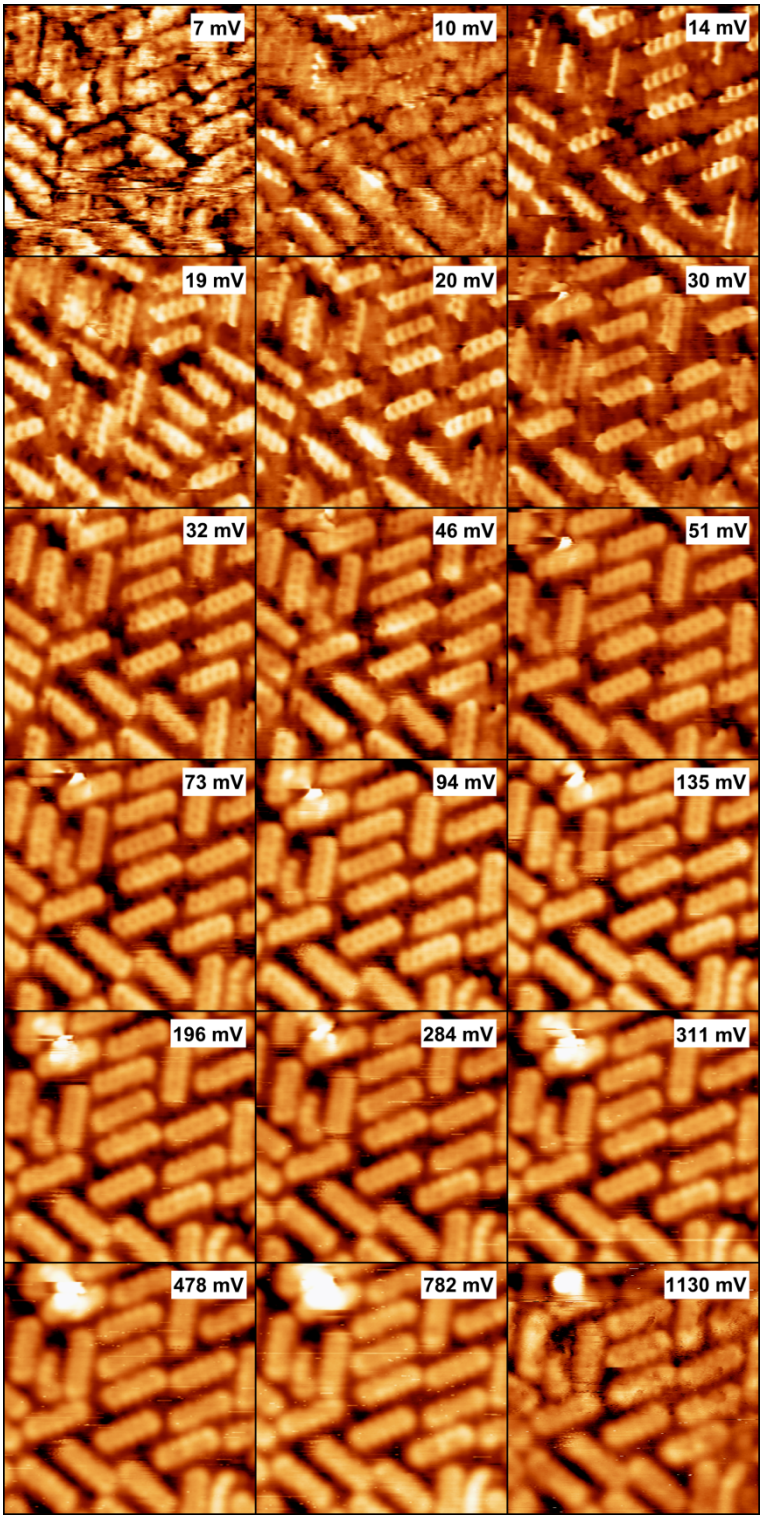

Fig. S2. Bias-dependent STM images of pentacene on Ni(111). Image parameters: 5×5 nm^2, 0.94 nA and bias voltage as indicated on the upper-right corner of each STM image.

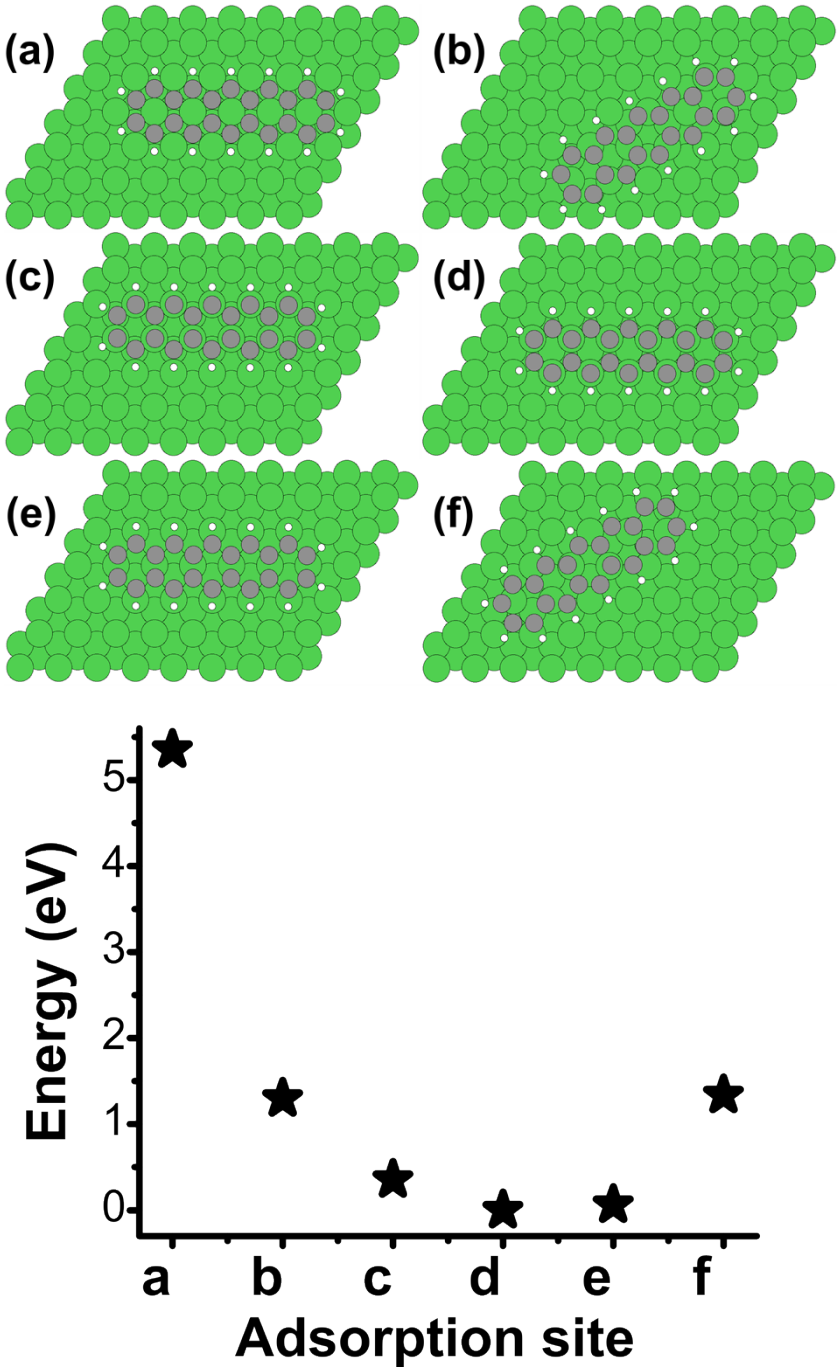

Fig. S3. Site dependent pentacene adsorptions on the Ni(111) substrate. The calculated binding energies (LDA) are visually represented with respect to the energetically most stable conformation in (d), which is the most negative value of the energy. Adsorption sites are graphically defined and represented as: planar pentacene adsorption with the central carbon ring on top of a nickel atom and aligned parallel to one lattice direction is depicted in the (a) top-0°, with the phenyl rings centered on nickel atoms along the $\langle 1\bar{1}0 \rangle$; (b) hollow-30°, where the pentacene is oriented along $[2\bar{1}1]$ with the central ring centered on a nickel fcc site; (c) hollow-hcp, the pentacene oriented along the $\langle 1\bar{1}0 \rangle$ with all the rings centered on fcc nickel sites, one

carbon is placed atop of a nickel atom and the next carbon above of a fcc site; (d) *hollow-fcc*, the pentacene oriented along the $\langle 1\bar{1}0 \rangle$ with all the rings centered on hcp surface sites, one carbon atom atop of a nickel atom and the next carbon above of a hcp site; (e) *bridge-top* and (f) bridge-30°, similar to bridge-top but rotated to 30° along the $[2\bar{1}1]$. Angles are expressed in reference to the $[1\bar{1}0]$ directions.

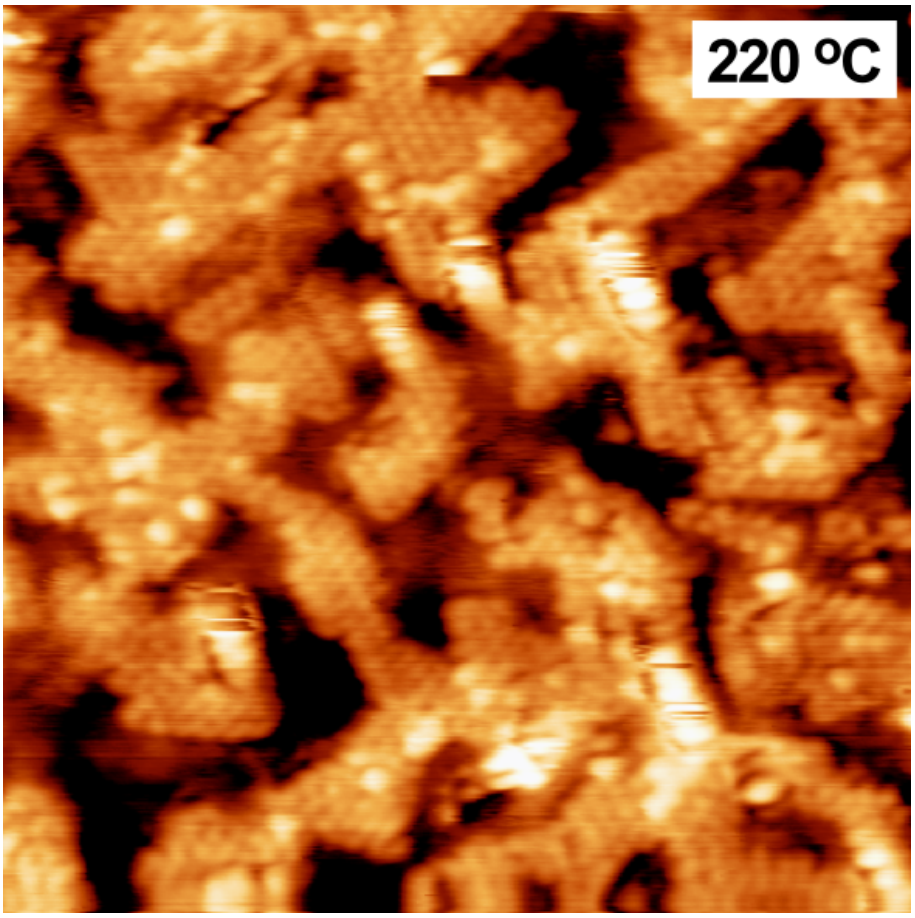

Fig. S4. High resolution 10×10 nm^2 STM image of graphitic domains on the Ni(111) substrate; prior to imaging the sample was annealed for 15 minutes at 220 °C. STM parameters: 1.47 nA, 10.68 mV.

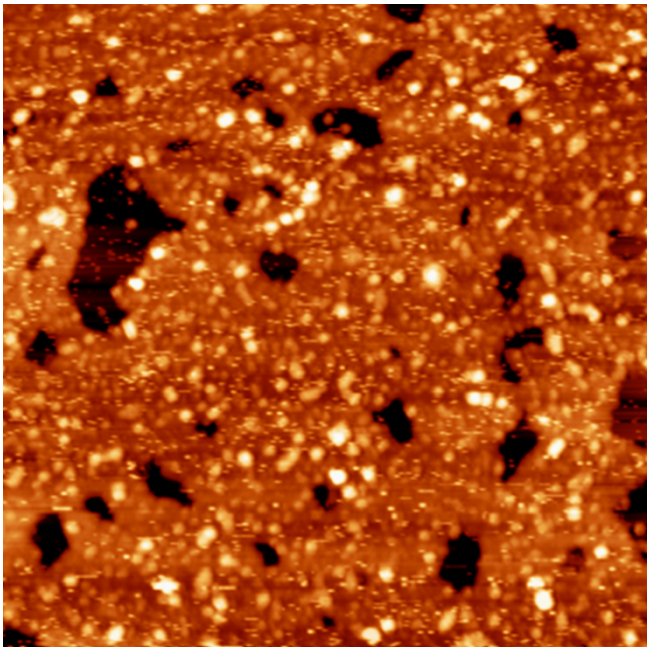

Fig. S5. 50×50 nm^2 STM image of graphitic domains on Ni(111), starting from pentacene coverage >ML; prior to imaging the sample was annealed for 15 minutes at 250 °C. STM parameters: -0.93 nA, -6.71 mV.

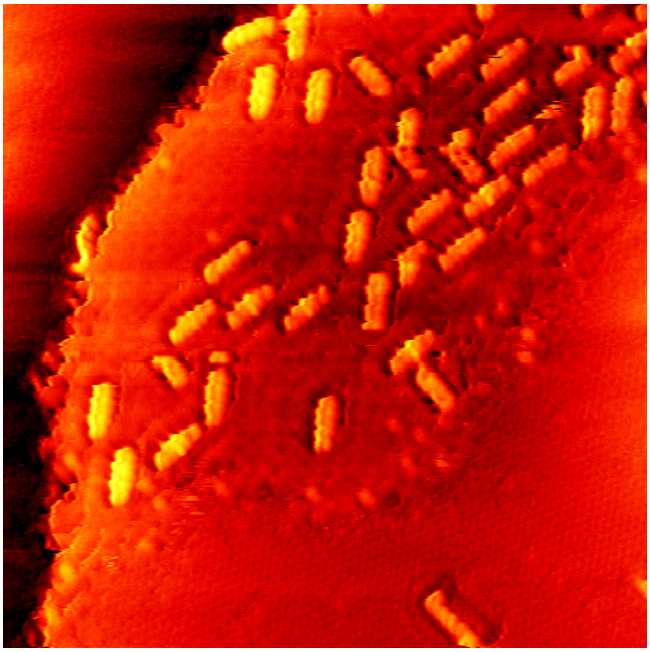

Fig. S6. Room temperature 15×15 nm^2 STM image of pentacene/Ni_2C, and graphene/Ni(111) obtained from pentacene precursor after annealing at 700 °C for 20 min. STM parameters: 1.24 nA, 3.05 mV.

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