SUPPLEMENTARY INFORMATION

Electronic effects of the Bernal stacking of graphite on self-assembled aromatic adsorbates

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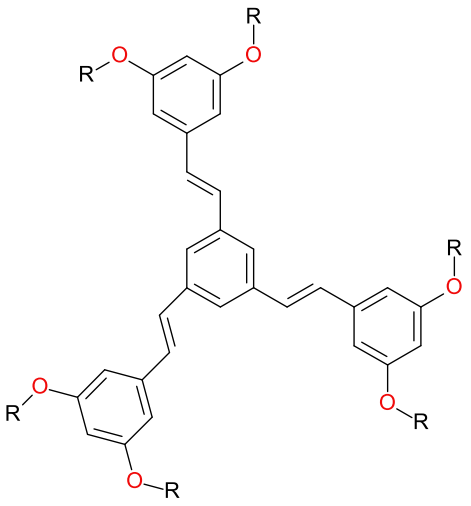
Method section

For this study, two related carbon based substrates, i.e. HOPG (SPI supplies, grade 2) and monolayer CVD graphene on copper foil (Graphenea), were used. Atomically clean surfaces were obtained either by cleaving the graphite substrate with the adhesive tape technique or by keeping graphene/copper substrate in a nitrogen sealed bag. After the atomic structure of both surfaces were checked by STM under air atmosphere the molecular monolayers were grown on top of both substrates by dropping a 5-µl phenyloctane solution of three similar in structure but different in size molecules from the TSB family:



TSB-C*n*

TSB-C*n* (see chemical formula above, R = C_nH_{2n+1}, with *n* = 8, 10 and 12) were synthesized and purified by adapting the procedure described in the litterature24 with 3,5-dialkyloxybenzaldehyde. 1-phenyloctane (Sigma-Aldrich, purity 98%) was used as received. Room temperature STM images were acquired using a homemade system operated in the height mode and liquid-solid interface. The tips were mechanically fabricated from a 250-µm Platinum-Iridium wire (Goodfellow, Pt80Ir20). The scanning parameters of STM images were: **1.a**: setpoint I_T = 16 pA, sample bias V_T = +890 mV; **1.b**: I_T = 15 pA, V_T = +1100 mV; **1.c**: I_T = 12 pA, V_T = +700 mV; **1.d**: I_T = 15 pA, V_T = +760 mV; **1.e**: I_T = 15 pA, V_T = +1100 mV; **1.c**: I_T = 24 pA, V_T = +850 mV ; **3.a**: I_T = 15 pA, V_T = -1000 mV; **1.c**: I_T = 16 pA, V_T = +890 mV; **4.a**: I_T = 19 pA, V_T = +1100 mV; **1.c**: I_T = 18 pA, V_T = +1000 mV.

Relative domain orientations for TSB-Cn on graphene

Because of the roughness of the underlying graphene substrate (copper foil) additional random bumps are superimposed to TSB-C*n* lattice, with a larger contrast. A Fourier analysis and high-pass filtering must be applied to isolate the molecular lattice prior to its analysis. The procedure is explained in figure SI-1*a*-*c* and its caption in the case of TSB-C8.

The results obtained with TSB-C10 are presented in figure SI-2.

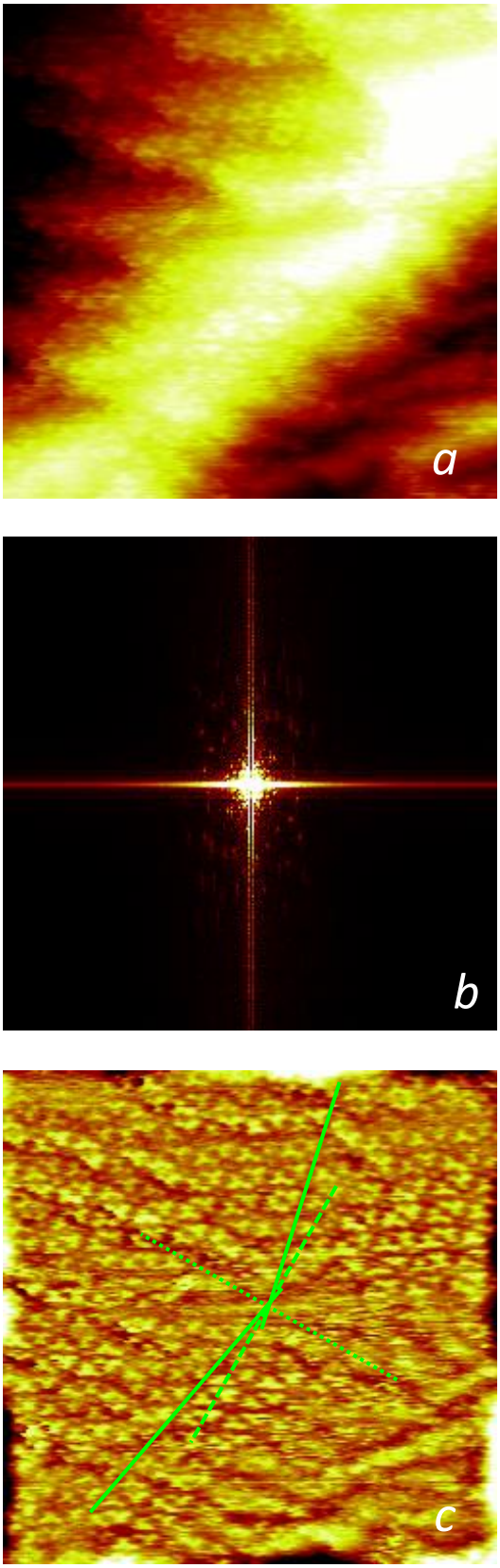


Figure SI-1 : Self-assembly of TSB-C8 on graphene. *a*: raw STM image of TSB-C8 on CVD graphene on copper foil (34nm×34nm, no drift correction). *b*: Fourier-transform of (*a*) showing the two hexagonal diffraction points for the L and R domains. *c*: high-pass filtered image (*a*) showing the above-mentioned L and R domains in the direct space. The lattice directions are highlighted in green.

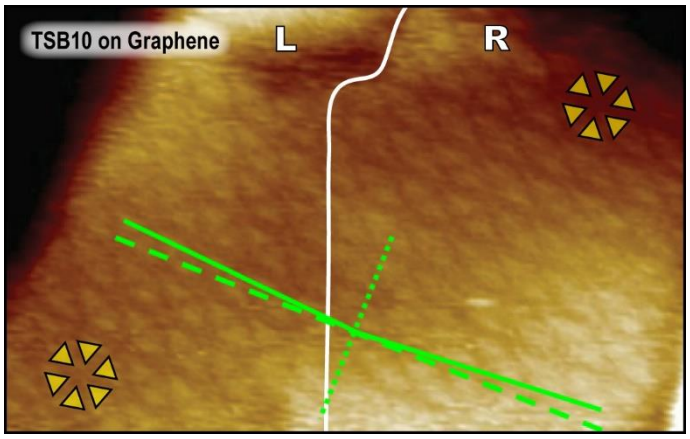


Figure SI-2 : STM image of TSB-C10 L and R domains on CVD graphene on copper foil. The domain delimitations (white line) and directions with respect to graphene (green lines) are superimposed.