Supporting Information for

Quasi-Layer-by-Layer Growth of Pentacene on HOPG and Au Surfaces

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1. Height profile of vacuum deposited *n*-dotriacontane on HOPG

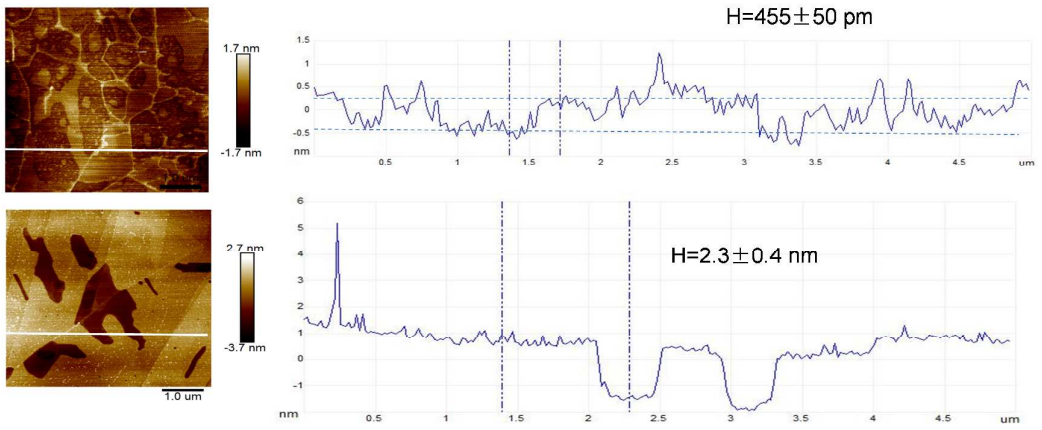

Figure S1. AFM height image of (upper) monolayer of vacuum deposited *n*-dotriacontane, (down) multiple layer of vacuum deposited *n*-dotriacontane.

2. Optical image of 2 nm vacuum deposited *n*-dotriacontane on HOPG

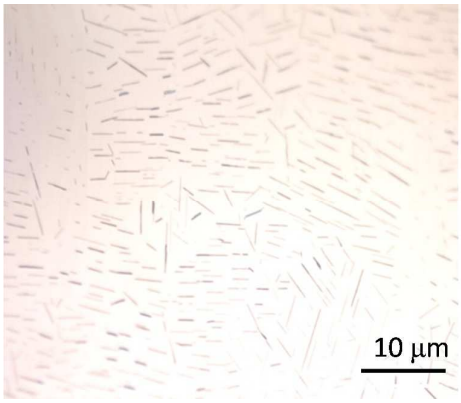

Figure S2. Optical image of *n*-dotriacontane(VD) on HOPG, many needle crystals were observed on the surfaces.

3. Monolayer determination by STM characterization

In order to confirm the thickness of $C_{32}H_{66}$, we performed STM in different conditions to check the information. The process is that: after the layer preparation, we first used STM to characterize the surface morphology, as shown in Figure S3a; and then we zoomed in and scarped the marked area by repeatedly fast scanning under different current and bias condition. Subsequently, we zoomed out and measured the same area and obtained the result in Figure S3b. The marked area presented some featureless morphology, suggested that the C32 layer was scraped off. We further characterized the packing of the substrate by zoomed in to the featureless area.

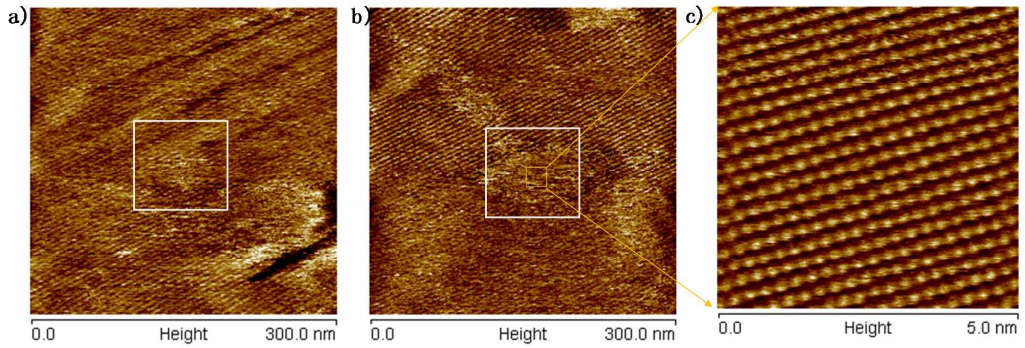

Figure S3. a) STM image of *n*-dotriacontane(SP) on HOPG before scraping, the inset marked the area for scraping. b) STM image of *n*-dotriacontane(SP) on HOPG after scraping, we can observe the marked present featureless morphology rather than the ordered assemble layer as that in a). c) the zoom in image of the scraped area, clear HOPG surface were observed.

4. Morphology or pentacene on SiO_2 and others

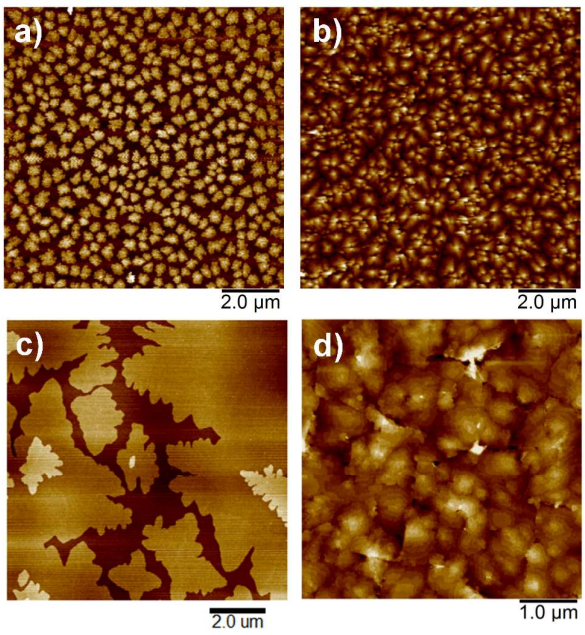

Figure S4. AFM height image of a) 2 nm and b) 10 nm pentacene on bare SiO_2 substrates. c) 2 nm *p*-6P on *n*-dotriacontane (SP) modified HOPG, d) 30 nm pentacene on *n*-dotriacontane (SP) modified graphene.

5. NEXAFS characterization

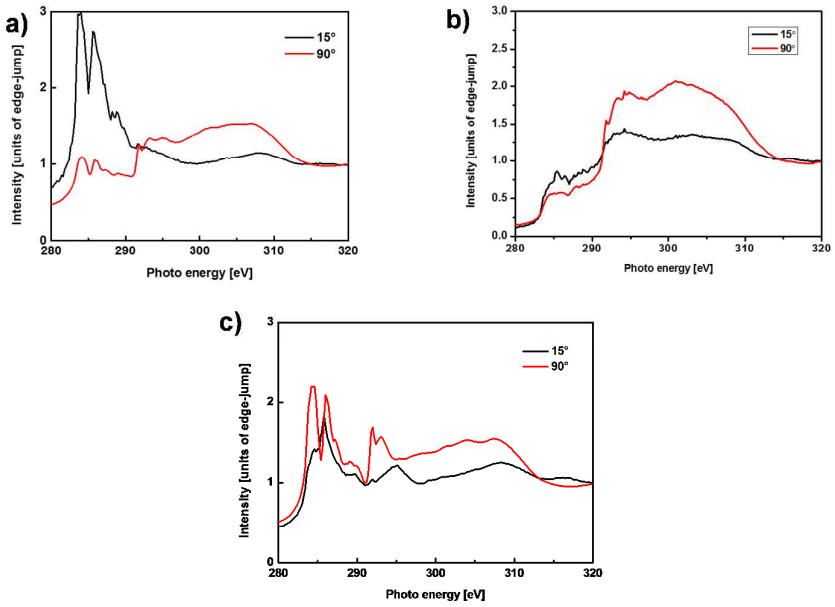

Figure S5. C1s NEXAFS spectra of the series of films: a) 1 nm pentacene on HOPG, b) 10 nm pentacene on HOPG, c) 10 nm pentacene on *n*-dotriacontane (SP) modified HOPG

6. DFT calculation.

The DFT calculation was based on the following condition: 1) VASP code, 2) GGA-PBE pseudopotential, 3) vdW-D3 method, 4) energy cutoff 400eV, 5) 20Å vacuum layer, 6) 1× 1 × 1 k-mesh for geometry optimization.

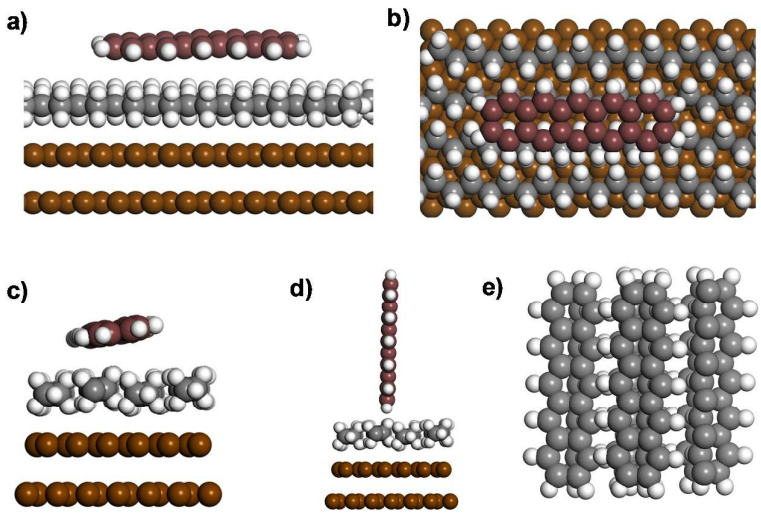

Figure S6 a-d) Absorption geometry of lying down (a-b), tilting (c), upright (d) pentacene on $C_{32}H_{66}$/HOPG, e) the packing mode of pentacene crystal. The interaction energy calculated between the lying down pentacene and the $C_{32}H_{66}$ layer is about -0.74 eV, while the interaction energy between the pentacene molecules is about -1.08 eV.

Table S1. Interaction energy of pentacene-modified substrate and the pentacene-pentacene in the crystals

Configurations	Molecular interaction (eV)
Lying (pentacene-C_{32})	-0.74
Standing (pentacene-C_{32})	-0.20
tilting (pentacene-C_{32})	-0.62
Lattice (pentacene-pentacene)	-1.08

7. Contact angle measurement

The static angle was characterized by the OCA 15 Full automatic optical contact angle measuring instrument (Dataphysics). Both HOPG and modified HOPG substrates were measured.

Table S2. The static contact angle of HOPG and C32/HOPG

	Water	**ethylene glycol**	**surface energy （mN/m）**
Bare HOPG	67.9^{o}	27^{o}	43.39
C32/HOPG	108^{o}	71^{o}	33.11