

Supporting information to Hexadecadienyl Monolayers on Si(111): Faster Formation, Improved Surface Coverage

Derivation of equation for monolayer thickness

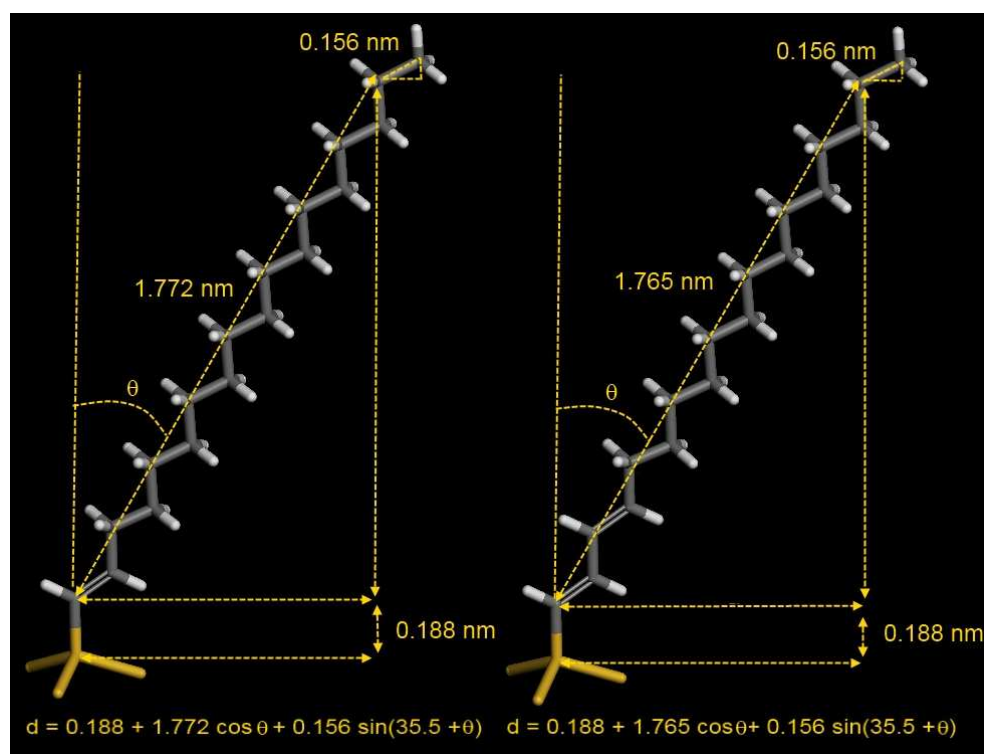


Figure S1. Derivation of the monolayer thickness by using the length of the carbon chain, the Si-C bond length and the tilt angle (θ).

Modeling studies in Materials Studio

The modeling of the monolayers on silicon was performed following the procedures as described previously.^{1,2} Since the packing energies were combined with the binding energies, only one series of coverage patterns was used. In order to allow comparison with literature values, a single set of patterns from ref. 1 (A series, See Figure S2) was used.

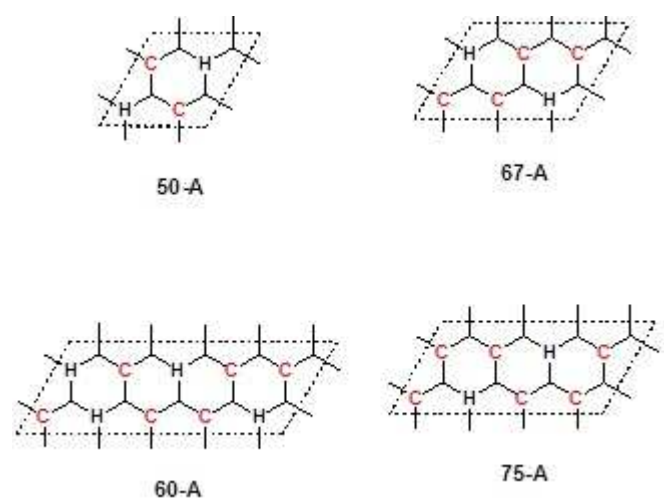


Figure S2. Patterns used in monolayer simulations.

Unit cells were constructed, with dimensions $a = b = 3.840 \text{ \AA}$, $c = 35 \text{ \AA}$, $a = b = 90^\circ$, and $g = 120^\circ$ (See Figure S3). The cells were expanded to larger cells (2 x2, 2x3, 2x4 or 2x5) and chains were replaced by hydrogen to achieve the desired pattern. The cells were then expanded to supercells of 12x12 units (33, 50, 67 and 75% surface coverage) and 10x15 units (60% surface coverage).³

The geometries were optimized using the polymer consistent force field (PCFF) (bottom two rows of Si atoms were constrained) as implemented in the Discover package in Materials Studio, using the ultrafine settings of the smart minimizer routine (line width 0,01 and convergence 10^{-5} , VdW and coulomb, atom centered and long-range correction switched off).

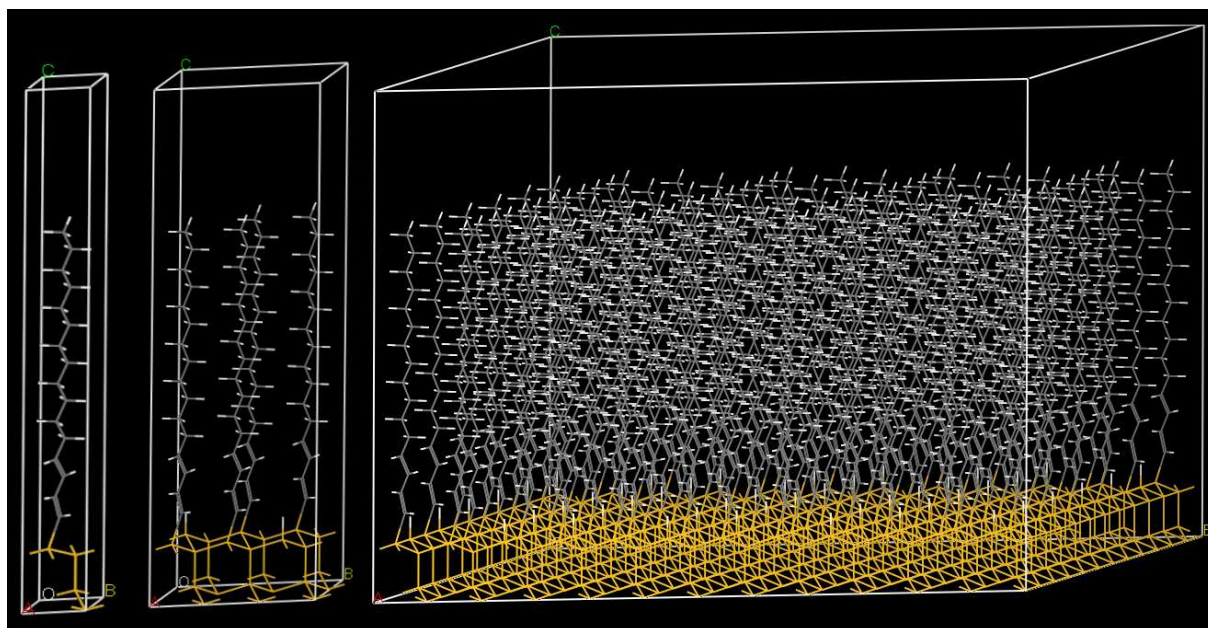


Figure S3. Construction of monolayer geometries from a single unit cell (left) to the desired pattern (middle), and finally the entire monolayer (right).

DFT calculations of XPS binding energies.

XPS binding energies were estimated by calculating the orbital energies of molecular analogues of chains attached to a silicon surface which was mimicked by a $\text{Si}(\text{SiH}_3)_3$ group (See Figure S3). The geometries were optimized with B3LYP/6-311G(d,p), using the Gaussian 09 package.⁴ The carbon binding energies were then estimated by calculating the 1s core energy versus the average of the 2p valence orbital energies (mimicking the Fermi level).

The calculations show that the peaks at 283.8 eV can be attributed to carbons attached to silicon. (both 283.9 eV, See Figure S3). Sp^2 hybridized carbons, show a binding energy around 285.7 eV, as the stronger electronegativity will increase the binding energy. Regular sp^3 hybridized carbons give a binding energy of 295.0 eV. Calculations of the binding energies of the hexadecenyl chain attached to the surface give three peaks: at 283.9 eV for the carbon attached to the silicon, at 285.0 eV for the aliphatic carbons, and at 285.8 eV for the

sp^2 carbons, in the ratio of 1:14:1 (See Fig. S3A). The different attachment modes of the 3-en-1-yne give a very different pattern of binding energies. Terminal attachment (Fig. 3B) gives three peaks (binding energies for the sp^2 hybridized carbons at 285.6-285.8 eV) in a ratio of 1:3:14. Double attachment (Fig. 3C) gives two carbons attached to silicon, which results in a ratio of 2:1:15. Another possibility is terminal attachment with retention of the triple bond (Fig. 3D). The triple bond results in distinct peaks at 284.3 eV for the carbon connected to silicon, and at 286.5 eV for the other sp hybridized carbon.

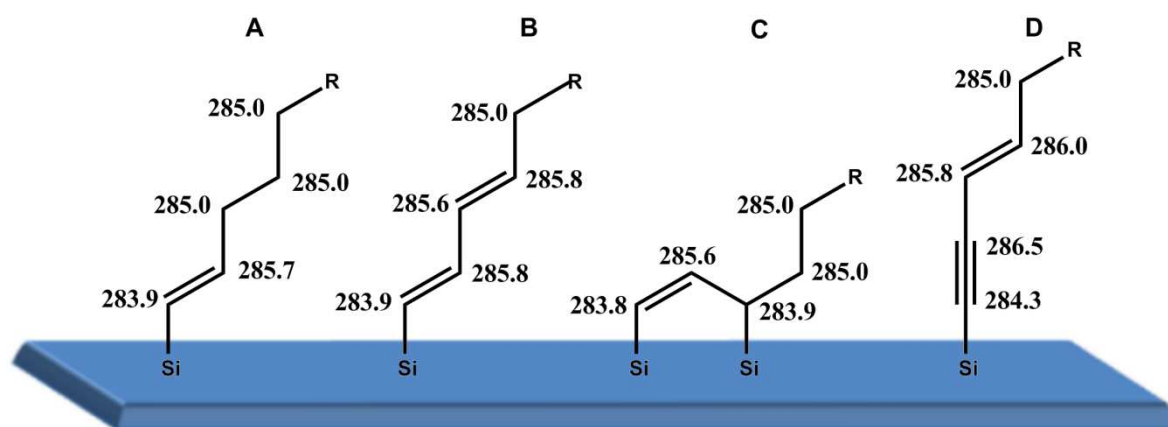


Figure S3. Self-Assembled monolayers on Si(111); **A)** hexadecenyl layers and **B-D)** possible modes of attachment of hexadeca-3-en-1-yne. Calculated binding energies per carbon atom are depicted in eV ($R = C_{11}H_{23}$).

Full IRRAS spectrum

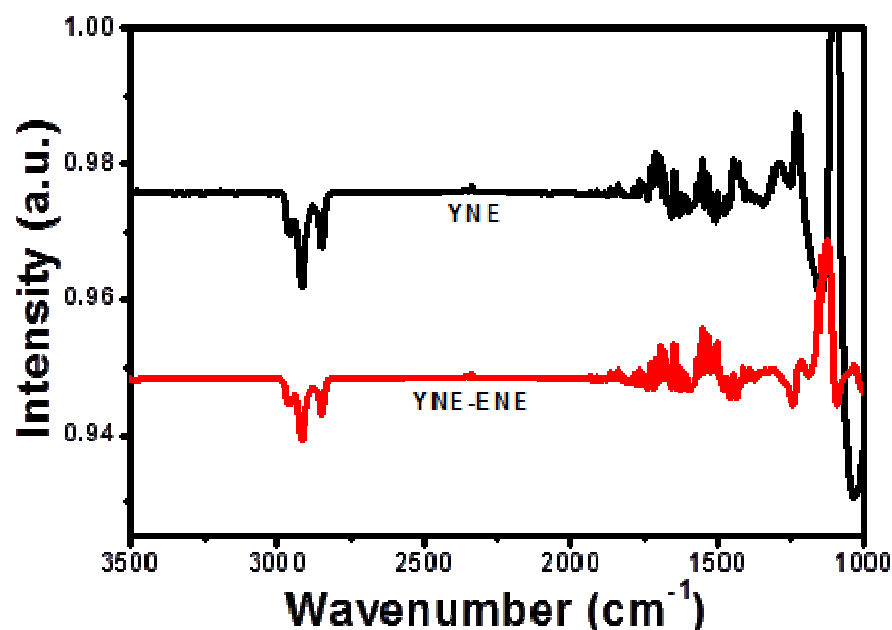


Figure S4. Full IRRAS spectrum of hexadec-3-en-1-yne (black) and 1-hexadecyne (red) derived monolayers on H-Si(111) at 80 °C.

Full reference of Gaussian 09

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References

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- (3) Scheres, L.; Giesbers, M.; Zuilhof, H. *Langmuir* **2010**, *26*, 10924.
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