Supporting Information

Theoretical Study on the Self-assembly of 1,3,5-triethynylbenzene on Si(100)2×1 and *In Situ* Polymerization via Reaction with CO to Fabricate A Single Surface-grafted Polymer

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Table S1: Calculated Energies with and without considering vdW interactions. E_{ads-1} and E_{ads-2} represent the energy of a H-Si(001)2×1 surface with a vinyl-centered radical and after H-abstraction respectively, while Δ represents the band gap of the surface polymer.

	with-vdW	*without-vdW*
E_{ads-1} (eV)	0.99	1.08
E_{ads-2} (eV)	2.11	2.17
Δ (eV)	0.91	0.98

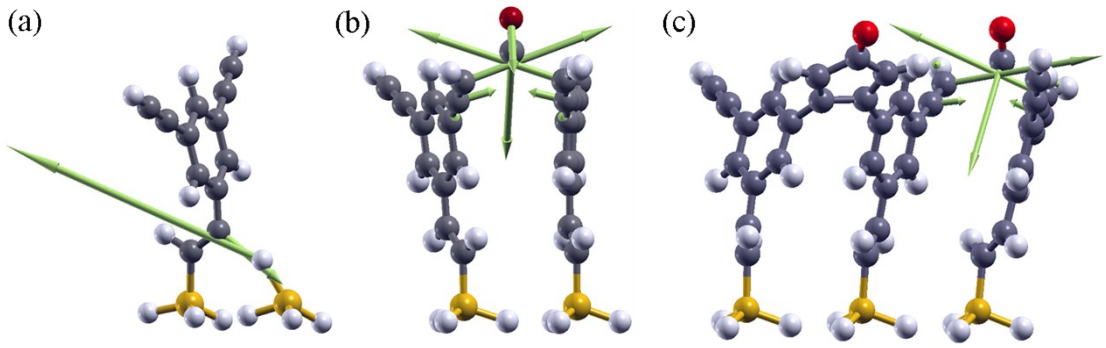

Figure S1. Schematic structures of the soft modes obtained from vibrational frequency calculations for transition state of (a) the H-abstraction process during TEB molecule growth on H-Si(100)2×1 surface; (b) the first and (c) the second cyclopentadienone ring formation during the polymer chain growth on the H-Si(100)2×1 surface.

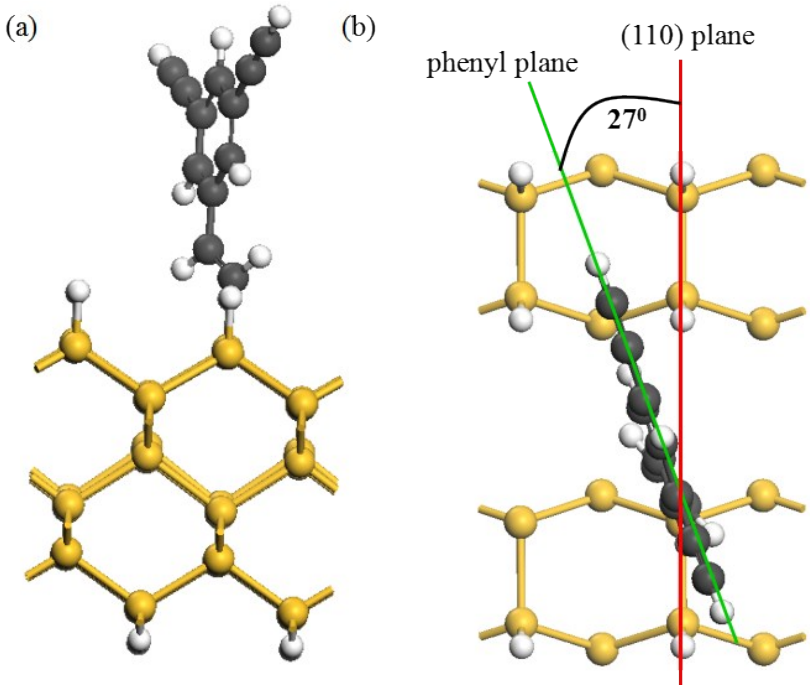

Figure S2. Schematic structures of an adsorbed DEB molecule on the Si surface (a) front view and (b) top view indicating the lowest energy position of 0 degree, where the phenyl is about 27° away from the (110) plane for single molecule adsorption.

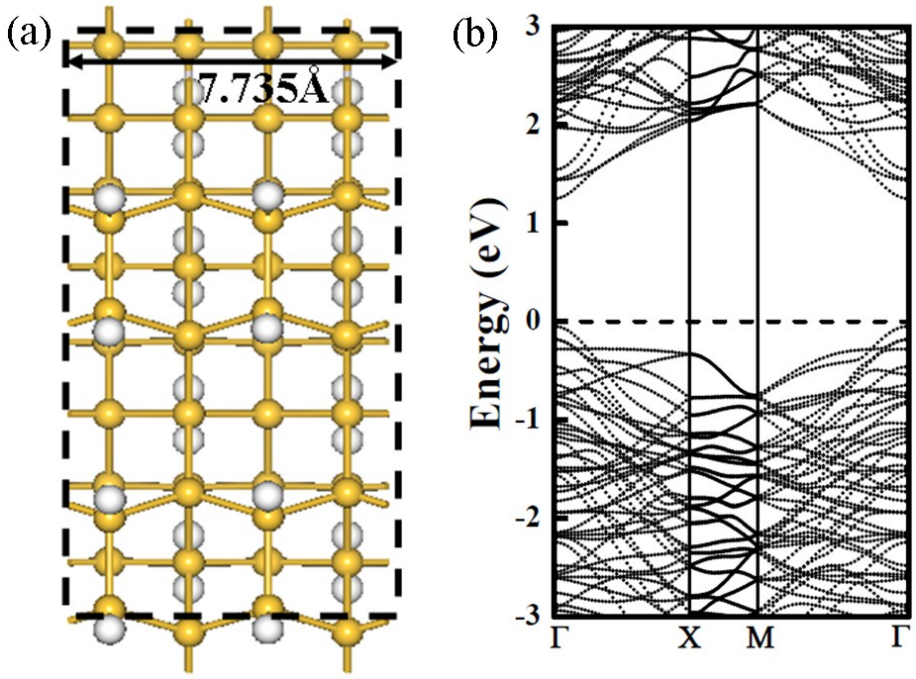

Figure S3. (a) Optimized structure of pristine H-Si(001)2×1 and (b) its band structure.

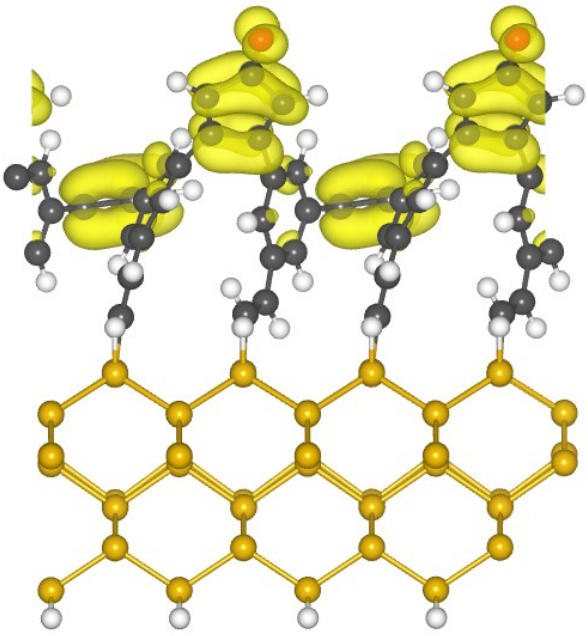

Figure S4. Isodensity surface of the polymer band as it crosses the Fermi level with 0.07 electrons/unit doping for the system.