Supporting Information

Theoretical Guide for Fabricating a Conducting Molecular Chain on Silicon Surface via *In Situ* Surface Polymerization Reaction

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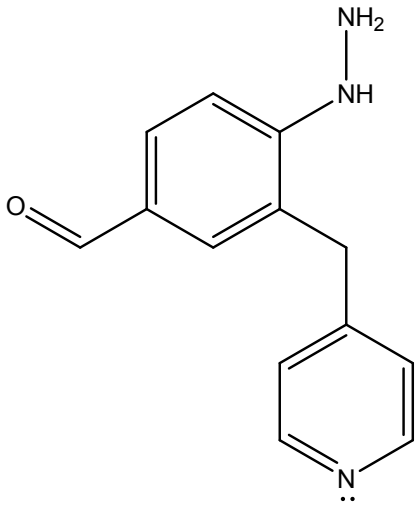

Figure S1: 4-hydrazinyl-3-(pyridin-4-ylmethyl)-benzaldehyde (HPyMB) molecular structure. Among all functional groups, the pyridine nitrogen atoms are the most reactive to exposed surface Si atoms.

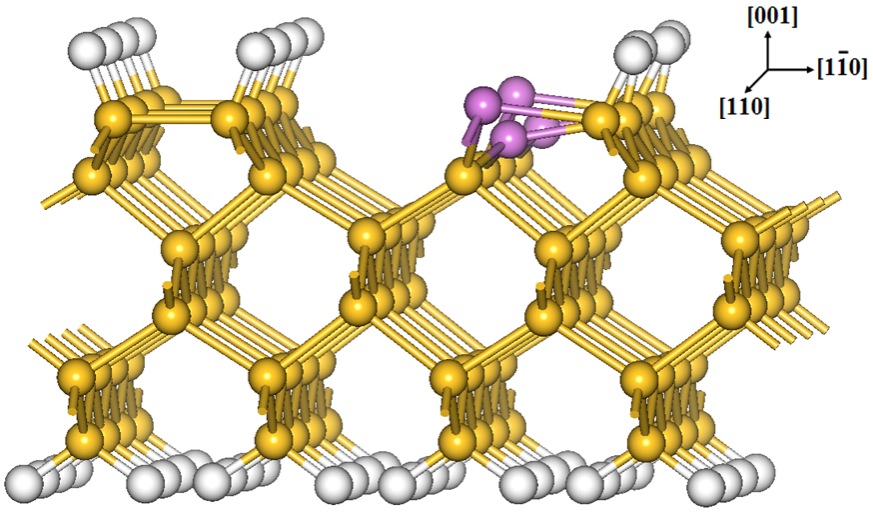

Figure S2: The alternating “ridge-valley” dangling-bond configuration of exposed surface Si atoms (denoted in pink color) for dimers along [110] direction on H-Si(001) surface.

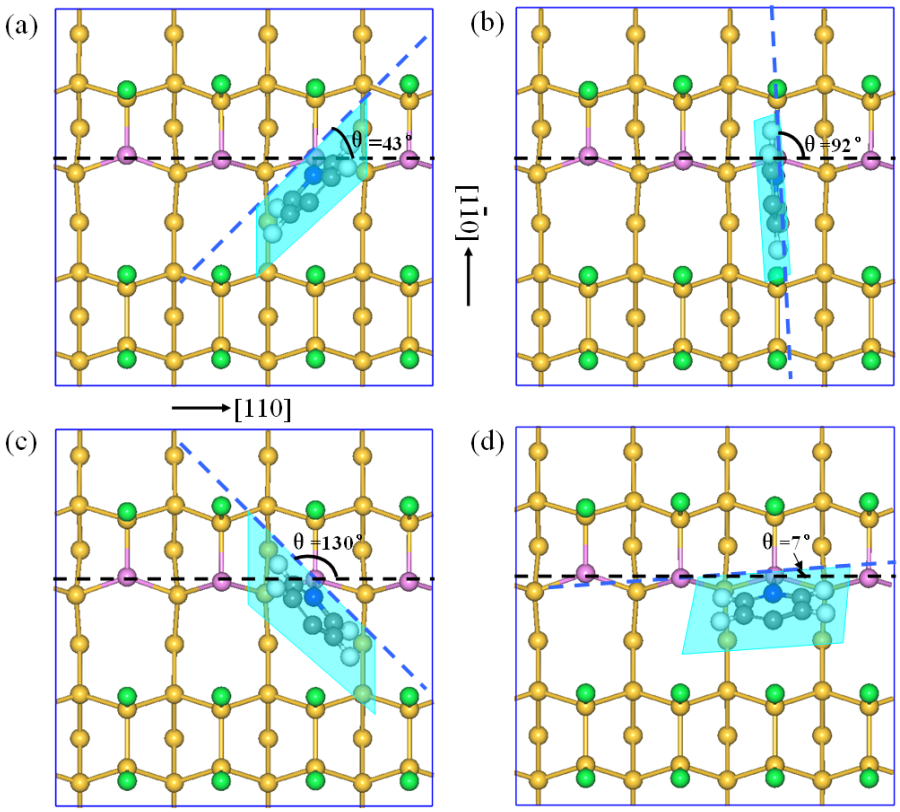

Figure S3: (a)-(d) are the top views of schematic structures for a single HPyMB molecule at intersecting angles (θ), 43, 92, 130 and 7 degrees respectively. Only pyridine ring and top surface layer of silicon atoms and hydrogen atoms are displayed for clarity. The black dash lines indicate [110] direction of Si(001) surface and blue dash lines represent the intersecting lines of the pyridine ring plane on Si(001) surface. The yellow and light magenta spheres represent saturated and unsaturated (with dangling bonds) surface silicon atoms respectively. And green ones denote hydrogen atoms.

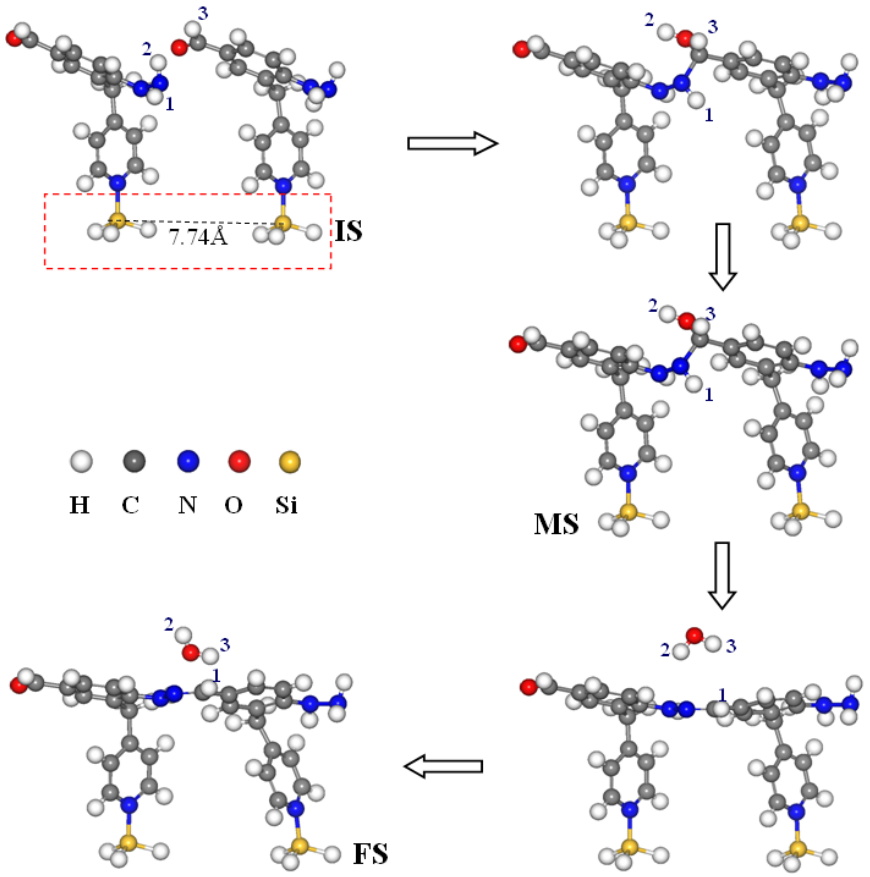

Figure S4: Schematic intermolecular dehydration reaction. To clarify the process, we label hydrogen atoms with numbers. The fixed atoms in this model are outlined within a red box.

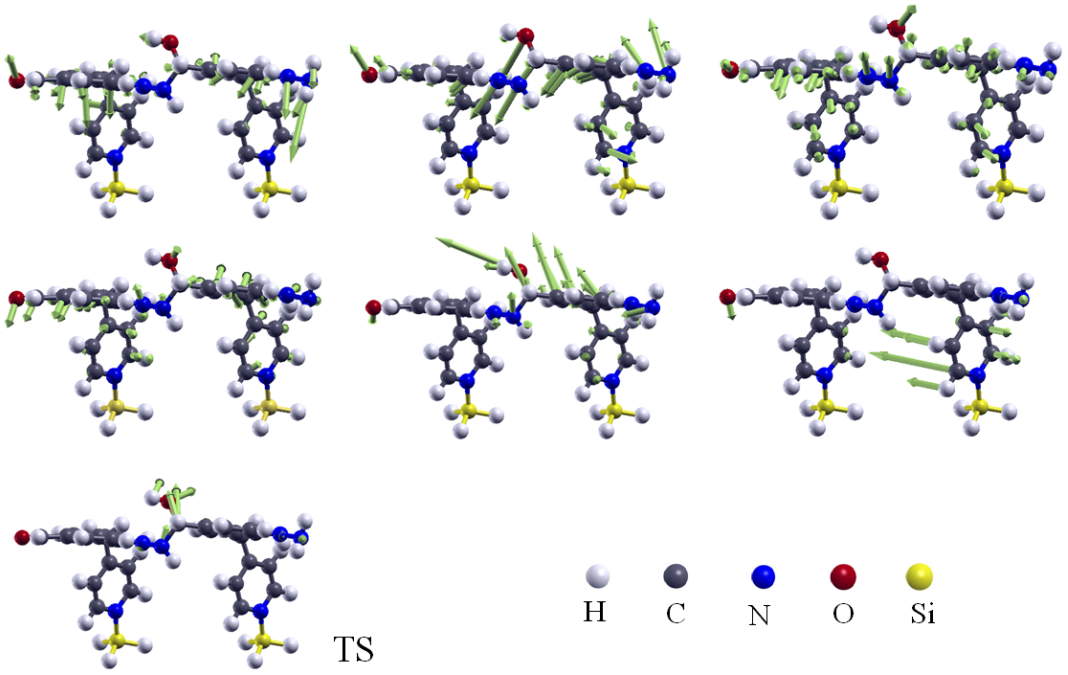

Figure S5: The seven soft modes obtained from vibrational frequency calculations. Six modes that tend to 'soften' due to the fixed SiH_3 groups and an additional soft mode corresponding to the final transition state.

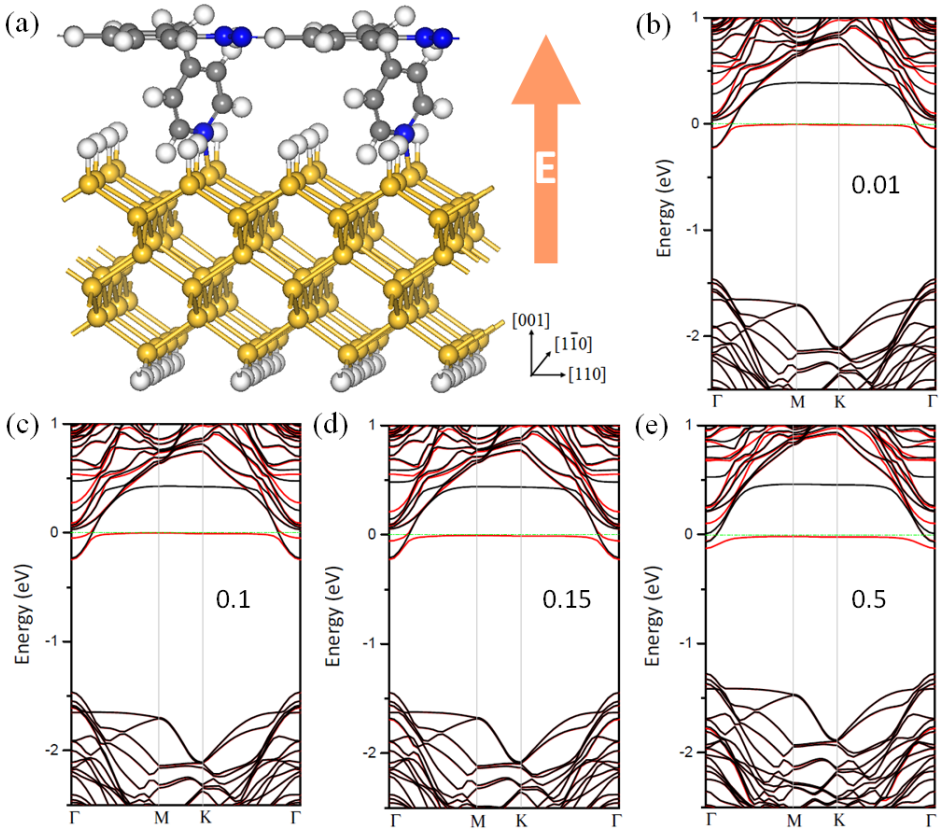

Figure S6: (a) Schematic of applying the electric field; (b-e) Band structures of the polymer/Si(001) under electric field of 0.01, 0.1, 0.15 and 0.5 (V/Å), respectively. Fermi Level is set to zero. Black and red lines indicate spin-up and spin-down channels, respectively.