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Atomic-scale Characterization of Free Radical Adsorption to the Si(111)-7 x 7 Surface NATHAN GUISINGER[1], SHAUN ELDER, NATHAN YODER, MARK HERSAM, Northwestern University — Ultra-high vacuum (UHV) scanning tunneling microscopy (STM) was employed to investigate free radical chemistry on the Si(111)-7 $\times$ 7 surface with atomic-scale spatial resolution. In particular, the nitroxyl free radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was explored, due to its single-site binding mechanism. UHV STM imaging of isolated molecules revealed that TEMPO covalently reacts with adatom dangling bonds with high affinity, while exhibiting a preference towards center adatom sites during the initial stages of adsorption. Adsorption to center and corner adatoms approached a ratio of 1:1 with increased surface coverage. Upon saturation, the surface exhibited long-range ordering. Following adsorption to a center adatom site, significant charge transfer occurred between TEMPO and a neighboring adatom. Scanning tunneling spectroscopy was utilized to investigate this delocalized effect by spatially mapping the local density of states. This study provides fundamental insight into free radical surface chemistry and suggests a direct pathway for forming nearly perfectly ordered organic adlayers on the Si(111)-7 $\times$ 7 surface.

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