281i Evidence of a Two Step Mechanism in Electronic Structure Selective Single-Walled Carbon Nanotube Reactions

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Single-walled carbon nanotubes (SWNT) possess unique electronic, optical, and mechanical properties. Individual carbon nanotubes are semiconducting or metallic, depending upon their chirality. Chemical reactions selective to the electronic structure of single-walled carbon nanotubes have become increasingly important from both technological and theoretical perspectives. Recently, an electronic structure selective chemistry was demonstrated using 4-chlorobenzene diazonium to react metallic over semiconducting nanotubes in an aqueous solution. SWNT electronic structure is based upon delocalized electrons occupying a 1-D density of states. However, covalent bonds are formed and broken between localized electrons. In the vicinity of localized electrons, the nanotube can no longer be described by a band model that assumes delocalized electrons moving in a periodic potential. So, how does the reagent detect a metallic or semiconducting species when the localization of the electrons necessary for covalent bonding changes the local electronic behavior? In this work, we answer this question by exploring the mechanism of the selective reaction of 4-chlorobenzene diazonium. Using transient Raman, photoluminescence, and photo-absorption spectroscopy, we take advantage of SWNT optical properties to probe what is happening near the nanotube surface. We show that selectivity proceeds by two distinct mechanistic steps: a selective non-covalent adsorption ($\tau = 2.4$ min) followed by a slower covalent reaction ($\tau = 73$ min) that need not be selective. The transient Raman and photoluminescence data are well described using a series of two first order reactions.