BASE STACKING, NOT BASE PAIRING, GOVERNS EXCITED-STATE DYNAMICS IN AT-CONTAINING DNA

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Although, base stacking and base pairing interactions are the major forces governing the macromolecular structure of DNA, their influence on electronic energy relaxation has remained elusive. This information is fundamental for understanding how excited states evolve to form photolesions. Over the years, much attention has been focused on dynamical processes in excited base pairs and their role in the evolution of electronic energy in DNA. Recent experimental and theoretical reports have suggested that light-triggered motion of a proton or hydrogen atom within an isolated base pair could initiate nonradiative decay to the electronic ground state. In this work, using transient absorption spectroscopy with femtosecond time resolution, we show that long-lived excited states in oligonucleotides composed of adenine (A) and thymine (T) bases are not quenched by base pairing. Proton transfer within AT base pairs is not competitive with decay channels created by vertical base stacking. Electronic energy in DNA containing AT base pairs evolves predominantly along strands and not across base pairs. The NIH supported this work.