Ultrafast Photodynamics in Diverse DNA Structures from A-tracts to Z-DNA
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The vulnerability of the genome to UV photodamage has sustained interest in excited electronic states in DNA for over 50 years. Progress in understanding the nature and dynamics of electronic excitations in DNA has accelerated rapidly thanks in part to ultrafast spectroscopy. Most excitations in single DNA bases decay nonradiatively in hundreds of femtoseconds. Surprisingly, much longer-lived excited states are observed in femtosecond pump-probe experiments on single- and double-stranded DNAs. Localized charge transfer states are prominent in runs of adenine bases (A tracts). DNA is polymorphic and can adopt a range of structures beyond the iconic B-form double helix. The effect of helix conformation on excited-state dynamics has been studied in a double-stranded oligonucleotide that can be switched between B- and Z-forms. Experiments on G quadruplex structures and on i-motif DNA reveal that these forms have significantly slower relaxation than B-DNA. By altering $\pi - \pi$ stacking and hydrogen bonding, structure profoundly affects the complex photoprocesses observed in DNA.

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