THE ROLE OF STRUCTURE AND SEQUENCE ON THE DYNAMICS OF EXCITED ELECTRONIC STATES IN GC-CONTAINING OLIGONUCLEOTIDES

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The sequence and secondary structure of DNA are expected to play a major role in shaping the dynamics of excited electronic states on account of the electronic couplings between proximal bases. Here we report the study by femtosecond transient absorption spectroscopy of long-lived singlet excited states in duplex systems comprised of alternating and consecutive sequences of guanine and cytosine. Under different solvent conditions, we studied the effects of base-stacking and base-pairing on the excited-state dynamics of the self-complementary oligonucleotide, d(GC)9. Under physiological conditions, d(GC)9 adopts the B-form double-helical conformation commonly found in genomic DNA. However, in the presence of high salt concentration, the sequence undergoes a structural transition to the left-handed Z-conformation. At low pH, protonation of cytosine induces a change in base pairing motif within the duplex from Watson-Crick to Hoogsteen. By using this unique oligonucleotide, we were able to adjust the overall secondary structure of DNA and monitor the excited state dynamics. Relatively long-lived excited states are formed in all of the GC systems studied. These results contrast with recent femtosecond fluorescence up-conversion experiments that only show emission on the time scale of hundreds of femtoseconds. In addition, we report that decay pathways for these dark long-lived states are relatively insensitive to changes in base-stacking geometries and base-pairing motifs, while sequence context plays a significant role in the excited-state dynamics.