DNA-Mediated Electron Transfer in Naphthalene-Modified Oligonucleotides

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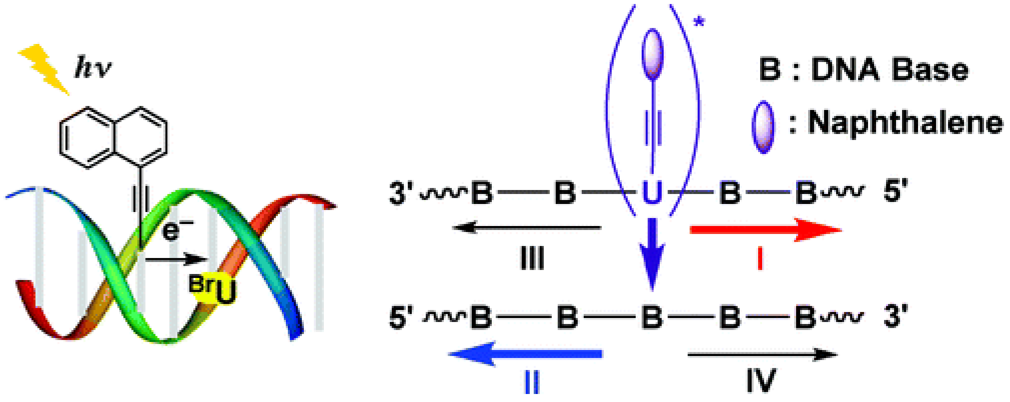
Abstract



Naphthalene-modified oligonucleotides have been synthesized and characterized with respect to electron transfer chemistry. Using the Sonogashira coupling reaction, naphthalene can be covalently anchored onto a modified uridine through an ethynyl linkage. This tethering allows for effective electronic coupling with the DNA bases, resulting in a significant red shift of the absorption bands of the naphthalenic chromophore. Modification with this chromophore does not appear to affect the overall stability and structure of the DNA. Upon selective irradiation of the naphthalene moiety at 340 nm, photoreduction of a distal electron trap, 5-bromouridine, embedded in the DNA base stack occurs. This DNA-mediated reduction from a distance was found to be significantly more efficient with substitution of 5-bromouridine toward the 5′-end than toward the 3′-end. These results support a general preference for electron transfer through DNA toward the 5′-end, irrespective of the donor. In addition, differences in efficiency of photoreduction through intrastrand and interstrand pathways are observed. For DNA-mediated reduction, as with DNA-mediated oxidation, significant differences in the charge transfer reaction are apparent that depend upon subtle differences in coupling into the DNA base stack.