SPECTROSCOPIC CHARACTERIZATION OF
DNA-MEDIATED CHARGE TRANSFER

Thesis by
Christopher R. Treadway

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Abstract

The DNA double helix, in addition to serving as a carrier of genetic information, provides a well-characterized molecular π stack through which charge transfer may be examined. Previous biochemical, photophysical, and electrochemical experiments have established that efficient charge transfer through DNA is mediated by the DNA base stack. To investigate the rates and efficiencies of that process we examined the spectroscopy of a series of DNA duplexes modified with a variety of photo- and redox-active moieties. Further, we examined the interactions and redox chemistry of a series of metallointercalators possessing high oxidation potentials with DNA.

The dynamics of photoinduced charge transfer through DNA were examined as a function of distance for a series of duplexes modified with 7-deazaguanine and a covalently attached ethidium chromophore. Over donor-acceptor distances of 10–17 Å, the dynamics of charge transfer were found to be distance independent. The observed decay times corresponding to charge transfer could be grouped into two components: (1) injection of charge into the DNA base stack, a process taking place on the 5-picosecond timescale, and (2) a correlated charge transfer rate corresponding to the reorientation of ethidium within the duplex, a process taking place on the 75-picosecond timescale. This study was the first definitive demonstration of the important role reactant dynamics play in DNA-mediated charge transfer.

Using the modified bases 2-aminopurine and 7-deazaguanine, intrastrand charge transfer through DNA was investigated. The photooxidation of guanine and 7-deazaguanine by 2-aminopurine was found to take place on the picosecond timescale. Charge transfer rates and quenching yields were also found to depend on the driving force for the reaction and the composition of the intervening base stack. These experiments again demonstrated that charge migration through the DNA π stack is a fast and efficient process.
The photooxidation of 7-deazaguanine by a ruthenium(II) intercalator in DNA was examined. Photoinduced charge transfer efficiencies over 7–14 Å were found to be shallow and dependent upon the chirality of the covalently attached metallointercalator. Nanosecond to subnanosecond decay rates were measured, and the spectroscopic signature of a charge transfer intermediate was observed.

A series of ruthenium(II) intercalators with high oxidation potentials was created. The spectroscopy of these complexes in the absence and presence of DNA was examined and compared to the well-known molecular “light switch” type complexes. Redox reactivity of the compounds with DNA did not correlate directly with oxidation potential and was found to be dependent on DNA binding and luminescence quenching abilities. Low-temperature EPR experiments revealed generation of long-lived radical species by the complexes in frozen DNA. These results demonstrated that redox potential may not be used as a sole predictor of reactivity with the base stack of DNA.

Finally, the binding of ruthenium(II) and rhodium(III) intercalators to DNA was investigated with CD and NMR spectroscopies. Data confirmed that metallointercalators do not preferentially bind next to each other along the double helix. Hence, direct contact of reactants cannot be used to explain fast and efficient charge transfer between metallointercalators bound noncovalently to DNA.

These studies have provided direct measurements of the dynamics of DNA-mediated charge transfer. Importantly, the stacking and dynamics of the reactants and DNA bases were found to affect the observed charge transfer behavior. These parameters, in addition to many others, must be included in any adequate description of the migration of charge through the DNA $\pi$ stack.
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