

Preparation and Regulation of Photoconductive DNA Duplex Nanowire

Prof. Sei-ichi Nishimoto

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,
Kyoto University

nishimot@scl.kyoto-u.ac.jp

Transport of charge, either positive charge (hole: h^+) or negative charge (electron: e^-), through p- p stacked bases in DNA duplex has been intensively studied during the last decade, in particular to get molecular insights into mechanism of DNA base damage and repair. Typically the hole transport is recognized to occur over a 20 nm range under certain conditions. DNA is thus expected to be a promising molecular material that may be employed for constructing nanoscale bioelectronic devices and electrochemical sensors, coupled with its characteristic ability for the self-assembly into various modes of higher-order structures dependent on the base sequences. For achieving this goal, minute regulation of the charge transport property of DNA duplex is considered as one of the key nanotechnologies. In the case of DNA nanomachines having gained a great deal of recent attention, synthetic DNA assemblies can switch between defined molecular architectures upon stimulation by external triggers, as regulated by a variety of methods such as pH changes and addition of the third molecular components.

In this study, photosensitizing chromophores possessing one-electron redox property in the electronically excited state were linked to specified positions of oligodeoxynucleotides (ODN's) with various base sequences and chain lengths. The resulting chromophore conjugate ODN was hybridized with a ^{31}P -radiolabeled complimentary ODN to obtain a DNA duplex. Photoirradiation of chromophores such as oxidizing anthraquinone (AQ) and reducing phenothiazine (PTZ) can induce electron extraction from and injection into the nearest neighboring base moiety of ODN to produce the corresponding base cation radical (hole carrier) and anion radical (electron carrier) intermediates, respectively. The transport of hole or electron through the ODN duplex was evaluated by detecting the ODN strand cleavages at the carrier-trapped sites, using a gel electrophoresis. Direct observation of the hole transport was achieved by photocurrent measurements.

Amperometry was used to characterize the AQ-photoinjected hole transports through 19-mer ODN duplex, as immobilized on the surface of gold electrode, and its triplex forms converted by association with several third oligopyrimidine (OPD) short-strands via Hoogsteen hydrogen bonding. While the cathodic photocurrent was observed upon irradiation at 365 nm of AQ-photosensitizer linked to the 3'-end of ODN duplex, a marked lowering of current density was identified to occur by the triplex formation of duplex with a given third OPD short-strand. In accord with this experimental evidence, photoinduced one-electron oxidative cleavage at remotely located guanine residues of ODN strands with several types of sensitizers was considerably suppressed by the triplex formation. The ODN triplex produces a cationic environment and altered stacking interactions of DNA bases at the duplex-triplex junctions, thereby presumably arresting the hole transport. The photocurrent through ODN duplex showed a reversible fall-rise response concomitant with alternating association-dissociation cycle of the OPD short-strand, as regulated by temperature change around the corresponding melting temperature of ODN triplex. Both the switched photoirradiation and the thermally alternating duplex-triplex conversion could provide tools of regulating the DNA hole transport.