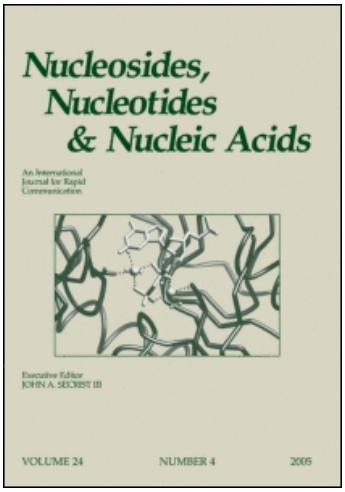

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Long Range Electron Transfer in PNA/DNA Duplexes

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LONG RANGE ELECTRON TRANSFER IN PNA/DNA DUPLEXES

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ABSTRACT: The conductive properties of PNA/DNA is examined. The electron donor is covalently linked to a fixed site in PNA which unambiguously places the acceptor in the hybrid duplex. The study shows that PNA/DNA acts like an insulator.

Electron transfer in biological material has attracted much attention and intense research has been devoted to this particular field[1-6]. The finding that the stacked bases in duplex DNA may form a unique conductive medium, a conduction band, has been intensively debated[7-9]. The general interest to analyse the conductive properties of stacked systems may motivated us to investigate electron transfer in PNA/DNA hybrids by using anthraquinones as electron acceptors. Excited anthraquinones are strong oxidants. Thus, electron transfer from the surroundings to the quinone is a very favored process. To incorporate a quinone acceptor unambiguously in a stacked system, we prepared a set of new PNA monomers (Fig. 1).

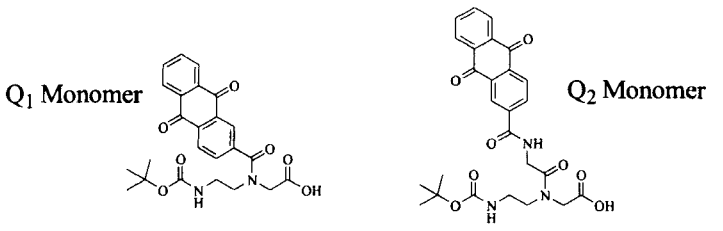


Figure 1.

These monomers can be incorporated in any position in PNA. Hybridization analyses showed that incorporation of either Q_1 or Q_2 in the central position of a PNA 19mer only gave rise to a modest reduction in T_m compared to the affinity of a fully matched 19mer PNA/DNA[10]. Irradiation of PNA/DNA hybrids created piperidine labile sites in the DNA strand (Fig. 2, X = abasic site in DNA, Y = Q_1). Irradiation of Q-PNA/DNA cleaved DNA with a preference for the 5'-G at GG-sites. When a single base pair mismatch was introduced between the quinone site and the GG site in the DNA the cleavage intensity was significantly reduced.

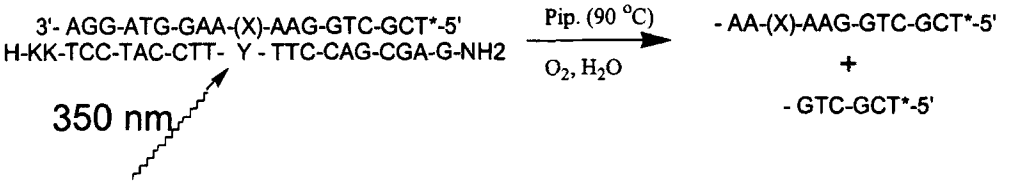


Figure 2.

Excited quinones have complicated photochemistry[11]. $^1O_2$ sensitizing and electron transfer both create base labile sites in DNA. We have made a series of control experiments to show that the primary oxidation event in DNA stems from the intramolecular electron transfer route, not the intermolecular $^1O_2$ route (e.g. diffusible species) (Fig. 3)[11].

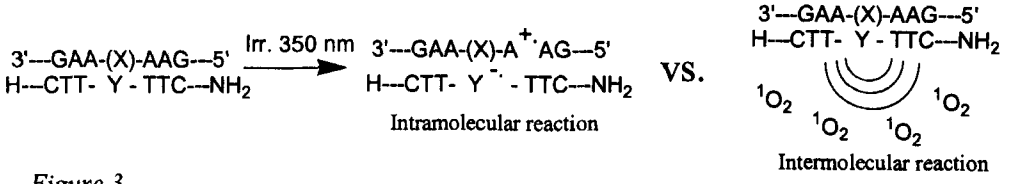
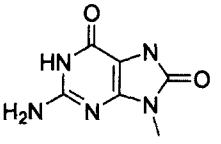


Figure 3.

The marked difference between A and G is caused by guanine having the lowest oxidation potential (0.1 V lower that adenine). By introducing a low oxidation potential trap (8-oxo-G), which has a 0.5 V lower oxidation potential than G, it is possible to describe the conductive properties of PNA/DNA hybrids, thus differentiate between the instantaneous delocalization model and a "hole hopping" model (hole = base cation radical). In the instantaneous delocalization model (PNA/DNA = a wire) cleavage would be inhibited at all sites except at the "trap" (8-oxo-G) since the duplex can be considered to be one continuous orbital system. We showed that 8-oxo-G inhibits the cleavage at the distal GG site (at the 3' direction), the cleavage at the GG site to the 5' end is not affected. Therefore, the hole cannot be in electronic contact with the trap as the instantaneous delocalization model predicts. Instead the base cation radical will migrate by a discrete hopping mechanism. Thus, PNA/DNA hybrids do not act as a wire but rather as an insulator.



8 Oxo-G

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