Direct Chemical Evidence for Charge Transfer between Photoexcited 2-Aminopurine and Guanine in Duplex DNA

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Abstract:

Photoexcited 2-aminopurine (Ap*) is extensively exploited as a fluorescent base analogue in the study of DNA structure and dynamics. Quenching of Ap* in DNA is often attributed to stacking interactions between Ap* and DNA bases, despite compelling evidence indicating that charge transfer (CT) between Ap* and DNA bases contributes to quenching. Here we present direct chemical evidence that Ap* undergoes CT with guanine residues in duplex DNA, generating oxidative damage at a distance. Irradiation of Ap in DNA containing the modified guanine, cyclopropylguanosine (^{CP}G), initiates hole transfer from Ap* followed by rapid ring opening of the ^{CP}G radical cation. Ring opening accelerates hole trapping to a much shorter time regime than for guanine radicals in DNA; consequently, trapping effectively competes with back electron transfer (BET) leading to permanent CT chemistry. Significantly, BET remains competitive, even with this much faster trapping reaction, consistent with measured kinetics of DNA-mediated CT. The distance dependence of BET is sharper than that of forward CT, leading to an inverted dependence of product yield on distance; at short distances product yield is inhibited by BET, while at longer distances trapping dominates, leading to permanent products. The distance dependence of product yield is distinct from forward CT, or charge injection. As with photoinduced charge transfer in other chemical and biological systems, rapid kinetics for charge injection into DNA need not be associated with a high yield of DNA damage products.

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