DNA getting sunburned

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Ultraviolet (UV) radiation induces various photo-damages in DNA. Among them the CPD (cyclobutane pyrimidine dimer) photo-damage caused by 2+2 photo-addition of adjacent thymine basis is the most abundant lesion. The formation of this photo-damage is discussed since the 1960ies: Dimerization of monomeric thymine in solution requires diffusion to bring thymine molecules in close contact. At reasonable concentrations contact formation is much slower than the 1 ps lifetime of the excited singlet state. Thus CPD-formation in solutions with monomeric bases can only occur via the long-lived triplet state. For thymine in DNA strands, where the thymine molecules are in close proximity, diffusion is not necessary and the singlet as well as the triplet channel may be involved. In this contribution we will present investigations on different dimerizable model systems using time-resolved IR techniques combined with quantum yield measurements and show, that the singlet channel dominates CPD-formation[1, 2].

The experiments show that in all stranded systems (different thymine dinucleotides as well as single stranded dT_{18}) the IR marker-bands of the CPD photo-damage appear within 1ps after UV irradiation (at 266 nm), i. e. with the decay of the originally excited singlet state of the thymine molecule. Thereafter the amplitudes of the marker-bands do not change on the 10 ps to ns timescale. This finding rules out the possibility of delayed CPD formation on this time scale. In addition we show that the quantum efficiency recorded from the IR absorption change on the 10 ps time scale matches the stationary values, indicating that the major fraction of CPD-damage is formed ultrafast and is directly related to the decay of the excited singlet state.

The observation of rapid CPD photo-damage formation within 1 ps yields interesting information regarding the evolutionary optimization of DNA stability. The time scale of 1 ps is to short to allow large scale structural changes of a DNA strand. Therefore CPD formation only takes place for thymine pairs prearranged in reactive conformations. Thus CPD photo-damage probability may be minimized by suitably designed DNA structures.

References

1. W.J. Schreier, T.E. Schrader, F.O. Koller, P. Gilch, C.E. Crespo-Hernandez, V.N. Swaminathan, T. Carell, W. Zinth, B. Kohler, Science 315 (2007) 625-29.
2. W. J. Schreier, J. Kubon, N. Regner, K. Haiser, T.E. Schrader, W. Zinth, P. Clivio, P. Gilch, J. Am. Chem. Soc.131 (2009), 5038-5039.