The Role of Cations in the Intrinsic Photostability of DNA

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The preservation of the genetic material is directly connected to the UV-light absorption in nucleic acids. Especially, DNA can dissipate the excess energy in a non-reactive way, leading to photostability, or it can suffer photoinduced lesions, ultimately leading to irreversible damage if the rate of DNA repair does not prevent accumulation of lesions.

In the present contribution we focus on this delicate interplay by studying, through a multi-scaling quantum mechanics/molecular mechanics computational protocol, the role played by excited electron, proton, and hydrogen transfer in a B-DNA model, especially pointing the attention toward the hydrogen-bonding pattern of Watson-Crick guanine/cytosine (G/C) base pairs within a double helix dynamic environment, including solvent and salt cations naturally occurring in the biological media. Depending on the Na^+ conditions, we observe the possibility of photoinduced double proton transfer following electron transfer among the two DNA strands, finally leading to photostability thanks to a backward pathway, once the electronic ground state is populated.[1]

In principle, this could pave the way not only toward novelties in fundamental nucleic acids' structure and function but also, in finding ways to possibly control the fate of UV-light energy dissipation in DNA through external salt conditions. Moreover, the stabilization/destabilization of the charge-transfer states' energy depending on the position of the cation were computationally considered, as they could serve as a reliable description of experimental spectroscopic measurements (electronic absorption, circular dichroism, etc.).[2]

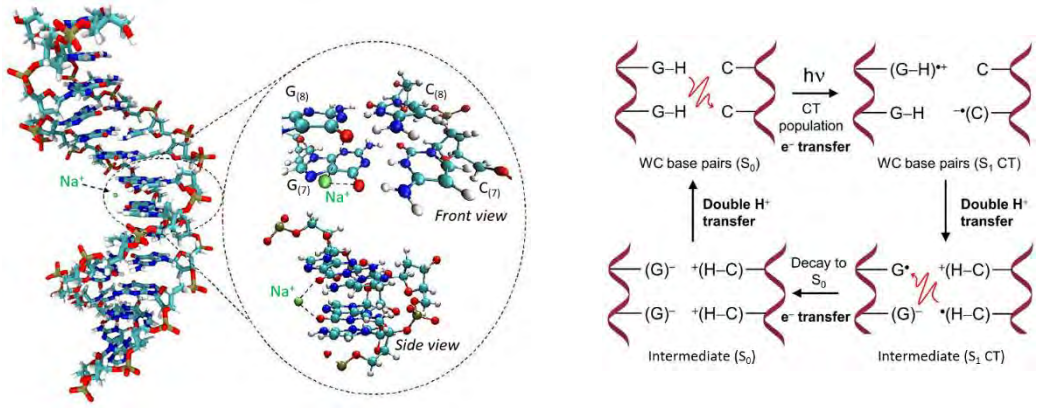

Figure. Left: 14 base pair (dG)·(dC) B-DNA model studied, with inset in the region affected by a sodium cation (for the sake of clarity, water molecules are omitted). Right: Scheme of the computationally observed excited-state forward/backward electron-coupled-double proton transfer in two π-stacked G/C base pairs, including the complete photostability cycle. Adapted from reference 1.

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References

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