

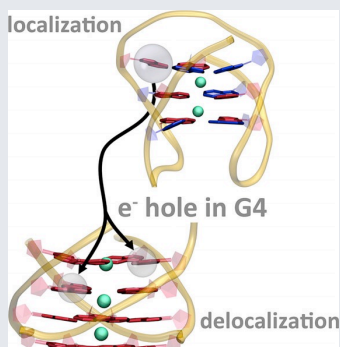
Optical spectra of G-quadruplexes: quantum chemistry calculations for identification of laser-induced species on the fs to ms time-scales

Dimitra Markovitsi (LIDYL), Pascale Changenet-Barret (LOB), Roberto Improta (Chaire D' Alembert UPSaclay/LIDYL), Lara Martínez-Fernández (LIDYL)

Four - stranded DNA structures (G - quadruplexes) are intensively studied because of their involvement in many biological processes and as promising architectures for molecular electronics. The OSPEG project funded by PALM focuses on the primary processes induced in G - quadruplexes by the absorption of low energy UV radiation. The objective is to identify the transient species evolving from the fs to the ms time - scale (various types of electronic excited states, reaction intermediates, and guanine radicals), combining time-resolved optical spectroscopy and quantum mechanical calculations.

We have shown that guanine radicals are generated in G-quadruplexes when they absorb UV photons with energy lower than the ionization potential of the DNA bases. The quantum yield for their one-photon ionization, of the order of 10^{-3} , is 3-4 times higher than that determined for DNA double helices. In order to explain such an unexpected photo-ionization process, we have established a working hypothesis: during the excited state relaxation, charge transfer excited states, in which the positive and negative charges are located on different DNA bases, are populated; under the effect of conformational motions, charge separation, charge migration and electron ejection from an "isolated" radical anion may take place. By performing a thorough photophysical study on human telomeric G-quadruplexes in the presence of sodium ions, we found that charge transfer excited states can indeed be populated in these systems. Thus, we confirmed the first requisite of our hypothesis but we still need to characterize the subsequent steps leading to radical generation.

We also demonstrated that the type of cationic radicals (electron holes) formed by ionization in G-quadruplexes depends on their topology: in the case of antiparallel structures the hole is localized on a single guanine, while in parallel ones they may be delocalized over two neighbouring guanines. As time goes on, cationic radicals deprotonate. The dynamics of both the deprotonation process and the reactivity of the deprotonated species are strongly affected by the G-quadruplex topology.



Time-resolved experiments and calculations were used to study the spectral properties of the ionized species created by UV light in G-quadruplexes. In sequences adopting an antiparallel structure, such as human telomere, the electron hole is localized on a single guanine. In parallel structures, the hole can be delocalized over two guanines.

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Résultats obtenus dans le cadre du projet OSPEG financé par le thème 3 du LabEx PALM et porté par Dimitra Markovitsi (LIDYL) et Pascale Changenet-Barret (LOB) en association avec Roberto Improta (Chaire d' Alembert UPSaclay/LIDYL).