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Complexity of excited state dynamics in DNA

Arising from: Base stacking controls excited state dynamics in A-T DNA *Nature* 436, 1141-1144 (2005)

Absorption of UV light by DNA is known to lead to carcinogenic mutations but the processes intervening between photon absorption and the photochemical reactions are poorly understood. Crespo-Hernández *et al.* studied the excited state dynamics of model DNA helices using femtosecond transient absorption spectroscopy¹ and by observing that the picosecond component of the transient signals recorded for (dA)₁₈.(dT)₁₈ is close to that determined for (dA)₁₈ but quite different from the one found for (dAdT)₉.(dAdT)₉, they conclude that excimer formation limits excitation energy to one strand at a time. Here, we show that, when excited state dynamics is probed by time-resolved fluorescence spectroscopy the picture changes dramatically, revealing the great complexity of these systems; we also comment on the pertinence of separating base stacking and base pairing when talking about excited states dynamics in double helices and we argue that the assignment of the long-lived signal component found for (dA)₁₈.(dT)₁₈ to adenine excimers is debatable. An oversimplification in the interpretation of the experimental data may be completely misleading for the understanding of the studied processes.

Figure 1A presents the fluorescence decays of (dA)₂₀ at three different wavelengths. Combining the present results with our previous measurements obtained for (dA)₂₀ by femtosecond fluorescence upconversion², at least five exponentials are needed to fit the decays on the 100 fs – 20 ns time range. A crucial point is that all time constants vary strongly with the emission wavelength. The same effect is encountered for (dAdT)₁₀.(dAdT)₁₀ and has been reported previously for poly(dA).poly(dT)³. We interpret this complex behaviour by a model stipulating the formation of a large number of excited states delocalized over several bases, which may be located both on the same strand and on opposite strands, and the subsequent energy transfer³. This model, based on calculations performed in the frame of the exciton theory and combining quantum chemistry data and molecular dynamics simulations⁴⁻⁷ accounts, not only for the decays but also the steady-state absorption and fluorescence spectra. Delocalization of the excitation energy is governed by the electronic coupling which depends on the oligomer conformation. Conformational changes occurring on the pico- and nano-second timescales are controlled by an ensemble of interactions involving not only the bases

but also the back-bone, counter-ions and water molecules^{5, 8}. In this sense, both base stacking and base pairing determine excited state dynamics.

For the abovementioned reasons the time constants provide a simply phenomenological description of the decays and do not correspond to specific excited states. However, it is possible to make a rough comparison of the overall excited state dynamics by considering the decays recorded at the maxima of the fluorescence spectra of the three oligomers (Figure 1B). In the case of (dAdT)₁₀.(dAdT)₁₀ and (dA)₂₀, the fluorescence maxima have been assigned to excimer emission^{9, 10}. We observe that, in contrast to the transient absorption signals, the fluorescence decay obtained for (dA)₂₀.(dT)₂₀ on the sub-nanosecond time-scale is much shorter than that observed for (dA)₂₀. The same observation is valid when comparing the decays of these single and double strands at identical wavelengths.

Neither in fluorescence nor in transient absorption experiments is the amplitude of the detected signals proportional to the excited state population. The transient absorption signals depend on the difference between the molar extinction coefficients of the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ transitions at the probed wavelengths. Since the steady-state absorption spectra of these oligomers correspond to a large number of transitions⁶ and nothing is known about the $S_1 \rightarrow S_n$ spectra of their various excited states, the percentage of the “excimer” population reported by Crespo-Hernández *et al.* is not necessarily correct.

The important difference between the transient absorption and fluorescence decays of (dA)_n.(dT)_n indicates the formation of dark transient species. If these dark species are adenine “excimers”, they must have different electronic structure from the fluorescent “excimers” of (dA)_n and, therefore, different lifetimes. Consequently, the similar time constants observed by transient absorption for (dA)₁₈.(dT)₁₈ and (dA)₁₈ may be fortuitous. The species observed by transient absorption in (dA)₁₈.(dT)₁₈ could as well be interstrand A-T charge transfer states, as suggested by recent theoretical calculations¹¹. The behaviour of such states in D₂O, examined by Crespo-Hernández *et al.*, is not easily predictable since water molecules form a variety of interstrand and intrastrand bridges between bases¹².

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Figure Caption

Fluorescence decays recorded by time-correlated single photon counting. **(A)** (dA)₂₀ at 330 nm (pink), 360 nm (red) and 420 nm (yellow). Black lines correspond to fits with multi-exponential functions yielding the following sets of time constants (3.2, 37.5, 186 and 748 ps), (11.6, 101, 253 and 1830 ps) and (39, 198, 551 and 5050 ps), respectively. The TMP decay (grey) corresponds to the instrumental response function. **(B)** (dA)₂₀ at 360 nm (red), (dA)₂₀.(dT)₂₀ at 330 nm (blue), (dAdT)₁₀.(dAdT)₁₀ at 420 nm (green).

Methods

DNA oligomers (Eurogentec), dissolved in phosphate buffer (pH = 6.8) were excited by femtosecond pulses (100 fs, 267 nm). All decays were reconstructed from the parallel (I_{par}) and perpendicular (I_{perp}) components according to: $F(t) = I_{\text{par}}(t) + 2GI_{\text{per}}(t)$. For further experimental details *cf.* reference 3.

