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Exciton Trapping Dynamics in DNA Multimers

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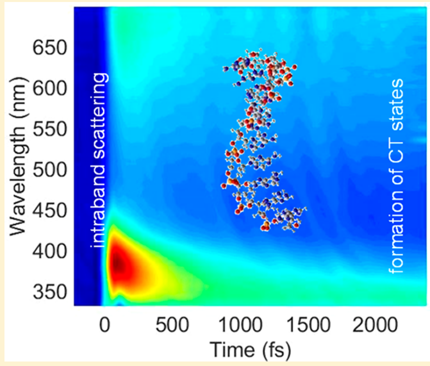
Supporting Information

ABSTRACT: Using as a model the single adenine strand $(dA)_{20}$, we study the ultrafast evolution of electronic excitations in DNA with a time resolution of 30 fs. Our transient absorption spectra in the UV and visible spectral domains show that internal conversion among photogenerated exciton states occurs within 100 fs. Subsequently, the $\pi\pi^*$ states acquire progressively charge-transfer character before being completely trapped, within 3 ps, by fully developed charge-transfer states corresponding to transfer of an electron from one adenine moiety to another (A^+A^-).



The electronic excited states of DNA multimers are studied in connection to the damage of the genetic code provoked by UV radiation.[1] Significant progress has been made in their characterization since the beginning of the 21st century thanks to femtosecond spectroscopy, which evidenced that interchromophore interactions play a key role.[2−8] On the one hand, transient absorption (TA) studies showed that excited charge-transfer (CT) states involving neighboring nucleobases are populated in high yield; the reported lifetimes of CT states range from 20 to 200 ps.[3,5,7] On the other hand, fluorescence upconversion measurements detected an important decrease of the fluorescence anisotropy occurring in less than 300 fs,[4,8] corresponding to the instrumental response function; this was attributed to ultrafast energy transfer among bases involving exciton states. However, neither the dynamics of the energy-transfer process nor that of the exciton trapping by CT states has been resolved to date. This is achieved in the present transient absorption study, performed with a time resolution of ca. 30 fs, exceeding by nearly an order of magnitude that used in previous studies on DNA multimers.

We focus on adenine single strands, which are known to adopt a helical structure and have been intensively studied on longer time scales.[9−16] Over the years, Kohler and co-workers studied $(dA)_n$ multimers in phosphate buffer with a time resolution of 250 fs by probing TA at selected wavelengths, typically 250 and 570 nm;[10,11,14,16] they fitted TA traces with biexponential functions attributing the shortest time constant (2.7 ps for $(dA)_{18}$)[16] to monomer like relaxation and the longest one to excimers with strong CT character (170 ps $(dA)_{18}$).[16] A more complex picture emerged from the work by Kwok and co-workers, who obtained TA spectra with time resolution of 150−250 fs, associated with Kerr-gated time-resolved fluorescence;[13] fits of the decays with three-exponential functions provided time constants of 0.4, 4.3, and 182 ps, correlated with the formation of two excimers, in addition to monomer-like decay. In parallel, fluorescence decays and fluorescence anisotropy decays showed that (i) part of the excited-state population survives down to the nanosecond time scale[12,15] and (ii) the maximum of the fluorescence spectrum (360 nm), decaying on the subnanosecond time scale, does not correspond to a CT state; this was attributed to "neutral" excimers identified by quantum chemistry calculations.[15]

Here we follow the differential absorption spectra of $(dA)_{20}$ from 280 to 700 nm on a time window reaching 3 ps. We show that internal conversion among Frenkel excitons occurs within 100 fs; subsequently, the nature of the excited states changes progressively and the appearance of CT states, identified unambiguously by their UV−visible absorption spectrum, requires 3 ps.

Our measurements were carried out on a homemade high time resolution pump−probe setup (see the Supporting Information), described in detail elsewhere.[17,18] Pump pulses had a bandwidth spanning between 260 and 280 nm (Figure 1a) and 16 fs duration; the energy per pulse was adjusted to 13 nJ, resulting in an excitation intensity of 10^{10} W cm^{-2}. Broadband white light continuum probe pulses covered the 280−700 nm spectral range. The instrumental response function decreased from 45 to 25 fs, when going from 280 to 700 nm; below 330 nm, the first 70 fs were distorted by the coherent artifact. Pump and probe polarizations were set at the magic angle. HPLC purified $(dA)_{20}$ multimers, purchased from Eurogentec Europe, were dissolved in saline phosphate buffer

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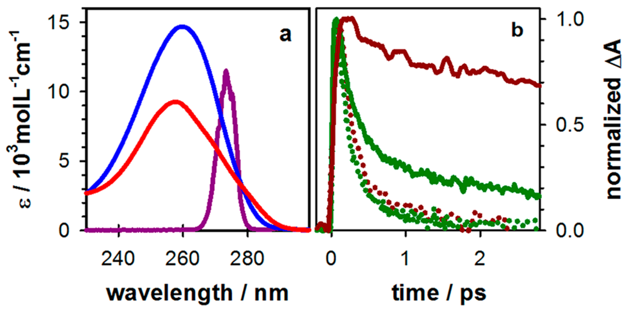

Figure 1. (a) Steady-state absorption spectra of the monomer (blue) and the multimer (red); the ε values, given per base, are taken from ref 25. The violet line represents the spectrum of the exciting pulse (arbitrary intensity). (b) Normalized transient absorption dynamics at 400 nm (green) and 570 nm (dark red) recorded for the monomer (dotted lines) and the multimer (solid lines).

(6×10^{-3} mol L^{-1}, pH 7.4); 15 mL of the solution were kept flowing in free jet so as not to excite helices containing photoinduced lesions.[19−21] For comparison, the adenosine monomer was also studied under identical conditions. The ground-state absorption spectra of the monomer and the multimer are shown in Figure 1a. The concentration of absorbed photons per pulse (1×10^{-5} mol L^{-1}) was significantly lower than the ground-state concentration of both the multimer (2×10^{-4} mol L^{-1}) and the monomer (4×10^{-3} mol L^{-1}), thus avoiding biphotonic events. We did not detect any signal from the neat solvent arising from hydrated electrons, which exhibit a broad peak around 700 nm;[22] such an undesired signal is an obstacle for recording full transient absorption spectra in the visible domain. In addition, electrons are also known to react with nucleic acids,[23,24] thus destroying the helix structure.

The transient absorption spectra of the monomer (Figure 2a−c) are rather simple to describe, as they are characterized by a photoinduced absorption band peaking at 380 nm and a

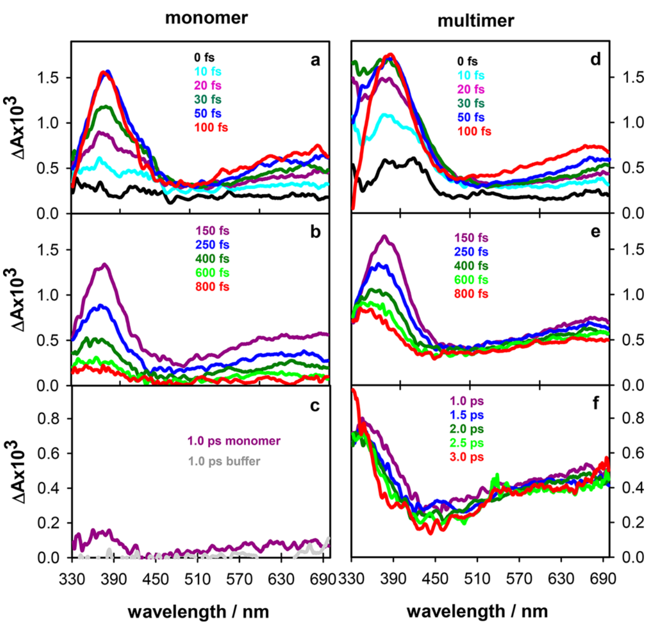

Figure 2. Transient absorption spectra obtained for the monomer (a−c) and the multimer (d−f) at selected times. The gray line in panel c corresponds to the spectrum of the aqueous solvent at 1 ps.

second one around 685 nm (noted B1 and B2, respectively, in Figure 3a) both of which decrease in intensity without

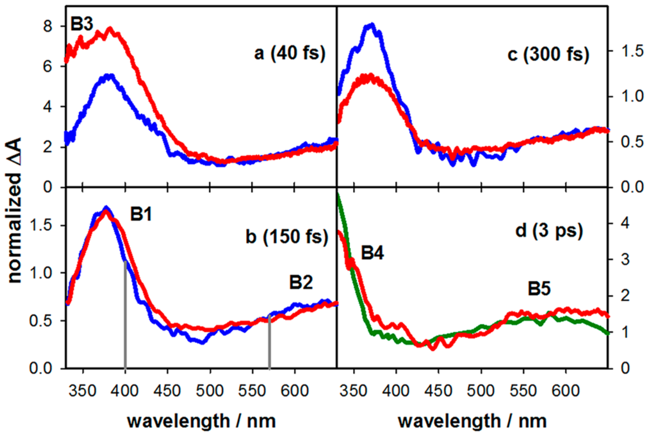

Figure 3. Comparison of the spectral shapes of the multimer (red) and monomer (blue) at selected times (a−c). The green spectrum in panel d corresponds to the sum of the spectra of the dAMP radical cation and dAMP radical anion. The spectral intensities have been normalized in an arbitrary way. The vertical lines in panel c indicate the wavelengths at which the decays in Figure 1b were recorded.

important changes in their shape. On the other hand, the evolution of the multimer TA spectra is quite complex. We can roughly distinguish three phases, depicted in Figure 2d−f. We note that our spectra recorded at longer times resemble those reported by Kwok et al.[13] To better grasp the spectral differences between multimer and monomer, we present in Figure 3a−c the monomer and multimer TA spectra recorded at selected delays normalized in intensity. Thus, it appears that the relative intensity of band B1 versus B2, which is initially higher for the multimer compared to the monomer, subsequently becomes equal and finally lower.

Looking more in detail at the multimer TA spectra recorded at early times (Figure 2d), we note the fast buildup of bands B1 and B2. However, while the intensity of B1 reaches its maximum within 30 fs, 100 fs are required for the latter. This is correlated with the disappearance of a second UV band (noted B3 in Figure 3a) around 330 nm, which cannot be properly resolved because of the coherent artifact, particularly important in this spectral domain, and with a change in the spectral profile from a two-peaked to a single-peaked structure (B1). We assign the spectral evolution observed during this first phase to intraband scattering, that is, internal conversion among exciton states. Theoretical studies reported the existence of exciton states in adenine single strands,[26−28] (persisting even in the presence of conformational disorder),[29] in line with the significant difference of the multimer steady-state absorption spectrum with respect to that of the monomer (Figure 1a), showing strong interactions among bases.

In the case of the monomer, the steady-state absorption spectrum corresponds to two close-lying $\pi\pi^*$ states, L_a and L_b. Predicted by quantum chemistry calculations,[30] their existence was experimentally evidenced by the low fluorescence anisotropy found for various adenosine derivatives, attributed to emission from the L_a state, following excitation of the L_b state.[31] The computed TA spectrum of L_a consists of an intense peak in the near UV and a weaker intensity band in the visible.[32] Such a description is in qualitative agreement with the present results, confirming that, in aqueous solution, L_a is

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the lowest-energy bright state. In line with recent studies on adenosine,[33,34] we did not detect any clear evidence for $L_b \rightarrow L_a$ internal conversion, meaning that the dynamics of this process is in the limit of our time resolution. More details on the adenosine are given in the Supporting Information.

Returning to the multimer behavior, we observe that its TA spectrum at 150 fs is quite similar to that of the monomer (Figure 3b). This similarity could be explained by localization of the exciton states and/or by the presence of collective states that are built on the monomer L_a states. Such exciton states being linear combinations of L_a, the position and shape of their absorption spectrum should coincide with those of L_a provided that they are isoenergetic to the monomer state. Our high temporal resolution thus enables us to visualize relaxation within the excitonic manifold of the multimer, which is completed within 100 fs. During the second phase (Figure 2e), lasting approximately from 150 to 800 fs, we observe that the bands B1 and B2 start decreasing and shifting to shorter wavelengths. This trend is much more pronounced for B1, which loses half of its intensity and undergoes a ~2200 cm^{-1} (40 nm) blue shift, versus 30% decrease and ~800 cm^{-1} (25 nm) shift for B2. We assign this intermediate regime of the excited-state relaxation to progressive alteration of the $\pi\pi^*$ character of the electronic excitations which start acquiring partial CT character while neighboring bases approach each other. This is in agreement with measurements performed by fluorescence upconversion, showing that, on this time scale, the emission spectrum shifts to longer wavelengths and the fluorescence anisotropy diminishes.[15] The anisotropy decrease upon increasing of the CT character of excited states is predicted by quantum chemistry calculations.[35] It is also possible that, in parallel, some localized excitations simply decay through monomer-like pathways. However, this path is not expected to concern a significant population of excited states in view of (i) the important differences in both the position and the intensity between the monomer and multimer TA spectra (Figure 2) and (ii) the strong hypochromism (42% at the maximum) exhibited by the steady-state spectrum of $(dA)_{20}$ (Figure 1a), showing very efficient base stacking.

The blue shift of the multimer absorption spectra continues on the picosecond time scale (Figure 2f), but the intensity changes are now weak. Progressively, a new spectral shape appears. At 3 ps we can distinguish a peak at 350 nm and another at around 600 nm (noted B4 and B5 in Figure 3d). The band B4 is better distinguished in Figure S1a in the Supporting Information, where spectra in the 280−350 nm region are shown. On the picosecond time scale, the monomer spectra (Figure S1b) correspond to the vibrationally excited ground state.[10,34]

As mentioned above, the long-lived excited states in $(dA)_n$ have been attributed to CT states. However, this attribution did not result from a spectral identification. As such, CT states correspond to transfer of an electron between two neighboring bases (A^+A^-); their absorption spectrum is expected to be the sum of the spectra of the adenosine radical cation[21,36] and the adenosine radical anion[24,37,38] reported in the literature. The spectra of these radicals have been obtained via photoionization[20,34] and pulse radiolysis measurements,[35−37] respectively. Thus, in Figure 3d we compare TA spectrum of $(dA)_{20}$ at 3 ps with the spectrum of an equimolar mixture of radical cation and the radical anion of the mononucleotide 2′-deoxyadenosine 5′-monophosphate (dAMP) considering their respective molar absorption coefficients. The agreement between the two spectra in Figure 3d is quite striking, further confirming the nature of this long-lived excited state.

Given the complex evolution of the multimer TA spectra, the decays strongly depend on the probe wavelength (Figure S2). They are longer than those of the monomer, which also exhibit a smaller but clearly detectable wavelength dependence (Figure S3). As an example, the decays recorded for both systems at 400 and 570 nm are shown in Figure 1b. The dynamics can be fitted with bi- or triexponential functions, but such fits do not have physical meaning because we deal with inhomogeneous systems. In the case of the monomer, we have continuous evolution along a nonplanar potential energy surface.[31] The multimer case is even more complicated because the helix geometry is highly anisotropic and undergoes dynamical conformational changes. CT formation, requiring the approach of two chromophores within the helix, can be considered as a bimolecular reaction. It is well-documented (see for example ref 39) that the dynamics of such reactions follow nonexponential patterns when they take place in restricted geometries. As a result, the time constants derived for this type of systems from fits with exponential functions depend not only on the wavelength but also on the time-window, explaining the diversity of the values reported in the literature. For the same reasons, fitting of the TA spectra with Gaussian curves is not appropriate.

With the above considerations in mind, in order to obtain a phenomenological description of the monomer decays, we fitted them with biexponential values (Table S1). The average decay times between 380 and 680 nm vary from 260 to 320 fs (Table S1), which fall in the range of previously reported values.[31,33,34]

In conclusion, our experiments on a model DNA helix provided unprecedented information on the ultrafast processes associated with exciton trapping; the successive steps of the complex process leading from the Franck−Condon to excited CT states are summarized in Table 1. The dynamics of intraband scattering, resulting from ultrafast energy transfer among bases,[1] was resolved. Moreover, the subtle and progressive evolution of $\pi\pi^*$ excitations toward CT states was evidenced. Finally, for the first time, full spectral identification was provided regarding the lowest bright excited state of the adenosine chromophore and the long-lived excited states of the multimer. This work paves the way toward the study of more complex DNA structures (duplexes, G-quadruplexes, i-motifs, etc.). We hope that it will stimulate theoretical studies, which could shed light on the transient absorption spectra of collective states and rationalize the observed spectral evolution through quantum dynamics calculations. Such calculations will possibly allow elucidating whether other types of excimers,[15,40] such as those dominating the fluorescence spectrum of $(dA)_{20}$, are populated in

Table 1. Processes Underlying the Time Evolution of the Multimer Transient Absorption Spectra

time	process
$t \leq 100$ fs	intraband scattering (internal conversion among exciton states)
150 fs < t < 800 fs	decrease in the interchromophore distance; the excited states start acquiring a CT character
0.8 ps < t < 3 ps	geometrical rearrangement resulting from the interchromophore charge transfer
t = 3 ps	stabilization of the CT state (A^+A^-)

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substantial yields during the excited-state relaxation of this DNA helix.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b00450.

Ultrafast transient absorption setup, multimer dynamics, fits of the monomer dynamics, and transient absorption spectra in the 280−360 nm domain (PDF)

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Notes

The authors declare no competing financial interest.

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