Distinctive Spectral Features of Exciton and Excimer States in the Ultrafast Electronic Deactivation of the Adenine Dinucleotide

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Abstract: We report the observation of distinctive spectro-temporal signatures of delocalized exciton vs. relaxed, weakly bound excimer states in the ultrafast electronic deactivation after UV photoexcitation of the adenine dinucleotide followed by transient absorption spectroscopy.

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1. Introduction

Extraordinarily efficient and ultrafast electronic deactivation processes in the natural nucleobases are widely considered as key factors determining the relative UV photostability of the DNA. Highly surprisingly, however, studies of single- and double-stranded DNA oligonucleotides revealed that the electronic lifetimes in these large base assemblies may be three to four orders of magnitude longer than in the monomers [1–3]. This huge discrepancy initiated intense debate, whether the long-lived excited states in the oligomers are due to dipole coupled, delocalized excitons extending over several bases [4] or whether they originate from localized excimers consisting of two neighboring, weakly bound π-stacked bases on the same strand with possible (partial) charge transfer (CT) character [5]. Here, we report the observation of distinct spectro-temporal signatures in transient excited-state absorption (ESA) spectra of the adenine dinucleotide $d(A)_2$ (Fig. 1a), which can be assigned to excitonic and to excimer-like excited states, respectively, shedding clear light on this important conundrum.

2. Experimental Results

The ultrafast electronic relaxation dynamics in the $d(A)_2$ dinucleotide were investigated following photoexcitation at $\lambda = 260$ nm in phosphate buffered aqueous solution (pH 7.0) by femtosecond UV/vis absorption spectroscopy with supercontinuum white-light and single-color deep-UV probe pulses [6]. The recorded two-dimensional (2-D) transient absorption map is displayed in Fig. 1b, the map for the mononucleotide dAMP is given for comparison in Fig. 1c. The vast differences between the two moieties are highlighted by the plots of the transient absorption spectra at selected delay times after excitation in Figs. 1d–e for the dimer vs. Fig. 1f for the monomer. In the first place, the long-lived ESA of the dinucleotide around $\lambda = 340$ nm is absent in the spectrum of the mononucleotide. Most importantly, however, the ESA spectra of $d(A)_2$ showcase not only substantial spectral evolution as function of time after excitation, but also partially resolved spectral structure, which is not visible in the considerably broader, unspecific transient spectra for dAMP. In particular, the broad initial ESA of the dinucleotide in the range 330–450 nm consisting of two overlapping, almost superimposed bands (Fig. 1d) collapses to the much longer-lived ($\tau \approx 400$ ps), and spectrally much narrower, single band around 340 nm (Figs. 1d–e). This striking transition happens on an ultrashort time scale, $\Delta t \lesssim 500$ fs. Attempts of a spectro-temporal band analysis of Fig. 1d even suggest first relaxation steps taking place within ≤ 100 fs. Additionally, the blue-shift of the ESA is accompanied by a corresponding red-shift in the fluorescence spectra of the excited dinucleotide molecules (not shown).

3. Discussion and Conclusions

The observed spectral evolution in Fig. 1d and the temporal dynamics shown in Figs. 1g–i reveal the ultrafast relaxation in the intially excited excitonically coupled ladder of states via intraband scattering within $\Delta t \lesssim 100-500$ fs followed by subsequent larger-amplitude rearrangement of the nucleobase moieties within a few ps from the original B-DNA configuration to an energetically relaxed and therefore much longer-lived ($\tau \approx 400$ ps) excimer with presumable structure [7,8] between near face-to-face or significantly distorted. With ongoing improvements of experimental time

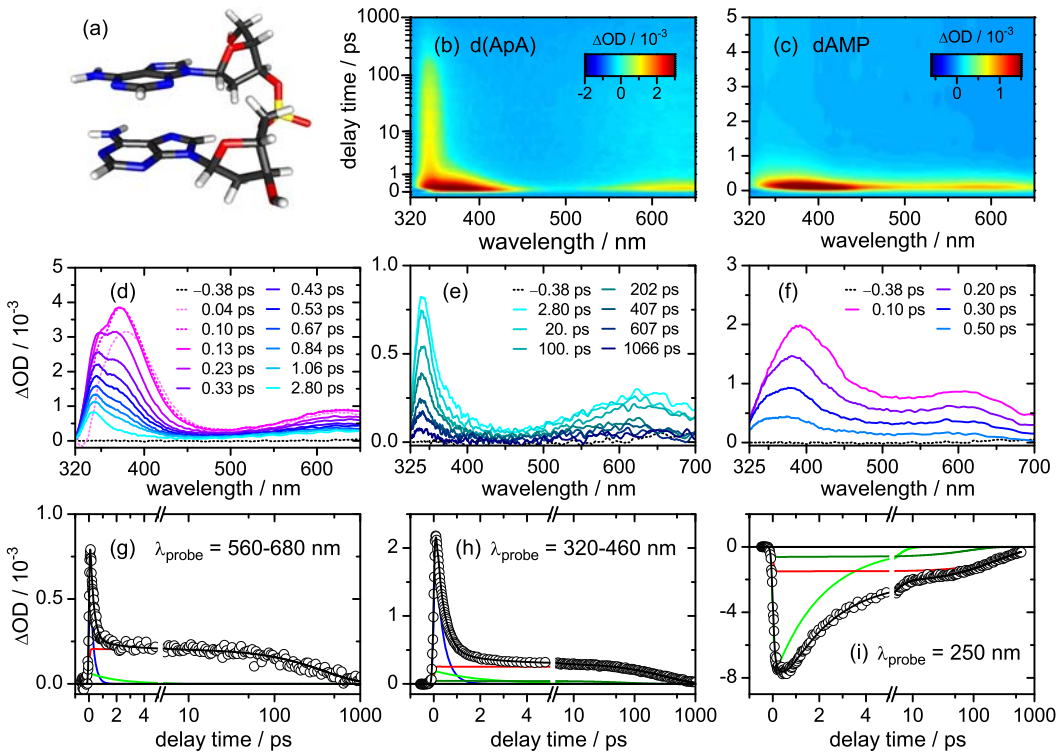

Fig. 1. a) Structure of the $d(A)_2$ dinucleotide (B-DNA conformation). b–c) 2-D transient absorption maps after 260 nm excitation of $d(A)_2$ and dAMP, respectively. d–f) Excited-state absorption spectra of $d(A)_2$ (panels d and f) and dAMP (panel f) at selected delay times. g–i) Temporal evolutions of the $d(A)_2$ ESA bands and recovery of the ground state bleach signal together with the respective least-squares fit curves.

resolution, critical tests of the excited-state structures and dynamics proposed by quantum chemical calculations (e.g. [7,8] and references therein) thus come into sight, which should resolve the challenging controversy surrounding the electronic dynamics in DNA oligonucleotides. Towards these ends, $d(A)_2$ constitutes an ideal model system.

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