Are Adenine Strands Helical H-Aggregates?

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On the basis of our quantum mechanical calculation, we propose that homogeneous single-stranded adenine bases (Ade-DNA) form helical H aggregates, and the photoexcited states can be described as Frenkel excitons. The calculated excitonic coupling between adjacent transition dipoles is in good agreement with the measured absorption spectrum of 20-base homogeneous adenine stacks that exhibits a blue shift of 2.6 nm relative to that of the monomeric species.

Excited states of nucleic acid bases are highly stable to photochemical decay of solar ultraviolet (UV) photons and this photostability reduces the need for costly enzymatic repair[1] of photodamaged DNA. However, this very high photostability of nucleic acids is not well-understood. In fact, the domain of human knowledge on the basic human genome has been only recently expanded to the configurational properties of nucleic acids with the advent of a full identification of the approximately 20 000 to 25 000 genes in human DNA. On the other hand, the dynamics of the photoexcited states and UV photochemistry of nucleic acids remain largely uncharted. Ultraviolet photoexcitation in single DNA bases is known to decay nonradiatively on a subpicosecond time scale.[2] In base-stacked DNA, however, much less has been understood regarding multichromophoric DNA photophysics in general and excess electronic energy elimination in particular. A long-lived emissive state in stacked DNA bases that is absent in base monomers has been observed by a number of authors[3−8] among which early studies on DNA base dimers were carried out three to four decades ago.[3−5] The long-lived excited states present in time-resolved studies of various single and double DNA strands with lifetimes in the 100−1000 ps regime[6−9] may increase their propensity toward photochemical reactions. Therefore, there has been some expectation about a direct link between these long-lived excited states and some important photolesions in living cells. This has led to intense experimental and theoretical interest on the photophysical nature of these states.[10]

In double-stranded DNA, bases form base-pairs horizontally and base-stacks vertically. The respective roles of base stacking and base pairing are controversial. Kohler and co-workers found that the singlet excited states reside on a single strand;[8] and Markovitsi et al.[11,12] found that the excited states located on both base-paired strands. To simplify the discussion, we focus on a B-form single stranded adenine DNA (Ade-DNA). In this paper, we propose that homogeneous single-stranded Ade-DNA forms an H aggregate with a helical shoulder-to-shoulder configuration of transition dipoles. The dipolar interactions in such a configuration render adjacent transition dipoles to have alternating directions in order to lower electronic energies.

TABLE 1: Singlet Excitation Energies and Their Corresponding Oscillator Strength from ZINDO, TDB3LYP, TDHF Calculations for a Monomer and a Dimer Segment Taken Out of a 20-Base Adenine Strand[a]

system	states	type	E_{ex} (eV) ZINDO	osc. str.
monomer	1	$\pi\pi^*$	4.3434	0.2435
	2	$n\pi^*$	4.5246	0.0044
dimer	1	$\pi\pi^*$ Frenkel exciton	4.2544	0.0343
	2	$\pi\pi^*$ Frenkel exciton	4.3654	0.3486
	3	$n\pi^*$	4.5111	0.0049
	4	$n\pi^*$	4.5166	0.0036
	⋮	⋮	⋮	⋮
	13	$\pi\pi^*$ charge transfer	5.3235	0.0200
	14	$\pi\pi^*$ charge transfer	5.4599	0.0109

system	states	type	E_{ex} (eV) TDB3LYP	osc. str.
monomer	1	$\pi\pi^*$	5.2100	0.2225
	2	$n\pi^*$	5.3131	0.0118
dimer	3	$\pi\pi^*$ Frenkel exciton	5.1611	0.0341
	4	$\pi\pi^*$ Frenkel exciton	5.2039	0.2660
	1	$\pi\pi^*$ charge transfer	4.8205	0.0122
	2	$\pi\pi^*$ charge transfer	4.8775	0.0006

system	states	type	E_{ex} (eV) TDHF[b]	osc. str.
monomer	1	$\pi\pi^*$	4.3642	0.4041
	2	$\pi\pi^*$	4.4752	0.0565
dimer	1	$\pi\pi^*$ Frenkel exciton	4.2760	0.0537
	2	$\pi\pi^*$ Frenkel exciton	4.3874	0.5581
	⋮	⋮	⋮	⋮
	19	$\pi\pi^*$ charge transfer	5.8956	0.0463
	20	$\pi\pi^*$ charge transfer	5.9916	0.0461

[a] The solvent effects have been included in TDB3LYP and TDHF calculations and the dielectric constant ϵ is 78.39. [b] Scaled by 0.70.[13]

Consequently, the oscillator strength is concentrated in several high-energy states of the exciton band leaving the low-energy states near the band bottom almost optically forbidden. Evidence from an absorption-spectral comparison between a single-base adenosine and 20-base homogeneous adenine strands lends strong support to our proposed picture. And this might offer a new way to study the excited-state properties of DNA.

To investigate the absorption spectra of a series of B-form homogeneous adenine DNA single-strands with one up to 20

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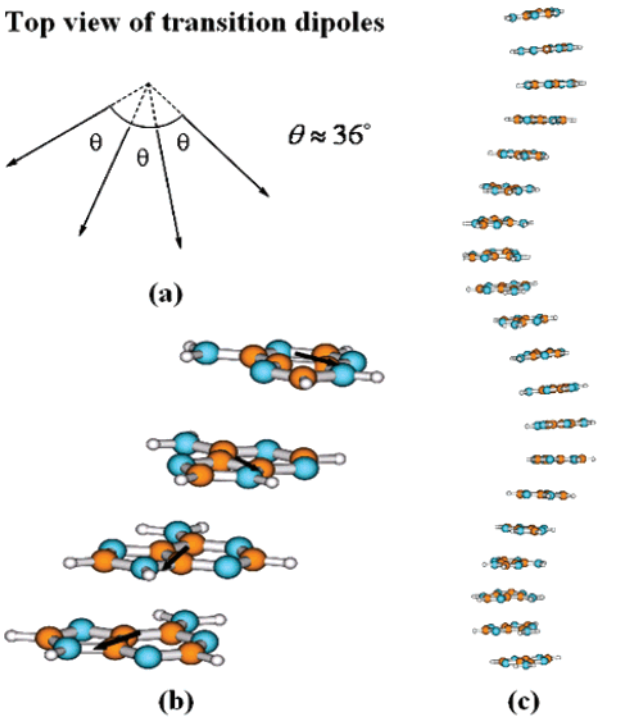

Figure 1. A B-form homogeneous single-stranded adenine oligomer with 20 bases (c). Adjacent bases, separated vertically by ~3.4 Å, are rotated by $\pi/5$ from each other (a). Two pairs of adenine bases are magnified with its calculated transition dipole orientation shown as the dark arrows (b).

adenine bases, the semiempirical ZINDO method[14−16] implemented in Gaussian program package[17] is adopted. The excitation energies for adenine and its dimer have also been calculated with TDDFT[18] and TDHF methods with the 6-311G(D) basis set for comparison. The solvent effects have been included in TDB3LYP and TDHF methods by adopting the polarizable dielectric model.[17] In Table 1, the results show that the excitation energy for the $\pi\pi^*$ optical transition state of adenine due to ZINDO is underestimated by 0.5 eV compared with experimental data (4.77 eV),[7] while it is overestimated by 0.5 eV with TDB3LYP. (There are some reports that showed their excitation energy results with TDB3LYP[19] and TDLDA[20] methods had better agreement with experiments.) However, TDDFT methods underestimate significantly the excitation energy of charge transfer states so that the charge transfer states are the lowest energy states in the TDDFT calculation results. The excitation energy calculated by TDHF is scaled by a factor of 0.7 in ref 13, since the TDHF method yields higher excited energies as compared to the experimental results. On the other hand, a more advanced ab initio method such as CASPT2[21] also gave rise to around 0.5 eV difference compared with the experimental data. For the adenine dimer, the trend for the excitation energies as well as the oscillator strength of optical transition states compared with adenine monomer due to ZINDO agrees qualitatively with that based on TDB3LYP and TDHF calculations. In addition, the computational effort of TDDFT, TDHF, and CASSCF[21] is already too demanding for oligomers containing more than three bases. On the basis of these arguments, we believe ZINDO is able to afford reasonable results for the excitation energies of the homogeneous adenine single strands.

The adenine monomer is studied first. The energies and oscillator strengths of its first two excited states with different methods are listed in Table 1. In the ZINDO calculation, the first excited state, a $\pi\pi^*$ excitation, has the largest oscillator strength, and its transition dipole moment, 3.84 D in size, lies mostly in the base plane. The orientation of the transition dipole is represented as the black arrow on each adenine base in Figure 1b. This is the same as in TDHF and TDDFT methods. Adenine dimers are studied as well. Table 1 lists a few low-lying excited-state energies and their corresponding oscillator strengths for a dimer segment taken out of a homogeneous adenine single strand with three calculation methods. In the ZINDO method, the lowest two excited states are results of $\pi\pi^*$ transitions, and moreover, the second $\pi\pi^*$ excitation has the largest oscillator strength. A detailed examination of their reduced single-electron transition density matrices reveals the electron−hole pairs of the two lowest excited states are confined almost to the same adenine base. In other words, little charge-transfer character is found for the lowest two excited states. Furthermore, their transition dipole moments are made up mostly of the separate transition dipoles of two adenine bases as indicated in Figure 1b. The wave functions of the lowest two excited states are as follows: where ψ_{S1} and ψ_{S2} are the wave functions of the first

$$\begin{aligned}\psi_{S1} \approx & -0.47|A_{HOMO} \rightarrow A_{LUMO}\rangle \\ & + 0.40|B_{HOMO} \rightarrow B_{LUMO}\rangle \\ & + 0.05|A_{HOMO} \rightarrow B_{LUMO}\rangle \\ & - 0.02|B_{HOMO} \rightarrow A_{LUMO}\rangle \\ \psi_{S2} \approx & \ 0.35|A_{HOMO} \rightarrow A_{LUMO}\rangle \\ & + 0.43|B_{HOMO} \rightarrow B_{LUMO}\rangle \\ & + 0.04|A_{HOMO} \rightarrow B_{LUMO}\rangle \\ & - 0.04|B_{HOMO} \rightarrow A_{LUMO}\rangle \end{aligned} \quad (1)$$

and second singlet excited states, respectively; $|A_{HOMO} \rightarrow A_{LUMO}\rangle$ and $|B_{HOMO} \rightarrow B_{LUMO}\rangle$ are the HOMO−LUMO transitions on monomers A and B, respectively; and $|A_{HOMO} \rightarrow B_{LUMO}\rangle$ ($|B_{HOMO} \rightarrow A_{LUMO}\rangle$) is the transition from A's (B's) HOMO to B's (A's) LUMO, which is of charge-transfer character. The lowest $\pi\pi^*$ transition on monomer A (B) is mainly $|A_{HOMO} \rightarrow A_{LUMO}\rangle$ ($|B_{HOMO} \rightarrow B_{LUMO}\rangle$). Therefore, the photoexcited states of the adenine monomers and the stacks of current interests can be modeled by Frenkel excitons with the following Hamiltonian:

$$\hat{H} = \sum_{nm} J_{nm} B_n^{\ddagger} B^{\dagger}{}_m \quad (2)$$

where J_{nm} is the interaction between the transition dipoles on bases n and m with the coupling between nearest neighbors $J = J_{n,n+1}$, and $B_n^{\ddagger}$ ($B_n^{\dagger}$) creates (annihilates) a Frenkel exciton on base n. In the TDB3LYP and TDHF calculations, the results for dimer have the same trend as that of ZINDO, except that in the TDDFT calculation the energies of the charge transfer states are lower than those of $\pi\pi^*$ optical transition states. And the energy split (0.04 eV) between the first and the second excited states calculated by TDDFT is much smaller than those of ZINDO and TDHF. The reason might be because the Hartree−Fock exchange part in the B3LYP method is smaller than that of the other two methods.

The orientations and positions of the calculated transition dipoles on four adjacent adenines (taken out from the 20-base strand in Figure 1c) are displayed in Figure 1a,b. By a simple inspection, the two adjacent transition dipoles are approximately parallel. We thus expect that the adenine strand forms an H-aggregate. This is supported by the fact that the second $\pi\pi^*$ excitation of the dimer has a much larger oscillator strength

TABLE 2: Singlet Excitation Energies and Their Corresponding Oscillator Strength of a B-Form Homogeneous Adenine Stack with 20 Bases[a]

state label	energies (eV)	osc. str. (ZINDO)	osc. str. [eq 2]
1	4.1760	0.000	0.00
2	4.1800	0.000	0.00
3	4.1843	0.000	0.00
4	4.1913	0.000	0.00
5	4.2003	0.000	0.00
6	4.2101	0.001	0.00
7	4.2223	0.000	0.00
8	4.2354	0.001	0.01
9	4.2500	0.001	0.00
10	4.2652	0.005	0.02
11	4.2819	0.004	0.00
12	4.2984	0.013	0.03
13	4.3149	0.007	0.00
14	4.3317	0.052	0.09
15	4.3472	0.063	0.02
16	4.3620	**1.046**	**0.93**
17	4.3728	**1.250**	**1.31**
18	4.3805	0.177	0.26
19	4.3857	0.046	0.01
20	4.3882	0.032	0.01

[a] To facilitate comparison, the oscillator-strength calculations based on eq 2 used a normalization factor from the ZINDO results.

than the first excited state. It has been postulated that the charge-transfer states may play an important role in the photophysics of adenine stacks.[5,11,12,22] However, charge-transfer states, such as States 13 and 14 of ZINDO results in Table 1, are made of mainly $|A_{HOMO} \rightarrow B_{LUMO}\rangle$ and $|B_{HOMO} \rightarrow A_{LUMO}\rangle$, and have much higher excitation energies. The charge transfer states might be important for double stranded DNA or other bases,[5,8,12] but for the homogeneous adenine single strand we can exclude them from our consideration for their much higher excitation energy than those of photoexcited states.

The fact that the homogeneous adenine strands are helical H-aggregates is further supported from our calculations for a 20-base adenine strand. Table 2 lists the 20 lowest energy excited states and their corresponding oscillator strengths from a ZINDO calculation of a 20-base strand of homogeneous adenine. It is found that the oscillator strength is concentrated on the 16th and 17th excited states counting from the lowest energy state due to the symmetry of the stacking. From Table 2, the bandwidth is estimated to be 0.212 eV implying that the near-neighbor coupling J is about 0.053 eV. This value of J has been corroborated by ZINDO calculations of dimers (0.055 eV), trimers (0.056 eV), and quadrumers (0.054 eV) of the adenine bases. The ZINDO results are in good agreement with a simple Frenkel exciton model that considers only the couplings between the transition dipoles of adjacent adenines and incorporates an angle of $\pi/5$ between them. Without loss of generality, the periodic boundary condition is employed first, and the oscillator strength is found to be shared entirely by the two degenerate states near the top of the exciton band with crystal momenta $K = \pm\pi/10a$ (a is the base spacing 3.4 Å). These two optically allowed states are exactly the 16th and 17th states counting from the lowest energy state at the bottom of the band, $K = \pi/a$, which is optically forbidden. After relaxing the periodic boundary condition, small leakage of the oscillator strength appears in other states, as shown in the fourth column of Table 2. To facilitate comparison, the oscillator-strength calculations based on eq 2 used a normalization factor from the ZINDO results. Excellent agreement has been found between the two sets of oscillator strengths. Taking into account only nearest-neighbor interactions $J = J_{n,n+1}$, energy eigenvalues of a 20-base strand with open boundaries are compared with those

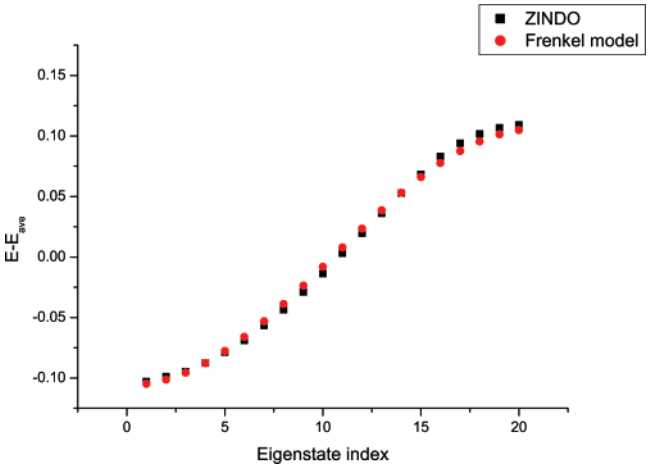

Figure 2. Energy plots (in eV) for the 20 lowest energy states from the ZINDO calculations (squares) and the Frenkel exciton model with $J = 0.053$ eV (filled circles). The average of the 20 ZINDO energies is set to zero. The horizontal axis labels the eigenstate index from 1 to 20.

from the ZINDO calculations in Figure 2 with a matching average energy value of zero. Again the agreement is good. Aside from finite-size effects (open boundaries), static disorder in the strand can also spread the oscillator strength to otherwise forbidden exciton states. In addition, this static disorder does not affect the conclusion that homogeneous adenine stacks are H-aggregates. Similar Frenkel exciton models have been applied with great success to model the excited state dynamics in purple-bacteria light-harvesting antenna complexes where arrays of bacterio-chlorophyll chromophores enable energy transfer in photosynthesis[23−26] and PPV aggregates.[27,28] In fact, applications of the excitonic model to Ade-DNA single strands, as suggested by Kohler and co-workers in their recent review article,[29] were also contemplated by Markovitsi et al. in their account of the observed decay of fluorescence and fluorescence anisotropy.[12]

In contrast to H-aggregates, the neighboring transition dipoles in J-aggregates are arranged in a head-to-tail configuration, and therefore, in low-lying excitonic states the transition dipoles are parallel to each other. J-aggregates were known from the mid-thirties to be highly fluorescent with absorption maxima red-shifted relative to those of their monomeric pigments.[30] On the other hand, H-aggregates exhibit weak or no fluorescence in addition to blue-shifted absorption spectra. The origin of the blue shift can be understood from the aforementioned oscillator-strength concentration near the top of the H-aggregate exciton band. Although absorption peaks of a DNA-base ensemble depend on a number of factors such as solvent effects, ensemble exciton−phonon coupling, and static disorder, the amount of the blue shift should be of the same order of magnitude as the coupling between the adjacent transition dipoles. The measured absorption spectra of a single-base adenosine and homogeneous single adenine strands containing 20 bases in aqueous solution (obtained from commercially available samples), as shown in Figure 3, give strong support to the proposed H-aggregation picture of homogeneous Ade-DNA-base strands. The absorption maxima of the 20-base strands (~257.2 nm) are found to be blue-shifted by about 2.6 nm (400 cm^{-1} or 0.05 eV) from that of the corresponding monomeric species (~259.8 nm), in good agreement with our calculated value of excitonic coupling strength between neighboring DNA bases, $J = 0.053$ eV. The measured absorption spectra have been fitted with a Brownian oscillator (BO) model in which a two-level electronic degree of freedom responsible for absorption is coupled to a phonon mode that is itself attached to a dissipative bath of harmonic

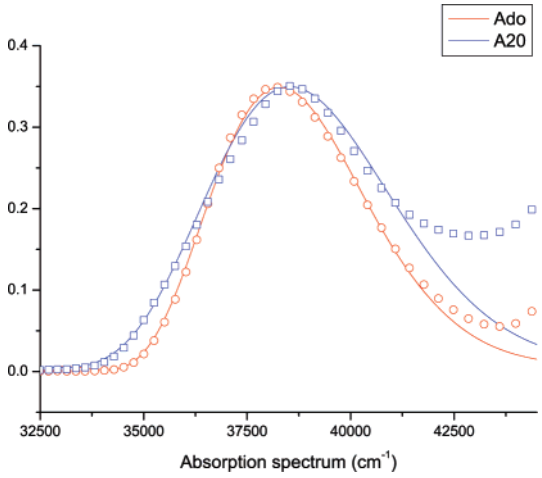

Figure 3. Measured absorption spectra in aqueous solution of single-base adenosine (Ado, red circle) and adenine strands that contain 20 bases ($(dA)_{20}$, blue square) in aqueous solution. The absorption maximum of the 20-base strands (~257.2 nm) is blue-shifted by about 2.6 nm relative to that of the single-base adenosine (~259.8 nm). Measured absorption spectra have been fitted with the BO model with an electronic degree of freedom coupled to a primary phonon mode of 1280 cm^{-1}, which in turn interacts linearly with a dissipative bath via a coupling strength of 1200 cm^{-1}. The BO fit for the single-base adenosine (red line) produces a Huang−Rhys factor $S = 2.9$, and that for the 20-base strands (blue line), $S = 4.1$.

oscillators.[31−33] A best fit is found with a phonon frequency of 1280 cm^{-1} and a system-bath coupling strength of 1200 cm^{-1}. So far we have not identified the vibration mode that is primarily responsible for the coupling. This mode may affect the lifetime of emission of homogeneous adenine oligo- and polynucleotides; and further work is being performed in this direction. The BO fit for the single-base adenosine (red line) produces a Huang−Rhys factor $S = 2.9$, and that for the 20-base strands (blue line), $S = 4.1$. Experimentally,[7] the monomer Stokes shift is found to be about 6000 cm^{-1}, in excellent agreement with our fitting-deduced Huang−Rhys factor $S = 2.9$. For 20-base adenine strands, the measured Stokes shift slightly exceeds that from the fitting. The spectral blue shift of the 20-base strand relative to the monomer, as calculated from the spacing between the zero-phonon lines of the two spectra, is about 1100 cm^{-1}, in agreement with the calculated value of 2*J*.

Fluorescence spectra for the 20-base homogeneous adenine strands show a broad structure with a half-width of about 10 000 cm^{-1} and a peak at 360−400 nm, while the fluorescence spectra for the single-base adenosine peak is at 307 nm.[7] The fact that the fluorescence spectra are red-shifted relative to those of the monomeric species sits well with our H-aggregate model because internal conversion to the lowest excitonic state in H aggregates happens much faster than emission, and fluorescence originates from the lowest energy exciton state (and perhaps even from defect states below the bottom of the exciton band, and thus the large half-width). Due to the small oscillator strength of the low-lying excitonic states which is generated by disorder and strand boundaries, the radiative lifetimes of the 20-base homogeneous adenine strands are greatly increased relative to their monomer species. This is in agreement with radiative rates estimated from measured absorption spectra of monomers and 20-base homogeneous adenine strands using the Strickler−Berg equation.[34] The radiative rate constant for monomeric emission is found to be 60 times that for 20-base homogeneous adenine strands.[7]

Despite much theoretical and experimental attention devoted to DNA photochemistry,[10,22] a clear description of the long-lived emissive state in DNA strands has remained elusive, and much contention still surrounds its physical nature and decay mechanisms. Here we have proposed an H-aggregation model for homogeneous single-stranded adenine DNA to give a simple, consistent explanation of various spectral observations for single-strand Ade-DNA. Calculated excitonic coupling between adjacent transition dipoles is in good agreement with measured absorption spectra of stacked and unstacked bases. In the literature, DNA strands have been used as templates for building H-aggregates of a cyanine dye.[35,36] Our work has been focused on the single-stranded Ade-DNA, and thus the results and conclusion cannot be extrapolated to heterogeneous DNA in general. Despite this, our work here might open up new venues to study photochemical decay of excited states in nuclei acid bases.

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