

Direct Observation of Triplet–Triplet Energy Transfer in DNA between Energy Donor and Acceptor C-Nucleotides

Sebastian Häcker,[§] Till J. B. Zähringer,[§] Hans-Achim Wagenknecht,^{*} and Christoph Kerzig^{*}



Cite This: *JACS Au* 2025, 5, 2770–2778



Read Online

ACCESS |



Metrics & More



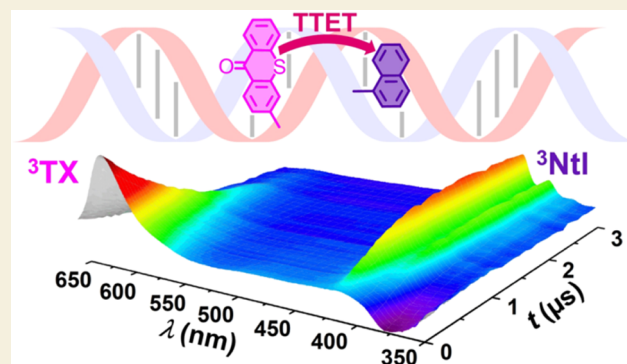
Article Recommendations



Supporting Information

ABSTRACT: Investigating the migration of excited-state energy in DNA is crucial for a deep understanding of protection mechanisms and light-induced DNA damage. While numerous reports focused on single electron transfer and Förster-type energy transfer in DNA, studies on the Dexter-type triplet–triplet energy transfer are scarce, in particular, those with direct detection of photoexcited triplet states. Herein, we present direct measurements of the distance-dependent triplet–triplet energy transfer rates through DNA by using transient absorption spectroscopy. This was achieved through the synthetic incorporation of thioxanthone as an energy donor and naphthalene as an energy acceptor into a DNA double strand at defined positions. The energy transfer rates strongly depend on the number of A-T base pairs (up to four) separating the energy donor from the energy acceptor. We observed a fast energy transfer rate with a time constant of 17 ns for the DNA sample in which the donor and acceptor are directly adjacent in the DNA. By analyzing two additional donor–acceptor distances, a steep exponential distance dependence with an attenuation factor of 1.15 \AA^{-1} could be obtained. Our results demonstrate that DNA acts as a poor conductor of triplet energy when energy donors with triplet energies below 2.7 eV are used, complementing more indirect studies on sensitized DNA damage.

KEYWORDS: DNA, energy transfer, oligonucleotides, photochemistry, time-resolved spectroscopy



INTRODUCTION

Solar ultraviolet (UV) light can be a threat to DNA, leading to light-induced DNA damage which, in the worst case, can lead to skin cancer.^{1–3} Nonetheless, in most cases, the excited states in DNA decay extremely fast (<1 ps) into charge-separated states. These return to their ground state through charge recombination, a property of DNA that protects it from light-induced damage.^{4–6} However, excited singlet states can also lead to photochemical reactions. For example, cyclobutane pyrimidine dimers (CPDs) are the most common DNA damage and are formed by singlet photochemistry on ultrafast time scale and in a nearly barrierless reaction at the site of excitation.^{7–9} In addition to the well-studied singlet photochemistry in DNA, it has been shown that excited triplet states also play an important role in the formation of DNA damage such as one-electron oxidation, cross-linking or CPDs.^{10–15} Singlet energy transfer typically occurs via dipole–dipole interactions, known as Förster Resonance Energy Transfer (FRET),¹⁶ from an excited donor to an acceptor. In contrast, triplet–triplet energy transfer (TTET) proceeds predominantly through the exchange mechanism (Dexter-type),¹⁷ which shares mechanistic similarities with electron transfer.¹⁸ Dexter energy transfer requires orbital overlap and, therefore, close proximity between the donor and acceptor. The range of

triplet energy transfer can be significantly extended by introducing bridging units that enable through-bond energy transfer,¹⁹ a phenomenon extensively studied in molecular systems.^{20,21} In certain cases, triplet-to-singlet energy transfer via dipole–dipole interactions has also been observed,²² or both mechanisms may operate in tandem.²³ Depending on the thermodynamic barriers introduced by the bridging units, energy transfer may occur sequentially through intermediate states via a hopping mechanism, provided these states are energetically accessible, or through tunneling. The mechanism by which triplet energy transfer in DNA leads to DNA damage is not yet fully understood, primarily because it is challenging to excite and localize triplet states in DNA at defined positions. Yet understanding the different photochemical mechanisms leading to DNA damage is crucial for elucidating the different pathways to skin cancer.

Received: March 31, 2025

Revised: May 19, 2025

Accepted: May 20, 2025

Published: May 27, 2025



Scheme 2. Synthesis of Naphthalene C-Nucleoside 4 and Phosphoramidite 6 as DNA Building Block

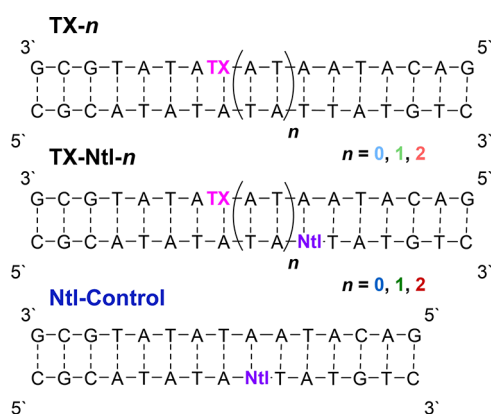
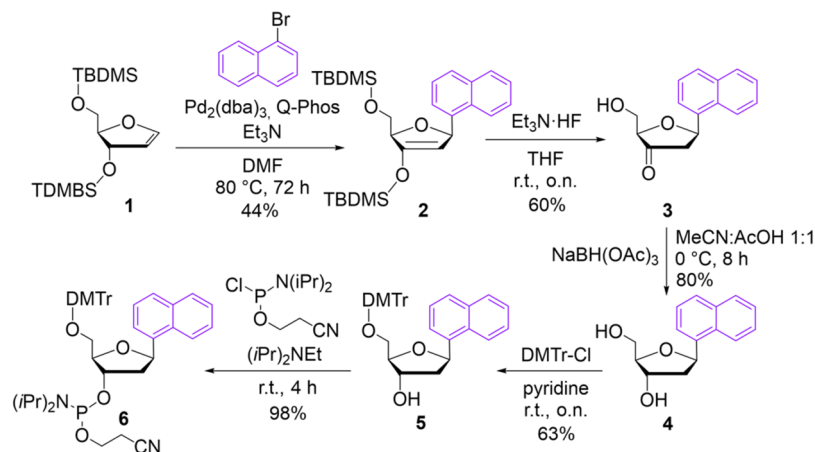


Figure 1. Top: Sequences of DNA double strands TX-*n* modified with TX and TX-Ntl-*n* modified with both TX and Ntl. Bottom: color-coded UV-vis absorption spectra of 90 μM DNA double strands TX-*n*, TX-Ntl-*n* and Ntl-Control (dark blue) in aqueous buffer solution (250 mM NaCl, 10 mM Na-P_i buffer, pH 7.0) and of 80 μM thioxanthone (pink) or 200 μM naphthalene (purple) in MeCN.

TX; see Figure 1 for its structure). The unmodified DNA single strands for the latter double strands were purchased.

Optical Spectroscopy

The UV-vis absorption spectra of all DNA double strands show ~ 20 nm red shifts of the long-wavelength absorption band of thioxanthone to 397 nm compared to the absorption spectrum of thioxanthone in acetonitrile with a maximum at 378 nm (Figure 1, bottom). The observed red shift can be explained by the more polar DNA environment, assuming that the TX chromophore is intercalated in the DNA base stack. This leads to a stabilization of the S₁ (π - π^*) state.⁴⁹ As a result, a relatively high concentration (90 μM , based on double-strand DNA) of the samples was required to ensure efficient excitation at our laser wavelength 355 nm and sensitive TA detection accordingly. As is evident from the reference spectra of naphthalene in MeCN and the DNA double strand Ntl-Control (see Figure 1), both the naphthalene chromophore and the conventional DNA bases do not absorb at 355 nm, ensuring selective laser excitation of TX (see Section S4.2 for further control experiments).

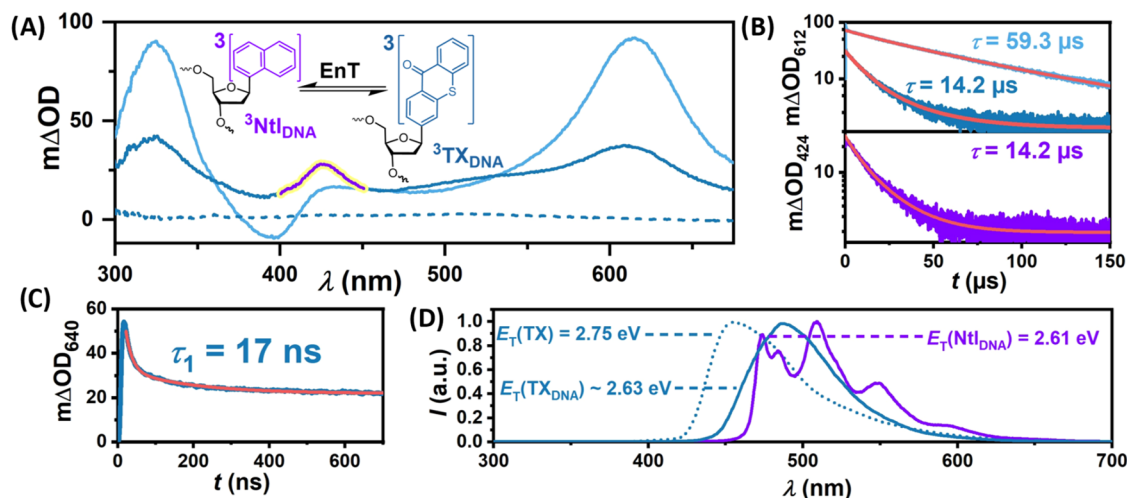


Figure 2. Mechanistic studies of TX-Ntl-0 (dark blue) and TX-0 (light blue) with 355 nm laser pulses. (A) Transient absorption spectra recorded 100 ns after excitation. The triplet-triplet absorption band of Ntl_{DNA} is highlighted in purple. (B) and (C) Time-resolved measurements at different detection wavelengths and time scales. (D) Time-gated 77 K emission of TX in MeCN (dotted line) and TX-Ntl-0 in aqueous buffer (250 mM NaCl, 10 mM Na-P_i buffer, pH 7.0) integrated 10 ms – 100 ms (blue) and 4.0 to 4.3 s (purple) after laser excitation.

Transient absorption spectroscopy employing a pulsed 355 nm laser (~ 20 mJ, ~ 5 ns pulse duration) was used to excite the DNA double strands in deaerated aqueous solution containing 250 mM NaCl and 10 mM Na–P_i buffer (buffer pH 7: 6.1 mM sodium phosphate monobasic and 3.9 mM sodium phosphate dibasic). The first sample we investigated was TX-Ntl-0, in which TX and Ntl are adjacent without any base pairs in between, together with the reference DNA double strand TX-0. We first analyzed the TA spectrum of TX-0. Immediately following excitation (100 ns), two absorption bands appeared at 320 and 612 nm, along with a ground-state bleach (GSB) observed at ~ 400 nm (Figure 2A).

These bands are associated with a TX-localized triplet state of the C-nucleotide of TX ($^3\text{TX}_{\text{DNA}}$),⁴⁶ which is rapidly generated via intersystem crossing from the singlet-excited state.⁵⁰ Compared to the triplet absorption spectrum of TX in MeCN (Figure S1A), the bands exhibit slight shifts, a phenomenon previously noted for TX in protic solvents and attributed to substitution at position 2.⁵¹ We obtain a triplet state lifetime of 59.3 μs for TX-0 (Figure 2B, top panel), within the lifetime range of unquenched ^3TX and its derivatives in aprotic and protic solvents.^{52–54} We conclude that the triplet-excited state of the C-nucleotide of TX is not quenched by the DNA bases in line with prior investigations, where CPD as a result of triplet–triplet energy transfer was only observed for triplet energy donors with higher triplet energies (>2.80 eV).²⁶ Exciting the DNA TX-Ntl-0 yielded an additional absorption band centered at 424 nm alongside the triplet absorption spectrum of TX directly after excitation (a 100 ns delay time was used to ensure the absence of stray light and fluorescence). This absorption band could be attributed to the Ntl-localized triplet state of the C-nucleotide ($^3\text{Ntl}_{\text{DNA}}$). Compared to the triplet absorption spectrum of Ntl in MeCN (Figure S1A), the fine structure is lost due to broadening and the spectrum is shifted to longer wavelengths. However, these observations can be traced back to the solvent influence on the Ntl triplet⁵⁵ and to the conversion of Ntl to the 2'-deoxyribofuranoside at the α -position.⁵⁶ In line with our observations, Kiefhaber et al. reported a similar transient absorption spectrum for ^3Ntl , with a peak at 420 nm, when they investigated the TTET dynamics between TX and Ntl connected by a peptide bridge.⁵⁷ We found that both transient species concurrently decay with a lifetime of 14.2 μs (Figure 2B). Assigning the species with the ~ 420 nm absorption band to $^3\text{Ntl}_{\text{DNA}}$ raises the question of why both $^3\text{Ntl}_{\text{DNA}}$ and $^3\text{TX}_{\text{DNA}}$ appear to form after excitation (100 ns delay) and decay with essentially identical lifetimes. This is particularly puzzling given that (i) we have ruled out the direct excitation of Ntl_{DNA} and (ii) the proposed energy transfer mechanism suggests that $^3\text{Ntl}_{\text{DNA}}$ should be generated during the quenching of $^3\text{TX}_{\text{DNA}}$. Indeed, the C-nucleotides of TX and Ntl in the TX-Ntl-0 DNA are in close proximity (3.4 Å based on regular stacking distance),⁵⁸ which is within the typical distance required for efficient Dexter-type energy transfer (<1 nm). Consequently, we expect the energy transfer to occur nearly instantaneously (<100 ns). However, detection in that range is challenging due to the strong fluorescence signal from TX (see also Section S4.4), which causes detector saturation. For this reason, a detection wavelength of 640 nm was chosen for $^3\text{TX}_{\text{DNA}}$ (Figure 2C), where the TX singlet state does not emit anymore. Time-resolved measurements show indeed a more complex kinetic scenario, and a biexponential fit resulted in a lifetime of 17 ns for the faster component, superimposed

by the longer lifetime (compare Figure 2B). The seemingly incomplete quenching of $^3\text{TX}_{\text{DNA}}$ prompted us to conduct time-gated 77 K emission spectroscopy. Interestingly, we observed two emission signals at different time intervals, which can be attributed to the phosphorescence of $^3\text{TX}_{\text{DNA}}$ followed by that of $^3\text{Ntl}_{\text{DNA}}$ (Figure 2D). Compared to the phosphorescence of TX in MeCN, the emission from the thioxanthone C-nucleoside is significantly red-shifted (~ 40 nm), indicating a decrease in triplet state energy. Similar environment effects on triplet-related properties in DNA were predicted and observed before.^{26,59,60}

We propose that the lower triplet state energy of TX_{DNA} reduces the energy gap to $^3\text{Ntl}_{\text{DNA}}$, which enables back energy transfer (bTTET) at room temperature reaching an equilibrated state.^{61–63} At 77 K bTTET becomes negligibly slow as is evident from time-gated emission spectra shown in Figure S11. Based on all these observations, we estimate the triplet state energy of Ntl_{DNA} to be 2.61 eV. Determining the triplet energy of TX_{DNA} is more challenging due to its broad phosphorescence spectrum. However, using the relative distribution of triplet states between Ntl_{DNA} and TX_{DNA} at 77 K and in the equilibrated state at room temperature, we estimate its energy to be approximately 2.63 eV (see Section S4.7 of the SI for details). These energy estimations support the assumption that TX has a lower triplet state energy than the DNA bases, consistent with the absence of characteristic transient absorption bands from the nucleotides.⁴⁰ Emission quenching of singlet-excited TX_{DNA} seems to be a minor process and occurs on a shorter time scale than the observed initial $^3\text{TX}_{\text{DNA}}$ decay and $^3\text{Ntl}_{\text{DNA}}$ formation (Section S4.4), ruling out significant contributions of Förster-like energy transfer processes. To summarize the results obtained for DNA TX-Ntl-0, after the formation of $^3\text{TX}_{\text{DNA}}$ we unequivocally observe rapid triplet–triplet energy transfer to Ntl_{DNA} with $k_{\text{TTET}} = (58.8 \pm 11.7) \times 10^6 \text{ s}^{-1}$ (see SI for calculation of k_{TTET}), reaching an equilibrated state⁶⁴ of $^3\text{TX}_{\text{DNA}}$ and $^3\text{Ntl}_{\text{DNA}}$ owing to the almost isoenergetic triplet states. These triplet states decay on a much longer time scale ($k_{\text{TTET}}, k_{\text{bTTET}} \gg k_{\text{TX}}, k_{\text{Ntl}}$). Interestingly such an energy transfer equilibrium has also been described by Kiefhaber et al. for the same donor–acceptor pair in a peptide environment.⁵⁷

Next, we examined the DNA double strand TX-Ntl-1, with two A-T base pairs separating the TX and Ntl C-nucleotides, in conjunction with the reference DNA TX-1. The TA spectra recorded 100 ns after 355 nm laser excitation are almost identical for these DNA samples (Figure 3A).

Yet, time-resolved measurements of $^3\text{TX}_{\text{DNA}}$ at 612 nm, where it can be monitored in isolation, reveal a faster deactivation in the presence of Ntl_{DNA} (TX-Ntl-1) in comparison to its absence (TX-1). This observation suggests $^3\text{TX}_{\text{DNA}}$ quenching by Ntl_{DNA} (Figure 3B). Indeed, we observe the formation of the $^3\text{Ntl}_{\text{DNA}}$ band at longer delay times (inset of Figures 3A, and S9). Comparative kinetic measurements at 424 nm show the slow formation of $^3\text{Ntl}_{\text{DNA}}$ in TX-Ntl-1 (Figure 3C). This signal rise cannot be observed for TX-1, which again shows a lifetime being typical for unquenched ^3TX . For this rather slow quenching process, we ruled out the possibility of inter-DNA energy transfer (from TX of one DNA double strand to Ntl in another DNA double strand, compare results with TX-Ntl-2 presented below) and attribute this to intra-DNA triplet energy migration from $^3\text{TX}_{\text{DNA}}$ to Ntl_{DNA} (in the same DNA double strand). Moreover, $^3\text{TX}_{\text{DNA}}$ was only moderately quenched by dissolved oxygen in the air-saturated

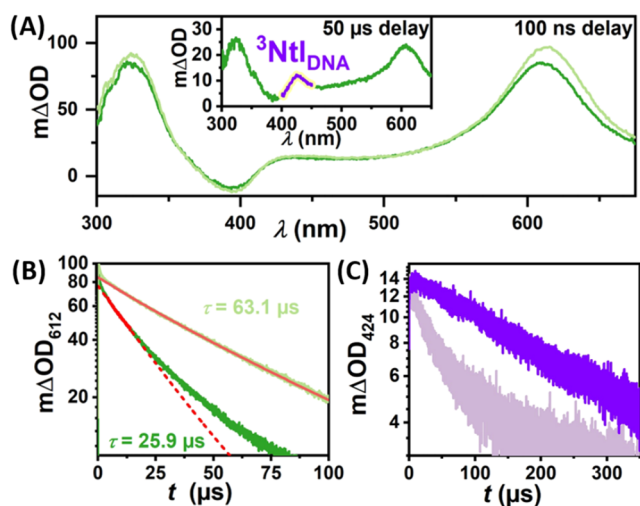


Figure 3. Mechanistic studies of TX-Ntl-1 (dark green) and TX-1 (light green) with 355 nm laser pulses. (A) TA spectra recorded 100 ns after excitation. Inset: TA spectrum of TX-Ntl-1 recorded 50 μ s after excitation. The triplet–triplet absorption band of Ntl_{DNA} is highlighted in purple. (B) Kinetic TA measurements at 612 nm. (C) Kinetic TA measurements of TX-Ntl-1 (purple) and TX-1 (light purple) at 424 nm.

solution of TX-0, underscoring the protective geometry of the DNA backbone. To determine the energy transfer constant, the decay trace of ³TX_{DNA} at 612 nm was fitted monoexponentially until the energy transfer efficiency η_{ET} reaches $\sim 30\%$ and back energy transfer has to play a minor role, making the reasonable assumption that TTET is faster than bTTET. Using the unquenched ($\tau = 63.1 \mu\text{s}$) and quenched lifetime of ³TX_{DNA} ($\tau = 25.9 \mu\text{s}$) we calculate an energy transfer rate constant of $k_{\text{TTET}} = (22.7 \pm 4.0) \times 10^3 \text{ s}^{-1}$. In contrast to TX-Ntl-0 the (back) energy transfer constant in TX-Ntl-1 is several orders of magnitude slower due to the larger separation of the C-nucleotides in the DNA (10.2 Å), and on the same order as the triplet decay constants of TX_{DNA} and Ntl_{DNA} ($k_{\text{TTET}} > k_{\text{bTTET}} \sim k_{\text{TX}} k_{\text{Ntl}}$). As a result, an equilibrium-like state is reached on a much slower time scale (Figure S9C).

Lastly, the DNA double strands TX-Ntl-2 and TX-2 were examined. Virtually identical TA spectra are observed after excitation (Figure 4A). However, in contrast to the pair with the shorter donor–acceptor distance investigated in Figure 3, kinetic traces of ³TX_{DNA} yield essentially identical lifetimes, taking experimental errors into account. Only a minor lifetime

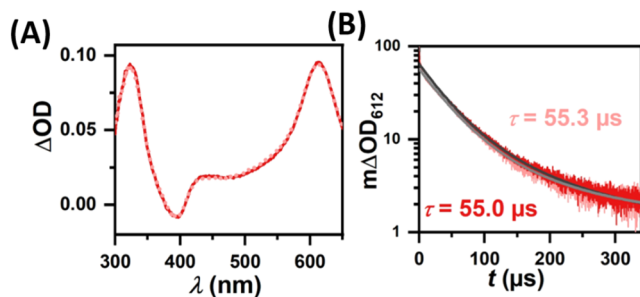


Figure 4. Mechanistic studies of TX-Ntl-2 (dark red) and TX-2 (light red) with 355 nm laser pulses. (A) TA spectra recorded 100 ns after excitation. (B) Kinetic TA measurements at 612 nm.

decrease from 55.3 ± 0.8 to $55.0 \pm 0.9 \mu\text{s}$ is observed with the introduction of the Ntl C-nucleotide into the DNA double strand (Figure 4B). The high photostability of the DNA samples allowed us to perform several independent sets of measurements, supporting the reliability of the obtained lifetimes (see Section S4.7). Based on this, we calculated an energy transfer constant of $(100 \pm 400) \text{ s}^{-1}$. However, we would like to note that the deviation is higher than the calculated energy transfer constant and should be seen as an upper limit while $k_{\text{TTET}} = 0 \text{ s}^{-1}$ sets the lower limit. In any case, at this donor–acceptor distance with four A-T base pairs in-between the donor and the acceptor (17 Å), TTET becomes negligibly small. Given that ³TX_{DNA} is virtually not quenched by Ntl in TX-Ntl-2 on this long time scale which would enable efficient diffusion of large DNA fragments, we can also exclude the possibility of inter-DNA energy transfer as a competing pathway alongside the primary intra-DNA energy migration. In a somewhat related system with a methoxyxanthone C-nucleoside as light absorber, the CPD yields are very similar for double stands with zero or four separating A-T base pairs.⁶⁵ The completely different behavior observed in this study with a drastically more pronounced distance dependence already indicates a Dexter-like instead of a FRET-like energy migration mechanism.

During our experimental work, we observed a secondary process in all TX-containing DNA samples following 355 nm laser excitation, likely associated with the neighboring DNA bases. However, this process is unrelated to the primary focus of this study on triplet energy migration and does not affect the results. A detailed description, along with several control experiments, is provided in the Supporting Information (Section S4.3).

Distance-Dependence of Triplet–Triplet Energy Transfer

The above-mentioned triplet–triplet energy transfer rates in the three DNA samples with varying donor–acceptor separation were plotted against the respective donor–acceptor distance on a semilogarithmic scale (Figure 5). The distance dependence of electron transfer (ET) and TTET, both governed by exchange-type mechanisms between a donor and an acceptor, is empirically described by the exponential rate equation $k_{\text{DA}} = k_0 \cdot \exp(-\beta \cdot r_{\text{DA}})$.^{20,21,66,67} Where β is the attenuation factor and it is fundamentally determined by the effective barrier height, ΔE_{eff} , which inversely correlates with the probability of electron tunneling.^{68,69} In the so-called superexchange mechanism, coupling between donor and acceptor is facilitated by orbitals of bridging units, which greatly surpasses the two-electron exchange integral in magnitude.^{70,71} In a simplified model proposed by Closs et al.,⁷² the attenuation factor for ET is approximately half that of TTET, which can be conceptualized as the simultaneous exchange of two electrons broadly supported by *ab initio* and semiempirical calculations.⁷³ However, this assumption does not hold true, when intermediate virtual donor–acceptor CT or bridge-localized excited states are involved in the energy transfer pathways.¹⁹ In such a scenario, the β value can be lower than the sum of the superexchange constants of electron and hole transfer (see Section S5 for further explanations).^{71,74}

In environments with high barrier heights ($\Delta E_{\text{eff}} > 1 \text{ eV}$), such as vacuum or certain solvents, β values typically range from 1.5 to 5 \AA^{-1} .^{74,75} Molecular bridging significantly enhances the exchange mechanism between donor and acceptor attributed to a reduced ΔE_{eff} and low lying virtual

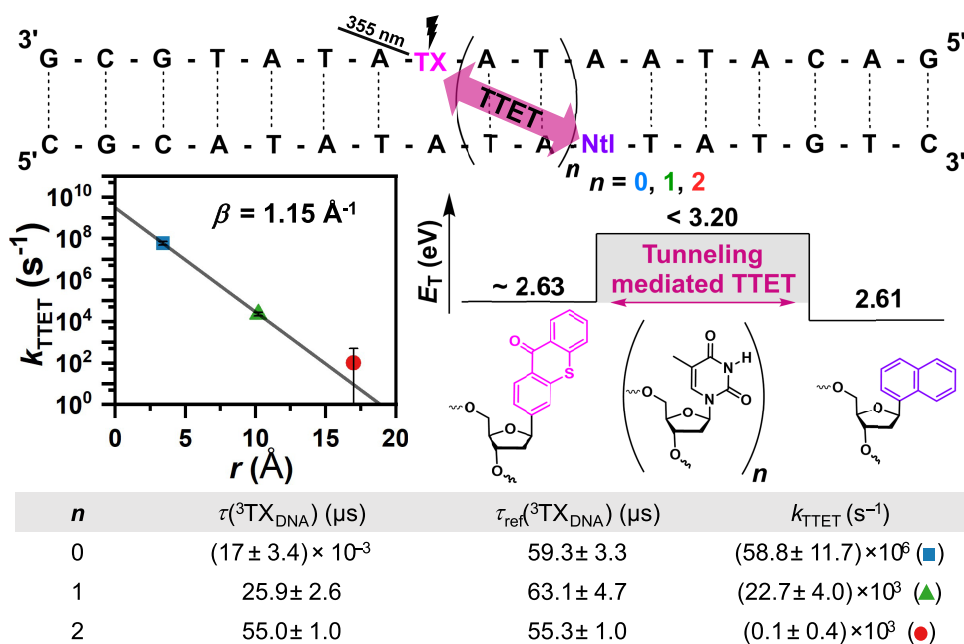


Figure 5. Sequences of DNA double strands TX-Ntl- n , experimentally observed distance dependence of triplet–triplet energy transfer from $^3\text{TX}_{\text{DNA}}$ to Ntl_{DNA} , schematic energy diagram of triplet–triplet energy transfer with plausible tunneling mechanism via the thymine triplet state. The table displays the quenched (τ for TX-Ntl- n) and unquenched (τ_{ref} for TX- n) TX triplet lifetimes and the resulting TTET rate constants. See Table S1 for details.

bridge states that mediate electronic coupling. For instance, TTET between Ru and Os complexes employing aromatic spacers such as phenyleneethynylene^{76,77} and phenylene⁷⁸ units are typically associated with attenuation factors $< 1 \text{ \AA}^{-1}$. If the effective barrier height approaches the available thermal energy, TTET and ET can occur via a hopping mechanism with real intermediate states, significantly extending the transfer range and reducing β to values as low as $< 0.1 \text{ \AA}^{-1}$.^{79,80}

The DNA double helix presents a distinctive structure with arrays of π -stacked nucleobases separated by 3.4 Å. This configuration favors charge and energy transfer along the bases (through-space) rather than along the sugar–phosphate backbone (through-bond).⁸¹ Tunneling and hopping mechanisms for charge transfer, particularly hole transfer, have been extensively studied in DNA systems.^{81–90} In contrast, research on TTET within DNA remains limited and is usually based on indirect detection methods.^{24,26,30,35} The handful of studies on this topic are further complicated by the combined effects of Förster- and Dexter-type energy transfer between intercalated donor and acceptor molecules.^{30,35} These interactions obscure a clear understanding of the underlying mechanisms leading to vastly different β values and contradicting interpretations.³¹

Among the free nucleotides thymidine has the lowest triplet state energy ($E_{\text{T}} = 3.2 \text{ eV}$).^{40,91,92} In recent studies, led by one of our groups, the distance dependence of triplet–triplet energy transfer in DNA using high triplet energy donors was thoroughly investigated by detecting the formation of T–T dimers. When sensitizers with $E_{\text{T}} > 3.0 \text{ eV}$ were employed, a shallow distance dependence ($0.13\text{--}0.37 \text{ \AA}^{-1}$) suggested that a hopping mechanism was operative.^{24,26} The triplet energies of the free nucleotides ($\geq 3.2 \text{ eV}$) cannot support such a hopping mechanism, however stabilizing effects in DNA can significantly lower triplet state energies.⁹³ For instance, an average triplet state energy of 2.8 eV has been inferred for thymine in supercoiled circular DNA.⁴⁷ Accurately determining triplet state energies of nucleobases within the DNA stack is

challenging, as they are influenced by distinct local environments. Recently, the triplet state energy of thymine in poly-A-T sequences – most relevant to our system – has been calculated at 3.0 eV using a free energy perturbation method that accounts for DNA effects.⁹⁴

Applying the above-mentioned fit function, we obtain an attenuation factor of 1.15 \AA^{-1} , which is considerably higher than values reported in previous studies of long-range TTET in DNA using triplet sensitizers with $E_{\text{T}} > 3.0 \text{ eV}$ ^{24,26} and more resembling reports of insulating bridging units in other molecular systems.^{68,95} Hence, a hopping mechanism involving intermediate states of DNA bases^{26,34,39} is unlikely, which is consistent with the absence of triplet state signals from DNA bases in the transient absorption spectra.⁴⁰ Considering the effective barrier height between the triplet donor ($\sim 2.63 \text{ eV}$) and the bridge (calculated at 3.0 eV for poly-A-T sequences) the attenuation factor supports a concerted TTET exchange mechanism, however, the involvement of virtual bridge or CT states cannot be excluded completely (see Section S5 for details).⁹⁴ Based on these findings, we propose that a tunneling mechanism facilitates intra-DNA energy transfer in TX-Ntl-1 and most likely in TX-Ntl-2 as well.^{70,76,77,96} The most plausible scenario involves a through-space mediated exchange interaction across the A-T pairs (Figure 5).

CONCLUSIONS

In this study, we have demonstrated that the DNA structure supports triplet energy transfer between thioxanthone (donor) and naphthalene (acceptor), which proceeds via a tunneling mechanism when a direct donor–acceptor orbital overlap is not feasible. Both chromophores were placed as artificial C-nucleotides at defined places in the DNA sequences. Through transient absorption spectroscopy, we provide direct evidence for triplet–triplet energy transfer and determined energy transfer rates for three specific donor–acceptor separations: directly adjacent (3.4 Å), separated by two (10.2 Å) and by

four alternating A-T base pairs (17 Å). From these measurements, we calculated an attenuation factor of 1.15 Å⁻¹, consistent with related DNA electron transfer studies. Notably, the energy transfer rate observed in the DNA double strand with longest separation between donor and acceptor shows that energy migration becomes negligible at a donor–acceptor separation of four base pairs (17 Å) comparable to molecular donor–acceptor systems with insulating bridging units.^{68,95} This highlights DNA as a relatively poor conductor of triplet energy when hopping is thermodynamically unfeasible. While the triplet state energy of nucleobases is reduced due to π -stacking in DNA, it remains sufficiently high to suppress long-ranged energy migration by UVA-absorbing triplet donors and is likely entirely impractical when using visible light-absorbing sensitizers, whose triplet energies are usually well below 2.7 eV.^{45,97} This serves as an effective protective mechanism for DNA against sunlight-driven sensitization. These findings align with the conclusions of Miranda et al., who established an alert limit for phototoxicity in chemicals at an $E_T \sim 2.8$ eV.⁴⁷

■ ASSOCIATED CONTENT

Data Availability Statement

All experimental data have been provided in the main text and the SI. The data sets shown in the main paper be found under <https://doi.org/10.25358/openscience-12363>.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.5c00364>.

Materials and methods, experimental details, characterization data, additional steady-state and time-resolved spectroscopic results, raw data sets, and control experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Hans-Achim Wagenknecht – Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe 76131, Germany; orcid.org/0000-0003-4849-2887; Email: wagenknecht@kit.de

Christoph Kerzig – Department of Chemistry, Johannes Gutenberg University Mainz, Mainz 55128, Germany; orcid.org/0000-0002-1026-1146; Email: ckerzig@uni-mainz.de

Authors

Sebastian Häcker – Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe 76131, Germany
Till J. B. Zähringer – Department of Chemistry, Johannes Gutenberg University Mainz, Mainz 55128, Germany

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacsau.5c00364>

Author Contributions

§S.H. and T.J.B.Z. contributed equally to this paper, names ordered alphabetically.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge generous financial support from the JGU Mainz the KIT and the German Research Foundation (DFG, grant number KE 2313/7-1). T.J.B.Z. is grateful to the German Federal Environmental Foundation (DBU) for a PhD fellowship (grant number 20022/028).

■ REFERENCES

- (1) Pfeifer, G. P.; Besaratinia, A. UV Wavelength-Dependent DNA Damage and Human Non-Melanoma and Melanoma Skin Cancer. *Photochem. Photobiol. Sci.* **2012**, *11* (1), 90–97.
- (2) Cadet, J.; Douki, T. Formation of UV-Induced DNA Damage Contributing to Skin Cancer Development. *Photochem. Photobiol. Sci.* **2018**, *17* (12), 1816–1841.
- (3) Taylor, J. S. Unraveling the Molecular Pathway from Sunlight to Skin Cancer. *Acc. Chem. Res.* **1994**, *27* (3), 76–82.
- (4) Crespo-Hernández, C. E.; Cohen, B.; Hare, P. M.; Kohler, B. Ultrafast Excited-State Dynamics in Nucleic Acids. *Chem. Rev.* **2004**, *104* (4), 1977–2020.
- (5) Middleton, C. T.; De La Harpe, K.; Su, C.; Law, Y. K.; Crespo-Hernández, C. E.; Kohler, B. DNA Excited-State Dynamics: From Single Bases to the Double Helix. *Annu. Rev. Phys. Chem.* **2009**, *60* (1), 217–239.
- (6) Kohler, B. Nonradiative Decay Mechanisms in DNA Model Systems. *J. Phys. Chem. Lett.* **2010**, *1* (13), 2047–2053.
- (7) Heil, K.; Pearson, D.; Carell, T. Chemical Investigation of Light Induced DNA Bipyrimidine Damage and Repair. *Chem. Soc. Rev.* **2011**, *40* (8), 4271–4278.
- (8) Cadet, J.; Grand, A.; Douki, T. Solar UV Radiation-Induced DNA Bipyrimidine Photoproducts: Formation and Mechanistic Insights. In *Photoinduced Phenomena in Nucleic Acids II*; Barbatti, M.; Borin, A. C.; Ullrich, S., Eds. Topics in Current Chemistry; Springer International Publishing: Cham, 2014; Vol. 356, pp 249–275 DOI: [10.1007/128_2014_553](https://doi.org/10.1007/128_2014_553).
- (9) Schreier, W. J.; Schrader, T. E.; Koller, F. O.; Gilch, P.; Crespo-Hernández, C. E.; Swaminathan, V. N.; Carell, T.; Zinth, W.; Kohler, B. Thymine Dimerization in DNA Is an Ultrafast Photoreaction. *Science* **2007**, *315* (5812), 625–629.
- (10) Cadet, J.; Douki, T.; Ravanat, J.-L.; Di Mascio, P. Sensitized Formation of Oxidatively Generated Damage to Cellular DNA by UVA Radiation. *Photochem. Photobiol. Sci.* **2009**, *8* (7), 903–911.
- (11) Epe, B. DNA Damage Spectra Induced by Photosensitization. *Photochem. Photobiol. Sci.* **2012**, *11* (1), 98–106.
- (12) Cuquerella, M. C.; Lhiaubet-Vallet, V.; Cadet, J.; Miranda, M. A. Benzophenone Photosensitized DNA Damage. *Acc. Chem. Res.* **2012**, *45* (9), 1558–1570.
- (13) Aparici-Espert, I.; Garcia-Lainez, G.; Andreu, I.; Miranda, M. A.; Lhiaubet-Vallet, V. Oxidatively Generated Lesions as Internal Photosensitizers for Pyrimidine Dimerization in DNA. *ACS Chem. Biol.* **2018**, *13* (3), 542–547.
- (14) Francés-Monerris, A.; Hognon, C.; Miranda, M. A.; Lhiaubet-Vallet, V.; Monari, A. Triplet Photosensitization Mechanism of Thymine by an Oxidized Nucleobase: From a Dimeric Model to DNA Environment. *Phys. Chem. Chem. Phys.* **2018**, *20* (40), 25666–25675.
- (15) Wagenknecht, H.-A. Remote Photodamaging of DNA by Photoinduced Energy Transport. *ChemBioChem* **2022**, *23* (2), No. e202100265.
- (16) Förster, Th. Mechanisms of Energy Transfer. In *Comprehensive Biochemistry*; Elsevier, 1967; Vol. 22, pp 61–80 DOI: [10.1016/B978-1-4831-9712-8.50010-2](https://doi.org/10.1016/B978-1-4831-9712-8.50010-2).
- (17) Dexter, D. L. A Theory of Sensitized Luminescence in Solids. *J. Chem. Phys.* **1953**, *21* (5), 836–850.
- (18) Hsu, C.-P. The Electronic Couplings in Electron Transfer and Excitation Energy Transfer. *Acc. Chem. Res.* **2009**, *42* (4), 509–518.
- (19) Skourtis, S. S.; Liu, C.; Antoniou, P.; Virshup, A. M.; Beratan, D. N. Dexter Energy Transfer Pathways. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113* (29), 8115–8120.

- (20) Wenger, O. S. Photoinduced Electron and Energy Transfer in Phenylene Oligomers. *Chem. Soc. Rev.* **2011**, *40* (7), 3538.
- (21) Albinsson, B.; Mårtensson, J. Excitation Energy Transfer in Donor–Bridge–Acceptor Systems. *Phys. Chem. Chem. Phys.* **2010**, *12* (27), 7338.
- (22) Galley, W. C.; Stryer, L. Triplet-Singlet Energy Transfer in Proteins. *Biochemistry* **1969**, *8* (5), 1831–1838.
- (23) Cravcenco, A.; Ye, C.; Gräfenstein, J.; Börjesson, K. Interplay between Förster and Dexter Energy Transfer Rates in Isomeric Donor–Bridge–Acceptor Systems. *J. Phys. Chem. A* **2020**, *124* (36), 7219–7227.
- (24) Antusch, L.; Gaß, N.; Wagenknecht, H.-A. Elucidation of the Dexter-Type Energy Transfer in DNA by Thymine–Thymine Dimer Formation Using Photosensitizers as Artificial Nucleosides. *Angew. Chem., Int. Ed.* **2017**, *56* (5), 1385–1389.
- (25) Gaß, N.; Wagenknecht, H.-A. Synthesis of Benzophenone Nucleosides and Their Photocatalytic Evaluation for [2 + 2] Cycloaddition in Aqueous Media. *Eur. J. Org. Chem.* **2015**, *2015* (30), 6661–6668.
- (26) Häcker, S.; Schrödter, M.; Kuhlmann, A.; Wagenknecht, H.-A. Probing of DNA Photochemistry with C-Nucleosides of Xanthenes and Triphenylene as Photosensitizers To Study the Formation of Cyclobutane Pyrimidine Dimers. *JACS Au* **2023**, *3* (7), 1843–1850.
- (27) Wang, X.; Martínez-Fernández, L.; Zhang, Y.; Wu, P.; Kohler, B.; Improta, R.; Chen, J. Ultrafast Formation of a Delocalized Triplet-Excited State in an Epigenetically Modified DNA Duplex under Direct UV Excitation. *J. Am. Chem. Soc.* **2024**, *146* (3), 1839–1848.
- (28) Eisinger, J.; Shulman, R. G. Excited Electronic States of DNA. *Science* **1968**, *161* (3848), 1311–1319.
- (29) Lamola, A. A.; Guéron, M.; Yamane, T.; Eisinger, J.; Shulman, R. G. Triplet State of DNA. *J. Chem. Phys.* **1967**, *47* (7), 2210–2217.
- (30) Hurley, D. J.; Tor, Y. Donor/Acceptor Interactions in Systematically Modified Ru^{II} – Os^{II} Oligonucleotides. *J. Am. Chem. Soc.* **2002**, *124* (44), 13231–13241.
- (31) Holmlin, R. E.; Tong, R. T.; Barton, J. K. Long-Range Triplet Energy Transfer between Metallointercalators Tethered to DNA: Importance of Intercalation, Stacking, and Distance. *J. Am. Chem. Soc.* **1998**, *120* (37), 9724–9725.
- (32) Lakowicz, J. R.; Piszczek, G.; Kang, J. S. On the Possibility of Long-Wavelength Long-Lifetime High-Quantum-Yield Lumino-phores. *Anal. Biochem.* **2001**, *288* (1), 62–75.
- (33) Kang, J. S.; Piszczek, G.; Lakowicz, J. R. Enhanced Emission Induced by FRET from a Long-Lifetime, Low Quantum Yield Donor to a Long-Wavelength, High Quantum Yield Acceptor. *J. Fluoresc.* **2002**, *12* (1), 97–103.
- (34) Giese, B. Long-Distance Charge Transport in DNA: The Hopping Mechanism. *Acc. Chem. Res.* **2000**, *33* (9), 631–636.
- (35) Brun, A. M.; Harriman, A. Energy- and Electron-Transfer Processes Involving Palladium Porphyrins Bound to DNA. *J. Am. Chem. Soc.* **1994**, *116* (23), 10383–10393.
- (36) Zhang, X.; Hu, H.; Liu, W.; Wang, Y.; Liu, J.; Wu, P. Selective Heavy Atom Effect Forming Photosensitizing Hot Spots in Double-Stranded DNA Matrix. *J. Phys. Chem. Lett.* **2021**, *12* (38), 9205–9212.
- (37) Jin, P.; Wang, J.-N.; Wang, X.; Jia, M.; Pan, H.; Mei, Y.; Chen, J. Tracking the Early Stage of Triplet-Induced Photodamage in a DNA Dimer and Oligomer Containing 5-Methylcytosine. *J. Phys. Chem. B* **2023**, *127* (31), 6878–6886.
- (38) Lu, C.; Gutierrez-Bayona, N. E.; Taylor, J.-S. The Effect of Flanking Bases on Direct and Triplet Sensitized Cyclobutane Pyrimidine Dimer Formation in DNA Depends on the Dipyrimidine, Wavelength and the Photosensitizer. *Nucleic Acids Res.* **2021**, *49* (8), 4266–4280.
- (39) Blancafort, L.; Voityuk, A. A. Thermally Induced Hopping Model for Long-Range Triplet Excitation Energy Transfer in DNA. *Phys. Chem. Chem. Phys.* **2018**, *20* (7), 4997–5000.
- (40) Gut, I. G.; Wood, P. D.; Redmond, R. W. Interaction of Triplet Photosensitizers with Nucleotides and DNA in Aqueous Solution at Room Temperature. *J. Am. Chem. Soc.* **1996**, *118* (10), 2366–2373.
- (41) Nakatani, K.; Yoshida, T.; Saito, I. Photochemistry of Benzophenone Immobilized in a Major Groove of DNA: Formation of Thermally Reversible Interstrand Cross-Link. *J. Am. Chem. Soc.* **2002**, *124* (10), 2118–2119.
- (42) Vendrell-Criado, V.; Rodríguez-Muñiz, G. M.; Cuquerella, M. C.; Lhiaubet-Vallet, V.; Miranda, M. A. Photosensitization of DNA by 5-Methyl-2-Pyrimidone Deoxyribonucleoside: (6 - 4) Photoproduct as a Possible Trojan Horse. *Angew. Chem., Int. Ed.* **2013**, *52* (25), 6476–6479.
- (43) Curutchet, C.; Voityuk, A. A. Triplet–Triplet Energy Transfer in DNA: A Process That Occurs on the Nanosecond Timescale. *Angew. Chem., Int. Ed.* **2011**, *50* (8), 1820–1822.
- (44) Klán, P.; Wirz, J. *Photochemistry of Organic Compounds: From Concepts to Practice*; Wiley: Chichester, West Sussex, U.K., 2009.
- (45) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*; CRC Press, 2006 DOI: 10.1201/9781420015195.
- (46) Zähringer, T. J. B.; Wienhold, M.; Gilmour, R.; Kerzig, C. Direct Observation of Triplet States in the Isomerization of Alkenylboronates by Energy Transfer Catalysis. *J. Am. Chem. Soc.* **2023**, *145* (39), 21576–21586.
- (47) Bosca, F.; Lhiaubet-Vallet, V.; Cuquerella, M. C.; Castell, J. V.; Miranda, M. A. The Triplet Energy of Thymine in DNA. *J. Am. Chem. Soc.* **2006**, *128* (19), 6318–6319.
- (48) Cameron, M. A.; Cush, S. B.; Hammer, R. P. Facile Preparation of Protected Furanoid Glycals from Thymidine. *J. Org. Chem.* **1997**, *62* (26), 9065–9069.
- (49) Dalton, J. C.; Montgomery, F. C. Solvent Effects on Thioxanthone Fluorescence. *J. Am. Chem. Soc.* **1974**, *96* (19), 6230–6232.
- (50) Ley, C.; Morlet-Savary, F.; Jacques, P.; Fouassier, J. P. Solvent Dependence of the Intersystem Crossing Kinetics of Thioxanthone. *Chem. Phys.* **2000**, *255* (2–3), 335–346.
- (51) Ferreira, G. C.; Schmitt, C. C.; Neumann, M. G. Dependence of the Thioxanthone Triplet-Triplet Absorption Spectrum with Solvent Polarity and Aromatic Ring Substitution. *J. Braz. Chem. Soc.* **2006**, *17* (5), 905–909.
- (52) Yip, R. W.; Szabo, A. G.; Tolg, P. K. Triplet State of Ketones in Solutions. Quenching Rate Studies of Thioxanthone Triplets by Flash Absorption. *J. Am. Chem. Soc.* **1973**, *95* (13), 4471–4472.
- (53) Amirzadeh, G.; Schnabel, W. On the Photoinitiation of Free Radical Polymerization-Laser Flash Photolysis Investigations on Thioxanthone Derivatives. *Makromol. Chem.* **1981**, *182* (10), 2821–2835.
- (54) Balta, D. K.; Temel, G.; Aydin, M.; Arsu, N. Thioxanthone Based Water-Soluble Photoinitiators for Acrylamide Photopolymerization. *Eur. Polym. J.* **2010**, *46* (6), 1374–1379.
- (55) Grabner, G.; Rechthaler, K.; Mayer, B.; Köhler, G.; Rotkiewicz, K. Solvent Influences on the Photophysics of Naphthalene: Fluorescence and Triplet State Properties in Aqueous Solutions and in Cyclodextrin Complexes. *J. Phys. Chem. A* **2000**, *104* (7), 1365–1376.
- (56) Takemura, T.; Hara, K.; Baba, H. Observation and Interpretation of Triplet-Triplet Absorption Spectra of Substituted Naphthalenes. *Bull. Chem. Soc. Jpn.* **1971**, *44* (4), 977–984.
- (57) Bieri, O.; Wirz, J.; Hellrung, B.; Schutkowski, M.; Drewello, M.; Kiefhaber, T. The Speed Limit for Protein Folding Measured by Triplet–Triplet Energy Transfer. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96* (17), 9597–9601.
- (58) Watson, J. D.; Crick, F. H. C. The Structure of DNA. *Cold Spring Harbor Symp. Quant. Biol.* **1953**, *18* (0), 123–131.
- (59) Nogueira, J. J.; Oppel, M.; González, L. Enhancing Intersystem Crossing in Phenotiazinium Dyes by Intercalation into DNA. *Angew. Chem., Int. Ed.* **2015**, *54* (14), 4375–4378.
- (60) Curutchet, C.; Voityuk, A. A. Environment Effects on Triplet–Triplet Energy Transfer in DNA. *Chem. Phys. Lett.* **2011**, *512* (1–3), 118–122.
- (61) Zähringer, T. J. B.; Moghtader, J. A.; Bertrams, M.; Roy, B.; Uji, M.; Yanai, N.; Kerzig, C. Blue-to-UVB Upconversion, Solvent Sensitization and Challenging Bond Activation Enabled by a

- Benzene-Based Annihilator. *Angew. Chem., Int. Ed.* **2023**, *62* (8), No. e202215340.
- (62) Strieth-Kalthoff, F.; Henkel, C.; Teders, M.; Kahnt, A.; Knolle, W.; Gómez-Suárez, A.; Dirian, K.; Alex, W.; Bergander, K.; Daniliuc, C. G.; Abel, B.; Guldi, D. M.; Glorius, F. Discovery of Unforeseen Energy-Transfer-Based Transformations Using a Combined Screening Approach. *Chem* **2019**, *5* (8), 2183–2194.
- (63) Mongin, C.; Moroz, P.; Zamkov, M.; Castellano, F. N. Thermally Activated Delayed Photoluminescence from Pyrenyl-Functionalized CdSe Quantum Dots. *Nat. Chem.* **2018**, *10* (2), 225–230.
- (64) Yarnell, J. E.; Wells, K. A.; Palmer, J. R.; Breaux, J. M.; Castellano, F. N. Excited-State Triplet Equilibria in a Series of Re(I)-Naphthalimide Bichromophores. *J. Phys. Chem. B* **2019**, *123* (35), 7611–7627.
- (65) Kuhlmann, A.; Bihl, L.; Wagenknecht, H.-A. How Far Does Energy Migrate in DNA and Cause Damage? Evidence for Long-Range Photodamage to DNA. *Angew. Chem., Int. Ed.* **2020**, *59* (40), 17378–17382.
- (66) Ricks, A. B.; Brown, K. E.; Wenninger, M.; Karlen, S. D.; Berlin, Y. A.; Co, D. T.; Wasielewski, M. R. Exponential Distance Dependence of Photoinitiated Stepwise Electron Transfer in Donor–Bridge–Acceptor Molecules: Implications for Wirelike Behavior. *J. Am. Chem. Soc.* **2012**, *134* (10), 4581–4588.
- (67) Lewis, F. D.; Wu, T.; Zhang, Y.; Letsinger, R. L.; Greenfield, S. R.; Wasielewski, M. R. Distance-Dependent Electron Transfer in DNA Hairpins. *Science* **1997**, *277* (5326), 673–676.
- (68) Andréasson, J.; Kajanus, J.; Mårtensson, J.; Albinsson, B. Triplet Energy Transfer in Porphyrin Dimers: Comparison between π - and σ -Chromophore Bridged Systems. *J. Am. Chem. Soc.* **2000**, *122* (40), 9844–9845.
- (69) Jensen, K. K.; Van Berlekom, S. B.; Kajanus, J.; Mårtensson, J.; Albinsson, B. Mediated Energy Transfer in Covalently Linked Porphyrin Dimers. *J. Phys. Chem. A* **1997**, *101* (12), 2218–2220.
- (70) Albinsson, B.; Mårtensson, J. Long-Range Electron and Excitation Energy Transfer in Donor–Bridge–Acceptor Systems. *J. Photochem. Photobiol., C* **2008**, *9* (3), 138–155.
- (71) Lai, R.; Liu, Y.; Luo, X.; Chen, L.; Han, Y.; Lv, M.; Liang, G.; Chen, J.; Zhang, C.; Di, D.; Scholes, G. D.; Castellano, F. N.; Wu, K. Shallow Distance-Dependent Triplet Energy Migration Mediated by Endothermic Charge-Transfer. *Nat. Commun.* **2021**, *12* (1), No. 1532.
- (72) Closs, G. L.; Piotrowiak, Piotr.; MacInnis, J. M.; Fleming, G. R. Determination of Long-Distance Intramolecular Triplet Energy-Transfer Rates. Quantitative Comparison with Electron Transfer. *J. Am. Chem. Soc.* **1988**, *110* (8), 2652–2653.
- (73) Clayton, A. H. A.; Scholes, G. D.; Ghiggino, K. P.; Paddon-Row, M. N. Through-Bond and Through-Space Coupling in Photoinduced Electron and Energy Transfer: An *Ab Initio* and Semiempirical Study. *J. Phys. Chem. A* **1996**, *100* (26), 10912–10918.
- (74) Curutchet, C.; Voityuk, A. A. Distance Dependence of Triplet Energy Transfer in Water and Organic Solvents: A QM/MD Study. *J. Phys. Chem. C* **2012**, *116* (42), 22179–22185.
- (75) Gray, H. B.; Winkler, J. R. Long-Range Electron Transfer. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102* (10), 3534–3539.
- (76) Eng, M. P.; Ljungdahl, T.; Mårtensson, J.; Albinsson, B. Triplet Excitation Energy Transfer in Porphyrin-Based Donor–Bridge–Acceptor Systems with Conjugated Bridges of Varying Length: An Experimental and DFT Study. *J. Phys. Chem. B* **2006**, *110* (13), 6483–6491.
- (77) Harriman, A.; Khatyr, A.; Ziessel, R.; Benniston, A. C. An Unusually Shallow Distance-Dependence for Triplet-Energy Transfer. *Angew. Chem., Int. Ed.* **2000**, *39* (23), 4287–4290.
- (78) Welter, S.; Salluce, N.; Belser, P.; Groeneveld, M.; De Cola, L. Photoinduced Electronic Energy Transfer in Modular, Conjugated, Dinuclear Ru(II)/Os(II) Complexes. *Coord. Chem. Rev.* **2005**, *249* (13–14), 1360–1371.
- (79) Huang, Z.; Xu, Z.; Huang, T.; Gray, V.; Moth-Poulsen, K.; Lian, T.; Tang, M. L. Evolution from Tunneling to Hopping Mediated Triplet Energy Transfer from Quantum Dots to Molecules. *J. Am. Chem. Soc.* **2020**, *142* (41), 17581–17588.
- (80) Welter, S.; Lafolet, F.; Cecchetto, E.; Vergeer, F.; De Cola, L. Energy Transfer by a Hopping Mechanism in Dinuclear Ir^{III}/Ru^{II} Complexes: A Molecular Wire? *ChemPhysChem* **2005**, *6* (11), 2417–2427.
- (81) Murphy, C. J.; Arkin, M. R.; Jenkins, Y.; Ghatlia, N. D.; Bossmann, S. H.; Turro, N. J.; Barton, J. K. Long-Range Photoinduced Electron Transfer Through a DNA Helix. *Science* **1993**, *262* (5136), 1025–1029.
- (82) Wagenknecht, H.-A. Reductive Electron Transfer and Transport of Excess Electrons in DNA. *Angew. Chem., Int. Ed.* **2003**, *42* (22), 2454–2460.
- (83) Wagenknecht, H.-A. Electron Transfer Processes in DNA: Mechanisms, Biological Relevance and Applications in DNA Analytics. *Nat. Prod. Rep.* **2006**, *23* (6), 973.
- (84) Murphy, C. J.; Arkin, M. R.; Ghatlia, N. D.; Bossmann, S.; Turro, N. J.; Barton, J. K. Fast Photoinduced Electron Transfer through DNA Intercalation. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91* (12), 5315–5319.
- (85) Giese, B.; Spichty, M. Long Distance Charge Transport through DNA: Quantification and Extension of the Hopping Model. *ChemPhysChem* **2000**, *1* (4), 195–198.
- (86) Kelley, S. O.; Barton, J. K. Electron Transfer Between Bases in Double Helical DNA. *Science* **1999**, *283* (5400), 375–381.
- (87) Siriwong, K.; Voityuk, A. A. Electron Transfer in DNA. *WIREs Comput. Mol. Sci.* **2012**, *2* (5), 780–794.
- (88) Kawai, K.; Majima, T. Hole Transfer Kinetics of DNA. *Acc. Chem. Res.* **2013**, *46* (11), 2616–2625.
- (89) Senthilkumar, K.; Grozema, F. C.; Guerra, C. F.; Bickelhaupt, F. M.; Lewis, F. D.; Berlin, Y. A.; Ratner, M. A.; Siebbeles, L. D. A. Absolute Rates of Hole Transfer in DNA. *J. Am. Chem. Soc.* **2005**, *127* (42), 14894–14903.
- (90) Takada, T.; Kawai, K.; Fujitsuka, M.; Majima, T. Direct Observation of Hole Transfer through Double-Helical DNA over 100 Å. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101* (39), 14002–14006.
- (91) Wood, P. D.; Redmond, R. W. Triplet State Interactions between Nucleic Acid Bases in Solution at Room Temperature: Intermolecular Energy and Electron Transfer. *J. Am. Chem. Soc.* **1996**, *118* (18), 4256–4263.
- (92) Nguyen, M. T.; Zhang, R.; Nam, P.-C.; Ceulemans, A. Singlet–Triplet Energy Gaps of Gas-Phase RNA and DNA Bases. A Quantum Chemical Study. *J. Phys. Chem. A* **2004**, *108* (31), 6554–6561.
- (93) Allahkaram, L.; Monari, A.; Dumont, E. The Behavior of Triplet Thymine in a Model B-DNA Strand. Energetics and Spin Density Localization Revealed by *Ab Initio* Molecular Dynamics Simulations†. *Photochem. Photobiol.* **2022**, *98* (3), 633–639.
- (94) García-Messeguer, R.; Navarrete-Miguel, M.; Martí, S.; Tuñón, I.; Roca-Sanjuán, D. DNA Triplet Energies by Free Energy Perturbation Theory. *J. Chem. Theory Comput.* **2025**, *21* (3), 1353–1359.
- (95) Keller, R. A. Intramolecular Energy Transfer between Triplet States of Weakly Interacting Chromophores. II. Compounds in Which the Chromophores Are Perpendicular to Each Other. *J. Am. Chem. Soc.* **1968**, *90* (8), 1940–1944.
- (96) Tan, Z.; Kote, R.; Samaniego, W. N.; Weininger, S. J.; McGimpsey, W. G. Intramolecular Singlet–Singlet and Triplet–Triplet Energy Transfer in Adamantyl-Linked Trichromophores. *J. Phys. Chem. A* **1999**, *103* (38), 7612–7620.
- (97) Dutta, S.; Erchinger, J. E.; Strieth-Kalthoff, F.; Kleinmans, R.; Glorius, F. Energy Transfer Photocatalysis: Exciting Modes of Reactivity. *Chem. Soc. Rev.* **2024**, *53* (3), 1068–1089.