Intra- to Intermolecular Singlet Fission

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Supporting Information

ABSTRACT: Singlet fission, the splitting of one singlet into two triplets, can potentially increase the efficiency of optoelectronic devices beyond conventional limits. Among the singlet fission molecules discovered to date, two mechanisms have emerged: intra- or intermolecular singlet fission. Here we show a combined intra- to intermolecular singlet fission mechanism in the model system of diphenyl-dicyano-oligoene (DPDC). Excitation of DPDC to the first optically bright state leads to the ultrafast formation of an intramolecular triplet pair, which decays in 40 ps in the solution phase but can also split competitively in 30 ps into two long-lived triplets (2×T₁) on adjacent molecules in solid films. These findings suggest a design principle for efficient singlet fission: the independent tuning of singlet—triplet pair coupling and triplet pair splitting from intra- and intermolecular interactions, respectively.

INTRODUCTION

An optically excited singlet state is converted into two triplet states in the energy and spin-allowed singlet fission process.1,2 Singlet fission was discovered 50 years ago,3,4 and recent surges in research activities5−11 are driven by exciting prospects in optoelectronic applications, such as photodetectors and solar cells.12−15 In photovoltaics, the power conversion efficiency of a conventional single-junction solar cell is constrained theoretically by the Shockley−Queisser limit of ~31% due in large part to the loss of excess photon energy above the semiconductor bandgap.16 When a singlet fission material absorbing at high photon energies is used in conjunction with a lower bandgap semiconductor, the theoretical power conversion efficiency can be increased to 44%.17,18 Singlet fission materials can also be used to increase the quantum efficiency of photodetectors from the conventional limit of 100% to 200%.12 A major obstacle to the realization of these potentials is the absence of a large toolbox of singlet fission materials from which engineers can make judicious choices in device fabrication.

In most molecular systems studied to date,1−11 singlet fission has been attributed to an intermolecular mechanism in which the optically excited singlet state (S) on one molecule couples with neighboring molecules to form an intermolecular triplet pair, i.e., a biexciton (BE), also called a multie exciton (ME). The BE in the solid state or an excimer in the solution19 can diffuse apart or form two individual triplets (2×T₁). Such an intermolecular mechanism is believed to be responsible for efficient singlet fission in crystalline solids or aggregates of tetracene,20−22 pentacene,8,11,23 1,3-diphenylisobenzofuran,9 rubrene,24,25 carotenoids,10 and perylenedimide.26 Theoretical studies point to the essential role of intermolecular charge transfer (CT) states in mediating the electronic coupling between S and BE.27−33

Intramolecular singlet fission, in which the BE and 2×T₁ states are located on the same molecule, has been suggested for isolated polymers, including poly- or oligoenes.34−39 Musser et al. found that the triplet lifetime was longer in a solid film than that in the solution phase for polythiophene.34 These authors suggested that the triplet pair separation via diffusion in the solid film might explain the increased triplet lifetime. From the point of view of creating robust design principles, intra-molecular singlet fission is particularly attractive. The critically important electronic coupling between S and BE (with or without CT intermediates) can be more easily designed and controlled within a single molecule than between molecules. A potential disadvantage with intramolecular fission is that the triplet pair confined to the same molecule can easily annihilate (back to the singlet and then ground state), resulting in a short lifetime of the triplet pair and limiting the charge extraction time window. One may envision an “ideal” mechanism where strong S/CT/BE coupling leads to the ultrafast formation of the intramolecular BE state, while intermolecular electronic interaction efficiently separates the triplet pair between neighboring molecules. Here we report the discovery of such an intra- to intermolecular singlet fission mechanism in the model system of modified oligoenes, a,ω-diphenyl-μ-μ-dicyano-oligoenes (DPDCs).

We chose DPDC molecules (Figure 1) for several reasons. A unique feature of oligoenes and similar carotenoid molecules is the presence of triplet pair states (TT), also called excited coherent states, as suggested in theoretical studies.40−42 The lowest singlet state in oligoenes is the “dark” S₁ state, which is formed on sub-ps time scales from the relaxation of the
optically bright S\(^*\) state. While the S\(^*\) state can be considered as a doubly excited TT state, the binding energy between these two closely interacting triplets is too high (>1 eV)\(^{40-42}\) to permit their separation into two individual triplets; as a result, S\(^*\) is only known to undergo nonradiative relaxation to S\(_0\).\(^{37-39}\) However, there is another well-known dark state S\(^*\) which is energetically between S\(_1\) and S\(_2\) and has been proposed as an intermediate for intramolecular singlet fission.\(^{43}\) The presence of a twist is expected to significantly weaken the coupling between the two triplets, permitting their separation. Our findings shown below suggest that the triplet pair (BE) may be interpreted as S\(^*\) which can split into two triplets on two adjacent molecules.

One limitation of naturally occurring carotenoids is the presence of side-chain methyl groups that may distort the planar conjugated oligoene structure, reduce the extent of conjugation, and prevent intermolecular close-packing. The DPDC molecules are designed to overcome these limitations.\(^{46}\) The addition of the two cyano (−CN) groups planarizes the oligoene backbone, making intermolecular close packing feasible and the extent of π-electron delocalization (thus, the optical gap) easily tunable with molecular length. The −CN groups are strong π-electron withdrawing\(^{40,44}\) and may introduce CT characters to the S\(_2\) state, potentially facilitate intramolecular BE formation. Singlet fission has been reported recently for solid films of a related molecule, diphenylhexatriene.\(^{45}\)

**EXPERIMENTAL SECTION**

**Sample Preparation.** The synthesis and characterization of the DPDC\(_n\) molecules have been reported elsewhere.\(^{46}\) Here \(n\) is the number of conjugated olefin in the molecule. All of the compounds have exclusively trans-stereochemistry in their double bonds. In this study, we chose five different lengths of DPDC\(_n\) molecules for investigation with \(n\) is an odd number from 3 to 11 (Figure 1). The solid films were prepared by drop-casting of the saturated solution of DPDC\(_n\) in chloroform onto sapphire coverslips. The optical density of the thin film samples in the visible range was typically 0.1.

**Transient Absorption.** The pump laser light (~100 fs pulse width, ~200 nJ pulse energy) comes from an optical parametric amplifier pumped by a Ti:sapphire femtosecond regenerative amplifier (800 nm, 1 kHz rep-rate). The probe light is a white-light supercontinuum (450–900 nm, ~100 fs pulse width). The pump and probe beams overlapped under a small angle. The detection consists of a pair of high-resolution multichannel detector arrays coupled to a high-speed data acquisition system. The pump laser pulse energy density on the sample was 20 \(\mu\)J/cm\(^2\), and the probe pulse energy density was approximately 1 order of magnitude lower.

**Triplet Sensitization Experiment.** We obtained the triplet state absorption spectrum of DPDC\(_n\) in the solution phase (in acetonitrile) using a nanosecond transient absorption setup (described elsewhere\(^{46}\)) and sensitization. The excitation laser pulse (355 nm, 5 ns pulse width, 10 Hz) was from a Nd:YAG laser (Spectra Physics). Thioxanthone (TX) was used as the solution phase sensitizer. After photoexcitation, singlet excitons are created in TX and then convert into triplet excitons via intersystem crossing (ISC).\(^{49}\)

**Phosphorescence Measurement.** We recorded phosphorescence spectra from solid DPDC\(_n\) using a modified spectrofluorometer (HORIBA Jobin Yvon, Fluorolog 3) in conjunction with a liquid nitrogen cooled Ge-diode detector (EO-817L, North Coast Scientific Corporation). The sample was placed in a 4 mm Pyrex tube and in a liquid nitrogen dewar with quartz windows and cooled down to 77 K.

**Grazing Incidence X-ray Diffraction (GIXD).** We carried out GIXD measurements at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory on beamline X-9 using 13.5 eV photon energy. The incident X-ray beam, \(k_{\text{in}}\), had a grazing incidence angle with the sample surface. A Photonic Science wide-angle X-ray scattering (WAXS) detector (pixel size of 0.11 mm) at the NSLS, positioned a distance \(L\) from the sample, recorded the scattered beam, \(k_{\text{out}}\). This was converted into an image of the reciprocal space (Q-space) with the scattering expressed as a function of the scattering vector \(Q = k_{\text{out}} - k_{\text{in}}\). Here, the sample-to-detector distance \(L\), calibrated with AgBH and LaB\(_6\) polycrystalline standards, was 244.9 mm. The samples were measured under a vacuum to minimize damage to the films from the intense X-ray beam and eliminate X-ray scattering from air.

**Time-Dependent Density Functional Theory (TD-DFT) Calculation.** In the TD-DFT calculation, we estimated the total energies of the S\(_0\), S\(_2\), and T\(_1\) states for each of the DPDC oligoenes using density functional theory (B3LYP functional, 6-31G\(^*\)*\(^*\)) basis sets, and Jaguar.\(^{50}\) For each molecule, we optimized the geometry of the S\(_0\) state. Keeping the geometry fixed, we then calculated the vertical T\(_1\) energy with RODFT and the vertical S\(_2\) energy using TD-DFT. The singlet and triplet energies for DPDC\(_n\), with different numbers of π-bonds (\(n\)) are presented in Table S1 (Supporting Information) and Figure 2C. In each molecule, the vertical excited states correspond to the promotion of one electron from the HOMO of the ground state to the LUMO of the ground state, which leaves two singly occupied orbitals. In the T\(_1\) state, these two electrons are high-spin coupled, and in the S\(_2\) state, they are low-spin coupled.

**RESULTS AND DISCUSSION**

Figure 2A shows the solution phase absorption spectra of DPDC\(_n\) (\(n = 3–11\), the number of π-bonds in the oligoene backbone, Figure 1). The peak absorption wavelength increases systematically with \(n\). Each absorption spectrum shows vibronic structure. We take the lowest energy peak (0–0 transition) in each as the optical gap and plot this as a function of \(n\) in Figure 2C (open circles). The experimental transition energies are in good agreement with calculations on DPDC\(_n\) from TD-DFT.
Figure 2. Absorption spectra of DPDC$_n$ with different numbers of π-bonds ($n = 3, 5, 7, 9, 11$) in a toluene solution (A) and in solid thin film (B). (C) Calculated S$_2$ (blue dots) and T$_1$ (red dots) excitation energies as a function of $n$ from TD-DFT. The open circles are from the lowest energy peak positions in panel A; the open squares are from the lowest energy peak in the phosphorescence spectrum from DPDC7 thin film. (D) The energy barrier for singlet fission, $\Delta E_{\text{SF}} = 2E_{T1} - E_{S2}$, from the TD-DFT results in panel B.

Figure 3. Transient absorption for DPDC$_7$ in solution. (A) 2D pseudocolor ($-\Delta T/T$) plots of TA spectra as functions of probe wavelength and pump–probe delay ($\Delta t$). The pump laser wavelength was 450 nm. The missing data points around 800 nm was due to saturation caused by high probe intensity. The ESA for BE, S$_0$, and S$_2$ are indicated. (B) TA spectra at different pump–probe delays. The open circles are the triplet induced absorption obtained via sensitization (see the Supporting Information). (C and D) Kinetic profiles for S$_0$ probed at 860 nm (red), S$_1$ at 700 nm (green), BE at 580 nm (blue), and bleaching at 493 nm (light blue, scaled by a factor of $-1$). The dotted curve is the instrument response.

(blue dots and line) detailed in the Supporting Information for vertical excitation to the first dipole-allowed singlet (S$_2$). Also shown in Figure 2C are the calculated triplet (T$_1$) energies (red dots and line), along with experimental values (open squares) obtained from phosphorescence of DPDC$_n$ ($n = 5, 7, 9$) thin films. In comparison to previous reports, the S$_2$ transition energies of DPDC$_n$ are in good agreement with those of diphenylpolyenes. Interestingly, the T$_1$ energies of DPDC$_n$ are lower than diphenylpolyenes or other polyenes. For example, our measured T$_1$ energies of DPDC$_5$, DPDC$_7$, and DPDC$_9$ are 1.34, 1.27, and 1.24 eV, respectively, while that of all trans retinal is 1.7 eV. We attribute the difference to the stabilization of T$_1$ by the −CN electron withdrawing groups. With our calculated S$_2$ and T$_1$ energies, we obtain the endoenergeticity for singlet fission, $\Delta E_{\text{SF}} = 2E_{T1} - E_{S2}$ shown Figure 2D. The singlet fission energy barrier (0.15 eV) is the smallest for DPDC$_7$.

Figure 2B shows absorption spectra of solid thin films of the DPDC$_n$ molecules. We observe a significant broadening of the absorption peak in the solid film as compared to the corresponding spectrum in the solution. While the trend of decreasing optical gap with increasing $n$ and the presence of vibronic progression are still observed in the solid film for $n = 3, 7, 9$, the spectra of $n = 9$ and 11 are broader and show no clear vibronic features. The latter results from a lack of crystallinity in these solid films, vide infra. For DPDC$_7$ thin film, the T$_1$ energy is 1.27 eV from phosphorescence (see below) and the S$_2$ state (lowest energy peak in the green spectrum in Figure 2B) is $\sim$2.34 eV; this gives an energy barrier for singlet fission in film of $\Delta E_{\text{SF}} \approx 0.2$ eV.

We use transient absorption (TA) spectroscopy to probe singlet fission. Figures 3A shows pseudocolor ($-\Delta T/T$) plots of TA spectra for DPDC$_n$ molecules in toluene solution as functions of probe wavelength and pump–probe delay time. In the experiment, the pump pulse at 450 nm excites the DPDC$_n$ molecules to the first optically bright state (S$_2$); after a controlled time delay ($\Delta t$), a white-light probe pulse follows the dynamics from the time-dependent ground state bleaching (GB) and excited state absorption (ESA).

The TA spectra (Figure 3A) consist of GB at $\leq$500 nm and ESA in three spectral regions that are very similar to those from the extensively studied carotenoids and related molecules. In carotenoids, the ESA from S$_2$ lies in the near-IR range of $\sim$800–1100 nm, while ESA peaks of S$^*$ and S$_1$ are in the visible range of $\sim$500–700 nm with S$^*$ on the blue side of S$_1$. In Figure 3A, we assign the short-lived ESA peak at $\geq$850 nm to the initially populated S$_2$ state; it rises with the laser pulse and decays in $\leq$0.5 ps. We assign the intense peak at $\sim$680 nm and a weak overlapping peak at $\sim$680 nm to the BE or dark S$^*$ and S$_1$ states, respectively. Figure 3B compares three TA spectra (at pump–probe delays: $\Delta t = 0.0, 0.4$, and 1.8 ps) with a spectrum of T$_1$ obtained from sensitization experiment (circles, see Figure S1 in the Supporting Information). The BE peak is similar to and slightly red-shifted (by $\sim$30 nm) from the T$_1$ peak; in contrast, S$_1$ is $\geq$100 nm red-shifted from T$_1$. This supports the notion that S$^*$ is a triplet pair state with characteristics of two individual triplets, e.g., due to the proposed twisting which weakens electronic coupling of the triplet pair. The strongest support for the triplet pair, $^3(\Pi \Pi)$, interpretation comes from results below for solid DPDC$_7$ film where BE is shown to further split into two triplets on adjacent molecules. Figure 3C shows kinetic profiles at indicated probe wavelengths (vertical cuts from Figure 3A). As expected, the formation of S$_0$ is concurrent with the bleach of S$_0$ within experimental resolution, as determined by the laser pulse and the thickness of the sample cuvette. In contrast, the formation of either BE or S$_1$ is delayed by $\sim$0.5 ps, suggesting that both come from the relaxation of the optically bright S$_2$ state. The S$_2$ decay dynamics is complex, with an initial nonexponential decay in $<0.5$ ps, with $<1$ ps of the residual signal on longer time scales. This complex dynamics can be...
attributed to the interconversion between \(S_2\) and BE. This is most obvious in Figure 3D: on the longer time scale, the dominant species, BE, decays with a lifetime of 40 ± 4 ps, matching that of ground state recovery. On this time scale, the weaker \(S_1\) and \(S_2\) signals exactly track that of BE. This can be accounted for by the interconversion between \(S_2\) and BE; both can decay to \(S_1\) and, finally, to \(S_0\). Supporting this, we note that the 40 ps lifetime of BE is 5–6 orders of magnitude shorter than the \(\mu s\) lifetime of a single triplet obtained in a sensitization experiment (see Figure S1 in the Supporting Information). We attribute the much shorter lifetime of BE, i.e., a strongly correlated triplet pair, to their easy annihilation to reform \(S_2\).

We conclude that intramolecular singlet fission takes place in DPDC\(_7\) in solution with the fission yield of 160%. The fission yield was determined based on the bleaching amplitudes at 0 and 2 ps delay times. At the latter delay time, \(S_2\) and \(S_1\) decays have almost completed.

We now turn to DPDC\(_7\) solid thin film and establish the successful separation of the intramolecular triplet pair into intermolecular triplets. Figure 4A shows a 2D pseudocolor plot of TA spectra from a DPDC\(_7\) thin film. We see three major changes from the solution spectra: (i) the GB and ESA peaks are all red-shifted in the solid state, and (ii) all ESA peaks overlap, especially for \(S_1\) and BE at 630 nm; (iii) in contrast to ESA, the GB signal is much longer lived and extends to well beyond nanoseconds. The long lifetime of bleaching signal is consistent with the formation of uncorrelated triplets (\(T_1\)), as is unambiguously verified by phosphorescence emission at 1000 nm (two peaks at 950 and 1055 nm, Figure 4B; see Figure S2, Supporting Information, for phosphorescence spectra from DPDC\(_5\) and DPDC\(_9\)). The phosphorescence signal decays with a time constant of \(\sim 15\ \mu s\) (inset in Figure 4B).

The presence of much longer-lived triplets only in the solid film, not in the solution phase, is a signature of intermolecular singlet fission reported for most molecular solids/aggregates.\(^7\)–\(^11\),\(^19\)–\(^23\) Intersystem crossing from \(S_2\) to the low-lying \(T_1\) should occur slower and similarly in both solution and solid film, in contrast to results presented here, and is excluded. We also exclude thermal artifacts which might result in a long living signal,\(^22\),\(^56\) as the observed GB dynamics is independent of laser power and substrates (see Figure S6, Supporting Information).

Figure 4C shows ESA kinetic profiles at 630, 765, and 1020 nm from the DPDC\(_7\) thin film. The initial excitation creates the optically bright \(S_2\) state (olive triangles and line) and subsequently decays on ultrafast time scales into BE and \(S_1\) states. While the signal at 765 nm is \(S_1\) that at 630 nm represents a mixture of BE and \(S_1\) (see global fitting analysis in the Supporting Information). Within the limited time resolution (\(\sim 100\ \text{fs}\)), BE seems to be formed on a faster time scale than \(S_1\). On longer time scales (ps), \(S_1\) and \(S_2\) show similar decay dynamics that can be attributed to the interconversion between \(S_2\) and BE and the decay of both via \(S_1\) to \(S_0\) similar to that of the solution phase. Note that the relaxation via the \(S_2 \rightarrow S_1 \rightarrow S_0\) channel is one of the two decay channels available to BE. The second decay channel is singlet fission, i.e., the splitting of the intramolecular triplet pair into two triplets on adjacent molecules.

The most critical evidence for the intra- to intermolecular singlet fission mechanisms comes from ground state bleaching."
intermolecular singlet fission mechanism, in which the spatial separation of $^1$(TT) to 2×T1 slows down the reverse of the singlet fission process. A long T1 lifetime is desirable for the harvesting of triplets in solar cells or other optoelectronic devices. The intra- to intermolecular singlet fission mechanism in Scheme 1 is likely responsible for singlet fission in the aggregates, but not in the solution, of zeaxanthin (a carotenoid analogue) reported by Wang and Tauber. Since intermolecular singlet fission depends strongly on pump photon energy, the rate of intermolecular singlet fission is approximately proportional to the negative slope of the GB signal change on the time scale of 10−40 ps, while the yield of singlet fission is approximately proportional to the GB signal at longer times (∼400 ps). Both the singlet fission rate and yield increase with increasing photon energy, as expected from the activated process due to the fact that the dark S1 state is formed on the sub-ps time scale. The oscillation has a time period of ∼300 ps. These oscillations are the well-known acoustic waves intrinsic to pulsed laser measurements on thin films, as detailed in the Supporting Information, Figure S9.

Since the energetics for singlet fission depends on the conjugation length of the DPDC$_7$ molecules, we expect the singlet fission yield to also depend on n, as confirmed in Figure 6A (see Figure S7, Supporting Information, for TA spectra for n = 3–11). The negligible singlet fission yield in DPDC$_7$ can be attributed to the large energy barrier (ΔE$_{SF}$ = 0.6 eV, Figure 2D). As expected from ΔE$_{SF}$, the singlet fission yield increases with n, maximizes for n = 7, and decreases again for n = 9 and 11. Interestingly, theory predicts that ΔE$_{SF}$ for n = 9 or
The propensity in DPDCₙ to preferentially form BE over S₁ may be attributed to the two electron withdrawing groups (−CN) that introduce CT character to the optically excited state and assist the localization of triplets. This issue deserves high-level theoretical investigation. For intermolecular design, we point out the need for sufficient HOMO–HOMO and LUMO–LUMO coupling to facilitate intermolecular triplet transfer, i.e., efficient Dexter energy transfer. Such design criteria are different than those outlined for intermolecular triplet pair formation, where balanced HOMO–HOMO, LUMO–LUMO, and HOMO–LUMO couplings are needed for efficient intermolecular singlet fission.

### ASSOCIATED CONTENT

3 Supporting Information

Details on experimental methods, sample preparation, additional experimental results, data analysis, and TD-DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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11 is only slightly higher than that for n = 7, but the singlet fission yield decreases significantly from ∼70% for DPDC₇ to 35 and 18% for DPDC₉ and DPDC₁₁, respectively. The singlet fission yields here are a net result of intramolecular triplet pair (BE) formation and intermolecular triplet pair splitting. While BE formation is an inherent property of the molecules, the separation of the triplet pair must compete with the relaxation of BE to S₀ and the rate depends on the intermolecular coupling and, thus, crystallinity of the solid. As shown by grazing incidence X-ray diffraction (GIXD) images in Figure 6B–D, the DPDCₙ films are highly crystalline for n ≤ 7 but amorphous for n ≥ 9 (see Figure S8, Supporting Information, for GIXD data from all samples). Compared to DPDC₇, the lack of crystallinity in DPDC₉ and DPDC₁₁ films leads to weaker intermolecular electronic interaction and slower rates of intra- to intermolecular BE → 2ₓT₁ transition.

### SUMMARY

While the mechanism established here comes from analysis of singlet fission in DPDCₙ molecules, oligoynes or polyynes may not be the best candidates for highly efficient singlet fission due to the endothermic process and the S₁ → S₀ loss channel. However, the intra- to intermolecular singlet fission should be of general significance to other potential candidates where an intramolecular biexciton may split into an intermolecular triplet pair. This mechanism suggests a new design principle for singlet fission: intramolecular electronic structure for the efficient formation of an intramolecular triplet pair (i.e., biexciton) upon optical excitation and intermolecular electronic interaction for the separation (fission) of the biexciton state into two individual triplets on adjacent molecules. For intramolecular singlet fission design, we note that the BE peak intensity dominates over that of S₁ in DPDC₇ (Figure 3A), while previous TA studies on carotenoids showed similar S* which was suggested as the triplet pair state and S₁ intensities.

![Figure 6: π-bond (n) dependence of singlet fission yields and crystallinity in DPDCₙ films.](image-url)


Jaguar, version 8.2; Schrodinger, Inc.: New York, 2013.


