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Is the Chemical Strategy for imbuing 'Polyene' Character in Diketopyrrolopyrrole Based Chromophores sufficient for Singlet Fission?

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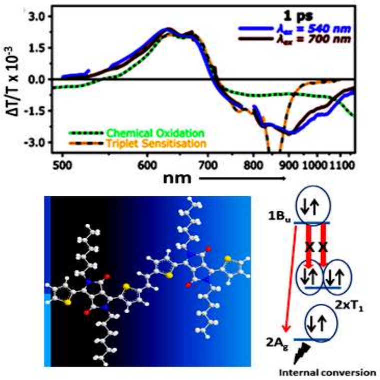
ABSTRACT. In this work, we have rationally designed and synthesized a novel thiophene-diketopyrrolopyrrole (T**DPP**)-vinyl based dimer. We have investigated the optical and electronic properties and have probed the photophysical dynamics using transient absorption to investigate the possibility of singlet exciton fission. These revealed extremely rapid decay to the ground state (< 50 ps), which we confirm is due to intramolecular excitonic processes rather than large-scale conformational change enabled by the vinyl linker. In all cases the main excited state appears to be 'dark', suggesting rapid internal conversion into a dark $2A_g$-type singlet state. We found no evidence of triplet formation in TDPP-V-TDPP under direct photo excitation. This may be a consequence of significant singlet stabilization in the dimer, bringing it below the energy needed to form two triplets. Our studies on this model compound set valuable lessons for design of novel triplet-forming materials, and highlight the need for more broadly applicable design principles.

TOC GRAPHICS



KEYWORDS singlet fission, donor-acceptor, vinyl, DPP, polyene, internal conversion, transient absorption

Considerable efforts have been directed towards the development of efficient excitonic solar cells based on organic materials, through a multitude of advancements in the design of appropriate molecular backbones, thin-film processing conditions and device-architectural engineering.[1, 2, 3 ,4, 5] To date, the highest power conversion efficiency achieved in organic solar cells is in the range of ~10%.[6] One critical limitation for these and indeed all other single-junction solar cell technologies arises from fundamental thermodynamic processes such as relaxation of high-energy carriers/excitons to the band edge. The consideration of such processes yields the Shockley-Quiesser efficiency limit of ~33% for single junction solar cells.[7, 8] One of the ways to circumvent this limitation is by invoking and implementing the concept of singlet exciton fission (**SEF**).[8, 9] This process involves the conversion of a singlet exciton into a pair of low-energy triplet excitons, which are initially coupled into an overall singlet state. This maintenance of singlet spin enables **SEF** to proceed on ultrafast time scales to out-compete other loss channels.[10]

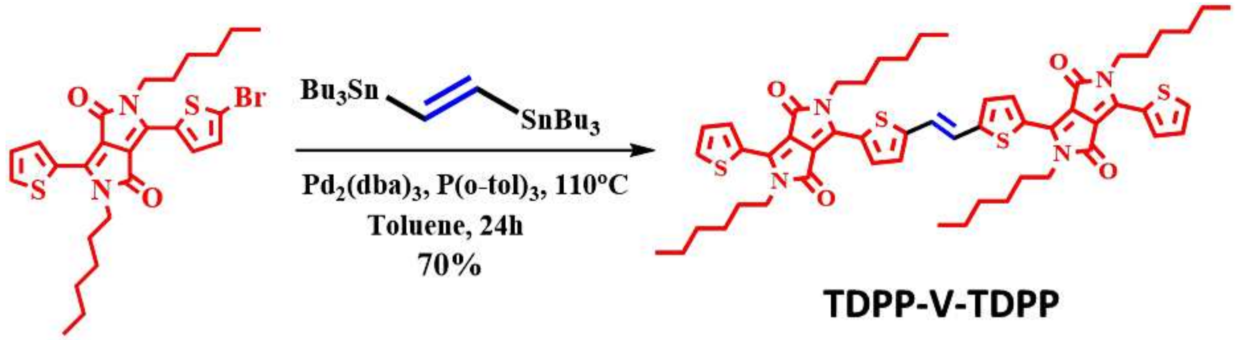
Efficient **SEF** relies on the correct alignment of the singlet and triplet energy states, such that $2\ E\ (T_1) \leq E\ (S_1)$.[11] By thereby splitting a high-energy exciton into two low-energy excitons, it becomes possible to harvest a significant proportion of the energy in 'visible spectrum' photons typically lost to thermalization, resulting in a new maximum efficiency limit of ~44%.[12] In the recent years, quantum chemical and experimental studies have demonstrated that acenes, for example pentacene, exhibit efficient **SEF** with ~200% triplet yield on time-scales as fast as 80 fs.[13-19] **SEF** proceeds either through the intermolecular or intramolecular mechanism.[20-24] For both mechanisms, **SEF** rates and efficiencies can be controlled by fine-tuning the strength of interchromophore coupling, which in the case of intermolecular fission entails the difficult task of optimizing chromophore packing within the film. [18, 24, 25] Furthermore, several groups have demonstrated that coupling between singlet and triplet-pair manifolds can be very effectively mediated by intermediate charge-transfer (**CT**) states.[21-23,26] This insight provides design criteria for the selection of building blocks for new intramolecular **SEF** materials that satisfy two key requirements for efficient **SEF**: an increased S_1-T_1 gap (to achieve $2x\ E\ (T_1) \leq E\ (S_1)$), and a lowest-lying optical excitation with significant charge-transfer character that can mediate the **SEF** process.[27-30, 31]

There is little knowledge about the degree of interchromophore coupling needed to make **SEF** competitive with fluorescence and to yet allow the component triplets of the singlet-coupled triplet pair to 'escape' and behave as independent excitations.[10,32,33] It is evident, however, that these processes require a delicate balance of chemical design parameters. These processes depend largely on the crystal environment, whether by positioning the molecules favourably for direct interaction or by stabilizing the low-energy charge transfer states which serve as virtual states in the coupling process.[26, 34] The interchromophore interaction can range from mere physical contact through indirect covalent coupling to direct covalent bonding that permits strong π-conjugation. The extent of coupling has direct effects on the **SEF** rate, but also indirectly affects the process by modifying the energy of the states of the isolated monomers and thus the exoergicity of **SEF**.[33, 35] This interchromophore coupling can be controlled by tailoring the chemical structure.[10,18, 24, 36, 37-40] One rational design approach to optimize this coupling for intramolecular **SEF** materials is based on alternately coupling electron-rich and electron-deficient moieties to form a quinoidal **D-A-D** backbone imparting significant charge-transfer character to the lowest energy optical excitation.[18,26,32,41] The resulting charge-transfer state possesses a large absorption cross-section and may couple more strongly to multi-exciton triplet states than pure singlet Frenkel excitons.[27, 42] We highlight in particular the design strategy proposed with this motif for conjugated polymers and oligomers. In that work, the oxidized thiophene acceptor found to be necessary to enable **SEF** simultaneously endows materials with significant oligoene/polyene character, suggesting a judicious balance of charge-transfer and polyene character is needed. [26, 43]

Indeed, the property of intramolecular **SEF** can also be achieved by incorporating oligoene-like moieties.[44, 45] In conventional polyenes, the lowest $2A_g$ states lie below the $1B_u$ states, enabling rapid (few ps) internal conversion to this 'dark' singlet that renders them largely non-emissive. It has long been considered that the $2A_g$ state is crucial to enable **SEF**, as it can be alternatively described as a bound triplet pair.[10, 46] However, more recent experimental evidence in oligoene aggregates [45, 47] and conjugated polyenes [48] has revealed direct triplet formation instead from the bright $1B_u$ state. It thus remains unclear what aspect of oligoene character enables **SEF** and precisely how the coupling between manifolds is achieved, though it is clear empirically that it is a powerful 'ingredient' for **SEF** materials.[26,48] Among the reported intramolecular **SEF** materials, vinylene-containing polymers have typically exhibited some form of optical activation, with fission enhanced by or even requiring excitation with a photon above the bandgap.[26, 48] The lack of intramolecular **SEF** in shorter oligoenes such as the carotenoids in spite of suitable energetics suggests that there is also a minimum size requirement for this **SEF** motif. On the other hand, non-activated intramolecular singlet fission has been observed in several pentacene and tetracene dimers, with efficiencies as high as 200%.[21-23, 24, 28, 38, 39] These results indicate that intramolecular **SEF** may be possible as long as two distinct sites for the product triplets are available.

The chemical design of charge-transfer **SEF** chromophores can be challenging, as it not only involves increasing the **S_1-T_1** gap, but also endowing the **S_1** state with sufficient charge-transfer character to enhance its coupling with the multiexcitonic triplet state. The former involves either the destabilization of the **S_1** state or stabilization of the **T_1** state by fine-tuning chromophore structural motifs. The latter is feasible when there is a large electronic coupling between donor and acceptor leading to a large HOMO-LUMO spatial overlap, hence large exchange energies.[49] The present understanding and the scarcity of appropriately designed materials provide little insight into the possible ways of harvesting multiple excitons in molecular materials. Diketopyrrolopyrrole (**DPP**)-based polymers and oligomers have attracted attention by virtue of high efficiencies in solar cells (~10%) and high hole (~20 $cm^2V^{-1}s^{-1}$) and electron mobilities (~12 $cm^2V^{-1}s^{-1}$) in **OFET**s. [50, 51] Their attractive properties such as high electron affinities and relatively low triplet energies can lead to the exploration of novel design principles for next-generation singlet fission materials based on **DPP** oligomers and polymers. Recent work has suggested that **DPP** derivatives can undergo **SEF** in the solid state [34] thanks in part to the charge-transfer character of their excitations, making them strong candidates for intramolecular **SEF** design motifs. This work addresses the challenge in developing intramolecular singlet fission materials.

In keeping with the aforesaid design principle of combining charge-transfer and polyene character, we coupled together two thiophene-**DPP** molecules (**TDPP**) with a vinyl linker to control the interchromophore coupling, yielding the dimer TDPP-V-TDPP. UV-Vis absorption measurements reveal substantial interaction between the **DPP** units, while photoluminescence (**PL**) spectroscopy shows the molecule to be non-emissive as typically observed in polyenes. Cyclic voltammetry (**CV**) measurements have been performed to elucidate the ionization



Scheme 1: Synthesis of TDPP-V-TDPP

potential and electron affinity. In order to probe the excited-state dynamics and better understand the interplay of bright and dark states, we performed transient absorption measurements on TDPP-V-TDPP in solution as well as in rigid polystyrene matrices. We observe in all cases that the initial 'bright' excited state appears to rapidly decay by internal conversion into a dark and extremely short-lived $2A_g$-type singlet, analogous to 'polyene' photophysics, because of the vinyl bridging unit. There is no evidence of triplet or charge formation, nor does substantial conformational change drive the rapid excited-state deactivation, which we consider instead to be analogous to the fast vibrationally-mediated decay active in carotenoids and other polyenes. Our experiments demonstrate that **SEF** is inactive in this material, which is likely a consequence of the strongly reduced singlet energy upon dimerization. Our study nonetheless sets important lessons for the design principles of **DPP**-based oligomers for future applications as next-generation **SEF** materials.

TDPP-V-TDPP was synthesized using a Stille coupling reaction involving a monobromo derivative of **DPP** and 1,2-bis(tri-sec-butylstannyl)ethene in molar ratios of 2:1 using catalyst $Pd_2(dba)_3$ and ligand $P(o\text{-}tol)_3$ in dry toluene as solvent. The synthesis of TDPP-V-TDPP is shown in **Scheme 1**. **DPP** was alkylated with the short hexyl chain to enhance the crystallinity. The intermediates and the final compounds were purified by silica gel chromatography. The monomers and final compounds were characterized and their purity was verified by ^{1}H NMR and ^{13}C NMR. The spectral data are described in supporting information.

The UV-Vis absorption spectra of TDPP-V-TDPP and the corresponding monomer unit are shown in **Figure 1**. The absorption exhibits a substantial red-shift of **TDPP** upon dimerization, from E_g~2.2 eV to ~1.75 eV, coincident with a shift in the 0-0/0-1 vibronic peak ratio from 1.2 to 0.95. These changes are indicative of substantial interaction between **TDPP** units and demonstrate effective conjugation across the central linker. While interaction between the constituent monomer units is important for processes such as **SEF**, the very strong effects here may prove detrimental. The triplet energy of the equivalent monomer molecule has been reported as ~1.1 eV, [34] which would result in very unfavourable **SEF** energetics if unchanged in the dimer. However, this electronic coupling is likely to alter the HOMO-LUMO overlap and

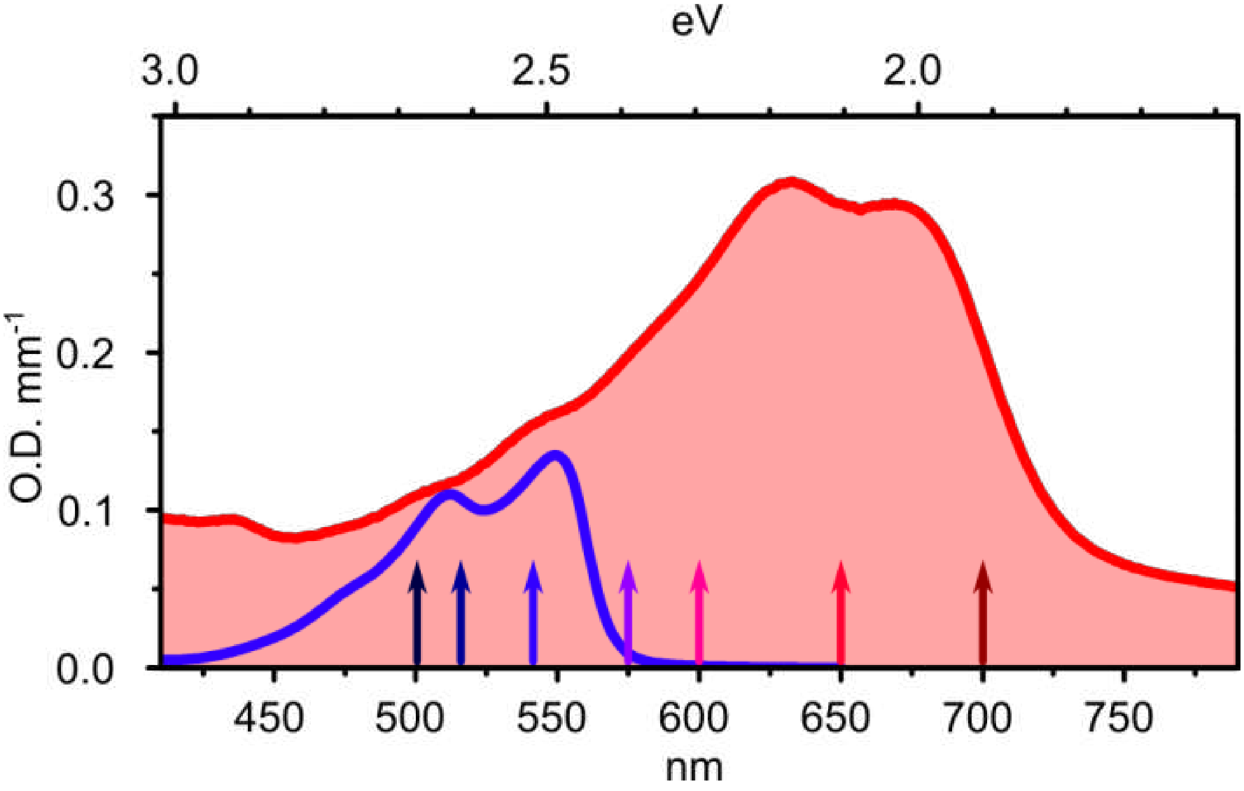


Figure 1. Normalized UV-vis spectrum of TDPP-V-TDPP (red) in chlorobenzene, at a concentration of 50 µg/mL. The weak features seen at ~500 and 550 nm closely match the absorption of the equivalent TDPP monomer (blue, arbitrary scale). The substantial red-shift upon dimerization is a signature of very strong interaction between the **TDPP** units. Arrows indicate pump wavelengths used in transient absorption measurements.

consequently the S_1-T_1 gap. In light of this, previous observations of changed triplet energies upon dimerization [24] and the typically large exchange energies in polyenes, the redshift of absorption alone is not sufficient to rule out **SEF** in TDPP-V-TDPP. Interestingly, we also detect slight vibronic features in the range 500-550 nm, in agreement with the peaks of monomer absorption. We do not anticipate any residual monomer in the solution following purification and detected no signs of such impurities using NMR. Nor do we find any evidence for gradual degradation of the TDPP-V-TDPP samples or powders into uncoupled, monomeric molecules. Instead, we attribute these bands to twisted conformers in which the conjugation between **TDPP** units is minimal. Heating the solution causes a reduction in the 0-0/0-1 vibronic ratio, consistent with increased torsional disorder on average, but the relative weight of these higher-energy peaks does not vary (**Figure S4, SI**). The barrier for interconversion between these states must be substantial, suggesting that these monomer-like bands represent a different stereoisomer which was kinetically trapped in a twisted configuration during synthesis.

We could detect no luminescence from TDPP-V-TDPP, whether in a standard fluorimeter (excitation from 400 nm to 750 nm) or following laser excitation at 550 nm or 650 nm. We thus conclude that the **PL** quantum efficiency in the dimer is extremely low, due to a short singlet excited-state lifetime. This result suggests similar behaviour to the polyenes, where rapid (<200 fs) deactivation of the bright $1B_u$ state through internal conversion to $2A_g$ results in **PL** quantum yields below 10^{-5}. The cyclic voltammograms are shown in **Figure S3, SI**. The extracted oxidation and reduction potentials are -5.00 eV and -3.44 eV respectively and the electrochemical gap is 1.56 eV. TDPP-V-TDPP exhibits reversible reduction cycle and a quasi - reversible oxidation cycle.

The low **PL** efficiency of TDPP-V-TDPP means that other spectroscopic tools are needed to build a comprehensive picture of the excited-state decay processes, namely transient absorption (**TA**) spectroscopy using a system described previously.[48] In this technique, the sample is excited with a short, tuneable pump pulse, followed at a precisely controllable time delay by a broadband (490-800 nm or 800-1175 nm) probe pulse. The transmission spectrum of the probe is measured in the presence and absence of the pump pulse, enabling a direct determination of the absorption spectrum of any excited states. Increased transmission of the probe (i.e. $\Delta T/T > 0$) can be attributed to bleaching of the ground-state absorption or stimulated emission from excited singlet states. A reduction in probe transmission ($\Delta T/T < 0$) gives the unique absorption signature of the excited state. In practice, these features tend to strongly overlap, making identification of distinct excited state difficult unless there is a clear change in the spectral shape over time or change in the decay kinetics across the detection bandwidth. Because this technique detects excited-state absorption, it is particularly well suited to materials and states which do not strongly emit, such as TDPP-V-TDPP.

In **Figure 2**, we present **TA** spectra (**a, c**) and decay kinetics (**b, d**) of TDPP-V-TDPP in chlorobenzene solution. Under band-edge excitation (**Figure 2, a-b**), we observe behaviour reminiscent of polyenes. The dominant $\Delta T/T > 0$ bands closely agree with the absorption spectrum (grey dashed), enabling assignment to ground-state bleach (**GSB**). Due to the absence of any additional positive features that could be attributed to stimulated emission, we consider the primary species observed (colored traces) to be an optically ‘dark’ state. On the very earliest timescales (thin black line) we detect additional spectral signatures such as a broadened photo-induced absorption (**PIA**) in the NIR, with distinct absorption >1075 nm, and a crossing point between positive and negative **TA** signals that is ~10 nm shifted to the red. The presence of this shifted crossing point is a potential sign of stimulated emission of photons from the bright initially excited state, characterized by extremely short lifetime. These features we assign as signatures of the initial singlet excited state, which converts on ultrafast timescales to a short-lived dark state, analogous to the rapid $1B_u \rightarrow 2A_g$ internal conversion well known in the polyenes. The timescale of this process is within our instrument resolution and should be <200 fs; the existence of such rapid internal conversion is consistent with the absence of detectable fluorescence. The lifetime of the second state is well described with biexponential decay, with the primary decay attributed to the 3.6 ps component. There is no evidence of changing spectral shape over the lifetime of this state, suggesting that the two time constants do not reflect internal conversion between different excited states.

Similar basic features are evident following excitation with excess pump photon energy, as at 540 nm (**Figure 2, c-d**). The same signatures of initial (thin black) and longer-lived (blue)

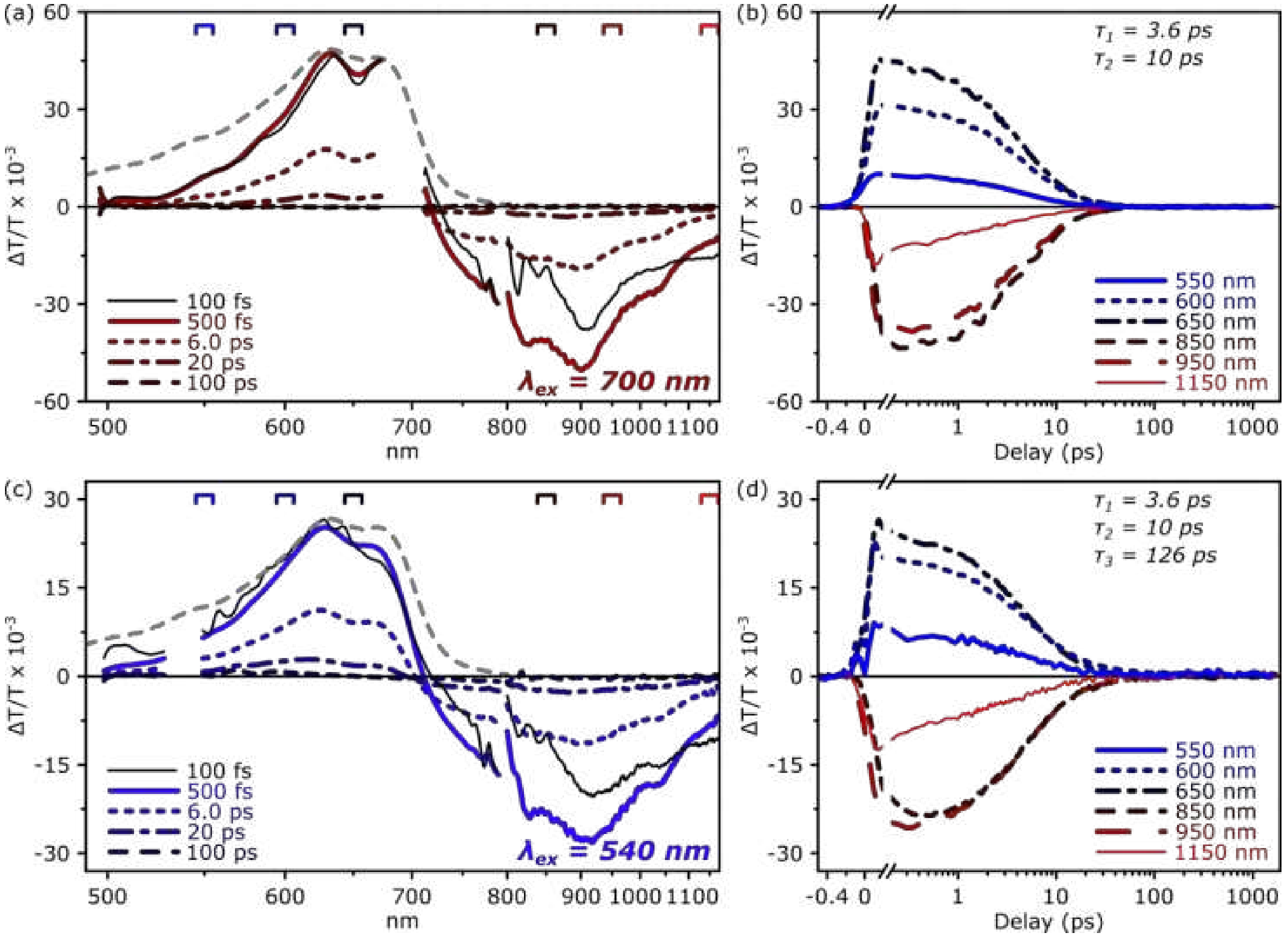


Figure 2. Sub-ps transient absorption measurements of TDPP-V-TDPP in solution with excitation (**a, b**) at the band edge and (**c, d**) well above the band edge reveal rapid internal conversion and excited-state quenching. (a) The initial excited state (thin black) converts within the instrument response to a second 'dark' state which exhibits no sign of stimulated emission. No further spectral evolution is detected during the rapid decay to the ground state. By 100 ps no signal can be detected. The UV-vis absorption spectrum (grey dashed) shows a close match to the positive **TA** signals observed, suggesting none can be attributed to stimulated emission. (b) Decay kinetics integrated over the bands indicated in (a). Following the initial fast kinetics, best observed in the 950 and 1150 nm traces, the kinetics can be well described with biexponential decay with the indicated time constants. (c) Excitation with significant excess energy results in the same overall spectral behaviour, but with slight broadening and a change in the shape of the ground-state bleach. New long-lived features are apparent, with faint bleach and accompanying photo-induced absorption detected at 100 ps and beyond. These features agree well with those of **TDPP** monomers. (d) The decay kinetics following excess-energy excitation reveals the same primary decay processes, but an additional decay component must be included in the fit to describe the new long-lived state. A very small fraction of the population persists beyond the limits of the measurement, into the nanosecond regime. Fits compared to raw data in **Figs. S6-7, SI**.

states can be observed, with only a slight difference in the shape of the **GSB**. However, on the longest timescales (100 ps and beyond) we can distinguish a faint **GSB** band at 600 nm and corresponding **PIA** at 700-800 nm. These are signatures of a new longer-lived state. We find an additional exponential component (126 ps) is needed to describe the decay dynamics, and a very small fraction of the population persists beyond the 1.5 ns range of our measurements. Such effects could be consistent with optically activated singlet fission, as has been observed in other polyenes, or the activation of other decay channels through excess-energy excitation. To clearly establish the nature of this behaviour, we systematically measured the pump wavelength dependence.

As shown in **Figure 3**, we detect qualitatively similar spectral effects of increased pump

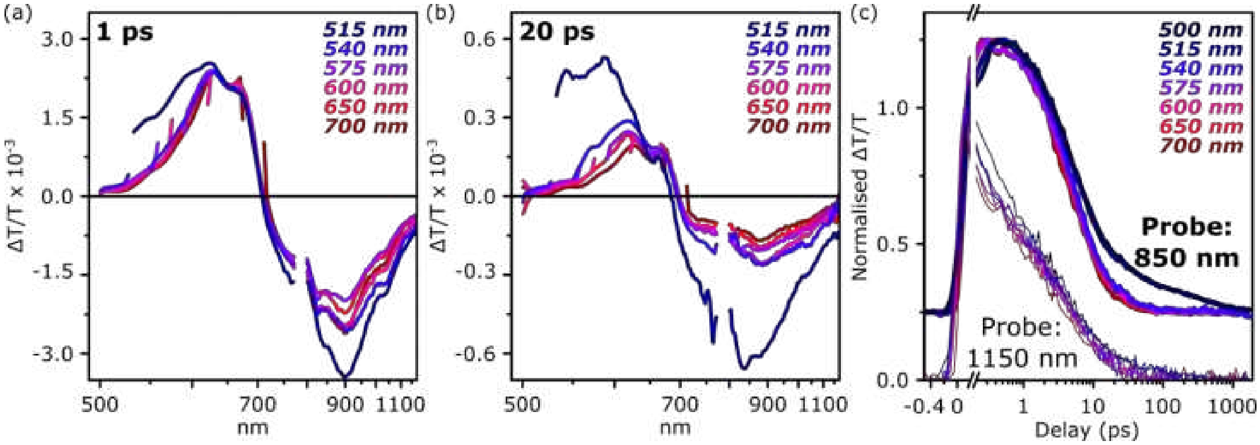


Figure 3. TA measurements at a range of excitation wavelengths reveal systematic spectral changes detectable at (a) early and (b) longer pump-probe delays. As the pump photon energy is increased, we detect an increase in the **PIA** signal in the **NIR** relative to **GSB**, and a shift in the peak ratio of the **GSB** spectrum (increasing 0-1 contribution). On longer timescales the enhancement of **PIA** and **GSB** features is still more pronounced, as excess photon energy slightly enhances the excited-state lifetime as well. (c) Integrated decay kinetics in the **NIR** show a small, systematic increase in the excited-state lifetime with pump photon energy until a sharp increase for 515 nm and 500 nm. This dramatic change is attributed to monomer-like TDPPs, whether arising from a small fraction of uncoupled precursors or from particular dimer conformations in which the **TDPP** units are not well conjugated. The smaller, systematic changes in the lifetime and **TA** spectra (particularly the **GSB**) reflect the pump-wavelength selectivity of particular sub-populations of TDPP-V-TDPP with varying conjugation length (i.e. torsional disorder). Full data presented in **Fig. S8, SI.**

photon energy both at (a) early and (b) long pump-probe delays. The primary effects are an increase in the relative weight of the **PIA** in the **NIR** and a change in the vibronic peak ratio in the **GSB**, with a progressive increase and broadening of the 0-1 peak.

These changes are particularly pronounced on longer timescales, as increased pump photon energy also increases the excited-state lifetime. In addition to this subtle but systematic effect in the decay kinetics (**Figure 3c**), we find a sharp change in behaviour for the two highest-energy pump wavelengths (500 and 515 nm). At these wavelengths a substantial amount of the longer-lived excited state is generated. We find no evidence, however, for an assignment to optically activated **SEF**, as the triplet spectrum obtained through an established sensitization method using N-methylfulleropyrrolidine as triplet donor[48]exhibits markedly different **PIA** (**Figure 4a**). Likewise, it is clear that this longer-lived species is not a charge-transfer state, as there is a poor match to the spectrum from chemical doping (**Figure 4a**). The match of all spectra at the short-wavelength edge of the excited-state absorption is intriguing. A similar shoulder ~700-800 nm is seen under all direct excitation conditions, as well as in the sensitized triplet spectrum and following chemical oxidation, albeit with much lower intensity relative to the **GSB**. While the onset of this band is largely governed by the position of the ground-state absorption, the similarity of the shoulder suggests a more fundamental relationship between the origin of the bands. We propose that the reason lies in the underlying charge-transfer character of excitations in **DPP** materials in general. This shoulder is evident in polaronic states (chemical reduction) and may be taken as a signature of charge-transfer character. Mixing of S_1 and T_1 states with charge-transfer configurations may then endow the **PIA** with such signatures, analogous to the singlet-triplet mixed features reported in bound ^{1}(TT) states in TIPS-tetracene solutions.[52]

Comparison of the long-lived spectra following excitation < 600 nm (**Figure S4 and S5, SI**) with published data reveals a striking similarity to the bright singlet state in a monomer **TDPP** derivative in solution.[34] Indeed, we find the largest effects in the pump wavelength dependence can all be accounted for as selective excitation at high pump photon energies of a sub-population of monomer-like molecules. As discussed above in the context of the absorption spectrum, we expect that these molecules are not chemical monomers, but rather conformers in which the conjugation between **TDPP** units is ineffective. We find that selectivity of different degrees of torsional disorder can explain the more subtle, systematic changes in **TA** spectra and kinetics observed across the entire pump wavelength series. Lower pump photon energies selectively excite molecules with more extended conjugation and presumably more planalized structure, as reflected in the 0-0/0-1 vibronic ratio observed in the **GSB** (a direct measure of the 'type' of molecules excited). Molecules in such geometry are likely closer to the equilibrium excited-state geometry, and thus have a greater radiative rate and need less time for vibrational relaxation, resulting in a slightly shorter excited-state lifetime. The pump wavelength dependence does not explain the surprisingly short primary excited-state lifetime, which is well described by the same 3.6 ps and 10 ps time constants in all cases (discounting the effects of the monomer-like species). As one of the most likely decay channels for such a covalent dimer is non-radiative decay via torsional relaxation about the central bond, [53, 54] we investigated the effects of geometric constraint in high viscosity polystyrene (**PS**) solution (95 mg/mL in chlorobenzene) and rigid **PS** matrix **(Figure 4, b-e).**

In **PS** solution we observe the same absorption line shape as in dilute chlorobenzene, while the spin-cast **PS** matrix exhibits pronounced broadening and a red-shift. These changes could suggest the presence of intermolecular interactions in spite of the relatively low TDPP-V-

TDPP loading (50 μg/mL). However, there is no corresponding change in the excited-state dynamics. We propose instead that the broadened and strongly red-shifted spectrum reflects the planarizing effects of the **PS** matrix, resulting in some molecules with significantly enhanced conjugation length. In viscous solution (**Figure 4c**) we observe the same spectral shapes and same pump wavelength dependence identified previously: an excitation-dependent vibronic structure in the **GSB**, no sign of stimulated emission and a **PIA** towards the **NIR**. While the **TA** spectra of the polymer matrix (**Figure 4d**) appear very different in shape, comparison with the absorption spectrum confirms that the entire spectral shape is consistent with **GSB**. There no new features corresponding to longer-lived excited states or a change in decay pathway due to conformational restriction. In fact, the overall behaviour appears to be entirely consistent with measurements in 'free' solution: as previously, excitation with higher-energy photons results in an enhancement of the **GSB** on the 'blue' side and a reduction on the 'red' side, pointing to the same selectivity of torsional conformers.

In no case do we observe a significant change in the excited-state lifetime (**Figure 4e**). The decay in **PS** solution and even **PS** matrix is almost indistinguishable from that in chlorobenzene solution, ruling out fast large-scale conformational change as the primary decay pathway. We thus consider that the photophysics observed here are most consistent with purely electronic dynamics, following the polyene model in which ultrafast internal conversion from the initial bright state forms a dark state of A_g symmetry. This state in turn exhibits very strong coupling to the ground-state vibrational manifold and rapidly decays through multi-phonon emission.

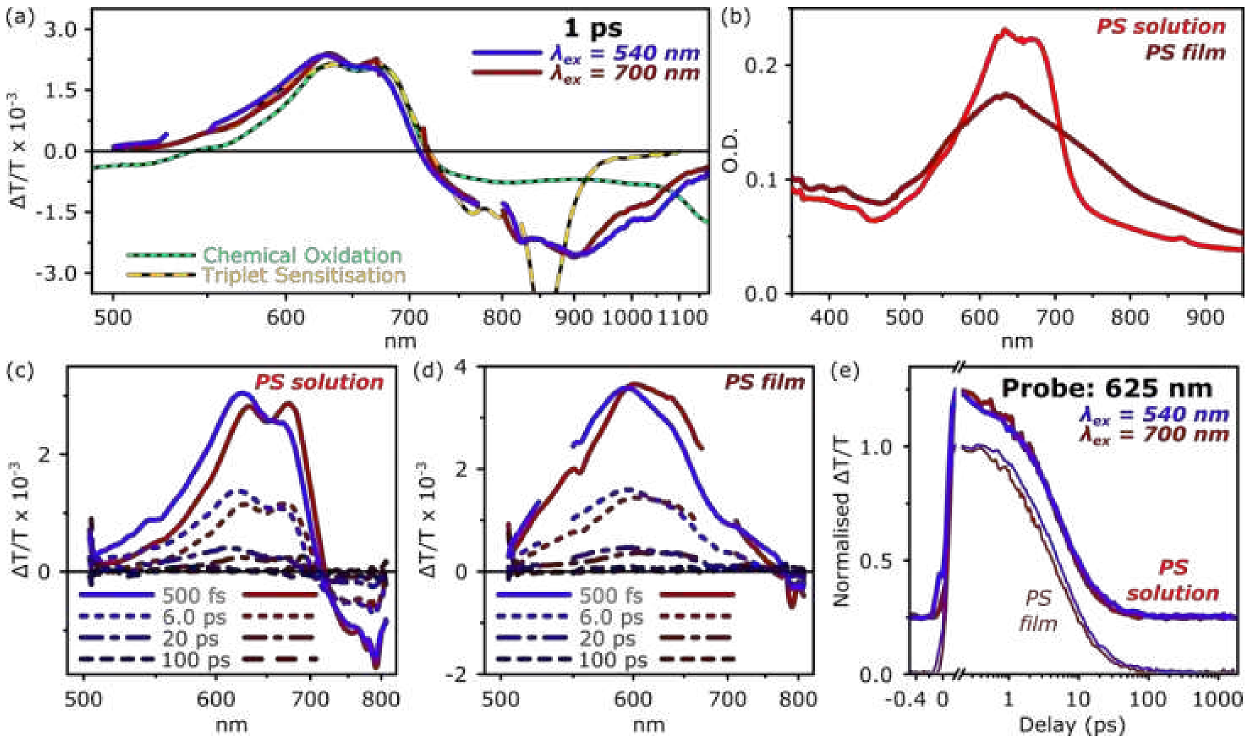


Figure 4. A series of control measurements were performed to identify the source of the ultrafast dynamics in TDPP-V-TDPP. (a) Chemical oxidation and triplet sensitisation spectra reveal no similarity to the observed transient absorption spectra following direct excitation, nor to the difference between band-edge and excess-energy excitation. There is thus no evidence for singlet exciton fission or ultrafast charge formation. Full sensitization data presented in **Fig. S9, SI**. (b) UV-Vis absorption spectra of TDPP-V-TDPP in high-viscosity solution and rigid polymer matrix. (c) **TA** spectra in concentrated **PS** solution are essentially indistinguishable from those obtained in chlorobenzene solutions, following both band-edge (dark red, 700 nm) and excess-energy (blue, 540 nm) excitation. (d) **TA** spectra in **PS** matrix reveal the same qualitative differences between excitation at 540 nm (blue) and 700 nm (dark red). (e) Integrated decay kinetics at the **GSB** peak reveal the same behaviour in viscous solution (thick) and **PS** matrix (thin) previously observed in chlorobenzene solutions: a slight enhancement of the lifetime following excess-energy excitation (blue), with the decay dominated by the same 3.6 ps and 10 ps time constants.

Our chemical strategy for imbuing ‘polyene’ character in a donor-acceptor-based covalent dimer appears to be successful, but results in no singlet fission. We expect that the primary reason for this behaviour lies in the energy balance. Dimerization into TDPP-V-TDPP results in a significant stabilization of the singlet energy, by ~400 meV. It is evident that there is no comparable reduction in the triplet energy, which is estimated at 1.1 eV in the monomer; the net result of this would be that triplet-pair formation in energetically inaccessible. Instead, inclusion of the vinyl linker creates the possibility of a dark, lower-energy state analogous to the $2A_g$ state analogous to polyenes, which decays rapidly and non-radiatively back to the ground state. This surprising effect reveals some of the possible pitfalls of small structural changes to design SEF dimers. However, the results also demonstrate that combining polyene character with charge-transfer chromophores can be straightforwardly achieved, and the features observed in the PIA spectra suggest that the charge-transfer character is maintained in the excited states. The remaining challenge, then, is to modulate the exchange energy to make **SEF** energetically accessible without too significantly perturbing the beneficial **CT** mixing. Destabilization of the $\mathbf{S_1}$ state should reduce the of $\mathbf{S_1}$ and **CT** states whilst simultaneously increasing the $\mathbf{S_1}$-$\mathbf{T_1}$ gap.[26, 49] This can be modulated by incorporating a covalent linker to control the extent of HOMO-LUMO spatial overlap in the chromophore. Rational choice or design of covalent linkers such as phenyls, biphenyls [55] or their substituted analogues can increase the energy of the $\mathbf{S_1}$ state by steric or hyperconjugation effects. End-capping the oligomer with strong electron withdrawing groups such as cyano, etc. will increase the proportion of quinoidal forms and form biradicals that stabilize the triplet state.[56] Such synthetic strategies are currently being implemented in our laboratory and the spectroscopic studies are underway.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge on the ACS Publications Website via pubs.acs.org

Materials and methods, Synthetic procedures, ^{1}H NMR, ^{13}C NMR, cyclic voltammograms, UV-Vis after doping, full transient absorption data and fitting, triplet sensitization (Figures S1-S5) (

PDF)

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Notes

The authors declare no competing financial interests.

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