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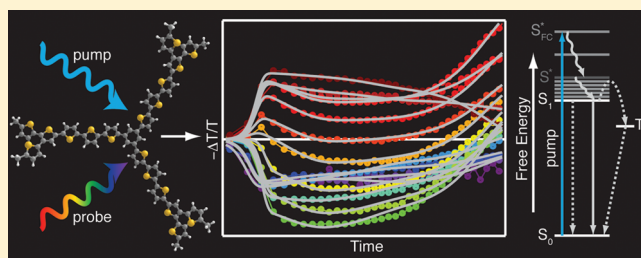
Allison C. Kanarr,[†] Benjamin L. Rupert,^{‡,§} Scott Hammond,[§] Jao van de Lagemaat,[§] Justin C. Johnson,^{*,§} and Andrew J. Ferguson^{*,§}

[§]National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, United States

[†]Department of Chemistry and Biochemistry, University of Colorado, UCB 215, Boulder, Colorado 80305, United States

 Supporting Information

ABSTRACT: First generation dendrimers with three oligothiophene arms (meta-arranged, 3G1-*n*S) and four arms (ortho- and para-arranged, 4G1-*n*S) connected to a central phenyl core were investigated spectroscopically in solution. In all dendrimers, on an ultrafast time scale (<10 ps), two “cooling” processes convert the initially generated, “hot” exciton into the geometrically relaxed, “cold” exciton. A decrease in the triplet yield, particularly evident for the 4-arm dendrimers; intersystem crossing rate; and nonradiative triplet decay time with increasing number of bridging thiophene units *n* all meet with expectations from prior studies on linear oligothiophenes. A relatively fast internal conversion process ($>0.6 \text{ ns}^{-1}$) is observed in both dendrimer series, possibly due to increased twisting about the phenyl core that reduces the triplet yields considerably with respect to oligothiophenes. An anomalous shifting of the triplet–triplet absorption spectra characterizes the 4G1-*n*S dendrimers as unique from the 3G1-*n*S series in terms of the hindrance of torsional motion and confinement of excited states enforced by the arrangement of dendrons.



1. INTRODUCTION

In the past few years optoelectronic devices based on organic semiconductors, such as organic light-emitting diodes (OLEDs) and organic photovoltaic (OPV) devices, have demonstrated remarkable levels of performance.^{1–3} Despite this recent progress, the search continues for chemical systems that combine the best aspects of conjugated polymers (e.g., solution processability) and small molecules (e.g., uniform, reproducible physical properties). Conjugated dendrimers fit this niche because they possess precisely defined molecular structures and can be processed easily from common organic solvents.^{4,5} Despite this promise, conjugated dendrimers have not been able to match the performance of, and therefore supplant, their rivals as the active components in the aforementioned devices.^{6–9} The fact that conjugated dendrimers have failed to realize their potential in optoelectronic devices highlights the need for comprehensive studies of excited state processes in such materials.¹⁰ Additionally, they remain an ideal candidate for conducting systematic studies of structure–property relationships, such as the understanding of their optical and electronic properties, of solution-processed organic semiconductors.^{10–14}

The thiophene repeat unit has been studied extensively as the fundamental building block for a plethora of organic optoelectronic systems, including polymers, oligomers, and more recently dendrimers, in the context of OLEDs,^{15–20} field-effect transistors (FETs),^{21–23} and OPV devices.^{24–27} The pervasive investigation

of thiophene-based semiconductor materials underlines the importance of developing an understanding of the interplay between the chemical structure and optical properties. Recently we reported on the synthesis and basic optical properties of a family of first-generation dendrimers in which conjugated thiophene dendrons of varying lengths are placed in different arrangements around a central phenyl core.¹³ The dendrimers prepared had either three or four dendrons, with a single branching point, around the core: the nomenclature *x*G1-*n*S is used to identify the dendrimers, where *x* is the number of first-generation dendrons and *n* is the number of bridging thiophene moieties between the phenyl core and branching point (Figure 1).¹³ This study demonstrated that an all-meta arrangement (3G1-*n*S) of the thiophene arms results in a chromophore that is localized to the α -conjugated thiophene segment and phenyl core, whereas ortho- and para-substitution (4G1-*n*S) permits electronic communication between two dendrons, although steric interactions between neighboring arms limits the effective conjugation length to less than the length of two α -conjugated segments coupled through the phenyl core.¹³

Of particular interest is whether triplet excitations should be as prominent in thiophene-based dendrimers as they are in oligothiophenes. Because ring twisting and σ – π mixing can

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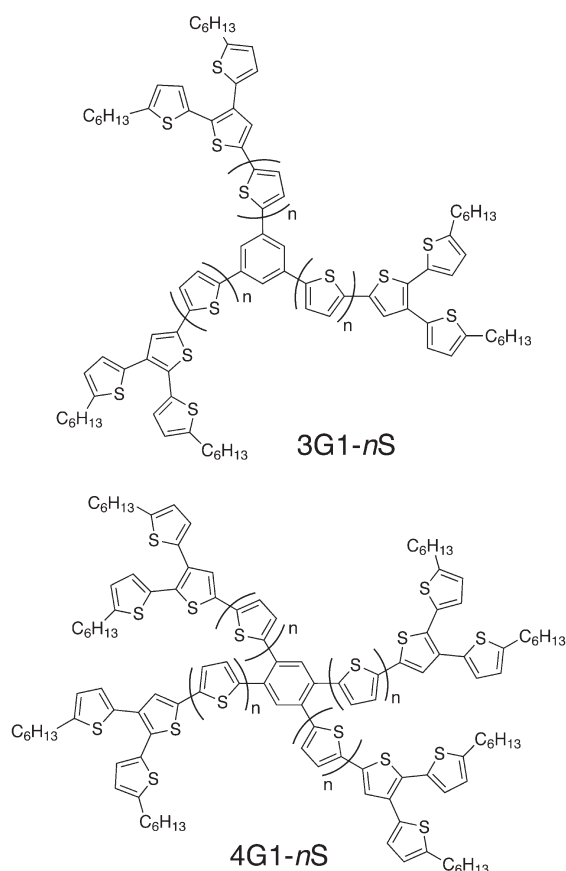


Figure 1. Chemical structures of the first-generation phenyl-cored thiophene dendrimers used in this study: *n* denotes the number of bridging thiophene rings between the phenyl core and branching point of the dendron.

modulate spin–orbit coupling strengths,²⁸ the geometrical conformations of the dendrimers in the excited state, as dictated by the generation number and length of thiophene chain, is expected to control the intersystem crossing (ISC) rate, k_{isc} , from the first excited singlet state, S_1 , to the first excited triplet state, T_1 . However, if higher-lying triplet states, T_N ($N > 1$), are energetically close to S_1 , the S_1-T_N channel becomes important, as dictated by the energy gap rule.²⁹ The exact S_1-T_N energy difference, determined primarily by the exchange interaction, which in turn depends on the amount of delocalization and charge transfer in the excited state, then plays a crucial role in determining k_{isc} . Competition between ISC and internal conversion (IC) will then likely determine the triplet yield. In the context of the mechanism and resultant efficiency of the conversion of solar photons into free carriers in light-harvesting systems based on organic semiconductors, triplet states are an often neglected but potentially influential species.^{30–32} These studies further highlight the need for a comprehensive understanding of how excited state processes, including triplet formation, can be controlled in model solar photoconversion systems.

In this work we present time-resolved studies, using nanosecond flash photolysis (ns-FP) and femtosecond transient absorption spectroscopy (fs-TAS) of the effect of dendron length and arrangement on the solution-phase excited-state processes in this family of thiophene dendrimers (Figure 1).

2. EXPERIMENTAL METHODS

All samples were prepared in an inert atmosphere and dissolved in 2-methyl-tetrahydrofuran (2-MeTHF; anhydrous,

>99.5%) from Sigma-Aldrich, which was degassed thoroughly by bubbling with argon for 30 min. UV–vis absorption was measured with a Shimadzu 3600, and fluorescence was collected with a Photon Technology International Quantamaster fluorimeter. Fluorescence quantum yields were determined using an absolute measurement in an integrating sphere.³³

Nanosecond time-resolved spectroscopic measurements were performed with an Edinburgh Instruments LP920 flash photolysis system. Pulsed excitation (10 Hz) at 355 nm was provided by the frequency-tripled output of a Q-switched Nd:YAG pump laser (Continuum, Surelite), with an average pulse power of approximately 5 mW. The photoinduced change in transmission was probed using a pulsed xenon arc lamp at a frequency of 10 Hz. The decadic molar extinction coefficients of the triplet states were measured using the ground state depletion method and the triplet quantum yields were measured using the relative actinometry method with anthracene in benzene as a reference.³⁴

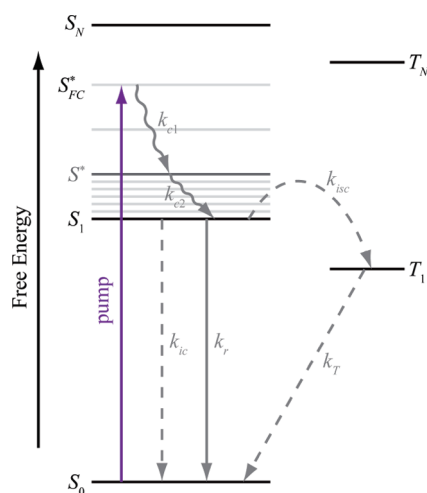
The time-resolved transient absorption spectroscopic experiments were performed using the second harmonic of a Ti:Sapphire laser (Clark, CPA-2001, 1 kHz, 775 nm, pulse duration ~ 130 fs) to pump at 388 nm (attenuated to approximately 0.5 mW average power) and a white-light probe produced by focusing 1 μ J of the fundamental into a continuously translated CaF₂ window, resulting in a continuum with a spectral range of approximately 400–800 nm. Time-resolved spectra were obtained at various delays between pump and probe by locking in to the 500 Hz modulation frequency of the pump while detecting identical copies of the monochromatized probe beam that traversed pumped and nonpumped regions of the sample. The two beams were incident on a balanced detector, with a small portion of the reference beam directed onto a second detector. The monochromator was scanned to produce data sets with $-\Delta T/T$ (where T is transmission) versus wavelength versus delay time ranging from 50 fs to 5 ns. Chirp in the probe pulse was accounted for by including an automatic wavelength-dependent delay determined by monitoring two-photon absorption in fused silica; the effective instrument response after chirp-correction was between 350 and 500 fs.

Spectrotemporal data acquired by the nanosecond flash photolysis (ns-FP) and femtosecond transient absorption spectroscopy (fs-TAS) methods were analyzed globally using the kinetic scheme in the main text (Scheme 1); further details about the fitting procedure can be found in the main text and Supporting Information.

3. RESULTS AND DISCUSSION

Flash Photolysis. The flash photolysis data (Figure 2) of all samples exhibit both bleach and excited-state absorption features, attributed to ground state depletion and triplet population, respectively. The same characteristic time (Table 1) can be used to describe the transient profiles associated with both features, for all dendrimers, indicating that in all cases the triplet state decays directly to the ground state according to simple first-order kinetics. This observation, along with the fact that the shape and position of the ground state bleach (GSB) are almost identical, in all cases, to the steady-state absorption of the dendrimers in solution, suggests that the photoinduced absorption at longer wavelengths is solely due to a triplet-state absorption (TSA), $T_1 \rightarrow T_N$. For the 3-arm dendrimers an increase in the length of the thiophene dendron results in a bathochromic shift of the TSA spectrum, with a concomitant narrowing of the absorption band,

Scheme 1. Kinetic Scheme Used To Analyze the Flash Photolysis and Transient Absorption Spectroscopy Data



consistent with the observed chain-length dependence for the linear α -oligothiophenes in a variety of solvents.³⁵ In contrast, the broad TSA absorption observed for the 4-arm dendrimers is almost unaffected by the number of bridging thiophene rings. In fact, there is a slight hypsochromic shift of the spectrum upon going from one to two bridging thiophene rings. For both the 3- and 4-arm dendrimers there is a clear decrease in the triplet lifetime, τ_T , as the number of bridging thiophene rings in the dendron increases. There is also a decrease in the triplet quantum yield, ϕ_T , with increasing dendron length, although this trend is much less pronounced for the 3-arm dendrimers, where the magnitude of the error reduces the statistical significance of the observed decrease. Both of these observations are consistent with the dependence of ϕ_T and τ_T on chain length for the linear α -oligothiophenes in a variety of solvents.³⁵

Transient Absorption. Figure 3 shows representative transient absorption spectra, as a function of delay time between the pump and probe pulses, for (a) 3G1–3S and (b) 4G1–3S. At long time delays (2.35 ns; brown traces), features similar to the GSB and TSA observed by flash photolysis dominate the measured spectra. At a time delay of 46 ps (yellow traces) the observed negative features with maximum amplitude at ~ 550 nm, for both dendrimers, have similar profiles to the steady-state photoluminescence (PL) spectra, implying that these result from stimulated emission from the first singlet excited state ($S_1 \rightarrow S_0$). At early times (820 fs; purple traces), a similar negative feature is observed at higher energies, indicating that the stimulated emission originates from the initially populated “hot” exciton, S_{FC}^* , which is generated by a vertical (Franck–Condon) electronic transition to an excited state in the same geometrical configuration as the ground state. As the time delay is increased from 820 fs to 46 ps, these features are observed to red-shift with time, indicating that the “hot” exciton either undergoes sequential energy transfer to molecular subunits capable of sustaining a more delocalized excited state¹⁰ or that geometrical relaxation to an energetically favorable molecular configuration occurs.^{36–39} Both processes will result in the excitation being located on a chromophore consistent with the observed steady-state PL spectra, and in the absence of additional experimental evidence it can be difficult to rule out either mechanism. In conjunction with this stimulated emission component a photoinduced absorption is also observed at lower energy, corresponding to excited state absorption to higher-lying singlet states ($S_1 \rightarrow S_N$).

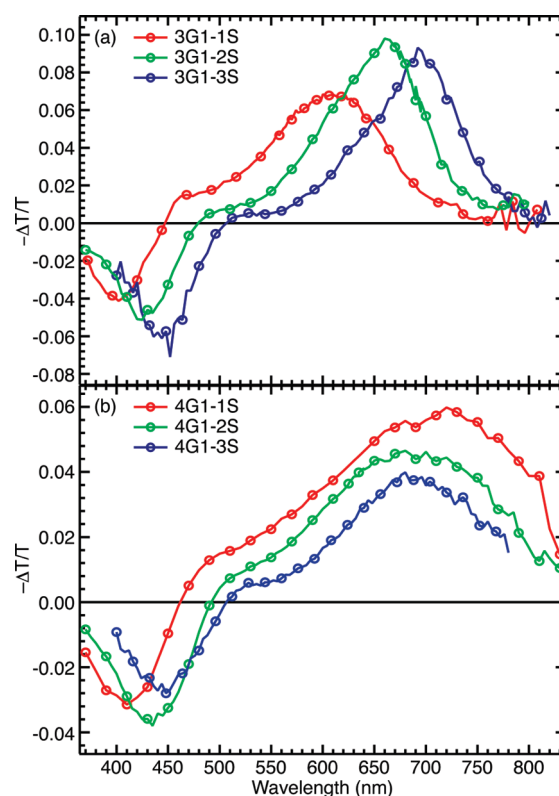


Figure 2. Peak transient absorption spectra, measured using flash photolysis, for (a) 3-arm dendrimers and (b) 4-arm dendrimers in degassed 2-MeTHF.

Kinetic Scheme. The observation of a single characteristic time to describe the first-order (exponential) decays of the ground state bleach and triplet state absorption, as measured by FP, and the previously observed single exponential photoluminescence decays (except for 4G1–3S),¹³ suggests that the excited state processes in the first generation phenyl-cored thiophene dendrimers can be described by the kinetic scheme (Scheme 1).

The excited state processes that take place upon photoexcitation (purple arrow) of the first-generation phenyl-cored thiophene dendrimers in solution are denoted by dark gray arrows. The states involved, processes that result in their interconversion, and the kinetic equations arising from this scheme are discussed in more detail in the text.

The previous studies of the time-resolved photoluminescence properties of the first-generation phenyl-cored thiophene dendrimers,¹³ along with the steady-state photoluminescence quantum yield and flash photolysis measurements performed as part of this study, allow the rate constants for a number of the excited state processes to be determined (Table 2); see the Supporting Information for full details.

At this stage it is worth noting that the radiative rate constants for the 3-arm dendrimers are similar to those observed for linear α -oligothiophenes in a variety of organic solvents.³⁵ This suggests that the all-meta arrangement of the dendrons around the phenyl core results in photophysical properties that are dominated by a single α -oligothiophene arm connected to a phenyl ring, as has been previously noted.¹³ That said, the presence of the additional arms results in a reduction in the rate constant for intersystem crossing with respect to those observed for linear

Table 1. Photophysical Properties of the First Singlet and Triplet Excited States of the First-Generation Phenyl-Cored Thiophene-Bridge Dendrimers in 2-MeTHF^a

compound	$\varepsilon(S_0 \rightarrow S_1)$ ($\times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$)	ϕ_{PL}	$\varepsilon(T_1 \rightarrow T_N)$ ($\times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$)	ϕ_{T}	τ_{T} (μs)
3G1-1S	0.93 ± 0.07	0.09 ± 0.01	1.50 ± 0.15	0.20 ± 0.03	38.37 ± 0.03
3G1-2S	1.25 ± 0.09	0.23 ± 0.02	2.50 ± 0.28	0.19 ± 0.03	28.55 ± 0.02
3G1-3S	1.56 ± 0.12	0.32 ± 0.03	2.80 ± 0.40	0.17 ± 0.03	20.10 ± 0.03
4G1-1S	0.96 ± 0.07	0.16 ± 0.02	1.01 ± 0.11	0.23 ± 0.03	45.47 ± 0.05
4G1-2S	1.47 ± 0.10	0.21 ± 0.02	1.56 ± 0.17	0.16 ± 0.02	28.48 ± 0.04
4G1-3S	1.71 ± 0.12	0.14 ± 0.01	2.45 ± 0.33	0.07 ± 0.01	20.10 ± 0.03

^a The calculations used to determine the errors for the parameters in Table 1 are described in further detail in the Supporting Information.

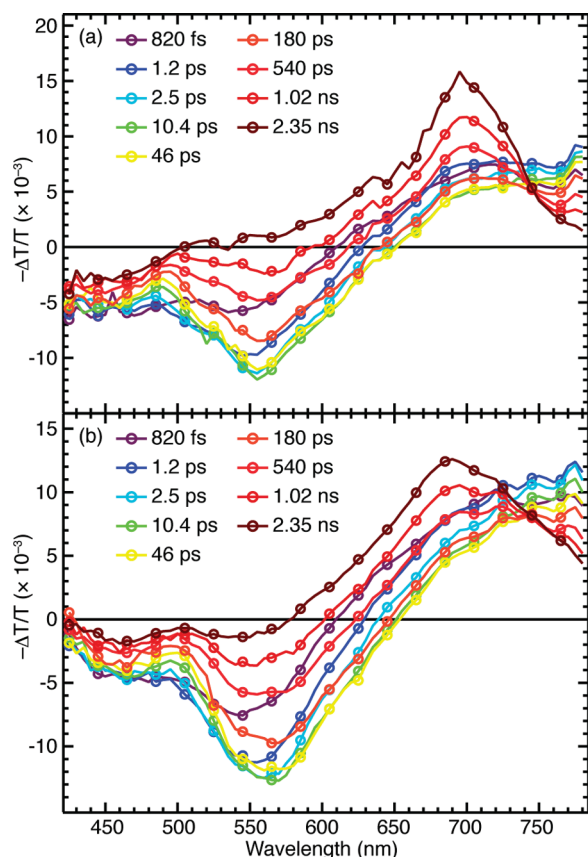


Figure 3. Representative transient absorption spectra, as a function of delay time (820 fs to 2.35 ns) between the pump and probe pulses for (a) 3G1-3S and (b) 4G1-3S in degassed 2-MeTHF.

α -oligothiophenes of similar length (number of conjugated rings),³⁵ which manifests itself as a dramatic reduction in the quantum yield for triplet formation. This may be due to a combination of factors that cannot be disentangled from available data. For oligothiophenes, it has been postulated that charge-transfer admixtures facilitate ISC and that these admixtures are more prevalent in shorter chains.³⁵ Although some partial charge-transfer character is expected for the dendrimers,⁴⁰ no experimental data verify this hypothesis, and solvent polarity effects were in fact found to be minor (data not shown). It is also possible that there is an increasing barrier for thermally activated ISC to T_N as the number of bridging thiophene rings, n , increases due to an expanding energy gap between S_1 and T_N .⁴¹ Temperature-dependent effects were measured but could not conclusively decouple trends in k_{isc} from k_{ic} (data not shown). Twisting of chains may also increase spin–orbit coupling strengths for the

shorter dendrimers; however, a clear correlation between twisting of chains and k_{isc} could not be found. The faster decay of the triplet to the ground state as n increases for both dendrimer series could be the result of the increasing likelihood of nonradiative decay as the T_1-S_0 energy gap decreases.

In contrast to the linear α -oligothiophenes, where the quantum yield for internal conversion, ϕ_{ic} , is small,³⁵ the incorporation of additional thiophene arms around the central phenyl core results in significant quenching of the excited state by internal conversion to the ground state, which results in the observed reduction of the photoluminescence quantum yield, ϕ_{PL} .¹³ The reduction of both k_{ic} and k_{isc} with arm length, in the case of the 3-arm dendrimers, indicates that the associated processes will compete less effectively with radiative decay from the first singlet state, which is reflected in the associated increase in ϕ_{PL} with the addition of more bridging thiophene units.

As has been previously noted, while the excited state in the 4-arm dendrimers is capable of extending through the phenyl core, it does not spread out over the full length of two dendrons; although, it was postulated that the relaxed exciton is larger in the 4-arm dendrimers than in the corresponding 3-arm compounds.¹³ With this in mind, it is evident that the values of the radiative and internal conversion rate constants, k_{r} and k_{ic} , are smaller and larger, respectively, than for linear α -oligothiophenes with comparable conjugation lengths (5–7 rings).³⁵ These two effects give rise to the dramatic reduction in ϕ_{PL} observed for the 4G1- n S series, compared to the linear α -oligothiophenes.³⁵ In contrast to the 3-arm dendrimers, no real trend can be observed in k_{r} and k_{ic} for the 4-arm dendrimers, suggesting that the nature of the relaxed excited state is likely to be quite different from that observed for the 3G1- n S dendrimers and, additionally, that it may even vary within the 4G1- n S series of dendrimers.

The position of the most prominent peak in the $T_1 \rightarrow T_N$ spectrum for the 3G1- n S series is a strong function of n , in analogy with oligothiophenes.³⁵ However, in the 4G1- n S series, the $T_1 \rightarrow T_N$ peak is almost independent of n , suggesting that the higher-lying triplet states do not spread along the thiophene chain as the length is increased. In fact, a slight blue-shift of the $T_1 \rightarrow T_N$ peak can be detected, although the considerable width of the peak precludes an accurate determination of its position. The increased broadening suggests that the increased conformational flexibility in the 4G1- n S series leads to a wider spread in T_N values. A similar effect is observed in the photoluminescence spectra of the 4-arm dendrimers, where enhanced coupling to vibrational/torsional modes results in increased broadening of the vibronic bands and a broader, less structured emission spectrum.¹³ While our measurements cannot rule out the possibility that intramolecular π – π interactions, between two thiophene arms arranged ortho to each other in the 4-arm

dendrimer, give rise to the negligible dependence of the observed triplet state absorption energy on the thiophene dendron length, theoretical calculations of the excited state geometries for the 4-arm dendrimers show no evidence for such an interaction.⁴⁰

It might seem unusual that the $T_1 \rightarrow T_N$ shift is larger than the $S_0 \rightarrow S_1$ shift with n for the oligothiophenes and for the 3G1- n S series but not for the 4G1- n S series, and this observation is worth considering further. In more rigid polycyclic aromatic systems such as polyacenes, both “cold” (i.e., vibrationally relaxed S_1) and “hot” excitons spread throughout the molecule to the same extent because there is little conformational disorder to produce localization on one portion of the molecule. The $T_1 \rightarrow T_N$ peak absorption shift in the polyacene series is smaller than that of $S_0 \rightarrow S_1$ going from naphthalene through pentacene,⁴² as is generally expected due to the size dependence of the exchange energy.⁴³ In systems with considerable conformational flexibility along the conjugated chain, such as oligothiophenes and the dendrimers considered here, there will be larger barriers to delocalization that the “cold” S_1 or T_1 excitons will be unable to surmount, thus, restricting them to roughly three α -conjugated thiophene units in the 3G1- n S series.⁴⁰ Therefore, although minor shifts in S_1 and T_1 do occur as n increases, higher energy electronic states are more able to sense the true size of the system, producing a larger change in T_N energies and a correspondingly larger shift in $T_1 \rightarrow T_N$ than $S_0 \rightarrow S_1$. “Hot” excitons are expected to delocalize over about five thiophene units, which is easily accommodated in 3G1–3S in just one arm but is more difficult in 3G1–2S and 3G1–1S.⁴⁰ In the latter two dendrimers, the “hot” exciton is “squeezed” into a smaller space forcing delocalization through the core to other arms, despite the unfavorable meta arrangement. This “nonlinear” delocalization comes at a considerable energetic cost compared with the para arrangement, similar again to linear versus bent polyacenes; however, coupling between arms in the excited state in meta-arranged phenylacetylene dendrimers has been observed.⁴⁴ Both oligothiophenes³⁵ and oligophenylenevinyls^{45–47} exhibit trends in n -dependent shifting of $T_1 \rightarrow T_N$ and $S_0 \rightarrow S_1$ similar to the 3G1- n S series (Figure S1, Supporting Information), suggesting the generality of this type of analysis for these families of chromophores. It should be mentioned that the most appropriate comparison of peak shifting would involve $S_1 \rightarrow S_N$ with $S_0 \rightarrow S_1$ transitions, but the true $S_1 \rightarrow S_N$ spectrum for most compounds is not available due to the relatively short singlet lifetime and difficulty in separating pure absorption, which appears to be rather broad and without structure, from stimulated emission.

The observation that there is essentially no shift of $T_1 \rightarrow T_N$ for the 4G1 series arises from the likelihood that the delocalization of excitation through the arms connected in para positions to the phenyl core already accommodates the largest “hot” triplet exciton size (defined by twisting of the thiophene backbone) for $n = 1$, and surmounting the barrier for producing a larger “hot” exciton apparently requires much more energy. Thus, the “hot” exciton wave function is unlikely to change significantly as n increases. Some delocalization can occur among the other arms, but this is unlikely to have a strong effect on the transition energies for the “hot” states. These constraints may be less applicable to studies of the dendrimers in films where some degree of intermolecular interaction can induce molecular configurations that reduce twisting and extend conjugation lengths. Investigations of the photophysical properties of films of 3G1- n S and 4G1- n S dendrimers are ongoing.

Global Spectrotemporal Analysis. Assuming, that a “hot” exciton, S_{FC}^* , has already been generated as a result of a

photoinduced, vertical electronic transition from the ground state, Scheme 1 results in the following differential equations (eqs 1–5) for the rate of change of the species involved:

$$\frac{d[S_{FC}^*]}{dt} = -k_{c1}[S_{FC}^*] \quad (1)$$

$$\frac{d[S^*]}{dt} = k_{c1}[S_{FC}^*] - k_{c2}[S^*] \quad (2)$$

$$\frac{d[S_1]}{dt} = k_{c2}[S^*] - (k_r + k_{ic} + k_{isc})[S_1] = k_{c2}[S^*] - k_f[S_1] \quad (3)$$

$$\frac{d[T_1]}{dt} = k_{isc}[S_1] - k_T[T_1] \quad (4)$$

$$\frac{d[S_0]}{dt} = (k_r + k_{ic})[S_1] + k_T[T_1] \quad (5)$$

where S_{FC}^* is the initially formed, “hot” exciton, S^* is an “intermediate”, “hot” exciton, S_1 is the relaxed, “cold” exciton, T_1 is the first excited triplet state, and S_0 is the ground state: k_{c1} is the first-order rate constant describing the cooling process of S_{FC}^* to yield S^* ; k_{c2} is the first-order rate constant describing the cooling process of S^* to yield S_1 ; k_r and k_{ic} are the first-order rate constants describing the radiative decay and internal conversion of S_1 to yield S_0 ; k_{isc} is the first-order rate constant describing intersystem crossing from S_1 to yield T_1 ; k_f is the inverse of the measured fluorescence lifetime; and k_T is the first-order rate constant describing decay from T_1 to yield S_0 .

The normalized, time-dependent trajectories of the species, $S_{FC}^*(t)$, $S^*(t)$, $S_1(t)$, $T_1(t)$, and $S_0(t)$, are described by the solutions to these differential equations and are described by exponential (first-order) decays (eqs 6–10) whose characteristic times are determined by the rate constants described above.

$$S_{FC}^*(t) = e^{-k_{c1}t} \quad (6)$$

$$S^*(t) = \frac{k_{c1}(e^{-k_{c2}t} - e^{-k_{c1}t})}{(k_{c1} - k_{c2})} \quad (7)$$

$$S_1(t) = \frac{k_{c1}k_{c2}[(k_{c1} - k_{c2})e^{-k_{c1}t} - (k_f - k_{c2})e^{-k_{c1}t} + (k_f - k_{c1})e^{-k_{c2}t}]}{(k_{c1} - k_{c2})(k_f - k_{c1})(k_f - k_{c2})} \quad (8)$$

$$T_1(t) = \frac{k_{c1}k_{c2}k_{isc}}{(k_{c1} - k_{c2})(k_f - k_{c1})(k_f - k_{c2})(k_{c1} - k_T)(k_{c2} - k_T)(k_f - k_T)} \times \left[\begin{aligned} &(k_{c2} - k_{c1})(k_{c2} - k_f)(k_f - k_{c1})e^{-k_{c1}t} \\ &- (k_{c1} - k_{c2})(k_{c1} - k_T)(k_{c2} - k_T)e^{-k_{c1}t} \\ &+ (k_f - k_{c2})(k_T - k_{c2})(k_T - k_f)e^{-k_{c1}t} \\ &- (k_f - k_{c1})(k_T - k_{c1})(k_T - k_f)e^{-k_{c2}t} \end{aligned} \right] \quad (9)$$

$$S_0(t) = \frac{-1}{(k_{c1} - k_{c2})(k_f - k_{c1})(k_f - k_{c2})(k_{c1} - k_T)(k_{c2} - k_T)(k_f - k_T)} \times \left[\begin{aligned} &k_{c1}k_{c2}k_{isc}(k_{c1} - k_{c2})(k_{c1} - k_f)(k_{c2} - k_f)e^{-k_{c1}t} \\ &- k_{c1}k_{c2}(k_{c1} - k_{c2})(k_{c1} - k_T)(k_{c2} - k_T)(k_T - (k_r + k_{ic}))e^{-k_{c1}t} \\ &- k_{c2}(k_{c2} - k_f)(k_{c2} - k_T)(k_f - k_T)(k_f k_T - k_{c1}(k_r + k_{ic}))e^{-k_{c1}t} \\ &+ k_{c1}(k_{c1} - k_f)(k_{c1} - k_T)(k_f - k_T)(k_f k_T - k_{c2}(k_r + k_{ic}))e^{-k_{c2}t} \end{aligned} \right] \quad (10)$$

In the case of the FP measurement, where the time-resolution is not sufficient to probe the fast processes associated with S_{FC}^* ,

Table 2. Rate Constants Determined from Steady-State and Time-Resolved Photoluminescence and Flash Photolysis Measurements^a

compound	k_r (ns ⁻¹)	k_{ic} (ns ⁻¹)	k_{isc} (ns ⁻¹)	k_T ($\times 10^{-5}$ ns ⁻¹)
3G1-1S	0.360	2.840	0.800	2.604
3G1-2S	0.393	0.991	0.325	3.534
3G1-3S	0.400	0.634	0.213	4.975
4G1-1S	0.286	1.089	0.411	2.198
4G1-2S	0.326	0.977	0.248	3.509
4G1-3S	0.207	1.170	0.104	4.975

^aThe simple equations used to determine these rate constants derive from the kinetic scheme (Scheme 1) described below, and are described in full in the Supporting Information document.

S^* , or S_1 , the scheme simplifies to decay of T_1 to S_0 , described by an exponential (first-order) decay with the rate constant k_T . The spectrottemporal FP data were analyzed according to this simplified scheme, resulting in the triplet lifetimes, τ_T , and the corresponding rate constants, k_T , presented in Tables 1 and 2, respectively.

Spectrottemporal TAS data were analyzed globally using weighted contributions of eqs 6–10 (eq 11), to account for the spectral dependence of the change in optical density for each species, after subsequent analytical convolution with an instrument response function described by a Gaussian function with full-width half-maximum ~ 350 –500 fs. Further details about the analytical convolution can be found in the Supporting Information.

$$\Delta OD(\lambda, t) = A_{S_{FC}^*}(\lambda)S_{FC}^*(t) + A_{S^*}(\lambda)S^*(t) + A_{S_1}(\lambda)S_1(t) + A_{T_1}(\lambda)T_1(t) + A_{S_0}(\lambda)S_0(t) \quad (11)$$

Initial attempts to model the spectrottemporal TAS data neglected any contribution from the initially formed, “hot” exciton, and were unsuccessful with respect to describing the early time (<10 ps) kinetics. Inclusion of two “cooling” processes, described by the rate constants $k_{c1} \geq 1000$ ns⁻¹ and $k_{c2} \geq 65$ ns⁻¹, resulted in an excellent description of the spectrottemporal TAS data for all six dendrimers; Figure 4 shows representative transients (colored symbols and traces) and their associated fits (solid gray traces) on a log time scale for (a) 3G1-3S and (b) 4G1-3S; the results of the full global spectrottemporal analysis for all the dendrimers are shown in the Supporting Information (Figures S2–S7).

At this stage it is worth describing how the spectrottemporal data were analyzed using the global analysis routine, which was optimized by reducing the global chi-squared for the full data set using a standard Levenberg–Marquardt algorithm in Igor Pro 6 (Wavemetrics). The following parameters were available to the global spectrottemporal analysis routine: the first-order rate constants k_{c1} , k_{c2} , k_r , k_{ic} , k_{isc} , k_T ; the spectral contributions (weighting factors) of the five species probed by the TAS measurement $A_{S_{FC}^*}(\lambda)$, $A_{S^*}(\lambda)$, $A_{S_1}(\lambda)$, $A_{T_1}(\lambda)$, $A_{S_0}(\lambda)$; and two parameters describing the position, G_{pos} , and full width at half-maximum, G_{fwhm} , of a unit-area Gaussian instrument response function. Additionally, because the GSB signal is expected to closely match the steady-state absorption spectrum $A_{S_0}(\lambda)$ was given by the normalized absorption at wavelength λ , multiplied by a constant determined from the relative magnitudes of

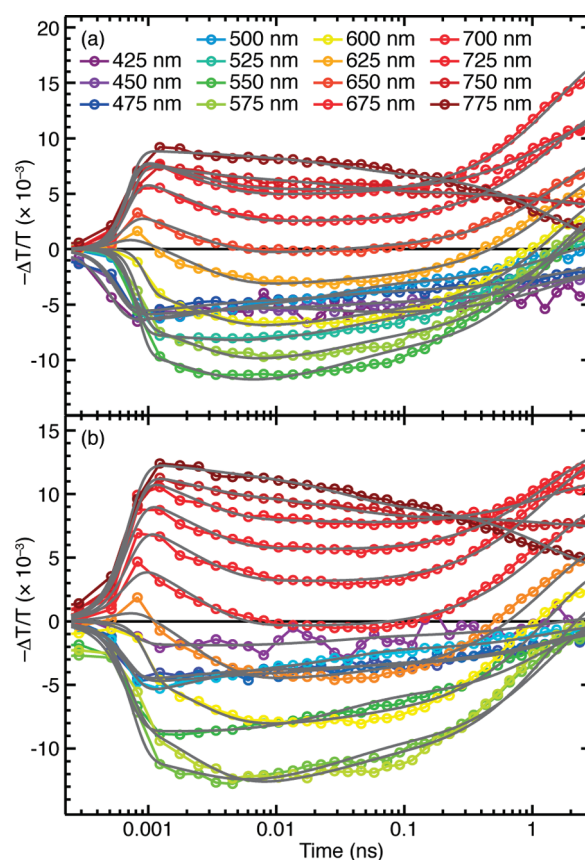


Figure 4. Representative transient absorption kinetic traces (symbols and colored traces) along with fits using the model described in the text (solid gray lines) as a function of probe wavelength (425–775 nm) for (a) 3G1-3S and (b) 4G1-3S in degassed 2-MeTHF.

the GSB and TSA from flash photolysis measurements (Figure 2). In this way the position and shape of the GSB were constrained to that of the steady-state absorption spectrum, allowing better (albeit not perfect) extraction of the TSA signal at high energies. However, the strong overlap of these two features made it difficult to extract the true TSA signal in this spectral region, and as a result $A_{T_1}(\lambda)$ was constrained to be greater than zero. With respect to the rate constants all were kept fixed at the values shown in Table 2, except that k_{c1} and k_{c2} were constrained to be greater than 1000 and 65 ns⁻¹, respectively. This meant that only $A_{S_{FC}^*}(\lambda)$, $A_{S^*}(\lambda)$, $A_{S_1}(\lambda)$, $A_{T_1}(\lambda)$, and G_{pos} were treated as local variable parameters (i.e., specific to an individual transient) and G_{fwhm} was kept as a global variable parameter (i.e., the same for all transients). As a result the spectral contributions for the five species described in Scheme 1 were extracted using the global spectrottemporal analysis for all six dendrimers; these are shown in Figure 5 for (a) 3G1-3S and (b) 4G1-3S.

The inclusion of the two “cooling” processes, that result in the conversion of S_{FC}^* into S_1 (via S^*) is justified on the basis of the time-dependent, red-shift of stimulated emission spectra observed in femtosecond transient absorption measurements of substituted oligothiophenes in solution.^{36–39} These studies obtained characteristic rate constants associated with internal energy redistribution processes of 1250–2000 ns⁻¹ and ~ 250 ns⁻¹, which were assigned to vibrational and torsional relaxation respectively.^{36–39} A more recent study of branched,

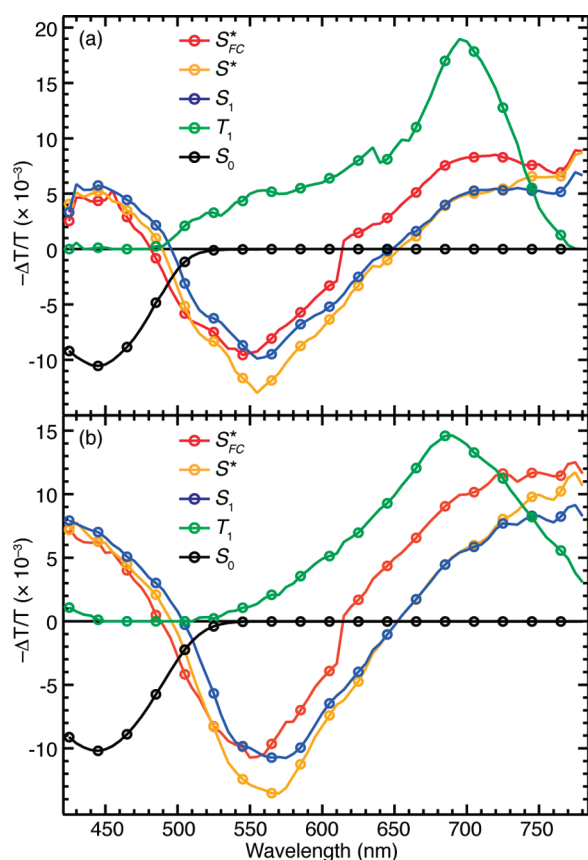


Figure 5. Representative spectral contributions, extracted using the model described in the text for the species described in Scheme 1 for (a) 3G1–3S and (b) 4G1–3S in degassed 2-MeTHF.

all-thiophene dendrimers also observed a fast process (described by a rate constant on the order of $3333\text{--}5000\text{ ns}^{-1}$), which was attributed to ultrafast energy transfer from the initially populated excited state to the lowest energy (longest conjugation length) oligothiophene segments.¹⁰ The same study by Ramakrishna et al. found that the torsional energy redistribution process, which was dependent on the dendrimer generation (number of branching points), was described by a rate constant on the order of $80\text{--}400\text{ ns}^{-1}$.¹⁰ Even though it was necessary to include the two “cooling” processes, denoted by k_{c1} and k_{c2} , to describe the sub-10 ps kinetics in our data, the number of points in the data on this time scale was insufficient to allow k_{c1} and k_{c2} to be used as completely free, variable parameters in the global fitting process. As a result, constraints were placed on these parameters to restrict the values to greater than 1000 and 65 ns^{-1} , for k_{c1} and k_{c2} , respectively. The nature of the measurements carried out in this work preclude us from distinguishing between fast vibrational relaxation or an ultrafast energy transfer process. However, the reduced branching in the 3- and 4-arm dendrimers used in this study, in comparison to the all-thiophene dendrimers studied by Ramakrishna et al.,¹⁰ suggests that the molecules already adopt a more planar structure, reducing the opportunity for energy transfer. In addition, the more symmetrical structures of the 3G1-*n*S and 4G1-*n*S dendrimers imply that there is a smaller distribution of chromophore energies, leading to only a minor role for energy transfer. These postulations intimate that vibrational and torsional energy redistribution are the more likely causes of the

observed bathochromic shift of the stimulated emission component.

4. CONCLUSION

Our results indicate that the wavelength-dependent transient absorption dynamics of first generation dendrimers, with three oligothiophene arms (meta-arranged, 3G1-*n*S) and four arms (ortho- and para-arranged, 4G1-*n*S) connected to a central phenyl core, can be described by a simple kinetic scheme including two “cooling” processes that convert the initially generated, “hot” exciton into the geometrically relaxed, “cold” exciton. Subsequent relaxation of the “cold” exciton via radiative decay or intersystem crossing to yield the triplet excited state then occurs. Our data are not sufficient to elucidate the precise mechanism of the “cooling” processes, but we attribute them to either sequential vibrational and torsional energy redistribution or to ultrafast energy transfer followed by torsional energy redistribution. We observe a decrease in the intersystem crossing rate and nonradiative triplet decay time with increasing number of thiophene units *n*, which is consistent with prior studies of the excited-state processes in oligothiophenes. We also measure a distinct decrease in the triplet yield for the 4G1-*n*S dendrimers with arm length, once again consistent with previous observations for linear oligothiophenes, while the observation of an apparent trend for the triplet yield for the 3G1-*n*S series must be tempered by the magnitude of the error associated with the calculated values. In contrast, however, our measurements reveal a relatively fast internal conversion process ($>0.6\text{ ns}^{-1}$) in both dendrimer series, possibly due to increased twisting about the phenyl core, that reduces the triplet yields considerably with respect to oligothiophenes. Even though the $T_1 \rightarrow T_N$ spectrum is observed to red-shift, as expected, with increasing number of thiophene units *n*, in the 3G1-*n*S dendrimers an anomalous blue-shift characterizes the triplet–triplet absorption in the 4G1-*n*S dendrimers. We attribute this observation to the hindrance of torsional motion and confinement of excited states enforced by the more crowded arrangement of dendrons in the 4-arm compounds.

■ ASSOCIATED CONTENT

S Supporting Information. Further information regarding calculation of the errors presented for the parameters given in Table 1; calculation of first-order rate constants from the kinetic scheme; analytical convolution of unit-area Gaussian instrument response with multiexponential decays; the dependence of ground state and triplet state absorption energies on the conjugation length for the first-generation phenyl-cored thiophene dendrimers in this study, along with those for linear α -oligothiophenes and oligophenylenevinyls; and experimental and simulated spectrotemporal TAS data for all six dendrimers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +1 (303) 384.6190 (J.C.J.); +1 (303) 384.6637 (A.J.F.). Fax: +1 (303) 384.6655 (J.C.J. and A.J.F.). E-mail: justin.johnson@nrel.gov (J.C.J.); andrew.ferguson@nrel.gov (A.J.F.).

Present Addresses

[‡]Lawrence Livermore National Laboratory, Livermore, CA 94550.

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