Oligothiophene Dendrimers as New Building Blocks for Optical Applications[†]

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Thiophene branched structures have been proposed as candidates for photon harvesting and electron−hole transporting materials in novel organic light emitting diodes and solar energy conversion devices. To understand the photoinduced processes in a novel thiophene dendrimer system, the excited state dynamics and nonlinear optical properties of 3D oligothiophene dendrimers have been investigated. The key point of this contribution is that we have found that with these thiophene dendrimer systems, the excitation is delocalized over a large number of thiophene units in the dendrimer and there is an ultrafast energy transfer (200−300 fs) to the longest branch of dendrimer, which can be utilized for future optical devices. In terms of nonlinear optics, it was found that a super-linear increase of two-photon absorption cross-section is observed with an increase in thiophene dendrimer generation that can be explained by the increased excitation delocalization. Generation dependent torsional energy redistribution has also been observed, which planarizes the final emissive state on a picosecond time scale.

Introduction

Organic materials possessing excellent optical and electrical properties have been the focus of intense research for several years because they have potential applications in photovoltaic devices,[1] light harvesting,[2,3] and organic electronics.[4] This is because of their ease of molecular synthesis and ability to fine-tune their physical properties for the need of technological applications. Among several methodologies for better functional organic materials, a building block approach based on the dendritic architecture with hierarchy of branched organic structures has been suggested to be an efficient design criterion for new artificial light harvesting and solar energy conversion devices.[5−10] Energy funneling from the peripheral chromophores of the dendrimer to the core[5] has been observed, and this has stimulated research in this field. Additionally, the enthusiasm in the field of organic dendrimers is also motivated by its possible applications in the areas organic light emitting diodes[11−15] and nonlinear optical devices.[16−24] Among several organic chromophores utilized to synthesize dendritic structures, thiophenes or oligothiophenes find a unique place, as they have been well investigated for their versatile chemistry,[25−29] applications in organic light emitting diodes,[30−32] field effect transistors,[33,34] and organic photovoltaic and light harvesting devices[35−39] such as solar cells. For example, organic solar cells based on P3HT (poly(3-hexylthiophene)) polymer/fullerene derivatives are one of the best available organic solar cells with an efficiency of 4−5%.[40] Although several oligomers and polymers of thiophene have been synthesized[41−46] and investigated extensively, not until recently has an all-thiophene dendrimer been synthesized.[47−51] Bauerle and co-workers[51] have synthesized space filling 3D-functionalized oligothiophene dendrimers for their application in light harvesting, solar energy conversion, and optoelectronics. Efficient excitation delocalization and excitation energy transfer are needed for the organic materials to mimic natural light harvesting systems, and conversion of solar energy and large electron mobilities are needed in organic light emitting diodes. Time-resolved measurements on these dendrimers as a function of generation can be able to evaluate the extent of excitation delocalization and energy transfer processes which are needed to evaluate their capabilities in optical applications.

In addition, strong intrachromophore interactions, efficient energy transfer, and migration through the structural design of dendritic architecture and formation of delocalized excited states render them to have enhanced nonlinear optical properties (especially two-photon absorption (TPA) cross-section) in comparison to their linear counterparts.[16−21,24] TPA properties of organic branched chromophores has been the subject under spotlight for past decade[52−64] or so because it has shown promising applications in 3D microfabrication,[65−68] photodynamic therapy,[69,70] multiphoton microscopy,[71−73] optical power limiting,[74,75] and sensing.[76] Several π-conjugated phenyl cored,[21] nitrogen centered[22,24] dendritic chromophores have been synthesized recently and their TPA cross-sections were measured, which have shown cooperative enhancement with an increase in dendrimer generation. In the context of these exciting nonlinear optical properties of dendrimers and branched organic structures, TPA cross-sections of thiophenes and their derivatives has also been investigated.[77−79] Since all-thiophene dendrons and dendrimers have the ability to form space filling solid state objects,[51] it will be interesting to utilize these thiophene dendrimers as potential two-photon absorbing materials in the solution and solid state in addition to their potential as artificial light harvesting systems. In a previous work on the TPA properties of macrocyclic thiophene derivatives with nanometer sized cavities,[79] we have shown that the TPA cross-section has increased to about 2.5 times that of smaller macrocycle. Time-resolved spectroscopic techniques were able to elucidate the

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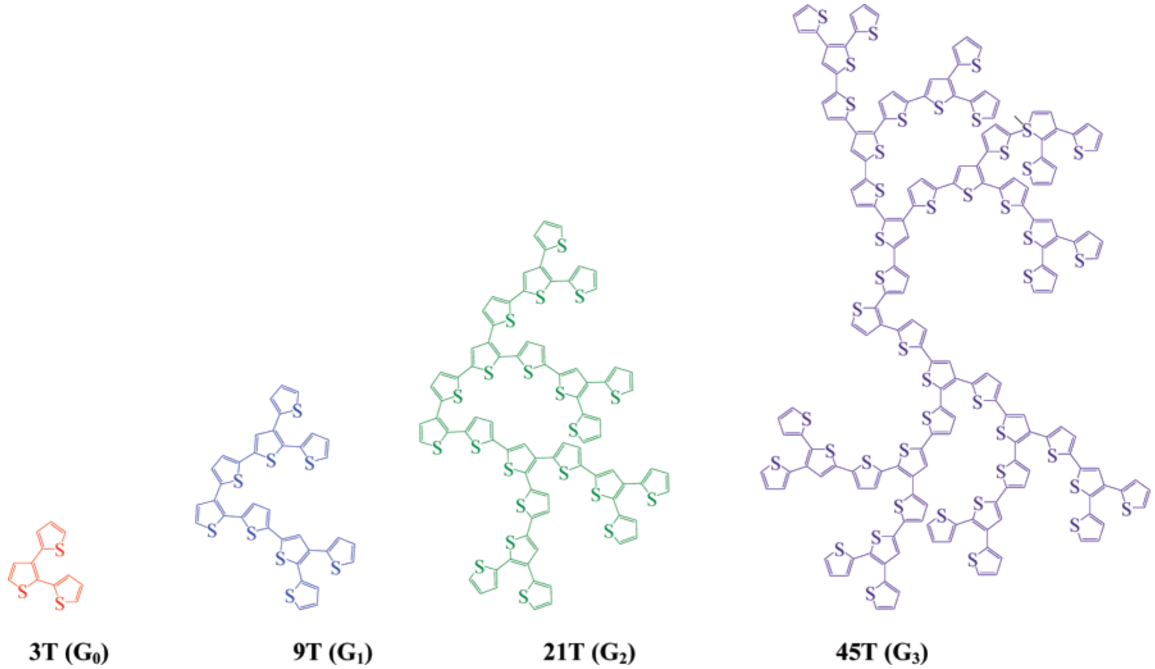


Figure 1. Molecular structures of the investigated 3D oligothiophene dendrimers.

delocalized excited states in these macrocyclic thiophene derivatives.[79]

As discussed above, thiophene dendrimers, oligothiophenes, and their derivatives are potential mimics of natural light harvesting systems; dynamics of photoinduced processes in them can give insight on their optical applications. Excited state dynamics of oligothiophenes and polythiophenes[80−95] has been investigated in the literature for understanding the fundamental mechanism behind their applications in light harvesting, solar energy conversion, and organic electronics. Several measurements on singlet and triplet states of thiophenes were carried out by femtosecond pump−probe spectroscopy[80−93] and the nature of singlet states by time-resolved fluorescence.[94,95] Westenhoff et al.[93] have reported the anomalous excitation energy transfer through torsional relaxation in the polythiophene derivative of poly[3-(2,5-dioctylphenyl)thiophene] (PDOPT). Kobayashi and co-workers[94,95] have reported chain length dependent stationary and time-resolved fluorescence spectra of α-oligothiophenes and shown that hydrodynamic slip model successfully explains the reorientation dynamics. Amidst several time-resolved experiments on oligothiophenes and polythiophenes, no experimental or theoretical investigation is available on the excited state dynamics of all-thiophene dendrimers and their generation dependence to prove their potential as light harvesting mimics.

In the present paper, we investigate the excited state dynamics and TPA properties of a thiophene dendrimer system up to the fourth generation (G_0 to G_3, molecular structures are shown in Figure 1). TPA cross-section sections have shown the superlinear increase of cross-section per unit thiophene with increase in dendrimer generation. Femtosecond time-resolved measurements have shown that the excitation is delocalized through a large part of the dendrimer and is responsible for the observed enhancement in TPA cross-sections and efficient light harvesting. Results also have shown the phenomenon of excitation energy migration to the longest emitting state in ultrafast time scale mimicking the energy funnel system. Additionally, generation dependent torsional relaxation in the emitting state has been observed which tends to assist in planarizing the molecule.

2. Experimental Section

a. Materials. Thiophene dendrimers were synthesized using the procedure described previously.[51] All the measurements were carried out in tetrahydrofuran (THF) (Aldrich) unless stated otherwise.

b. Steady State Measurements. Optical absorption measurements were carried using Agilent UV/vis absorption spectrometer. Fluorescence measurements were carried out using a Jobin Yvon Spex Fluoromax-2 spectrofluorometer. The quantum yields of the molecules were measured using a known procedure, and Coumarin 307 was used as the standard.

c. Two-Photon Excited Fluorescence Measurements. To measure the two-photon absorption cross-sections (δ), two-photon excited fluorescence (TPEF) method[96] has been employed. A 10^{-4} M Coumarin 307 solution in methanol was used as the reference over a wavelength range of 700−800 nm. To measure the TPA cross-sections for wavelengths less than 700 nm, *p*-bis(*o*-methylstyryl)benzene (MSB) dissolved in cyclohexane was used as the reference. A mode-locked Ti:sapphire laser (Kapteyn Murnane (KM)) was used for determining the δ over 760-820 nm. For the remaining wavelengths (630−760 and 820−900 nm), an Optical Parametric Amplifier (OPA-800C, Spectra physics) was employed. The seed used was a mode locked Ti:sapphire laser (Tsunami, Spectra Physics). This was amplified using a regenerative amplifier (Spitfire, Spectra Physics) which in turn was pumped by a Nd:YLF laser (Empower, Spectra Physics). The amplified pulses were obtained at 1 kHz, 800 nm, and ∼100 fs, which was used for pumping the OPA.

d. Fluorescence Lifetime Measurements. Time correlated single photon counting (TCSPC) was used to determine the fluorescence lifetimes of the thiophene dendrimers used in this study. The laser used was the KM system described earlier. The second harmonic from the 800 nm output was used for these measurements.

e. Femtosecond Transient Absorption Measurements. Transient absorption was used to investigate the excited state dynamics of the thiophene dendrimers at different excitation wavelengths and the description of the system has been provided

TABLE 1: Linear Optical Properties of Thiophene Dendrimers[a]

compound	$\lambda_{\mathbf{abs}}$ (nm)	$\lambda_{\mathbf{em}}$ (nm)	$\Phi_{\mathbf{f}}$	$\tau_{\mathbf{f}}$ (ps)	M (D)
G_0	302	440	0.02	-	4.9
G_1	371	517	0.09	790	9.6
G_2	382	542	0.05	500	14.8
G_3	385	565	0.06	690	19.2

[a] Φ_f is the emission quantum yield, τ_f is the fluorescence lifetime obtained from time-correlated single photon counting, and M is the absorption transition dipole moment in Debye.

elsewhere.[63,64] Briefly, the pump beam was produced by the OPA-800C described above. The pump beams used in the present investigation were obtained from the fourth harmonic of signal and idler beams and were focused onto the sample cuvette. The probe beam was delayed with a computer controlled motion controller and then focused into a 2 mm sapphire plate to generate white light continuum. The white light was then overlapped with the pump beam in a 2 mm quartz cuvette containing the sample and the change in absorbance for the signal was collected by a CCD detector (Ocean optics). Data acquisition was controlled by the software from Ultrafast Systems Inc. A typical power of probe beam was less than 30 nJ, and the pump beam was around 50−400 nJ per pulse. For the present transient absorption measurements of G_1 to G_3, we have used the pump power of 250 nJ per pulse and the kinetics was found to be independent of pump-power for all the investigated dendrimers. Magic angle polarization was maintained between the pump and probe using a wave plate. The pulse duration was obtained by fitting the solvent response, which was ∼130 fs. The sample was stirred with a rotating magnetic stirrer and no photodegradation of the sample has been observed.

3. Results and Discussion

3.1. Linear Optical Properties. Optical absorption and emission properties of these all-thiophene dendrimers have been briefly discussed in an earlier publication.[51] For the sake of completeness and clarity, ground state absorption and fluorescence spectra of the increasing generation of dendrimers (G_0 to G_3) dissolved in THF are shown in Figure 1. The absorption of the smallest system (G_0) is around 270 and 310 nm and that of G_1 has a maximum around 378 nm, and it increases with an increase in dendrimer generation (Table 1). An interesting aspect to note here is that for the higher generations of dendrimers not only is there a red shift of the absorption maximum but also there is a broadening of the absorption spectrum to red wavelength regions.[51] This is ascribed to the fact that the higher generation of dendrimers consists of several linear α-oliogthiophene branching units whose absorption spectra shifts to longer wavelengths with increasing the chain length.[44] In a simpler arithmetic calculation of the number of α-oligothiophenes in each dendrimer yields following trend (G_0 (α-2T + α−T), G_1 (α -4T + α-3T + 2 α-T), G_2 (α-6T + α-5T + 2 α-3T + 4 α-T), G_3 (α-8T + α-7T + 2 α-5T + 4 α-3T + 8 α-T)). This is clearly manifested in the increase in extinction coefficients as well as the red shift and broadening of absorption spectra.

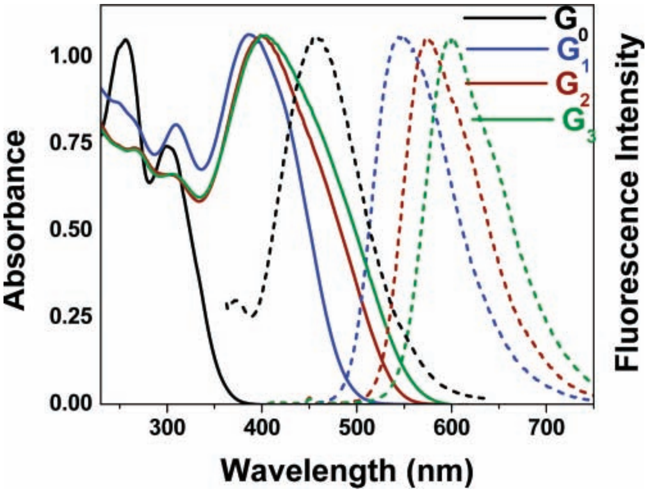


Figure 2. Optical absorption (solid lines) and fluorescence spectra (dashed) of different generation of thiophene dendrimers. It can be observed that both the optical absorption and emission spectra are red-shifted with an increase in dendrimer generation.

However, one finds a very interesting trend in the case of fluorescence spectra with increasing dendrimer generation. The emission spectra are shifted to longer wavelengths as the generation is increased (Figure 2 and Table 1), but there is no broadening of the emission spectra and the emission maximum has a good correlation with the highest linear oligothiophene branching unit in each dendrimer, such as α-4T for G_1 and α-8T for G_3.[44] It appears that the fluorescence comes from the longest chromophoric α-conjugated unit in a branched structure and is invariant to the excitation wavelength. This behavior indicates intramolecular excitation energy transfer from shorter chromophores to the longest chromophore, which then emits energy. From the optical absorption measurements, it was observed that the absorption spectrum is a linear combination of the absorption spectra of several linear α-oligothiophene units and different excitation wavelengths can excite preferentially different linear oligothiophenes which make the dendrimer. However, the fluorescence spectra of the dendrimers suggest a possibility of intramolecular excitation energy transfer to longest oligothiophene in respective dendrimer. Time-resolved measurements have been carried out to understand the actual mechanism of excitation (whether it is localized or delocalized) and to probe the phenomenon of intramolecular excitation energy transfer and are described below.

3.2. Two-Photon Absorption Properties. Having investigated the one-photon absorption measurements and found that the absorption can be a linear combination of several α-oligothiophene units, it is interesting to see how the nonlinear optical properties such as the TPA cross-section vary with dendrimer generation. To do this, TPA cross-section estimations have been carried out with the aid of a two-photon excited fluorescence (TPEF) method.[96] It has been shown in our previous investigation that when the thiophenes are arranged in a circular topology, excitation can be delocalized over an entire macrocycle and the TPA cross-section can be enhanced.[79] Shown in Figure 3A are the TPA excitation spectra for G_1 to G_3 dendrimer generations. For presentation the data from G_0 is not shown because it spans the wavelength region 550−640 nm and has very low TPA cross-section of less than 6 GM. Peak cross-section for the dendrimers increase from 6 to 700 GM for G_0 to G_3, respectively. To understand how the cross-section correlates with the chromophore density, the TPA cross-section per unit thiophene is calculated and plotted as a function of dendrimer generation in Figure 3B. It can be seen from figure that the TPA cross-section has enhanced with an increase in dendrimer generation and showed seemingly saturation like behavior at higher generation of dendrimers. If there was no super-linear increase in TPA cross-section with dendrimer generation, a straight line parallel to cross-section of one thiophene should have been observed (Figure 3B) for the plot of TPA cross-section per unit

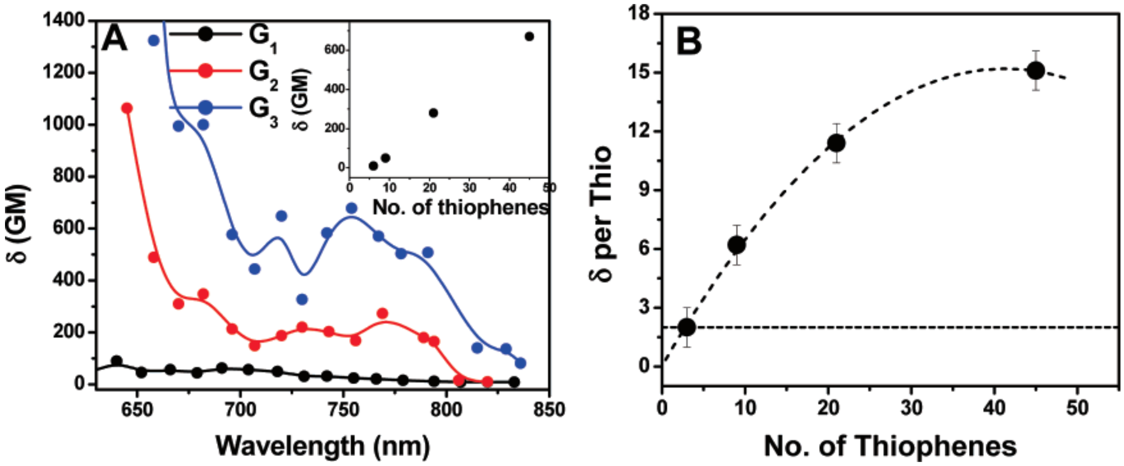


Figure 3. (A) Two-photon excitation spectra of the thiophenes of different dendrimer generations. The inset shows the plot of peak TPA cross-section versus thiophenes in each dendrimer. (B) Plot of TPA cross-section per unit thiophene with number of thiophenes in dendrimer.

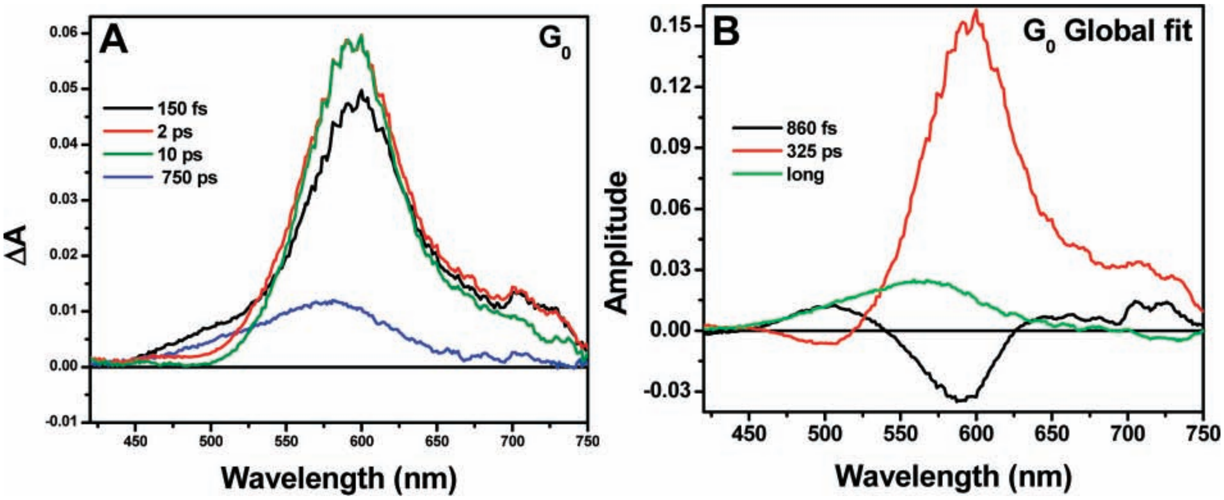


Figure 4. (A) Transient absorption spectra at different time delays for G_0 in THF after excitation at 330 nm. (B) Transient spectra of principle coefficients at different time constants obtained from single value decomposition and consequent global fit analysis.

thiophene versus dendrimer generation. However, the plot deviates and shows a super-linear behavior. This phenomenon is reminiscent of what has been observed in the case of cooperative enhancement of the TPA cross-section with an increase in branching in branched chromophores,[53,64] as well as an increase of cross-section in nitrogen centered dendrimers[24] and macrocyclic thiophenes.[79] Time-resolved spectroscopic techniques can probe the mechanism behind such enhancement in TPA cross-section, as has been proven in our earlier investigations.[62−64,79]

3.3. Excited State Dynamics of Oligothiophene Dendrimers. To understand the mechanism behind the enhanced TPA cross-sections with an increase in dendrimer generation as well as to explore the fundamental excitation and energy transfer processes in 3D oligothiophene dendrimers that have potential applications as light harvesting mimics and solar energy conversion devices, femtosecond transient absorption measurements have been carried out. Several investigations on dynamics of excited states of oligothiophenes and polythiophenes have been carried out in the literature by means of transient absorption and time-resolved fluorescence techniques.[80−95] Lanzani et al.[81] have measured the excited state dynamics of α-4T with and without substituents using femtosecond pump−probe spectroscopy. It has been shown that for the case of substituted 4T that there are two main components of the relaxation of the excited state other than the singlet state decay that have been explained by invoking a two-dimensional model consisting of vibrational or vibronic relaxation and torsional relaxation. A fast component of around 700 fs was observed for a decay of the excited state absorption (ESA) of α-4T and is ascribed to vibrational relaxation that is present in both unsubstituted and substituted α-4T whereas the torsional relaxation component of 4 ps is observed only in substituted α-4T, suggesting that it needs additional planarization.[81] Similar torsional relaxation has been observed in several oligothiophenes with different substituents.[80,82] Interestingly, torsional relaxation assisted excitation energy transfer has also been observed for the case of polythiophene (PDOPT) polymer by Sundstrom and co-workers.[93] It will be interesting to know how these ultrafast processes will change when the emission is localized on the longest oligothiophene in case of these thiophene dendrimers. To understand if the excitation is localized or delocalized, measurements have also been carried out after excitation at different wavelengths for the higher generation of dendrimers, which can excite different α-oligothiophene units preferentially.

Dynamics of Go. Transient measurements have been carried out for G_0 in THF after excitation at 330 nm with the fourth harmonic of signal beam from optical parametric amplifier. Transient absorption spectra at 150 fs, 2 ps, 60 ps, and 750 ps time delays for G_0 are shown in Figure 4A. It can be observed from figure that the transient absorption spectra at 150 fs (instantly after excitation) consisted of a weak shoulder at 500

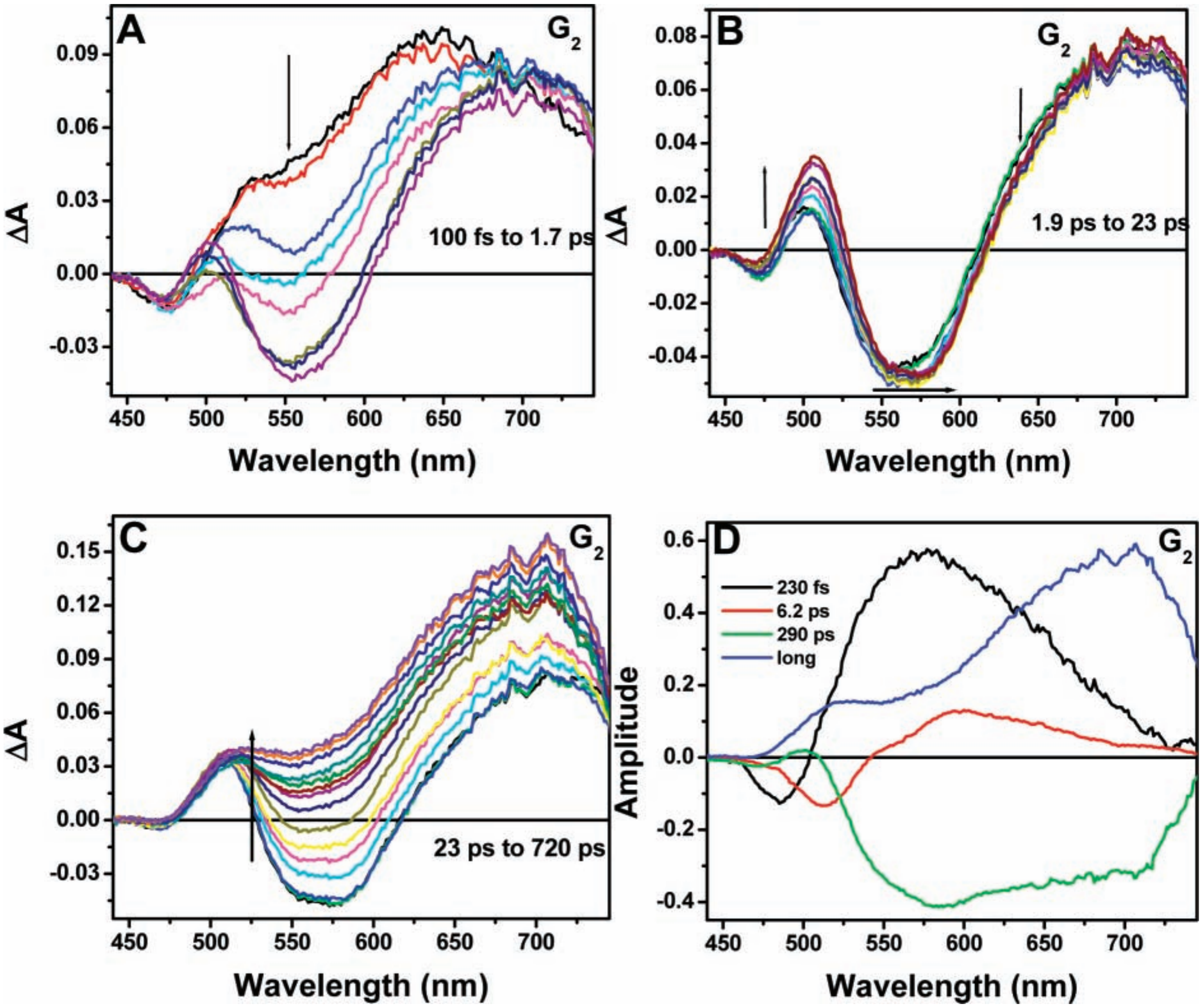


Figure 5. (A) Transient absorption spectra of G_2 in THF at different time delays from 100 fs to 1.7 ps depicting the intramolecular excitation energy transfer from the delocalized state to the longest oligothiophene present in the dendrimer, i.e., α-6T. (B) Transient absorption spectra of G_2 in THF at time delays from 1.9 to 23 ps showing the dynamic Stoke's shift in stimulated emission. (C) Transient absorption spectra of G_1 in THF from 23 to 720 ps showing the recovery of stimulated emission to give rise to triplet−triplet absorption. (D) Transient spectra of principle coefficients of G_1 in THF after single value decomposition and global fit analysis.

nm with a maximum at 600 nm. The excited state absorption (ESA) at 600 nm increased in amplitude at a time delay of 2 ps and the shoulder's amplitude at 500 nm decreased and one can observe a further decrease in amplitude of ESA at 10 ps. This ESA absorption with a maximum at 600 nm cam be ascribed to the singlet−singlet absorption, and it decays to give the transient absorption at 750 ps with ESA maximum of 580 nm, which is long-lived (triplet−triplet transition) (Figure 4B). Transient spectra of principle coefficients for different time constants obtained from single value decomposition and consequent global fit analsysis are shown in Figure 4. A close analysis of the figure reveals that the transient spectrum corresponding to 860 fs time constant shows decay in both sides of the maximum of ESA whereas growth is observed at the maximum wavelength region of 600 nm. This phenomenon resembles the narrowing of ESA with time, which can be ascribed to the well-investigated vibrational cooling of the molecule in the excited state. Thus, the 860 fs component has been attributed to vibrational cooling of the excited state of G_0. A similar time scale for vibrational relaxation has also been observed for other oligothiophenes.[80−83] Transient spectra of principle coefficients of the 320 ps component show the decay of singlet−singlet absorption and concurrent growth of triplet state absorption (long component spectrum) which suggest that the singlet state of G_0 decays to ground state mostly by intersystem crossing to give rise to the triplet state with a time constant of 320 ps.

Dynamics of Higher Generation of Dendrimers (G_1 to G_3). In addition to what has been observed for G_0, interesting additional excited state features and dynamics are observed for the case of higher generation dendrimers G_1 to G_3. It has been observed that the basic transient absorption features of dendrimers G_1 to G_3 are similar in a larger perspective though with different ESA maxima and stimulated emission as well as subtle differences in their dynamics. To avoid recurrence, detailed excited state dynamics and transient absorption features of one of the dendrimer G_2 are discussed here along with comparison of the dynamics with other dendrimers (for complete transient absorption features of G_1 and G_3, see the Supporting Information). Figure 5A shows the transient absorption spectra at initial time delays from 100 fs to1.7 ps for G_2 in THF after excitation at 425 nm (pump photon energy of 2.92 eV) with a pump power of 250 nJ per pulse. It can be observed from the figure that at 100 fs (immediately after photoexcitation) the transient absorption spectrum consists of bleach with a maximum around 480 nm and ESA with a maximum around 640 nm and a shoulder at 540 nm. The bleach at 480 nm is due to the depletion of the ground state, and the ESA with a maximum at 640 and 540 nm is ascribed to the singlet−singlet absorption of the Franck−Condon (FC) state of G_2, where the excitation is probably delocalized through a larger part of thiophenes in the dendrimer. Presumption of delocalized excited state came from the similar ESA spectra of FC state of G_2 even though the excitation wavelength is changed from a very blue wavelength of 360 nm to the furthest red side of the absorption spectrum at 425 nm (Supporting Information). This observation suggests that the absorption spectrum is completely delocalized and what we are observing instantly after photoexcitation is the delocalized excited state. These results are also further supported by faster fluorescence anisotropy with an increase in dendrimer generation in fluorescence upconversion measurements, which will be published elsewhere.[97]

However, this ESA of the delocalized state decays very fast and concurrent negative signal with a maximum around 560 nm starts to grow at the same time scale (Figure 5A). This negative signal is ascribed to that of the stimulated emission arising out of the longer oligothiophene present in the G_2, i.e., is of α-conjugated 6T. Mechanistically similar features are also observed for G_1 and G_3 immediately after photoexcitation, which proceeded to give the stimulated emission from the longest thiophene in their respective dendrimer in similar time scales. The time scale for the growth of the bleach is around 250 fs for G_2, which has been ascribed to ultrafast excitation energy transfer from the collective excitation of thiophenes in the dendrimer to the lowest energy absorbing α-6T. Interesting supplementary features are observed at intermediate time delays of 1 to 10 ps, which are shown in Figure 5B.

A dynamic Stoke's shift in the stimulated emission is observed in Figure 5B as the time delay is changed to 1.9−23 ps, which can be explained by invoking the phenomenon of torsional energy redistribution or relaxation in the longest branch of the oligothiophene. Torsional relaxation is associated with the slow rotation of the C−C single bond connecting two thiophene units of the longest oligothiophene, which lowers the energy of excited state and in the process tends to assist in planarizing the emitting state.[80] Since the ground state is in a twisted configuration because of heavy substitution at β-sites for the present dendrimers, there is a need for the planarization of the final emitting state wherein the emission is localized in the longest oliogothiophene branch. This phenomenon is similar to the torsional relaxation of the excited state of highly substituted α-4T and hexamethylsexithiophene, which planarizes it.[81] However, the final emitting state decays (the stimulated emission recovers) as shown in the transient absorption spectra at time delays from 23 to 720 ps. Because there is an overlap of other excited state absorption that arose due to the triplet−triplet absorption in the same wavelength region as of stimulated emission, it tends to recover faster than its actual singlet state lifetime. The stimulated emission recovery time of 290 ps is faster than the singlet state lifetime of 500 ps observed from time-correlated single photon counting (Table 1). Transient spectra of principle coefficients for different time constants obtained from global fit analysis are shown in Figure 5D and this sums up the complete excited state dynamics of G_2. The faster time constant of 250 fs is ascribed to ultrafast energy transfer from the delocalized excited state of the dendrimer to give the emission from the longest oligothiophene present in the dendrimer system followed by a torsional relaxation with a time constant of 6.2 ps and the intersystem crossing to give triplet state with a time constant of 290 ps. Further, excitation wavelength-dependent excited state dynamics measurements have been carried out for all the dendrimers and it has been shown that the ESA features for a given dendrimer are quite similar and did not vary with excitation wavelength. Corresponding excited state decay time constants for all dendrimers at different excitation wavelengths are summarized in Table 2, and they did not differ much. These results suggest that the excitation is delocalized all over the chromophore and there is no preferential excitation of certain parts of oligothiophenes in dendrimers. Also, the ESA of FC state of each dendrimer differs from each other, suggesting different excitation delocalization lengths for each dendrimer, and they are much larger than the small subunits. This phenomenon of excitation delocalization as a function of dendrimer generation has also been confirmed by femtosecond fluorescence anisotropy decay measurements which will be published elsewhere.[97]

TABLE 2: Excitation Wavelength-Dependent Lifetimes of the Dendrimers

sample	360 nm	380 nm	425 nm
G_0	τ_1 = 860 fs, τ_2 = ----, τ_3 = 330 ps, long		
G_1	τ_1 = 250 fs, τ_2 = 3.5 ps, τ_3 = 560 ps, long	τ_1 = 260 fs, τ_2 = 3.5, ps τ_3 = 480 ps, long	τ_1 = 220 fs, τ_2 = 2.5 ps, τ_3 = 330 ps, long
G_2	τ_1 = 230 fs, τ_2 = 4.5 ps, τ_3 = 410 ps, long	τ_1 = 250 fs, τ_2 = 4.9 ps, τ_3 = 280 ps, long	τ_1 = 230 fs, τ_2 = 6.2 ps, τ_3 = 290 ps, long
G_3	τ_1 = 280 fs, τ_2 = 10.7 ps, τ_3 = 410 ps, long	τ_1 = 290 fs, τ_2 = 9.1 ps, τ_3 = 350 ps, long	τ_1 = 300 fs, τ_2 = 12.2 fs, τ_3 = 420 ps, long

Generation Dependence of Excited State Dynamics. As stated earlier, the excited state dynamics obtained from transient absorption for G_1 to G_3 are quite similar and a comparison of the observed time constants provides their generation dependence. Photoexcitation of the dendrimers yielded two fast decay components (one in the range 200−300 fs and another from 2 to 12 ps) apart from singlet state decay (Table 2). Faster decay in all the dendrimers is associated with a growth and shift of stimulated emission to longer wavelengths to give the emission from the longest oligothiophene present in the dendrimer and hence has been ascribed to ultrafast energy transfer from the delocalized excited state of the dendrimer. However, it can be argued that this time scale is closer to the vibrational relaxation time (600−800 fs) that has been observed for linear oligothiophenes.[80−82] But the time scales observed for the dendrimers are way faster than what has been observed for vibrational cooling of oligothiophenes. If vibrational cooling is the reason for fast decay, the time scale for higher dendrimers should have been much higher than that of the time scale observed for smaller linear oligothiophenes. Thus, we attribute this time constant to the ultrafast excitation energy transfer funneling the energy to the lowest energy state, a phenomenon that has been observed in phenylacetylene cored dendrimers.[98] A similar time scale for excitation energy transfer has also been observed for polythiophenes in solution and in thin films by Sundstrom and coworkers.[93] Comparative kinetic decay traces with an increase in dendrimer generations suggest that there is a small increase in the fast time constant for higher generation dendrimer G_3 when compared to G_1 (Figure 6A, Table 2). This can be ascribed to the fact that the Forster's overlap to the lowest energy absorbing oligothiophene tends to decrease with an increase in dendrimer generation, thereby slowing down the rate of excitation energy transfer though marginally.

Similar to what has been observed above, the picosecond time scale component also increases with an increase in dendrimer generation. The time scale for G_1 is around 2.3 ps, and it increases to around 12 ps for G_3 at the excitation wavelength of 425 nm (Figure 6B, Table 2). As explained earlier in this

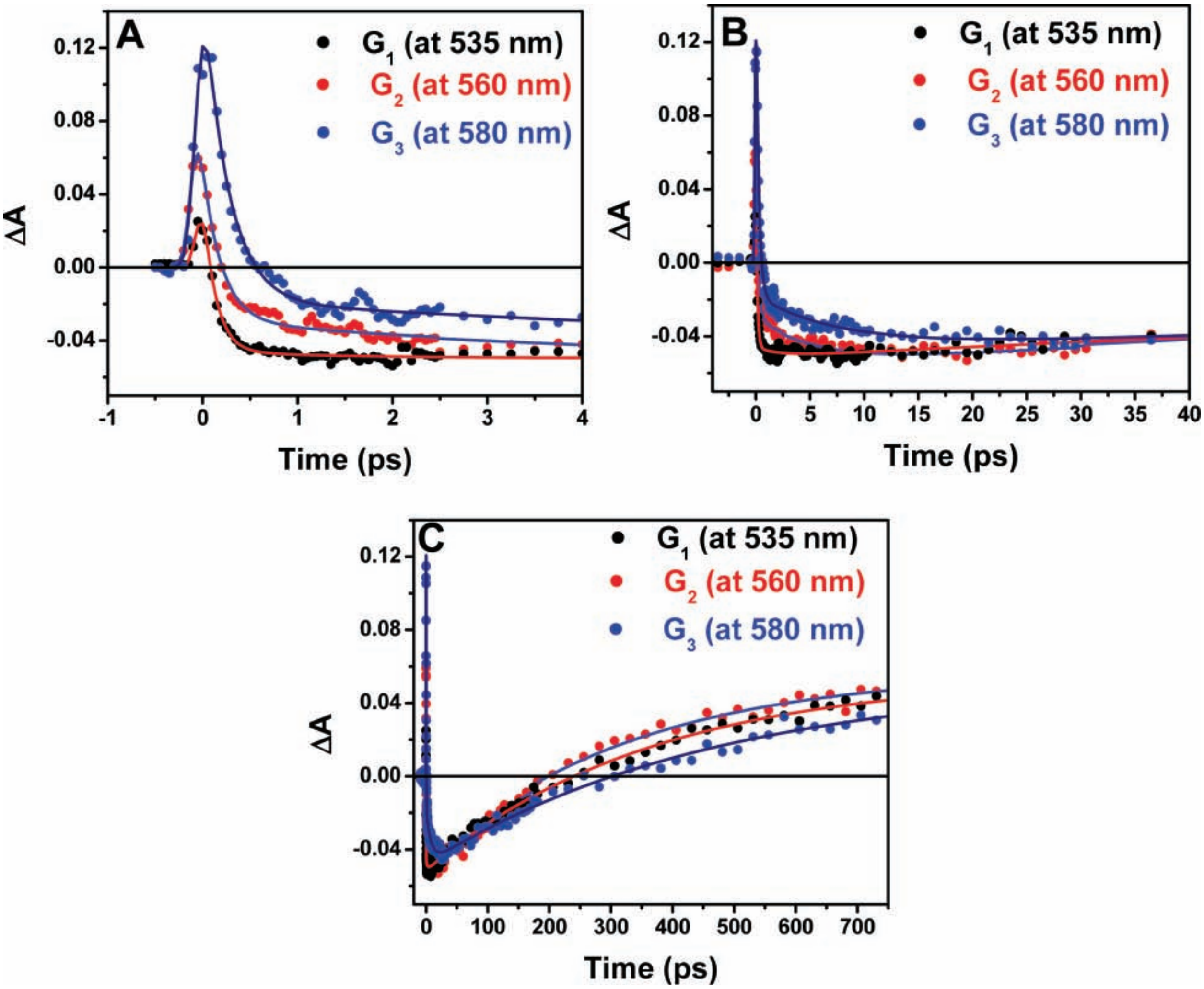
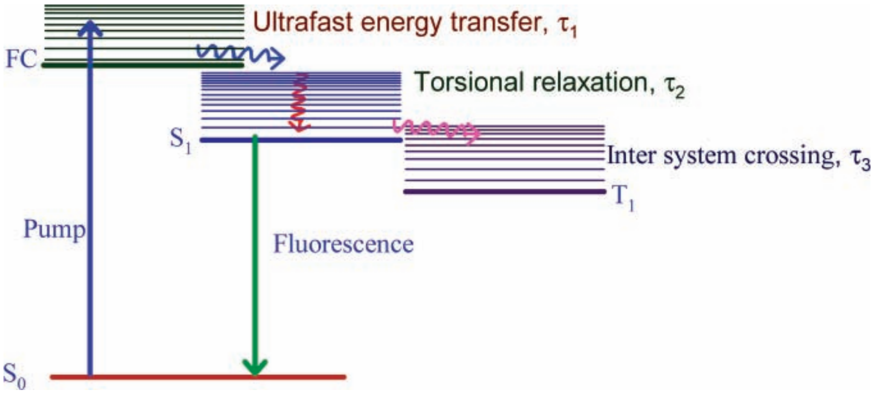


Figure 6. (A) Kinetic decay traces of growth of stimulated emission in all dendrimers in short time window depicting the phenomenon of excitation energy transfer. (B) Kinetic decay traces of growth of stimulated emission in all dendrimers in the intermediate time scale depicting the picosecond scale torsional relaxation assisted excitation energy transfer. (C) Kinetic decay traces of growth of stimulated emission in all dendrimers in longer time scales showing the process of stimulated emission recovery to give triplet−triplet absorption with intersystem crossing.

SCHEME 1: Mechanism of Excited State Deactivation of Higher Generation Thiophene Dendrimers



paper, this component has been ascribed to that of the slow torsional energy redistribution assisted with the planarization of the longest oligothiophene (which emits) present in each dendrimer. Because the emitting oligothiophene increases in chain length with increase in size of dendrimer, it can be suggested that it takes longer torsional relaxation time for the planarization of the emitting state. However, Lanzani et al.[81] have not observed any dependence of torsional relaxation time on the chain length of oligothiophene pn 4T and 6T. This suggests that in higher generation dendrimers, there may be an additional involvement of slow excitation energy transfer or slow energy trapping that is also accompanying the torsional energy redistribution, thereby increasing the time scale of the picosecond component with an increase in dendrimer generation. Similar torsional relaxation assisted excitation energy transfer has been observed for the case of PDOPT polythiophene from ultrafast transient absorption anisotropy measurements.[93]

The longer time scale kinetic traces show that the stimulated emission recovers with a time scale of 300−500 ps at an excitation wavelength of 425 nm (Table 2, Figure 6C). It can be observed from the figure that in all the cases the presence of a long-lived transient is observed, which has an overlapping absorption in the stimulated emission region. This transient has already been ascribed to the long-lived triplet−triplet absorption. Because there is additional overlapping triplet−triplet absorption at the same wavelength as that of stimulated emission, the recovery kinetics of stimulated emission became faster than the actual singlet state lifetime observed in the time-correlated single photon counting technique (long time decay constant in Table 2 with respect to τ_f of Table 1). Overall, the excited state deactivation of the thiophene dendrimers can be summarized in Scheme 1.

Photoexcitation takes the population vertically to the FC state, which is a delocalized excited state from where ultrafast intramolecular excitation energy transfer to the lowest energy absorbing longest oligothiophene takes place. In addition, the emitting oligothiophene reaches the bottom of the potential energy surface by torsional energy redistribution, which tends to planarize the emitting state on the picosecond time scale. Finally, the excited state decays to give via intersystem crossing to the triplet state (Scheme 1). In the present case of dendrimers, the excited state dynamics differs with linear oligothiophenes by the presence of a delocalized excited state, ultrafast energy transfer, and the supplementary torsional relaxation, which are not present in the case of unsubstituted linear oligothiophenes. Delocalization of the excited states through a larger part of the dendrimer explains the higher absorption transition dipole (*M*, Table 1) moment with an increase in dendrimer generation and thereby observed enhanced TPA cross-sections. The presence of delocalized excited states are also very important for applications such as efficient light harvesting devices because it increases their ability to harvest light much more effectively.

4. Conclusions

All oligothiophene dendrimers have been investigated for their application in solar energy harvesting and nonlinear optical devices. We have investigated the coupling between the thiophenes within the dendrimer where energy could migrate between the chromophores. Femtosecond transient absorption measurements have shown the excited state delocalization spanning the large part of dendrimer and ultrafast energy transfer to the longest oligothiophene in each dendrimer unit, which enables them to serve as efficient light harvesting antennae for solar cell devices. A super-linear increase in TPA cross-section has also been observed with an increase in dendrimer generation, which is again ascribed to a greater degree of excitation delocalization with dendrimer generation, making them suitable as good building blocks for larger TPA materials. Additional torsional energy redistribution assisted energy trapping in the final emitting state, which tends to planarize the emitting state has also been observed in higher generation dendrimers with the aid of a dynamic Stokes's shift observed in the picosecond time scale from transient absorption measurements.

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Supporting Information Available: Complete details of transient absorption spectra of all the thiophene dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Halls, J. J. M.; Friend, R. H. In *Clean Electricity from Photovoltaics*; Archer, M. D., Hill, R., Eds.; Series on Photoconversion of Energy; Imperial College Press: River Edge, NJ, 2001; Vol. 1, p 377.

(2) (a) Padinger, F.; Rittberger, R. S.; Sacriftci, N. S. *Adv. Funct. Mater.* **2003**, *13*, 85. (b) Jinag, D.-L.; Aida, T. *Nature* **1997**, *388*, 454.

(3) Morisue, M.; Yamatsu, S.; Haruta, N.; Kobuke, Y. *Chem. Eur. J.* **2005**, *11*, 5563.

(4) Forrest, S. R. *Nature* **2004**, *428*, 911.

(5) Kopleman, R.; Shortreed, M.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Moore, J. S.; Bar-Haim, A.; Klafter, J. *Phys. Rev. Lett.* **1997**, *78*, 1239.

(6) (a) Bari-Haim, A.; Klafter, J.; Kopleman, R. *J. Am. Chem. Soc.* **1997**, *119*, 6197. (b) Bar-Haim, A.; Klafter, J. *J. Phys. Chem. B* **1998**, *102*, 1662.

(7) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402.

(8) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635.

(9) (a) Adronov, A.; Frechet, J. M. *J. Chem. Soc., Chem. Commun.* **2000**, *18*, 1701. (b) Kawa, M.; Frechet, J. M. J. *Chem. Mater.* **1998**, *10*, 286.

(10) Gilat, S. L.; Adronov, A.; Frechet, J. M. J. *Angew. Chem. Int. Ed.* **1999**, *38*, 1422.

(11) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449.

(12) Wang, P. W.; Liu, Y. J.; Deavadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237.

(13) Glebler, C.; Antoniadis, H.; Bradley, D. D. C.; Shirota, Y. *Appl. Phys. Lett.* **1998**, *72*, 2448.

(14) Halim, M.; Samuel, I. D. W.; D.; Pilow, J. N. D.; Monkman, A. P.; Burn, P. L. *Synth. Met.* **1999**, *102*, 1571.

(15) Markham, J. P. J.; Lo, S.-C.; Magennis, S. W.; Burn, P. L.; Samuel, I. D. W. *Appl. Phys. Lett.* **2002**, *80*, 2645.

(16) Goodson, T., III. *Ann. Rev. Phys. Chem.* **2005**, *56*, 581.

(17) Goodson, T., III. *Acc. Chem. Res.* **2005**, *38*, 99−107.

(18) Chuang, S.-J.; Liu, T.-C.; Kim, K. S.; He, G. S.; Swiatkiewicz, J.; et al. *Chem. Mater.* **2001**, *13*, 4071.

(19) Varnavski, O.; Leanov, A.; Lih, L.; Takacks, J.; Goodson, T., III. *J. Phys. Chem. B* **2000**, *104*, 179.

(20) Varnavski, O.; Samuel, I. D. W.; Palsson, L.-O.; Beavington, R.; Burn, P. L.; Goodson, T., III. *J. Chem. Phys.* **2002**, *116*, 8893.

(21) (a) Varnavaski, O. P.; Ostrowski, J. C.; Sukhmolinova, L.; Tweig, R. J.; Bazan, G. C.; Goodson, T., III. *J. Am. Chem. Soc.* **2002**, *124*, 1736. (b) Ranasinghe, M. I.; Varnavaski, O. P.; Pawlas, J.; Hauck, S. I.; Lowie, J.; et al. *J. Am. Chem. Soc.* **2002**, *124*, 6520.

(22) Dorbizhev, M.; Karotki, A.; Dzenis, Y.; Rebane, A.; Suo, Z.; Spangler, C. W. *J. Phys. Chem. B* **2003**, *107*, 7540.

(23) Poliakov, E. Y.; Chernyak, Y.; Treitak, S.; Mukamel, S. *J. Chem. Phys.* **1999**, *110*, 8161.

(24) Varnavski, O.; Yan, X.; Mongin, O.; Blanchard-Desce, M.; Goodson, T., III. *J. Phys. Chem. C* **2007**, *111*, 149.

(25) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93.

(26) Bauerle, P. In *Electronic materials: The oligomer approach*; Mullen, K., Wegner, G., Eds.; Wiley-VCH: New York, 1998.

(27) *Handbook of Ologo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999.

(28) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(29) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571.

(30) Braun, D.; Gustaffson, G.; McBranch, D.; Heeger, A. J. *J. Appl. Phys.* **1992**, *72*, 564.

(31) Mitschke, V.; Bauerle, P. *J. Chem. Soc., Perkin Trans.* **2001**, 740.

(32) Vatterlin, C.; Neureiter, H.; Gebauer, W.; Ziegler, B.; Sokolowski, M.; Bauerle, P.; Umbach, E. *J. Appl. Phys.* **1997**, *82*, 3003.

(33) Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *270*, 26.

(34) Katz, H. E.; Bao, N.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359.

(35) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.

(36) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

(37) Granstrom, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257.

(38) Brabec, C. J.; Sacrittel, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 85.

(39) (a) Noma, N.; Tsuzuki, T.; Shirota, Y. *Adv. Mater.* **1995**, *7*, 647. (b) Kopidakis, N.; Mitchell, W. J.; van de Legemaat, J.; Ginley, D. S.; Rumbles, G.; Shaheen, S. E.; Rance, W. L. *Appl. Phys. Lett.* **2006**, *89*, 103524.

(40) Reyes-Reyes, M.; Kim, K.; Caroll, D. J. *Appl. Phys. Lett.* **2005**, *87*, 083506.

(41) Kromer, J.; Rios-Carreras, I.; Fuhrmann, G.; Musch, C.; Wunderlin, M.; Debaerdemaeker, T.; Mena-Osteritz, E.; Bauerle, P. *Angew. Chem. Int. Ed.* **2000**, *39*, 3481.

(42) Mena-Osteritz, E.; Bauerle, P. *Adv.Mater.* **2001**, *13*, 243.

(43) Fuhrmann, G.; Bauerle, P. *Chem. Commun.* **2003**, 926.

(44) Bauerle, P.; Fishcer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 303.

(45) Nicolas, Y.; Blanchard, P.; Levillain, E.; Allain, M.; Mercier, N.; Roncali, J. *Org. Lett.* **2004**, *6*, 6433.

(46) Mitchell, W. I.; Kopidakis, N.; Rumbles, G.; Ginley, D. S.; Shaheen, S. E. *J. Mater. Chem.* **2005**, *15*, 4518.

(47) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C. *Org. Lett.* **2002**, *4*, 2067.

(48) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C.; Gies, A.; Nonidez, W. *J. Am. Chem. Soc.* **2004**, *126*, 8735.

(49) Locklin, J.; Patton, D.; Deng, S.; Baba, A.; Millan, M.; Advincula, R. C. *Chem. Mater.* **2004**, *16*, 5187.

(50) Deng, S.; Locklin, J.; Patton, D.; Baba, A.; Advincula, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 1744.

(51) Ma, C.-Q.; Mena-Osteritz, E.; Debaerdemaeker, T.; Wienk, M. M.; Janssen, R. A. J.; Bauerle, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 1679.

(52) Albota, M.; Beljonne, D.; Bredas, J.-L.; Ehrlich, J. E.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653.

(53) Chung, S.-J.; Kim, K.-S.; Lin, T.-C.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem. B* **1999**, *103*, 10741.

(54) Beljonne, D.; Wenseleers, W.; Zojer, E.; Shuai, Z.; Vogel, H.; Pond, S. J. K.; Perry, J. W.; Marder, S. R.; Bredas, J.-L. *Adv. Funct. Mater.* **2002**, *12*, 631.

(55) Kogej, T.; Beljonne, D.; Meyers, F.; Perry, J. W.; Marder, S. R.; Bredas, J. L. *Chem. Phys. Lett*. **1998**, *298*, 1.

(56) Lee, H. J.; Sohn, J.; Hwang, J.; Park, S. Y.; Choi, H.; Cha, M. *Chem. Mater.* **2004**, *16*, 456.

(57) Katan, C.; Terenziani, F.; Mongin, O.; Werts, M. H. V.; Porrés, L.; Pons, T.; Mertz, J.; Tretiak, S.; Blanchard-Desce, M. *J. Phys. Chem. A* **2005**, *109*, 3024.

(58) Lahankar, A. S.; West, R.; Varnavski, O.; Xie, X.; Goodson, T., III; Sukhomlinova, L.; Twieg, R. *J. Chem. Phys.* **2004**, *120*, 337.

(59) Wang, Y.; Ranasinghe, M. I.; Goodson, T., III. *J. Am. Chem. Soc.* **2003**, *125*, 9562.

(60) Varnavski, O.; Goodson, T., III; Sukhomlinova, L.; Twieg, R. *J. Phys. Chem. B* **2004**, *108*, 10484.

(61) Wang, Y.; He, G. S.; Prasad, P. N.; Goodson, T., III. *J. Am. Chem. Soc.* **2005**, *127*, 10128.

(62) Ramakrishna, G.; Goodson, T., III. *J. Phys. Chem. A* **2007**, *111*, 993.

(63) Ramakrishna, G.; Bhaskar, A.; Goodson, T., III. *J. Phys. Chem. B* **2006**, *110*, 20872.

(64) Bhaskar, A.; Ramakrishna, G.; Lu, Z.; Twieg, R.; Hales, J. M.; Haga, D. J.; Van Stryland, E.; Goodson, T., III. *J. Am. Chem. Soc.* **2006**, *128*, 11840.

(65) Zhou, W.; Kuebler, S. M.; Braun, K. L.; Yu, T.; Cammack, J. K.; Ober, C. K.; Perry, J. W.; Marder, S. R. *Science* **2002**, *296*, 1106.

(66) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X. L.; Marder, S. R.; Perry, J. W. *Nature (London*) **1999**, *398*, 51.

(67) Kawata, S.; Sun, H.-B.; Tanaka, T.; Takada, K. *Nature (London*) **2001**, *412*, 697.

(68) Maruo, S.; Nakamura, O.; Kawata, S. *Opt. Lett.* **1997**, *22*, 132.

(69) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73.

(70) Bhawalkar, J. D.; Kumar, N. D.; Zhao, C. F.; Prasad, P. N. *J. Clin. Laser Med. Surg.* **1997**, *15*, 201.

(71) He, G. S.; Markowicz, P. P.; Line, P.-C.; Prasad, P. N. *Nature* **1999**, *415*, 767.

(72) Xu, C.; Zipfel, W.; Shear, J. B.; Williams, R. M.; Webb, W. W. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 10763.

(73) Larson, D. R.; Zipfel, W. R.; Williams, R. M.; Clark, S. W.; Bruchez, M. P.; Wise, F. W.; Webb, W. W. *Science* **2003**, *300*, 1434.

(74) He, G. S.; Xu, G. C.; Prasad, P. N.; Reinhardt, B. A.; Bhatt, J. C.; McKellar, R.; Dillard, A. G. *Opt. Lett.* **1995**, *20*, 435.

(75) Ehrlich, J. E.; Wu, X. L.; Lee, I.-Y. S.; Hu, Z.-Y.; Röckel, H.; Marder, S. R.; Perry, J. W. *Opt. Lett.* **1997**, *22*, 1843.

(76) Bhaskar, A.; Ramakrishna, G.; Twieg, R.; Goodson, T., III. *J. Phys. Chem. B* **2007** (submitted).

(77) Zhao, M.-T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535.

(78) Marder, S. R.; Kippelen, B.; Jen, A. K.; Peyghambarian, N. *Nature* **1997**, *388*, 845.

(79) Bhaskar, A.; Ramakrishna, G.; Hagedorn, K.; Varnavski, O.; Mena-Osteritz, E.; Bauerle, P.; Goodson, T., III. *J. Phys. Chem. B* **2007**, *111*, 946.

(80) (a) Lanzani, G.; Nisoli, M.; De Silvestri, S.; Tubino, R. *Synth. Met.* **1996**, *76*, 39. (b) Lanzani, G.; Nisoli, M.; De Silvestri, S.; Barbarella, G.; Zambianchi, M.; Tubino, R. *Phys. Rev. B.* **1996**, *53*, 4453. (c) Lanzani, G.; Nisoli, M.; Magni, V.; De Silvestri, S.; Barbarella, G.; Zambianchi, M.; Tubino, R. *Phys. Rev. B* **1995**, *51*, 13770.

(81) Lanzani, G.; Nisoli, M.; De Silvestri, S.; Tubino, R. *Chem. Phys. Lett.* **1996**, *251*, 339.

(82) Lanzani, G.; Cerullo, G.; Stagoara, S.; De Silvestri, S. *J. Photochem. Photobiol. A* **2001**, *144*, 13.

(83) van Hal, P. A.; Janssen, R. A. J.; Lanzani, G.; Cerullo, G.; Zaveleni-Rossi, M.; De Silvestri, S. *Chem. Phys. Lett.* **2001**, *345*, 33.

(84) Cerullo, G.; Lanzani, G.; Muccini, M.; Taliani, C.; De Silvestri, S. *Synth. Met.* **1999**, *101*, 614.

(85) Grebner, D.; Helbig, M.; Rentsch, S. *J. Phys. Chem.* **1995**, *99*, 16991.

(86) Paa, W.; Yang, J.-P.; Rentsch, S. *Appl. Phys. B.* **2000**, *71*, 443.

(87) Yang, J.-P.; Paa, W.; Rentsch, S. *Synth. Met.* **1999**, *101*, 624.

(88) Paa, W.; Yang, J.-P.; Rentsch, S. *Synth. Met.* **2001**, *119*, 525.

(89) Kodara, T.; Watanabe, A.; Ito, O.; Watanabe, M.; Saito, H.; Koishi, M. *J. Phys. Chem.* **1996**, *100*, 15309.

(90) Frolov, S. V.; Kloe, Ch.; Berg, S.; Thomas, G. A.; Batlogg, B.; Tubino, R. *Phys. Rev. B* **1996**, *53*, 4453.

(91) Klein, G. *Chem. Phys. Lett.* **2000**, *320*, 65.

(92) Grage, M. M.-L.; Zaushitsyun, Y.; Yartsev, A.; Chachivilis, M.; Sundstrom, V.; Pullerits, T. *Phys. Rev. B* **2003**, *67*, 205207.

(93) (a) Westenhoff, S.; Beenkem, W. J. D.; Friend, R. H.; Greenham, N. C.; Yartsev, A.; Sundstrom, V. *Phys. Rev. Lett.* **2006**, *97*, 166804. (b) Westenhoff, S.; Daniel, C.; Friend, R. H.; Silva, C.; Sundstrom, V.; Yartsev, A. *J. Chem. Phys.* **2005**, *122*, 094903.

(94) Cheng, X.; Ichimura, K.; Fichou, P.; Kobayashi, T. *Chem. Phys. Lett.* **1991**, *185*, 286.

(95) Yang, A.; Kuroda, M.; Shiraishi, Y.; Kobayashi, T. *J. Phys. Chem. B* **1998**, *102*, 3706.

(96) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481.

(97) Ramakrishna, G.; Baurle, P.; Goodson, T., III. To be published.

(98) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.