

Time-Resolved Fluorescence Investigation of Energy Transfer in Compact Phenylacetylene Dendrimers[†]

Mahinda I. Ranasinghe,[‡] Michael W. Hager,[§] Christopher B. Gorman,[§] and Theodore Goodson III^{*,‡}

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, and
Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695

Received: September 26, 2003; In Final Form: April 12, 2004

Excitation energy transfer dynamics in light-harvesting dendritic macromolecules has generated a great deal of interest due to the fact that such systems can be used in photovoltaic and light-emitting devices. Studies on phenylacetylene-based dendrimers played a key role in stimulating this interest and extensive theoretical as well as experimental investigations have been carried out to get a better insight into the phenomena behind the excitation energy transfer dynamics of these dendrimers. In this manuscript, time-resolved femtosecond fluorescence and fluorescence anisotropy dynamics as well as temperature dependent steady state spectral studies of a second generation homogeneous (compact) phenylacetylene dendrimer are reported. The low-temperature fluorescence spectrum of the dendrimer showed two distinctive emission peaks that can be related to the existence of two closely spaced electronic states of the chromophore. Time-resolved fluorescence results suggest delocalization of the excitation energy in the excited state. The ultrafast fluorescence anisotropy decay dynamics further supports the existence of a delocalized state.

I. Introduction

Organic dendrimers have been considered as potential candidates for use in artificial light-harvesting systems, nonlinear optical devices, and light-emitting devices as well as medicinal applications.^{1–5} There are several key studies that have been carried out to understand the mechanism of optical excitations and excitation energy transfer in several types of organic dendrimers with conjugated units.^{1,2,6,7} A fundamental advantage of dendrimers over its linear (monomer) counterparts stems from the possibility that a number of chromophores may be held together in an ordered and confined geometry⁸ giving a very high density of transition dipoles for optical excitation. Similarly, this type of three-dimensional arrangement of chromophores may lead to the arrangement of transition dipoles in a regular geometrical orientation and this may ultimately lead to an enhanced transition dipole moment and new optical properties³ of the branching macromolecules with respect to its monomeric chromophore (basic building block). Phenylacetylene dendrimers have been synthesized for the purpose of light-harvesting antenna applications.^{9a} Energy transfer dynamics in compact dendrimers has been investigated utilizing time correlated single-photon counting measurements. The compact dendrimer showed fluorescence decay dynamics that can be fitted with a single exponential decay function with a decay time of approximately 3 ns.^{9b} For the case of the phenylacetylene dendrimers, first prepared by Moore et al., the conjugation among chromophores is broken at the branching center by virtue of the meta substitution.¹⁰ Therefore, the interactions among chromophores may be described as purely Coulombic through dipole–dipole interactions.¹⁰ The strength of interactions among chromophores

is mainly determined by the electronic properties of the branching center in a dendrimer.¹¹

To get a better understanding of the phenomenon behind the light-harvesting properties of these phenylacetylene dendrimers, they have been subjected to both theoretical and experimental investigations,^{2,10,12,13} as well as nonlinear optical investigations.¹⁴ Initial studies by Kopelman, Moore, and co-workers^{2a} using steady-state absorption spectra showed that in the homogeneous phenylacetylene dendrimer the optical excitation is localized. This localization is evident from the nonreduction of energy of the dendrimer with the increasing generation. Mukamel's^{10b} initial calculation using the collective electronic oscillator method determined that the excitation is localized within the basic units. The latter studies by Mukamel and co-workers¹⁰ focused on constructing the Frenkel Exciton Hamiltonian using collective electronic oscillator approach to theoretically predict the optical response as well as energy transfer and funneling in these phenylacetylene dendrimer systems. In their investigations they found that the calculated absorption spectrum is comparable with the experimental absorption spectrum suggesting that localized one-exciton states dominate the spectrum. Those states are found to occupy the periphery of the molecule. In these calculations, weak exciton–phonon (low-temperature limit) coupling was considered, and it was shown that the delocalized states can give rise to weaker absorption peaks. It was found that although the electron–hole pair can be localized on various chromophores the excitation energy of excitons can be delocalized due to Coulombic interactions between optically induced charge redistribution on different segments. In another report, Reineker and co-workers¹⁵ found that the lowest absorption peak of a homogeneous phenylacetylene dendrimer is gradually red-shifted with increasing dendrimer generation. This study again confirmed that the steady state absorption of phenylacetylene dendrimer is dominated by the peripheral chromophores and energetically lowest

* Corresponding author. E-mail: tgoodson@chem.wayne.edu.

[†] Part of the special issue "Alvin L. Kwiram Festschrift".

[‡] Wayne State University.

[§] North Carolina State University.

and highest absorption peaks originate from contributions from all the chromophores.¹⁵ Also, Melinger and co-workers^{12a} have carried out a femtosecond degenerate pump–probe spectral investigation and revealed that stepwise energy transfer from outer dendrons to the energy trap takes place in extended phenylacetylene dendrimer (inhomogeneous) and such an energy transfer is discussed in terms of a Forster model.^{12a}

The theoretical and steady-state optical experimental studies on compact phenylacetylene dendrimers have led to the conclusion that the optical excitation is confined to the basic building block irrespective of the dendrimer generation, and an outward flow of energy may take place which is disadvantageous for light-harvesting purposes.^{2,12} However, the investigations on the phenylacetylene-based extended dendrimer have shown that it can funnel optical excitation energy into a core molecule efficiently.^{2,12,13} The stepwise energy transfer mechanism^{12a} as well as direct energy transfer to the core^{13a} was found to play a significant role in the energy transfer dynamics of the extended dendrimer. Although several theoretical¹⁰ and steady-state optical studies as well as femtosecond pump–probe investigations^{2,12,13} on extended homogeneous PA dendrimer have been reported, no femtosecond time-resolved fluorescence studies have been reported for either compact or extended PA dendrimers. Time-resolved fluorescence and fluorescence anisotropy decay measurements are important in gaining insight in to the energy transfer dynamics of these homogeneous compact dendrimers. Recent investigations^{6,7,16,19–22} have shown that the fluorescence anisotropy decay dynamics and hence depolarization rates can be utilized to understand the energy transfer dynamics in this type of branched macromolecular architecture. Studies on various dendritic systems with different branching centers have provided a better insight into the role of the branching center. For example, it has been found that for a nitrogen branching system,^{6,7} strong electronic coupling leads to very strong interchromophoric interactions and fast anisotropy decay dynamics. Such strong interchromophoric interactions results in an energy delocalization in the dendrimer forming a domain of excitations that may be as large as the size of the dendrimer itself.⁶ Similarly, the other branching centers such as adamantane,^{7a} carbon,^{7a,20} phosphorus,²⁰ and benzene²¹ act as weak electronic couplers giving rise to weak interchromophoric interaction among chromophores. This type of weak interaction leads to comparatively slower energy transfer and hence slow anisotropy decay dynamics.

On the basis of these investigations, there are two different distinct energy transfer mechanisms that can be identified in these dendritic branch systems. One of the mechanisms involves the discussion of energy transfer through space (Forster) and such a mechanism, characterized as incoherent hopping dynamics, is associated with relatively long depolarization times.^{20,21} This incoherent mechanism originates from the weak interchromophoric interactions determined by the electronic coupling ability of the branching center. The Forster type energy transfer mechanism has been utilized to discuss the energy transfer dynamics in phenylacetylene-based extended dendrimers where stepwise energy transfer from periphery to a perylene core takes place efficiently.^{12a} Some reports support the stepwise energy transfer mechanism¹² to the core in these dendrimer while others¹³ suggest the possibility of the direct energy transfer to the core from the periphery dendrons. The other energy transfer mechanism, characterized as a coherent process,^{6,7,19} originates from the very fast energy redistribution among branching chromophores. Basically, there are several important physical parameters of the branched chromophore system that will

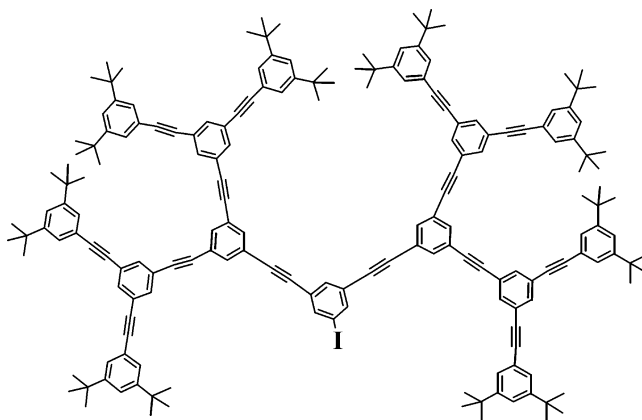


Figure 1. Structure of phenylacetylene dendrimer (PA-G2) used in the investigation.

determine the type of dominant energy transfer mechanism. Leegwater²² has proposed a model by considering the ratio of the homogeneous line width and interaction strength between chromophores as well as the depolarization time. This model can be used to qualitatively distinguish between hopping (incoherent) dynamics and exciton (coherent) dynamics. In this report femtosecond time-resolved fluorescence anisotropy decay dynamics as well as low-temperature steady-state spectral measurements of a second generation (G2) compact phenylacetylene dendrimer are reported. This study provides additional understanding of the energy transfer dynamics in compact phenylacetylene dendrimers. The objective of this investigation is to understand the excitation energy transfer dynamics among the self-similar dendrons in the compact phenylacetylene dendrimer before it transfers to a core chromophore.

II. Experimental Section

Figure 1 shows the structure of the dendrimer system, without any energy trapping core chromophore, that was utilized in our investigation. The synthesis and purification of the phenylacetylene dendrimer (PA-G2) shown in Figure 1 have been described in a previous publication.²³ The optical experiments were carried out with a solution prepared by dissolving the sample in degassed dry methylene chloride. The absorption and emission spectra were obtained by using the Ocean Optics spectrometer (USB2000). The time-resolved fluorescence measurements were carried out using our time-resolved femtosecond fluorescence Upconversion setup. The experimental setup is discussed in details in our previous publications.^{6b,c} Briefly, the fundamental femtosecond mode-locked Ti–sapphire laser pulses with a pulse width of about 55 fs (Tsunami, Spectra Physics) was used to generate frequency doubled light using a BBO crystal (NC1). The second harmonic light was separated from the fundamental using a beam splitter and the polarization of the second harmonic was adjusted to horizontal polarization. The second harmonic pulses were mixed with fundamental pulses in another nonlinear crystal (NC2) to generate a third harmonic light (273 nm). The sample, which is in a rotating cell, was excited using the third harmonic radiation and fluorescence was collected with an achromatic lens and directed to another BBO crystal (NC3). The rest of the fundamental light was passed through a motorized optical delay and mixed with the fluorescence at the NC3 to generate sum frequency light. The sum frequency light was dispersed using a monochromator and detected using a photomultiplier tube (Hamamatsu R1527P). The polarization of excitation pulses for the anisotropy measurement was controlled with a berek compensator. The temperature-dependent

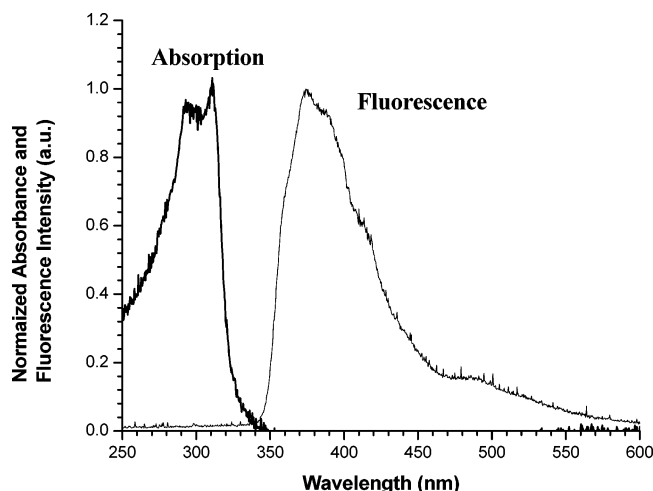


Figure 2. Absorption and emission spectra of PA-G2 in dry degassed CH_2Cl_2 at room temperature.

absorption and fluorescence spectra were obtained using an Oxford Instruments continuous flow cryostat and the Ocean Optics (USB2000) spectrometer.

III. Results and Discussion

A. Steady-State Absorption Measurements of Phenylacetylene Dendrimer. Shown in Figure 2 is the room temperature absorption spectrum and emission spectrum of the homogeneous dendrimer in degassed dry MeCl solution. The absorption spectrum is centered approximately at 320 nm (3.88 eV), which resembles the absorption spectrum reported by Kopelman and Moore² for this particular type of dendrimer. The $\pi \rightarrow \pi^*$ electronic transition can be considered as the dominant transition that is responsible for the observed absorption spectrum. Similarly, it was shown that the main absorption feature arises from the vibrationless electronic transition in the basic repeating unit. This vibrationless feature in the absorption spectrum was used to show that the optical excitations are localized on chromophore segments.^{2,13} The energy localization is found to be concentrated on the branching chromophore unit due to the nodes of the Cayley tree. Another characteristic for the localized excitation is the nonreduction of the energy of the macromolecule with the increase in the generation, because any delocalization of energy should result in a reduction of energy of the macromolecule. Red shift of the lowest absorption band indicates the delocalization of excitation energy. The optical excitations in this type of dendrimer (with nonoverlapping charge distribution) have been described in terms of the Frenkel excitation Hamiltonian (eq 1) by Mukamel et al.¹⁰

$$H \equiv \sum_m \Omega_m B_m^\dagger B_m + \sum_{m \neq n} J_{mn} B_m^\dagger B_n - P \cdot \epsilon(t) \quad (1a)$$

$$P = \sum_m \mu_m (B_m^\dagger + B_m) \quad (1b)$$

where Ω_m represents the transition energy from the ground state to the excited state of the m th chromophore. The hopping parameter J_{mn} is determined by the Coulombic interaction between chromophores. The B_m^\dagger and B_m are the creation and annihilation operators, if excitation localized is on the m th chromophore, respectively. The exciton parameters obtained in their calculation have been used to describe the optical response of a dendritic nanostar using eq 2. The calculated absorption spectrum by Mukamel indeed resembles (both energy and shape)

our experimental absorption spectrum supporting the idea of localized excitation in these branching systems in the ground-state configuration. Mukamel's calculations considering the nearest neighbor interactions among the chromophores, those are considered as two level systems in the branching macromolecules, led to the conclusion that the electron-hole pairs could transfer coherently or incoherently across a collection of transition dipoles confined in certain geometry. These calculations concluded that the electron hole pairs of a branched molecular system that have para substitution can be delocalized, but their motion is strictly confined by meta substitution. The lack of electronic delocalization across meta position suggest that one can consider the excitation is localized into weakly interacting segments. Only the nearest neighbor coupling has been considered in this calculation.¹⁰ The optical response (absorption) of these types of branching chromophores is given by

$$\sigma(\omega) \equiv \sum_{\alpha} \frac{2|\mu_{\alpha}|^2 \Gamma}{(\omega - \epsilon_{\alpha})^2 + \Gamma^2} \quad (2)$$

where ϵ_{α} represents the eigenvalues of the Frenkel exciton Hamiltonian without external field, μ_{α} is the transition dipole moment of the α th exciton and Γ is the exciton-dephasing rate. This calculation concluded that strongly localized one-exciton states dominate the linear optical response of the dendrimer. These states are found to be localized on the periphery of the dendrimer. Our steady-state absorption measurements of the homogeneous (compact) dendrimer were compared with this calculated absorption spectrum for a similar phenylacetylene-based dendrimer.¹⁰ Although the measured absorption spectrum resembles the calculated spectrum in shape and in energy, no exciton splitting was observed in the experimental spectrum as predicted by the calculation. This observation may suggest that the interchromophoric interactions are weak in the phenylacetylene dendrimer. All of these observations strongly suggest that the optical excitation in these branching macromolecules is localized due to the lack of electronic coherence across the branching center.

B. Steady-State Emission Measurements. Figure 2 also shows the fluorescence spectrum of the dendrimer obtained by exciting the sample at 273 nm. The fluorescence spectrum of the PA dendrimer may be compared with the fluorescence spectrum of the diphenylacetylene branched system which resembles the emission spectrum of diphenylacetylene.^{18,24} It has also been reported that two emitting singlet states with symmetries of B_u and A_g are responsible for the fluorescence in poly(phenylacetylene).^{18a} However, it should be mentioned that only one of the transitions (i.e., $B_{2u} \leftarrow A_{1g}$) is symmetry allowed and the other transitions are orbitally (or parity) forbidden.²⁴ The emission of the dendrimer is similar to the emission from the emission spectrum reported by Moore for a similar type of PA dendrimer with different generations.^{9b} Therefore, it can be suggested that the fluorescence of the dendrimer also originates from the same emissive state as that of the DPA. As the electronic absorption of phenylacetylene dendrimer is solely determined by the basic repeating unit, it can be suggested that the steady-state fluorescence spectral properties of the PA dendrimer may also be governed by the electronic properties of the basic repeating unit, diphenylacetylene. However, in a recent study by Bardeen et al.¹⁷ it was shown that the absorption and emissive states in phenylacetylene dendrimer with meta substitution may be different with a strong Stokes shift in the PA dendrimer spectra. This conclusion, based

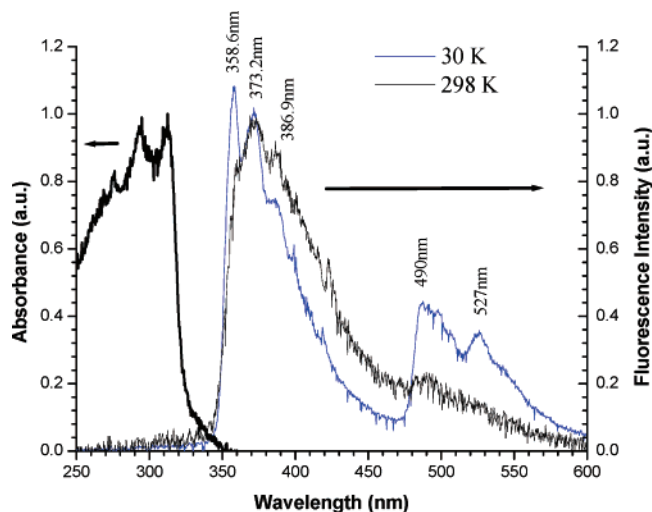


Figure 3. Absorption and fluorescence spectra of PA-G2 at 298 and 30 K in a PVB thin film.

on several factors that are discussed later, may give rise to different electronic properties in the ground and excited states.¹⁷ Time-resolved fluorescence decay investigations may be very helpful in understanding this difference in the steady-state spectral properties of phenylacetylene dendrimer.

C. Temperature-Dependent Steady-State Spectral Measurements. Figure 3 shows the temperature-dependent absorption and emission spectra of phenylacetylene dendrimer in a poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate) (PVB) thin film matrix. The absorption spectrum of the PA dendrimer fabricated in a thin film is comparable in shape and energy with the absorption spectrum of the dendrimer in solution. The absorption spectrum did not show significant dependence on the temperature even at 30 K. In contrast to this, the fluorescence spectrum showed significant differences at 298 and 30 K. First, the main emission band showed a trend of decreasing spectral line width with decrease in temperature. Also, the amplitude of the weak band at 490 nm was significantly enhanced with decreasing temperature. Second, the room-temperature emission spectrum showed one peak at 373 nm and shoulders at 358.6, 386.9, and 490 nm while the low-temperature fluorescence spectrum showed peaks at 358.6, 373, 490, and 527 nm with a shoulder at 386.9 nm. The low-temperature steady-state spectrum provides several key pieces of information about the dendrimer and its electronic structure. The appearance of two distinct emission bands, one centered at 373 nm and the other around 490 nm, clearly suggest that there are two emissive species present in the dendrimer sample. The emission at 490 nm increases with decreasing temperature. Kopelman et al.^{13b} have demonstrated the formation of excimers in different solvent environments due to the coupling of the perylene moieties. A recent investigation by Melinger and co-workers²⁵ has suggested that the presence of strong interactions between dendrons in a thin film compared to a dilute solution is responsible for excimer formation in thin films. Therefore, the emission band at 490 nm could be due to excimer emission of the excimer in the thin film. It is important to mention that at low temperature the excimer population can be significantly higher than that at room temperature as at low temperature the suppression of vibrational and rotational modes may improve the orientation of the dendrons such that excimer formation becomes favorable in the thin film.

The low-temperature absorption and fluorescence spectral measurements of the dendrimer showed another important

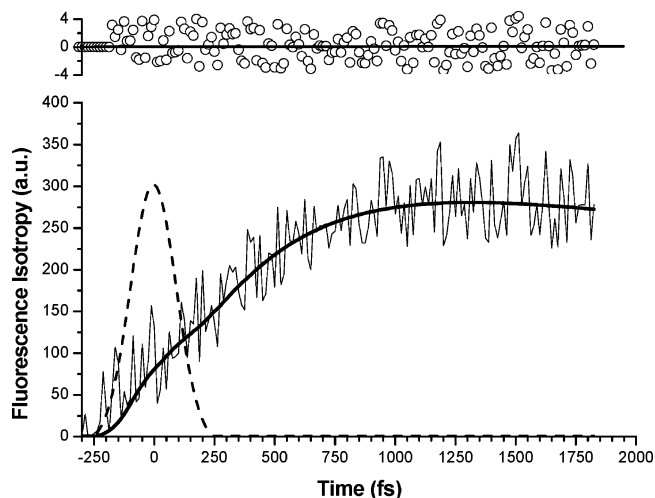


Figure 4. Fluorescence isotropy decay curve of PA-G2 in dry degassed CH_2Cl_2 at room temperature with residuals of the best fit curve.

feature which is not seen in the DPA molecule. The Stokes shift in the case of PA dendrimer is very strong when compared with the DPA molecule.²⁴ This strong Stokes shift can be explained by considering the excited-state relaxation. In a recent investigation of Bardeen and Martinez,^{17b} a clear picture about this type of Stokes shift in homogeneous phenylacetylene dendrimer was provided. In this study, it was shown that the Stokes shift can get larger with an increase in the dendrimer generation. It has been shown that such a large Stokes may be related to three major changes to the potential energy surfaces of the molecular system.^{17b} First, the increase in the energy of the ground state as the molecule relaxes to the emitting configuration. This raises the ground state energy which in turn reduces the energy gap between excited state and ground state. This will shift the emission spectrum further to the red. Second, a change in geometry accompanies a decrease in the excited state energy that further shifts the emission to the red. Finally, splitting in the excited state will lower the energy gap between the electronic levels further shifting the emission spectrum to the red. All of these factors can lead to a larger Stokes shift than what was initially expected. During the initial electronic transition, the ground-state configuration might be preserved, and due to the vibronic relaxation, the transition dipole may possess a new excited state configuration that is different from the ground-state configuration. The peaks in the low-temperature fluorescence spectrum of the dendrimer could be related to the vibronic progression that is comparable with the vibrational progression of the DPA molecule.²⁴ On the other hand, the low-temperature emission spectrum may also suggest that there are two closely spaced^{18a} emissive states at 358 and 373 nm. These excited states are so closely spaced that they are overlapped at room temperature. Such closely spaced excited states may have a significant impact on the emission transition dipole moment and hence the polarization of the emitted radiation by the chromophore.²⁶ Fluorescence anisotropy measurements might also provide more evidence about these two emissive states (see below). However, emission from such two states may be negligible unless the orbital symmetry of one of the states is altered adversely to make a transition from that particular state to the ground-state allowed.

D. The Time-Resolved Femtosecond Fluorescence Decay Measurements of Phenylacetylene Dendrimer. The isotropic fluorescence decay dynamics for the PA is shown in Figure 4. The time-resolved fluorescence decay dynamics were obtained by femtosecond time-resolved fluorescence upconversion spec-

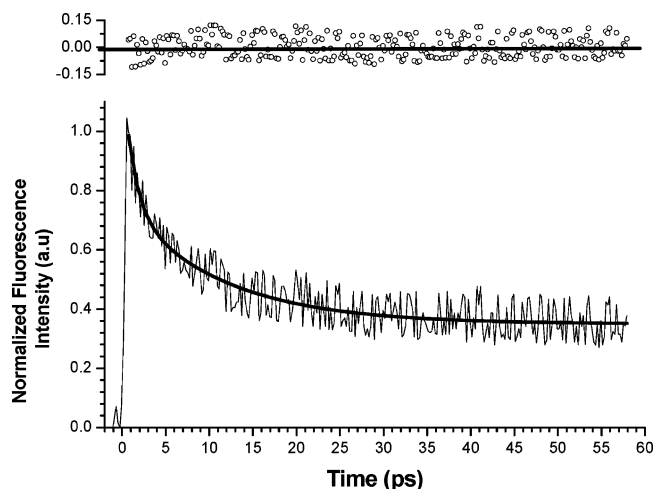


Figure 5. Long fluorescence decay dynamics of PA-G2 in dry degassed CH_2Cl_2 at room temperature with residuals of the best fit curve.

troscopy. The laser excitation power had to be minimized in order to preserve the sample from photodecomposition, and therefore, the signal-to-noise ratio is lower than expected. However, due to the high sensitivity of the upconversion system it was still possible to obtain a reasonable set of data to determine the fluorescence decay dynamics. The fluorescence dynamics curve showed two-component initial rise times of 0.5 ± 0.2 and 2 ± 0.75 ps. The initial rise time of 0.5 ± 0.2 ps may be associated with the solvent rearrangement as well as a conformational rearrangement of the chromophore in the excited state of the branched dendritic system. Similarly, as there are two excited states, the optical excitation energy may equilibrate between those two states before decaying, and this process could make an additional contribution to the rise time. The second rise time of 2 ± 0.75 ps can be associated with the possible energy transfer between initial excited state to the relaxed excited state of the chromophore unit in the dendrimer. The rise time has been used to discuss the energy transfer dynamics in dendrimers.⁷ It could be suggested that if the fluorescence originates from two different states, two distinct decay times may be observed in the fluorescence decay dynamics as the higher energy component has a shorter lifetime than the lower energy component.^{18a} Therefore, the fluorescence decay would consist of a fast decay component and a slow decay component. To determine whether two closely spaced excited states contribute to the fluorescence decay dynamics in these types of dendrimers, a longer fluorescence decay profile was obtained as shown in Figure 5. This long decay can be fitted reasonably well with a two exponential decay function using eq 3, and the fitting yielded approximate decay times of 4 and 100 ps.

$$y = A_1 e^{(-x/t_1)} + A_2 e^{(-x/t_2)} + y_0 \quad (3)$$

This suggests that the emitting chromophore of the dendrimer could contain two emissive pathways that could be associated with two excited states. These two emissive states are spaced closely in energy, and it will be impossible to distinguish the emission from each state using the steady state spectroscopy at room temperature. The only spectroscopic evidence of the existent of the two excited states that we could use is the presence of two fluorescence decay components in the fluorescence decay profile and the behavior of the fluorescence anisotropy decay profile at room temperature. Although the solvent polarizability can alter the energy gap between the two excited states, such a change in the energy gap may not be

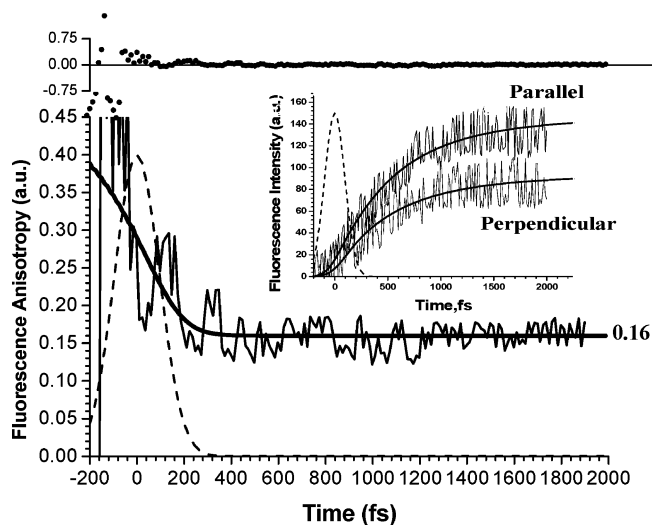


Figure 6. Fluorescence anisotropy decay of PA-G2 in dry degassed CH_2Cl_2 at room temperature with residuals of the best fit curve. Inset: parallel and perpendicular fluorescence curves of DPA-G2 in dry degassed CH_2Cl_2 at room temperature.

sufficient to cause significant differences in the steady-state spectral properties of the molecular system. The 4 ps time component could be related to the emission from the forbidden excited state after distortion in the symmetry of the chromophore. The 100 ps decay time could be associated with the emission from the transition-allowed excited state.

E. Time-Resolved Fluorescence Anisotropy Decay Measurements of Phenylacetylene Dendrimer. The fluorescence anisotropy decay curve for the PA dendrimer at room temperature is shown in Figure 6. The sample was excited at 273 nm and the emission was measured at 380 nm. The initial anisotropy decayed to a residual value of 0.16 with a decay time shorter than the instrument response function (IRF) of our experimental setup. Our investigations on other branching systems have shown anisotropy decay times as short as 50 fs can be determined using our experimental setup. The anisotropy decay times were obtained by convoluting the experimental results with the instrument response function. For example, nitrogen^{6,7,19–21} centered system showed the anisotropy time less than 100 fs while carbon-,^{7a} phosphorus-,²⁰ and benzene-centered²¹ systems showed anisotropy decay times closer to 1 ps at room temperature. All the previous investigations on phenylacetylene dendrimer led to the conclusion that the optical excitation is localized on the branch due to weak electronic coupling across the branching center. Such localization in excitation can give rise to slow depolarization rates that can yield longer anisotropy decay times. Interestingly, the phenylacetylene dendrimer system that contains benzene at the branching center showed a very fast anisotropy decay time, which is even shorter than the IRF. This type of fast depolarization of excitation can be discussed considering the excited-state properties of phenylacetylene dendrimer. As discussed above, the depolarization time could be used to understand the energy transfer dynamics. A recent report^{7a} using the Leegwater model clearly discusses this phenomenon in details. According to this report the behavior of depolarization time on interaction strength (J) for a given homogeneous line width (Γ/J) (see Figure 9 in ref 7a) can be used to distinguish the energy transfer dynamics in a branched chromophore system. According to the calculation, incoherent hopping energy transfer is characterized by the longer depolarization times (i.e., >200 fs) while very fast coherent energy delocalization is characterized by short depolarization times. The depolarization time for the phenylacetylene dendrimer can be

estimated as being to be shorter than 50 fs. On the basis of the calculation mentioned above it is impossible to consider the incoherent energy transfer dynamics as the dominant energy migration process. The phenylacetylene dendrimer's depolarization time falls within the coherent regime, and there were no additional depolarization decay components except for the long rotational diffusion time. The fast depolarization time was a surprising result, as it was expected that the depolarization time would lead to the conclusion that the incoherent hopping type of energy transfer mechanism dominates in the phenylacetylene dendrimer. Recent investigations on the excited state of the phenylacetylene dendrimer by Bardeen and Martinez,¹⁷ containing both theoretical and experimental results, may provide a rationalization that can be used to understand our present anisotropy results and observed short depolarization time. These investigations showed that it is possible that strong dipole coupling may occur in the phenylacetylene dendrimer in its relaxed excited state although the subunits are weakly coupled in the ground state configuration. This strong coupling in the excited state was evident in the emission spectra of the different generations of the PA dendrimer as the emission spectrum shifted gradually to the red with the increasing generation. This strong coupling has been shown to arise mainly due to the vibrational distortions and broken symmetry of the geometry in the excited state of the chromophore unit. These factors can give rise to stronger electronic coupling in the relaxed excited state although the coupling is weaker in the ground state.¹⁷ This geometry dependent electronic coupling can determine the mode of energy transfer in phenylacetylene dendrimers. The strong coupling may result in fast energy delocalization in the excited state that could give rise to the very fast depolarization decay we observed. Therefore, it might be inferred that a delocalized state of the dendrimer exists when the chromophore units are in the relaxed excited state even though energy localization takes place in the ground state of the dendrimer.

It should also be mentioned that such a fast anisotropy decay may not only be a reflection of a fast energy delocalization process in some cases. For example, the emission from two closely spaced excited states that contribute to the fluorescence in phenylacetylene dendrimer may also play a role here as well. But, as discussed above, the contribution to the emission from one state (A_g) will be smaller as the transition from that state is generally forbidden. The orientation of the emitting dipoles of the excited states contributing to the fluorescence decay may be polarized in two different directions.²⁴ This kind of dipolar orientation will destroy the initial optical polarization information. However, it is suggested that the contribution to the emission from the forbidden state is small and therefore, the decay of initial anisotropy value to its residual value is mainly due to the fast energy redistribution of delocalized states.

It has been shown previously that the optical excitation is localized in the ground state due to the lack of electronic coupling among chromophores in these types of dendrimer, and such a conclusion can lead to the assumption that incoherent hopping energy transfer dominates the optical excitation energy transfer mechanism. The anisotropy decay for such a weakly interacting chromophore system was expected to be slow as directed by a Forster type incoherent energy transfer process. However, this was not observed for the PA dendrimer investigated in this report. In a separate study,²¹ it was found that the methyl-substituted benzene branching center (1,3,5-tris((*E*)-2-{4-[(*E*)-2-pyridin-4-ylvinyl]phenyl}vinyl)-2,4,6-trimethylbenzene) indeed acts as a weak electronic coupler leading to slower

energy transfer dynamics that can be discussed in terms of Forster Theory. The room temperature measurements of this system yielded an anisotropy decay time of 815 fs, which clearly indicates the incoherent hopping type of energy transfer dynamics dominates in this benzene-centered system. This observation might be explained by considering the steric factors of the branching center. In this case, the additional substituents in the benzene branching center may hinder any vibrational distortion of the chromophore by exerting an additional steric hindrance. This may aid in keeping the symmetry of the branching center intact, even in the excited state, and hence the benzene will maintain its character as a weak electronic coupler. However, such a steric hindrance is not present in the phenylacetylene dendrimer investigated here. This may result in more freedom for the chromophores to undergo vibrational distortions in the excited state and subsequently the breaking of the symmetry in the excited state, making the benzene center a strong electronic coupler.

In conclusion, we have shown that the excited state of the basic building block, diphenylacetylene, defines the steady-state emission properties and the fluorescence decay dynamics of the phenylacetylene dendrimer. Although the steady-state spectral measurements of the dendrimer resembles those of basic building blocks, the time-resolved fluorescence dynamics of the dendrimer support the idea of energy delocalization in the relaxed excited states. There are two important characteristics of the time-resolved fluorescence studies that can be crucial in discussing the possibility of fast energy transfer dynamics in the dendrimer. First, the rise time in the fluorescence decay dynamics can be considered due to the energy transfer from initial excited state to the relaxed excited state. Second, we have shown that the fast anisotropy decay dynamics is indeed associated with the fast energy migration among branching chromophores of a dendrimer.¹⁰ This type of fast depolarization may suggest the existence of very strong electronic interactions among branching chromophores in the relaxed excited state of the chromophore.

Acknowledgment. T.G.III. acknowledges the National Science Foundation, Air Force Office of Scientific Research, and Sloan Foundation for the financial support for this investigation.

References and Notes

- (1) (a) Adronov, A.; Gilat, S. L.; Frechet, J. M. J.; Ohta, K.; Neuwahi, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175–1185. (b) Jiang, D. L.; Aida, T. *Nature (London)* **1997**, *388*, 454. (c) Yeow, E. K. L.; Ghiggino, K. P.; Reek, J. N. H.; Crossley, M. J.; Bosman, A. W.; Schenning, A. P. H. J.; Meijer, E. W. *J. Phys. Chem. B* **2000**, *104*, 2596. (d) Liu, D.; De Feyter, S.; Cotlet, M.; Stefan, A.; Wiesler, U.-M.; Herrmann, A.; Grebel-Koehler, D.; Qu, J.; Muellen, K.; De Schryver, F. C. *Macromolecules* **2003**, *36*, 5918.
- (2) (a) Kopelman, R.; Shortreed, M.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Moore, J. S.; Bar-Haim, A.; Klafter, J. *Phys. Rev. Lett.* **1997**, *78*, 1239. (b) Swallen, S. F.; Shi, Z. Y.; Tan, W. H.; Xu, Z. F.; Moore, J. S.; Kopelman, R. *J. Luminesc.* **1998**, *76–77*, 193. (c) Xu, Z.
- (3) (a) Drobizhev, M.; Karotki, A.; Rebane, A.; Spangler, C. W. *Opt. Lett.* **2001**, *26*, 1081–1083. (b) Ma, H.; Chen, B.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 986–987. (c) Nomura, Y.; Sugishita, T.; Narita, S.; Shibuya, T.-i. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 481–486. (d) Drobizhev, M.; Karotki, A.; Dzenis, Y.; Suo, Z.; Spangler, C. W.; Rebane, A. *J. Phys. Chem. B* **2003**, *107*, 7540.
- (4) (a) Ma, D.; Lupton, J. M.; Beavington, R.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2002**, *12*, 507–511. (b) He, G. S.; Lin, T.-C.; Cui, Y.; Prasad, P. N.; Brousmiche, D. W.; Serin, J. M.; Frechet, J. M. J. *Opt. Lett.* **2003**, *28* (10), 768.
- (5) (a) Balogh, L.; Bielinska, A.; Eichman, J. D.; Valluzzi, R.; Lee, I.; Baker, J. R.; Lawrence, T. S.; Khan, M. K. *Chim. Oggi* **2002**, *20*, 35–40. (b) Liu, M.; Frechet, J. M. J. *Pharm. Sci. Technol. Today* **1999**, *2*, 393–401. (c) Roberts, J. C.; Adams, Y. E.; Tomalia, D. A.; Mercer-Smith, J. A.; Lavalley, D.-+ K. *Bioconjugate Chem.* **1990**, *1*, 305–308. (d) Dass C. R. *J. Pharm. Pharmacol.* **2002**, *54*, 3.

- (6) (a) Ranasinghe, M. I.; Varnavski, O. P.; Pawlas, J.; Hauck, S. I.; Louie, J.; Hartwig, J. F.; Goodson, T., III. *J. Am. Chem. Soc.* **2002**, *124*, 6520–6521. (b) Varnavski, O.; Menkir, G.; Burn, P.; Goodson, T. *Appl. Phys. Lett.* **2000**, *78*, 1120. (c) Varnavski, O.; Leanov, A.; Liu, L.; Takacs, J.; Goodson, T. *Phys. Rev. B* **2000**, *61*, 12732.
- (7) (a) Varnavski, O.; Ostrowski, J. C.; Sukhomlinova, L.; Twieg, R. J.; Bazan, G. C.; Goodson, T., III. *J. Am. Chem. Soc.* **2002**, *124*, 1736–1743. (b) Varnavski, O.; Samuel, I. D. W.; Palsson, L.-O.; Beavington, R.; Burn, P. L.; Goodson, T., III. *J. Chem. Phys.* **2002**, *116*, 8893.
- (8) (a) Tomalia, D. A.; Frechet, J. M. J. *Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (16), 2719. (b) Tomalia, D. A.; Dvornic, P. R. *Nature (London)* **1994**, *372* (6507), 617.
- (9) (a) Xu, Z.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537. (b) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635.
- (10) (a) Poliakov, E. Y.; Chernyak, V.; Tretiak, S.; Mukamel, S. *J. Chem. Phys.* **1999**, *110*, 8161. (b) Tretiak, S.; Chernyak, V.; Mukamel, S. *J. Phys. Chem. B* **1998**, *102*, 3310. (c) Chernyak, V.; Minami, T.; Mukamel, S. *J. Chem. Phys.* **2000**, *112*, 7953. (d) Minami, T.; Tretiak, S.; Chernyak, V.; Mukamel, S. *J. Luminesc.* **2000**, *87–89*, 115.
- (11) Lupton, J. M.; Samuel, I. D. W.; Burn, P. L.; Mukamel, S. *J. Phys. Chem. B* **2002**, *106*, 7647.
- (12) (a) Kleiman, V. D.; Melinger, J. S.; McMorrow, D. *J. Phys. Chem. B* **2001**, *105*, 5595. (b) Melinger, J. S.; Pan, Y.; Klieman, V. D.; Peng, Z.; Davis, B. L.; McMorrow, D.; Lu, M. *J. Am. Chem. Soc.* **2002**, *124*, 12002.
- (13) (a) Swallen, S. F.; Kopelman, R.; Moore, J. S.; Devadoss, C. *J. Phys. Chem. B* **2000**, *104*, 3988. (b) Swallen, S. F.; Zhu, Z.; Moore, J. S.; Kopelman, R. *J. Mol. Struct.* **1999**, *485–486*, 585. (c) Shortreed, M. R.; Swallen, S. F.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Devadoss, C.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **1997**, *101*, 6318.
- (14) Nakano, M.; Fujita, H.; Takahata, M.; Yamaguchi, K. *J. Am. Chem. Soc.* **2002**, *124* (32), 9648.
- (15) Reineker, P.; Engelmann, A.; Yudson, V. I. *J. Luminesc.* **2001**, *94–95*, 203.
- (16) Varnavski, O.; Ispasoiu, R. G.; Balogh, L.; Tomalia, D. A.; Goodson, T. G. *J. Chem. Phys.* **2001**, *114*, 1962.
- (17) (a) Gaab, K. M.; Thompson, A. L.; Xu, J.; Martinez, T. J.; Bardeen, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9288. (b) Thompson, A. L.; Gaab, K. M.; Xu, J.; Bardeen, C. J.; Martinez, T. J. *J. Phys. Chem. A* **2004**, *108*, 671.
- (18) (a) MacCallum, J. R.; Hoyle, C. E.; Guillet, J. E. *Macromolecules* **1980**, *14*, 1647. (b) Andrews, J. R.; Hudson, B. S. *J. Chem. Phys.* **1978**, *68*, 4857. (c) Borst, D. R.; Chou, S. G.; Pratt, D. W. *Chem. Phys. Lett.* **2001**, *343*, 289.
- (19) Ranasinghe, M. I.; Wang, Y.; Goodson, T., III. *J. Am. Chem. Soc.* **2003**, *125*, 5258.
- (20) Wang, Y.; Ranasinghe, M. I.; Goodson, T., III. *J. Am. Chem. Soc.* **2003**, *132*, 9562.
- (21) Ranasinghe, M. I.; Murphy, P.; Lu, Z.; Huang, S. D.; Twieg, R. J.; Goodson, T., III. *Chem. Phys. Lett.* **2004**, *383*, 411.
- (22) Leegwater, J. A. *J. Phys. Chem.* **1996**, *100*, 14403.
- (23) Gorman, C. B.; Smith, J. C.; Hager, M. W.; Parkhurst, B. L.; Sierzputowska-Gracz, H.; Haney, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 9958.
- (24) (a) Hirata, Y.; Okada, T.; Mataga, N. *J. Phys. Chem.* **1992**, *96*, 6559. (b) Hirata, Y.; Okada, T.; Nomoto, T. *Chem. Phys. Lett.* **1998**, *293*, 371.
- (25) Melinger, J. S.; Davis, B. L.; McMorrow, D.; Pan, Y.; Peng, Z. *J. Fluorine* **2004**, *14*, 105.
- (26) van Gurp, M.; van Heijnsbergen, T.; van Ginkel, G.; Levine, Y. K. *J. Chem. Phys.* **1989**, *90*, 4103.
- (27) Demidov, A. A.; Andrews, D. L. *Photochem. Photobiol.* **1996**, *63*.