

Optical Excitations in Organic Dendrimers Investigated by Time-Resolved and Nonlinear Optical Spectroscopy

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ABSTRACT

Our research is concerned with the optical properties of covalently bound branched multichromophore systems. The presence of strong intramolecular interactions in dendrimers and other branched macromolecules has stimulated new approaches toward improved energy transfer and light-emitting and enhanced nonlinear optical materials, as well as the possibility of delocalized (exciton) excitations in molecular aggregates. This Account summarizes some of our investigations, which combine the use of different time-resolved techniques to examine the dynamics in organic (conjugated) branched structures and provide important structure–function correlations necessary for applications.

Introduction

There is presently a need for superior optical and electronic materials to generate a deeper understanding of the fundamental chemistry and physics of various organic molecules as well as for engineering new applications.¹ One particular area that organic materials have made great progress involves the creation of novel optical devices.² A number of different organic molecular architectures have emerged through creative synthetic methodologies. This has included chromophore aggregates as well as organic conjugated dendrimers. The use of organic dendrimers for artificial light harvesting (and for other optical applications) is advantageous for several important reasons. The branched organic structure suggests that it is possible to bring a number of chromophores together in a defined geometry. Also, there is the possibility of strong intramolecular interactions in the branched multichromophore system.³ The electronic coupling of the chromophores at a particular branching point could result in an enhanced transition dipole moment⁴ and enhanced nonlinear and quantum optical effects.⁵ Finally, the use of certain organic conjugated systems may act as an efficient sink of energy along a directed energy transport mechanism.⁶ Time-resolved spectroscopy provides the capability of understanding the detailed mechanisms of energy redistribution and the dynamics of electronic coupling in the dendritic structures, and this may provide the necessary under-

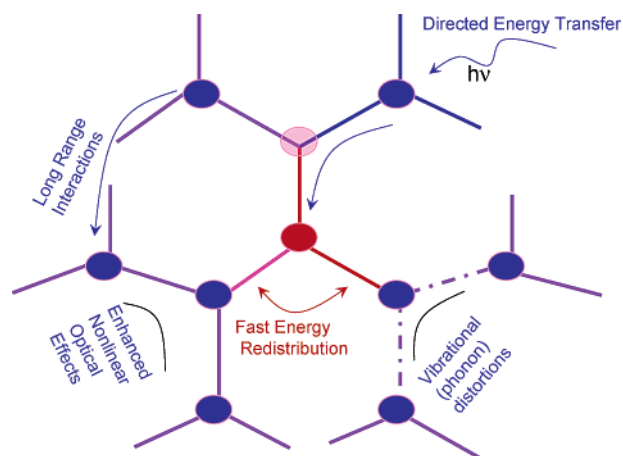


FIGURE 1. Schematic representation of different dynamical processes observed in branched macromolecules that are discussed in this Account.

standing of structure/property relationships in aid of designing new materials.

A major issue in branched structures concerns excitation localization, delocalization, and the role of through-space interactions. Localization of the excitation on a single branch has been reported because of the contribution of strong inhomogeneous broadening in the multichromophoric system.⁷ For the case of stronger intramolecular coupling in the chromophore system, a Frenkel exciton model has been invoked. Here, Coulombic coupling between chromophores leads to the description of the wave function to be a linear superposition of excitations on the individual branches. The absorption spectra may be analyzed using the collective electronic normal modes representing the changes in charge and bond-order distributions by the optical field. In the chromophore aggregate system, excitons (Frenkel) can migrate coherently or incoherently across the aggregate.⁸ This approach has been applied theoretically by Mukamel et al.⁴ for the phenylacetylene dendrimers. This analysis showed that electron-hole pairs of molecules are sharply affected by the meta substitution on the interlinking benzene rings.⁴ It was thus suggested that the localization of these pairs controls the nature of the optical excitation.⁴ However, evidence of delocalized excitons, which have been shown to have enhanced nonlinear susceptibilities,⁹ is a major focus of our previous time-resolved investigations.

The correlation of structure/property relationships with ultrafast dynamics in branched organic macromolecules is the focus of this Account. Specifically, this Account reviews our investigations of (see Figure 1 for illustration) (1) the time scale and efficiency of excitation energy transfer in organic dendrimers, (2) the relative strength of interactions between chromophores in branched structures, (3) the structure–function relationships that give rise to high intramolecular energy-migration rates, and

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(4) the effects of the intramolecular interaction in branched structures on the enhancement of two-photon absorption. The time scale of the fluorescence depolarization process in certain branched systems is used as a signature of delocalized excitonic states resulting from strong electronic interactions.¹⁰ Through these investigations, it may be suggested that the branching macromolecular architecture is indeed an exciting avenue toward significantly enhanced nonlinear optical (NLO) effects in comparison to their linear chromophore systems, which is possible through the existence of a delocalized excitation in the system.

Novel Organic Dendrimers for Optical Applications

Many of the early synthetic strategies of creating large branched macromolecular systems were initially carried out by the investigations of Tomalia et al.,¹¹ as well as Fréchet et al.¹² and Vögtle et al.¹³ In regards to the use of conjugated branched systems, Moore et al.¹⁴ utilized divergent, convergent, and double-stage convergent methods for synthesizing phenylacetylene dendritic macromolecules. Kopelman and Klafter et al.¹⁵ investigated the linear optical properties of two different variants of phenylacetylene dendrimers: the compact system, which consists of three Cayley trees with common origin and 3-fold symmetry, and the extended system, which has a completely ordered structure but possesses only an approximate self-similarity.^{15,16} What was found with these two relatively similar systems was that for the compact dendrimers the energy of 0–0 peak absorption was not affected by an increase in dendrimer generation, while for the extended dendrimers, an apparent hierarchy of localization lengths was observed.¹⁵ A number of systems were both synthesized and investigated after the initial reports.^{17,18} A number of research groups have also focused on the creation of dendritic structures based on important conjugated repeat motifs, such as triarylamine.¹⁹ There is still a great interest in creating novel organic branched systems for possible future light-emitting and NLO applications.

Experimental Methods for Investigations of Ultrafast Dynamics in Dendrimers

The experiments that we have utilized to probe the ultrafast dynamics and NLO properties in particular organic macromolecules are time-resolved fluorescence (upconversion),²⁰ transient absorption,²¹ degenerated four-wave mixing,²¹ nonlinear absorption,^{22–24} and three-pulse photon-echo spectroscopy.²⁵ Fluorescence upconversion measurements provided compelling evidence of strong intramolecular interactions and coherent energy-transfer dynamics in branched macromolecules. The optical setup has been reported previously, but briefly, it includes a ~50 fs Ti/sapphire oscillator that delivers ~800 nm pulses, which are converted to the excitation frequency by the use of NLO crystals.^{10,20,25b} The fluorescence from the

organic macromolecular material is collected and focused onto a NLO BBO crystal, which is overlapped (temporally) with the probe beam, and the sum-frequency-generated light is selected by a monochromator and detected by photon-counting electronics.^{3,10,20,24} The fast time resolution of this technique allows for a relatively sensitive detection of ultrafast dynamics in organic molecules. Another major advantage of this measurement is the ability to measure the depolarization contribution of the emission decay by anisotropy measurements, which can ultimately lead to analysis of the time scale and mechanism of energy migration in the system. We have used this methodology extensively for branched macromolecular systems, which may (or may not) follow a Förster energy-transfer mechanism.^{10,26} For the case of a “hopping” energy-transfer mechanism, the anisotropy decay time in the planar symmetrical system is related to the chromophore relaxation time and angle between the chromophores by²⁷

$$r(t) = \frac{1}{10} [1 + 3e^{-t/\tau_D}] \quad \tau_D = \frac{\tau_{\text{hopping}}}{4(1 - \cos^2 \theta)} \quad (1)$$

Initial anisotropy decay times on the order of a few picoseconds to as fast as 60 fs have been analyzed for different branched structures depending on the intramolecular interactions in the system.

Time-resolved absorption measurements have also been used to probe the dynamics of excitations in the branched macromolecules.²¹ For example, the transient absorption signals were analyzed to compare the anisotropy decay obtained from emission (relaxed) with that obtained from direct excitation. The experimental apparatus used to perform the time-resolved absorption measurements has been reported in a recent publication.²¹ Another important technique that we have utilized to probe the fast dynamics in branched macromolecules involves the use of photon-echo spectroscopy.²⁵ A major issue regarding the excitations in organic branched structures concerns the possibility of a coherent excitation process because of the strong interaction among chromophores. An interesting feature of the integrated three-pulse photon-echo intensity regards its connection to the dephasing time and the magnitude of the transition dipole moment. The product of these two values contributes (nonlinearly) to the amplitude of the integrated echo signal and gives information regarding the high transition dipole moment and slow dephasing rates in organic macromolecules.²⁸ The photon-echo peak-shift method^{25a,b} has been applied to organic branched structures (which showed enhanced NLO effects).^{25c} Information obtained from this method is useful in estimating the reorganization energy as well as coupling constants related to the coupling of the transition frequency to the nuclear motion of the bath.²⁹ This powerful tool, in combination with others described above, has and will continue to give greater insight into the electronic effects in organic branched structures.

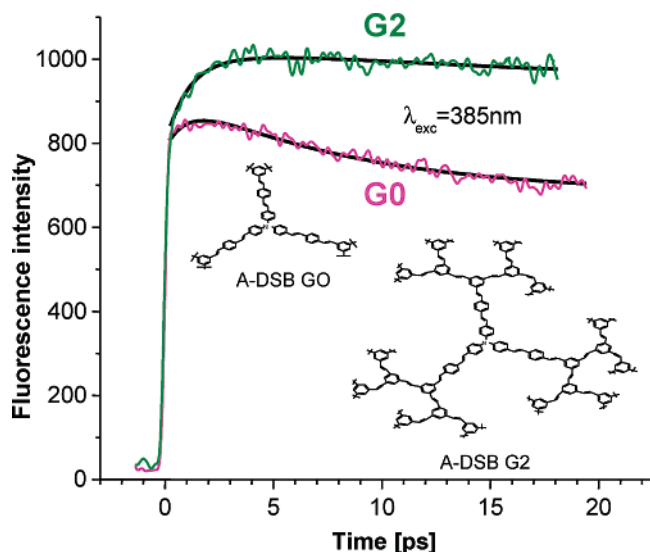


FIGURE 2. (Inset) Representative molecular structures of the N-DSB dendrimers. The time-resolved fluorescence decay profiles for the G0 and G2 generations are shown. The G2 shows the characteristic rise time signal, which is not present for G0.

Investigation of Excitations in Organic Dendrimers by Time-Resolved Spectroscopy

Directed Energy-Transfer Dynamics in Branched Structures. We have carried out time-resolved fluorescence measurements on a dendrimer system with conjugated building blocks to probe the specific energy-transfer dynamics and the pathway of the energy-transfer process.²⁶ The specific system created by Burn et al.²⁶ contained distyrylbenzene (DSB) unit building blocks at the core, where a nitrogen atom served as the center of the “three-arm” core (see Figure 2). The dendrons were composed of meta-substituted stilbene units (weak conjugation across the branching point). This provided the necessary donor (stilbene)–acceptor (DSB) chromophore topology for directed energy transfer to the core. Utilization of fluorescence upconversion allowed the excitation of the dendrons and subsequent emission of the DSB core molecules. A relatively fast (~ 7 ps, Figure 2) rise time

feature of the fluorescence decay profile for the G2 dendrimer (with stilbene dendrons) was used to analyze the time scale of the energy-transfer process.²⁶ With this result (along with the decay time of the stilbene dendrons), a very efficient ($\sim 99\%$) energy-transfer process was obtained for this dendritic system. There have been other examples of energy transfer directed by a Förster mechanism in branched dendritic structures in the literature as well in photosynthetic natural-light-harvesting systems, where the energy-transfer time in the LH-II aggregate is ~ 100 fs.^{10,30,27,31}

Energy-Migration Dynamics at the Branching Center.

To probe the process of intramolecular interactions in organic dendrimers, time-resolved techniques may also be employed. For certain excitonic system where the building blocks are not completely linked together in a conjugated structure (for example, meta-position substitution on benzene), time-resolved methods such as excited state and fluorescence anisotropy measurements have been used in a variety of systems. De Schryver et al.³² investigated the time-resolved polarized transient absorption decay of a dendrimer bearing eight perylene-imide chromophores on a polyphenylene core and compared these results to those of similar model compounds. The chromophore–chromophore energy-migration process was analyzed under the context of the Förster model.³²

We have also investigated the process of energy migration using ultrafast fluorescence anisotropy decay measurements such as in the nitrogen-cored DSB dendrimer system.²⁶ For example, with the good time resolution of the upconversion technique, we were able to capture the dynamics within the first picosecond (< 1 ps) of relaxation, presumably during the redistribution of energy. Shown in Figure 3a (and 3b) is the anisotropy decay (along with the parallel and perpendicular components of the fluorescence decay in the inset) of the N-DSB dendrimer system at room (and low) temperature. From convolution procedures, an initial fast anisotropy decay component of ~ 60 fs was obtained.²⁶ As expected, the longer time

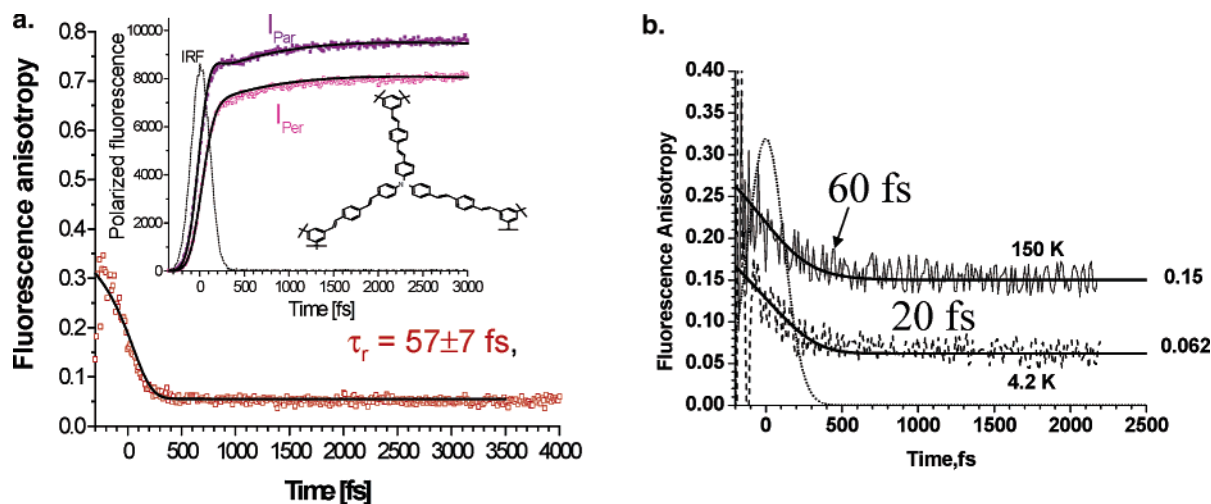


FIGURE 3. (a) Time-resolved fluorescence anisotropy decay for the N-DSB branching center system. (b) Anisotropy decay result for N-DSB at low temperatures.

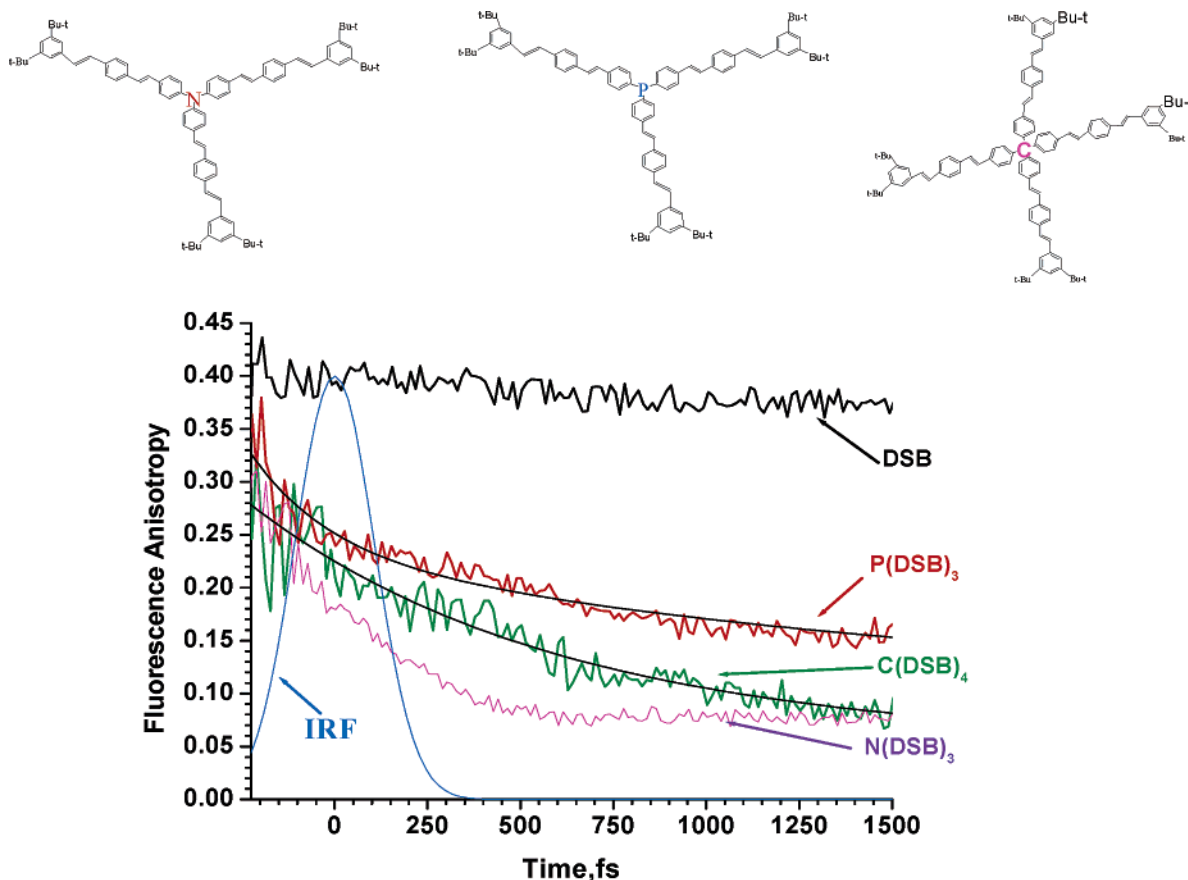


FIGURE 4. Molecular structures used in investigations of fast energy redistribution with model-branched systems with similar chromophore ligands. The anisotropy decay for the different systems shows the dependence of the branching center on the dynamics of the depolarization time.

components were also detected but were attributed to the rotational motion of the entire branched structure and not because of fast energy-migration processes.

It appears that this fast delocalization of energy mainly concerned the excitation of chromophores around the branching center. To understand the important structure–function relationships, investigations were carried out with a number of different branched structures with similar building-block chromophores. For example, while utilizing the DSB chromophores as building blocks, branching centers composed of nitrogen (N), carbon (C), phosphorus (P), and benzene (meta substituted) were investigated by ultrafast fluorescence anisotropy measurements (see Figure 4).^{3,33}

With similar chromophores attached, the other branched-centered systems showed significantly different anisotropy dynamics compared to the nitrogen-centered system (Figure 4).³³ For example, the carbon- and benzene-centered systems showed a considerably slower anisotropy decay compared to that of nitrogen, and the phosphorus system was intermediate between these two systems.³³ Of course, the linear chromophore system itself (MSB, a DSB analogue) showed the expected slower rotational motion of the chromophore in solution and was independent of any fast time-scale dynamics.¹⁰ It becomes clear that the relative interaction as expressed by fast depolarization measurements can be altered synthetically by placing the

appropriate building blocks in a particular orientation, as well as the appropriate use of branching centers to tune the interaction among chromophores. From our experience, it appears that the nitrogen-centered system (via a mesomeric effect) may possess the strongest intramolecular interactions and subsequently lead to larger enhancement values for the NLO effects.

The explanation of the fast kinetics observed in the depolarization process draws new questions concerning the mechanism of the energy-redistribution process in dendritic structures. To consider this process in terms of the Förster model, it is important to consider the interaction radius in regards to the possibility of a fast energy-redistribution process. Calculations of the expected energy-migration time under the Förster model for the N-DSB dendrimer system gave a hopping time of ~ 4 ps.¹⁰ This result is approximately 2 orders of magnitude slower than what was observed in the experiment (see Figures 3 and 4). This suggests that the Förster model may not be the only explanation of the extremely fast kinetics related to the energy-redistribution (migration) process around the branching center, which results from strong intramolecular interactions.

Another model that may describe the fast energy-redistribution process (at least qualitatively) connects the anisotropy decay kinetics to the ratio of the interaction strength (A) and the homogeneous line width (Γ).³⁴ This

model has its limitations regarding the issue of exciton–phonon coupling, which is somewhat suppressed by approximating the system at high temperatures (fast modulation limit).³⁴ However, it allows for a qualitative description of the strength of interaction and the mode of energy transport. An expression, which relates these two parameters to the depolarization time, is given by^{10,34}

$$t_{\text{dep}} = \frac{1}{\Gamma(1 - A)} \quad (2)$$

where

$$A = \frac{1}{N} \sum_{k=1}^N \frac{\Gamma^2}{\Gamma^2 + 16J^2 \sin^2(2\pi/N) \sin^2(2\pi k/N)} \quad (3)$$

Here, N is the number of chromophores contributing to the energy-redistribution process.

Thus, if the depolarization kinetics are obtained from the experiment, then calculated curves with eq 2 for particular values of the homogeneous line width may result in an estimate of the interaction strength.^{34,35} This model has been applied to previous systems for the purpose of describing the point at which the energy-redistribution dynamics reaches the crossover region from incoherent (hopping) dynamics to coherent (exciton) dynamics.^{10,26,34} This was also applied toward the analysis of ultrafast fluorescence dynamics of the natural-light-harvesting system (LH2) as well.^{34,35} Studies with different organic branching centers allowed for the estimation of the regime at which the interaction of participating chromophores resides. For example, for the N-DSB dendritic branching center with a fast (~60 fs) depolarization time (Figure 3),²⁶ it was indeed found that the mode of transport could be described as being in the crossover region from hopping dynamics to a coherent energy-migration process. This effect was also obtained for other dendritic structures as well, suggesting a general trend toward the synthesis and investigation of strongly (coherently) interacting branched systems. It appears that the dominant factors affecting the ultrafast dynamics are the electronic coupling through the core atom and the electronic and geometrical properties of the branch structure. The nitrogen-centered system possesses the appropriate geometrical and electronic properties that demonstrate ultrafast energy-redistribution processes.

Low-Temperature Measurements of Energy-Redistribution Dynamics in Branched Structures. Measurements at significantly lower temperatures, where the contribution from phonons might be significantly suppressed, add to the description of fast energy migration in aggregated systems.³⁶ Investigations of several branching centers at low (4 K) temperature were reported by our group.^{37,38} For consistency, the N-DSB dendritic system was also investigated by preparing a thin film of the active branched structure doped in an inert organic host polymer (PVB) (Figure 3b).³⁷ The first observation was that the (initial) anisotropy decay time was still fast at lower temperatures. This gave stronger justification that the effect of a fast depolarization at room temperature is indeed related to

an electronic mechanism. Second, it was found that the depolarization time decreased with decreasing temperature. These measurements, which were very challenging, pushed the limits of the fluorescence upconversion spectroscopic measurement and to our knowledge served as the first report for an organic macromolecular system with a branching chromophore geometry.³⁷ The explanation for the suppression of the depolarization decay with decreasing temperature was not based on a change of the strength of interactions but primarily on the line-broadening mechanisms. The effect of the competition between these two broadening mechanisms has been reported for other organic excitonic (LH2) systems,³⁶ where it was found that it is important to consider the ratio (σ_h/σ_{inh}) of the two line-width contributions. This relationship suggests that with the increase in the ratio of the homogeneous and inhomogeneous line widths (σ_h/σ_{inh}) there should be a decrease in the depolarization time. Reported calculations also showed a systematic decrease in the residual value of anisotropy with a decrease in inhomogeneous broadening (disorder) for light-harvesting antenna systems.³⁹

Enhanced NLO Properties of Branching Chromophore Systems. One consequence of the strong intramolecular interactions is the possibility of observing enhanced NLO effects.²⁴ This issue, in regards to dendrimers and other multichromophore-branching structures, has recently been enthusiastically investigated by both synthetic organic chemistry and optical characterization methods.⁴⁰ Measurements of the two-photon absorption cross-section for branching chromophore macromolecule materials has resulted in new information regarding the specific synthetic design criteria for the fabrication of superior NLO materials for device applications. While the idea of a multichromophore macromolecular system for NLO-enhanced effects had been investigated in the past, the issue related to branching structures both experimentally and theoretically has been addressed in a slightly different manner. Experimentally, two-photon absorption (and subsequently fluorescence) results have been obtained for dendrimers of different generations.^{23a,41} There have been results that suggest cooperative enhancement, linear (additive) behavior, and even reduction of the two-photon absorption cross-section in certain multichromophore systems. Detailed calculations of the nonlinear response in these systems have also been carried out to explain this behavior.^{40,42} Our investigation (and several others) with a branched trimer system involving a nitrogen center with charge-transfer (nitroaminotolane) chromophores showed a significant enhancement in the two-photon absorption effect per chromophore.²¹ This prompted further investigations to probe the mechanism of this enhancement.

Time-Resolved Spectroscopy of Branched Structures with Enhanced NLO Properties. To probe the mechanism of the enhanced NLO effects in branched chromophore systems more closely, we have carried out detailed investigations with both trimer and monomer systems. The first of these important investigations was carried out with a nitroamino tolane building-block chromophore system (see inset of Figure 5 for structures), which was

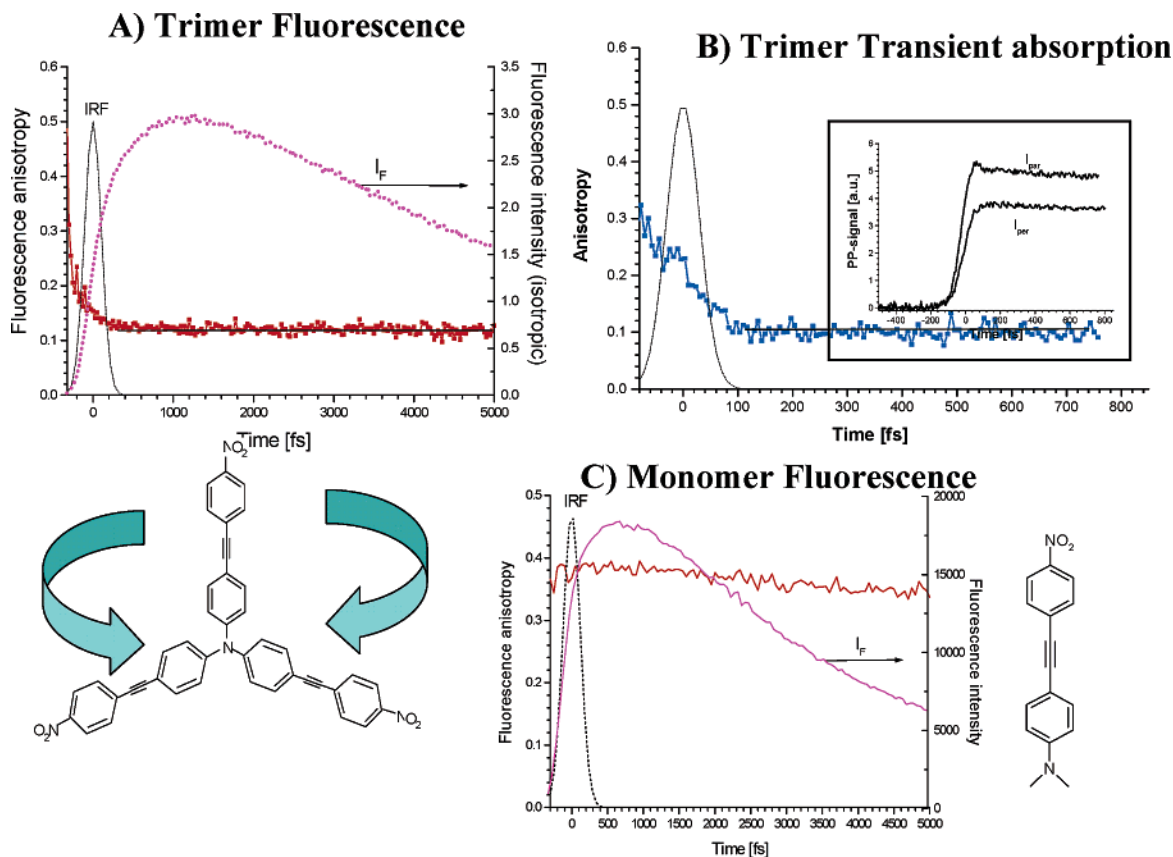


FIGURE 5. Comparison of the ultrafast dynamics in a NLO branched chromophore with its monomer analogue. The fluorescence decay was affected in a similar way for the two systems by the solvent polarity. A long rise time was observed in both cases. The fluorescence anisotropy decay for the trimer (inset of A) was very different compared to that of the monomer. Also, the transient absorption anisotropy decay (B) for the trimer was similar to the fluorescence anisotropy decay.

synthesized in Twieg's laboratory.^{10,21} As shown in Figure 5, the fluorescence anisotropy decay of this particular NLO branched system was similar to that obtained for the N-DSB described above. The fast anisotropy decay was also observed for the transient absorption measurement with the branched chromophore system (also seen in Figure 5). However, a fast anisotropy decay was not observed for the linear chromophore system. This suggested that the fast energy migration could be related to exciton delocalization in the branched structure and connected with the enhanced NLO effects. Further measurements were carried out to probe the mechanism for the observed differences in NLO properties in the trimer and monomer systems by three-pulse photon-echo peak-shift spectroscopy.

Three-Pulse Photon-Echo Measurements of Branching Chromophore Systems with Enhanced NLO Properties. The issue of dephasing may also play a significant role in describing the changes in the NLO effects of branched structures in comparison to the linear molecular analogues. Several methods have been employed to probe this fast process in organic systems in the past, and they constitute a large degree of understanding about the connection of disorder and coherent polarization decay.^{25a,b,43} One such technique is a variation of multiple wave mixing called photon-echo spectroscopy.²⁵ This

technique has been thoroughly applied to the natural-light-harvesting system and in semiconducting nanoparticles.⁴⁴

As outlined in the literature, the photon-echo technique has also been utilized for investigation of dephasing and quantum beats in semiconducting nanoparticles, as well as solvent dynamics in selected systems.^{44b,45} It should be mentioned that our own interest in the use of photon-echo spectroscopy is for a characterization of delocalized excitations and an estimation of real inhomogeneous broadening in the system. The specific echo experiment that we have utilized in this regard is the three-pulse photon-echo peak-shift method, which was first described by Fleming and Wiersma et al.²⁹ The details of this method have been the focus of a number of comprehensive reports.^{25a,b} Briefly, the four-wave-mixing experiment encompasses three sequential pulses with time delays (τ), the coherence time (between the first and second pulse) and the population time (T) (between the second and third pulse).^{25,29} In the peak-shift method, signals in the two phase-matching directions ($k_1 - k_2 + k_3$ and $-k_1 + k_2 + k_3$) are collected as a function of the coherence delay for a particular T .^{25,29} Half the distance between the maxima of the two photon-echo signals is the measure of the peak-shift value. It has been suggested that the peak-shift value may be interpreted as a measure of the

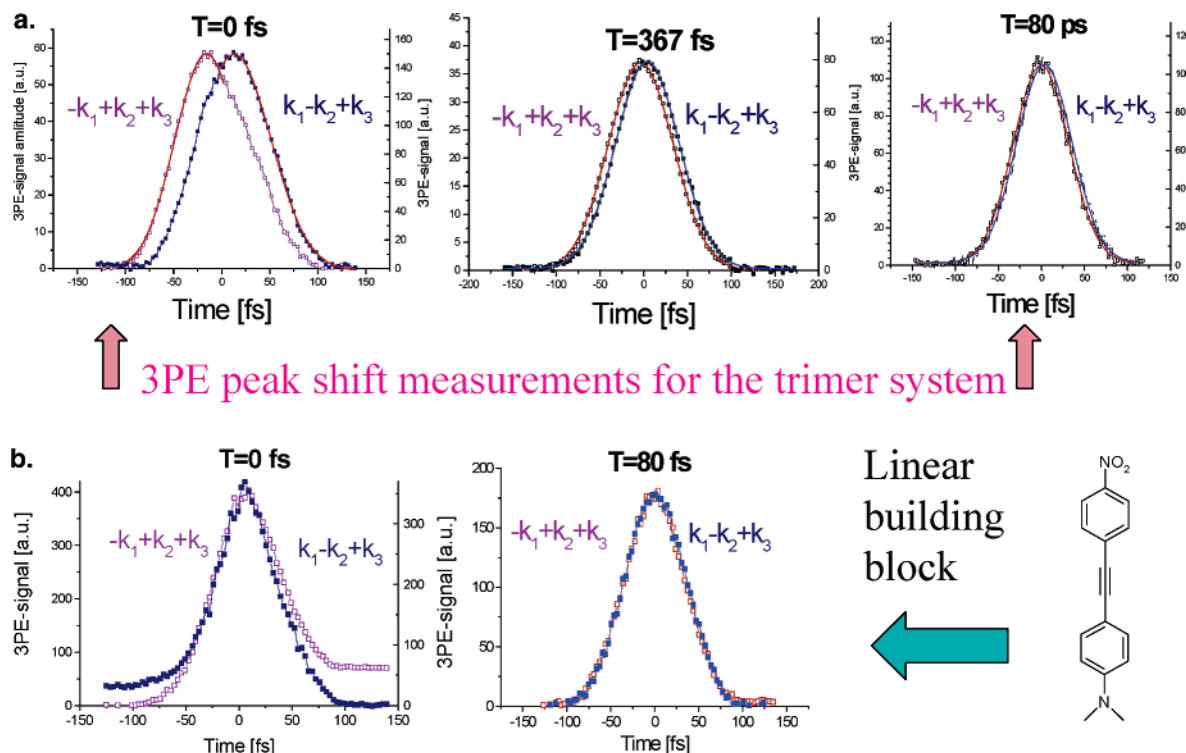


FIGURE 6. (a) Integrated three-pulse photon-echo signals for T-NPTA for the following population periods: $T = 0$ fs, $T = 367$ fs, and $T = 80$ ps. (b) Integrated three-pulse photon-echo signals for DMNAT for $T = 0$ and 80 fs.

coupling to the bath (environment) as well as the reorganization energy (in solution).^{25a} Our purpose here is to compare the parameters related to the coupling constant (Δ), reorganization energy (λ), and the contribution real inhomogeneous broadening (Γ_{inhomo}) for the branching structures and the linear chromophore analogue.

Shown in Figure 6 are the representative photon-echo decay profiles (both phase-matching directions) for the linear and trimer nitroamino tolane system.^{25c} Each of these echo profiles depicts a particular population time either at very short times (where the maximum peak-shift value is found) or at longer population times (where relatively small peak-shift values are observed). As it can be seen in the Figure 6, there is a significant peak shift for the trimer system at a smaller (~ 6 fs) population time. This effect is smaller at longer (~ 80 ps) population times. However, for the monomer system, the peak-shift value is very small (close to 0) for short population times as well as longer population times.^{25c} This result immediately suggests that there is a qualitative difference between the two systems constructed from the same building blocks. This result was also in accordance with our time-resolved fluorescence polarization measurements, indicating the possibility of the initial delocalized state in the trimer. The initial peak-shift value is determined largely by the total coupling strength between the electronic transition and the bath (a higher coupling strength leads to a smaller peak shift). Thus, the low initial peak shift for the monomer is reasonable, because this system possesses a strong coupling to the bath and charge-transfer character. A weaker interaction with the bath (smaller reorganization energy) is in accordance with the suggestion of a delo-

calized character of the initial state of the trimer, because the state delocalized over several chromophores usually possesses lower electron–phonon coupling compared to that for the single chromophore because of possible motional narrowing effects.

Another interesting and important feature of the 3PEPS of the T-NPTA is a nonzero asymptotic peak-shift value at large population periods (T). This residual peak shift reflects the retained transition frequency memory at long times, which results from the static inhomogeneity in the system. It should also be mentioned that the absolute photon-echo signal for the trimer system was considerably larger than that observed for the monomer system when the linear optical density (concentration) was normalized between the two system solutions. This observation may be connected with differences between the two systems in terms of the important product of the transition dipole moment (μ) and the dephasing time.²⁸ The enhanced transition moment for the trimer system as a result of the delocalized state is apparent in this comparison and gives further information regarding the NLO enhancement processes.

Concluding Remarks

It appears that the optical properties of branching chromophore aggregates are significantly different from the properties observed for their linear monomer analogues. We have demonstrated this by measurements of ultrafast dynamics in the excited and relaxed states. Ultrafast fluorescence anisotropy measurements gave rise to the observation of fast and predominately coherent energy-

redistribution processes, which are the result of strong intramolecular interactions. These results are connected with the existence of a delocalized excitation, which may give rise to enhanced NLO effects in certain branched structures. As mentioned above, the focus of this Account was to present some of the important results of our investigations regarding the excitation dynamics in novel organic branched structures. While there has been some improvement in our understanding of the mechanism of excitations in these systems, there is still much to be learned from further focused investigations. For example, the issue of the contribution from various broadening mechanisms is still not completely understood for this particular type of molecular aggregate. Further insight into the mechanism of enhancement of NLO effects observed in branched structures in comparison to their linear analogues is still necessary before superior device applications based on this process may be utilized.

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