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Voltaic and Light Emitting Materials**

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# Investigations of the Photo-Physical Properties of Novel Photo-Voltaic and Light Emitting Materials

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## **Abstract**

Understanding photophysical properties of optoelectronic materials and the discovery of new materials provide a great challenge for researchers interested in applications. This report highlights the distinctive optical properties of dendrimers; branched chromophore systems as well as dendrimer encapsulated metal nanoparticles which provide a novel approach toward this challenge. Excitation energy transport properties in these materials were investigated by ultrafast fluorescence anisotropy decay. It was found that the strength of interactions among chromophore units determines the mechanism of the mode of energy transport. The synthesis of several novel branching structures, photoactive dendrimers as well as dendrimer encapsulated lanthanide and metal nanoparticles was achieved. Local field effects contributed strongly to the enhanced nonlinear properties in chromophore-functionalized dendrimer nanocomposites. The sensitized lanthanide emission suggested that this material was useful for light-emitting and optical amplifier. Correlation of anisotropy decay time with the enhanced two-photon absorption provided a new design criterion for large two-photon materials. Furthermore, various techniques including steady-state optical measurements, time-resolved upconversion spectroscopy, nonlinear absorption, transient absorption were used to characterize a variety of optical properties of the materials of interest.

## **Introduction**

Investigations of energy transfer in dendritic macromolecules are of great importance in creating artificial light-harvesting and -emitting systems as well as molecular electronic/photonic devices. The research supported by AFOSR in the PI's laboratory has primarily involved the investigations of optical excitation energy transfer in novel dendritic and branching light-emitting materials as well as the synthesis of new materials with enhanced optical properties. The principle issue was to understand excitation energy transfer between subunit and the degree of excitation delocalization in dendrimers and branching structures. We utilized steady-state and time-resolved fluorescence spectroscopy to characterize energy migration and intramolecular interaction in these dendritic macromolecules. A major challenge is to understand the patterns of energy transfer that relates to specific dendritic geometry and applications.

Our initial investigations in this field were predominantly focused on the optical properties of dendrimers, polymers and novel metal nanoparticle topologies in collaboration with Profs. Guillermo C. Bazan (University of California, Santa Barbara), John F. Hartwig (Yale University), Robert J. Twieg (Kent State University), Donald A. Tomalia (University of Michigan), Jim Takacs (University of Nebraska), Timothy M. Swager (MIT) and Paul. L. Burn (University of Oxford). Indeed, these early investigations helped to pave a path toward future studies involving organic branched chromophore systems. To produce systems that were more specific toward the needs of the research supported by the AFOSR, we synthesized a series of novel organic conjugated branching structures, photoactive dendrimers as well as organic-inorganic nanohybrids.

To characterize these materials of interest, various techniques including steady-state and time-resolved upconversion spectroscopy as well as nonlinear and transient absorption have been used in the PI's laboratory. Specifically, excitation energy transfer, intermolecular and intramolecular interactions have been investigated by ultrafast time-resolved fluorescence spectroscopy. We have found that the strength of interactions among intersegmental branches governed the mechanism of optical excitation, the pattern and the efficiency of energy transport. This important discovery is of great importance in characterizing and tuning the performance of materials that were incorporated into light-emitting, photovoltaic devices. In addition, we also carried out the characterization of novel dendrimer nanocomposites (DNCs) with different metals and topologies of dendrimers. The finding of large optical power limiting and the enhanced nonlinearity in DNCs has opened up potential applications of these nanostructured materials in nonlinear optics. Also, the nanohybrid materials prepared by encapsulation of metal nanoparticles into an artificial light antenna (chromophore-functionalized dendrimer) are promising materials for photovoltaic devices due to the large surface binding potential and possibly efficient charge separation at the interface. To find materials with large two-photon cross-sections, we carried out the measurements of two-photon cross section in the number of different branching structures. We have observed significant enhancements of TPA in these multi-branched structures. Correlation of this enhancement with the interaction strength among the branched chromophores provides a new design criterion for large two-photon materials.

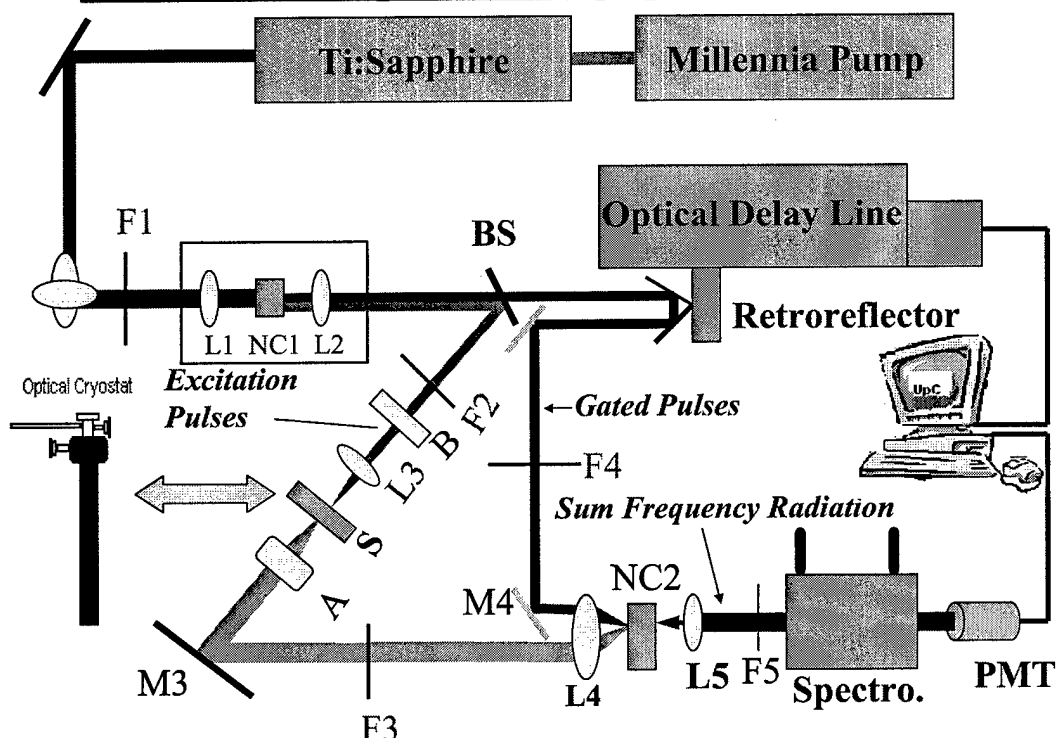
## **1. Investigation of excited state dynamics in dendrimers and branching structures**

### **1.1 Excitation energy transfer in dendrimers**

The investigation of optical excitation energy transport in dendrimers and branching structures are motivated by the prospect of using these materials as active components in light-emitting and photovoltaic devices as well as creating artificial light-harvesting systems. Understanding of photodriven energy transfer in these materials provides valuable information in evaluation of performance of these materials in device structures and the efficiency of electronic/photonic devices. Under the support of AFOSR, we have built a femtosecond time-

resolved fluorescence upconversion apparatus to systematically investigate excitation energy transfer in certain organic dendrimers and branched structures. Figure 1 shows the optical diagram of our setup. This apparatus consists of the basic unit of FOG-100 system. Briefly, the fundamental femtosecond mode-locked Ti-Shapphire laser pulses with pulse width of about 55fs (Tsunami, Spectra Physics) was used to generate frequency doubled light using a BBO crystal (NC1). The sample was excited using the second harmonic radiation and fluorescence was collected with an achromatic lens and directed to another non-linear crystal (NC2). The rest of the fundamental light was passed through a motorized optical delay and mixed with the fluorescence at the NC2 to generate sum frequency light. The sum frequency light was dispersed using a monochromator and detected using a photo-multiplier tube (Hamamatsu R1527P). The polarization of excitation pulses for the anisotropy measurement was controlled with a Berek compensator. The low temperature measurements were carried out using an Oxford Instruments continuous flow cryostat using liquid helium as the cryogen. The cryostat was interfaced electronically and optically to our upconversion system. The sample chamber is thoroughly flushed with helium gas and a helium gas filled rubber bladder is always connected to the sample chamber during the course of the experiment.

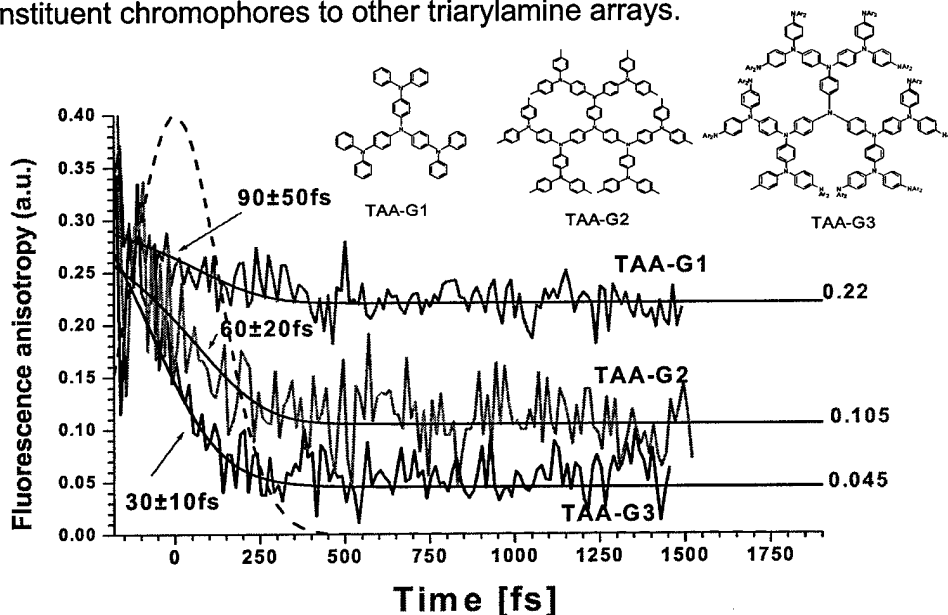
### *Femto-Second Optical Gating Spectroscopy Unit*



**Figure 1** Femtosecond ultrafast fluorescence upconversion set up

Our initial investigation is to probe excitation energy transfer in homogenous triarylamine (TAA) based dendrimers. The results of ultrafast fluorescence

measurements revealed that the delocalized excitations could persist over a large number of participating chromophores. In this case there was a significant red-shift in the absorption spectra and a systematic decrease in the residual anisotropy value and decay time as a function of increasing dendrimer generation (see Figure 2). This effect, although hypothesized by a number of authors, had never been reported before our manuscript in *J. Am. Chem. Soc.* Indeed, this system is also very useful in understanding energy migration process in a strong interaction regime in light of the similarity in overall structures and constituent chromophores to other triarylamine arrays.



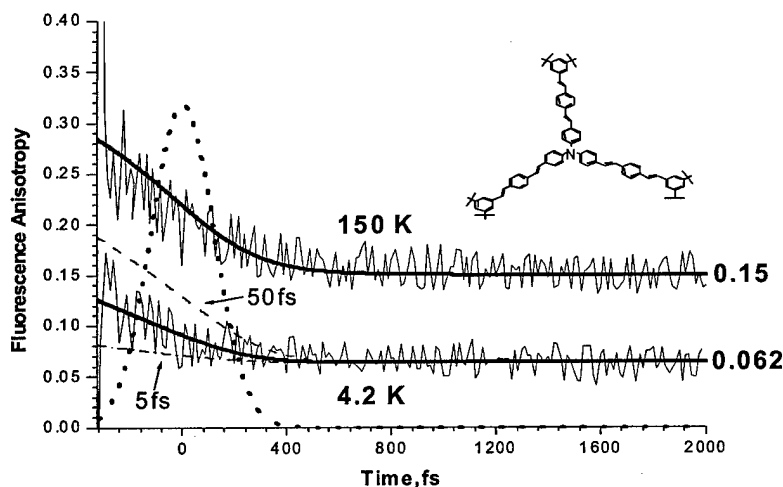
**Figure 2** Fluorescence anisotropy decay dynamics in TAA based dendrimers

This result motivated the PI's group to explore energy transport phenomena in dendrimers with different cores. The cores were composed of either organic chromophores or elements (atoms). The investigations with a nitrogen cored distyrylbenzene (A-DSB, synthesized by Paul Burn at Oxford University) dendrimers demonstrated that the efficiency of energy transfer from dendron to core is very close to unity. Time-resolved fluorescence measurements showed the transfer rate to be approximately 7 ps; therefore, the Förster model was suggested to describe the mechanism of energy transfer. We also carried out the investigations of ultrafast dynamics in a novel porphyrin cored dendrimer. This investigation was carried out by an undergraduate student (Ms. Nicole Dolney) with the help from a postdoctoral assistant (Dr. Oleg Varnavski) in the group. Steady-state absorption and emission spectroscopy were also used to probe the energy transfer efficiency in the stilbene dendrons and the porphyrin dendrimer systems. Ultrafast fluorescence dynamics as well as the anisotropy decay measurements indicated that complete (efficient) energy transfer was blocked due to the orientation of the dendrons. The anisotropy decay of the Pt-porphyrin dendrimer system shows two components, one is associated with the fast

depolarization in the porphyrin complex and another is associated with the polarized emission from the dendrons as a result of incomplete energy transfer to the core.

### 1.2 Excited-state dynamics of branching structures at low temperature

As we have investigated the energy migration processes in branching structures at room temperature to be very fast ( $\sim 70$  fs), we would very much like to know what kinetic contributed to the fast depolarization. As was a major goal in our AFOSR program, constructing the low temperature apparatus and investigations of systems at  $\sim 4$  K have already been carried out. In general the main parameter that we seek to modify is the homogeneous linewidth by cooling the branching structures close to liquid helium temperatures. We have already obtained an interesting result with the nitrogen cored DSB system. The result and structure are shown in Figure 3. As it can be seen from this figure the anisotropy residual value decreases with decreasing temperature. What was also surprising was that the anisotropy decay time also decreases with decreasing temperature. These measurements push the limits of the fluorescence upconversion technique. The time resolution is affected by a number of optical parameters in the system, and the deconvolution procedure has also been revisited in order to characterize the very fast decay times that we observed.



**Figure 3** Fluorescence anisotropy result of the  $N(DSB)_3$  system at low temperature

While the measurement and characterization of ultrafast anisotropy has not been measured in organic conjugated dendrimers, it has been investigated in natural photosynthetic light harvesting systems. Here, the competition between homogeneous and inhomogeneous (static) broadening of the system is affected by lowering of the temperature. It was found that a change in the ratio of these two could dramatically change the residual anisotropy value and also the



anisotropy decay time. This relationship can be understood by use of following expression,

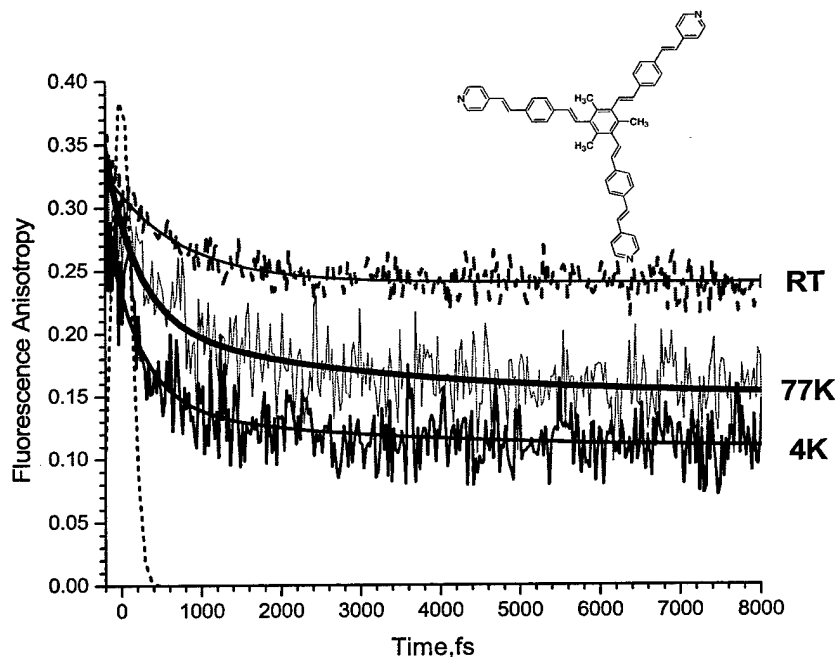
**Equation 1**

$$\tau_d = \frac{\tau_{hop}}{\left( \pi^{d/2} \sqrt{\frac{2s}{d}} \frac{\Gamma(1-d/s)}{\Gamma(1+d/2)} \frac{\sigma_h}{\sigma_{inh}} e^{-(E-E_0/0.6\sigma_{inh})^2} \right)^{s/d}}$$

Reasonable estimates of the homogeneous linewidth ( $\sigma_h$ ) and the inhomogeneous linewidths ( $\sigma_{inh}$ ) were made for our N(DSB)<sub>3</sub> system in order to estimate the possible change in depolarization time ( $\tau_d$ ). These estimates turned out to agree well with the change of anisotropy decay and residual value measured at two temperatures. This work suggests that the “coherent” nature of the excitation is enhanced at low temperature as the “locking-in” of the static disorder is completed at ~4K and the residual anisotropy value reaches the lowest limit which is then as a function of the equilibrium static geometry of the molecule. This entire important (and very difficult) investigation was carried out by a graduate student (Mr. Mahinda Ranasinghe) under the AFOSR program.

We have found that the nitrogen atom acts as a very efficient electronic coupler-giving rise to strong intersegmental interactions at low temperatures. To understand the energy transfer dynamics completely, we also investigated the different branching center system to probe the strength of interactions amongst chromophores and the energy transfer dynamics at low temperatures. Instead of nitrogen core, a system containing benzene branching center and three pyridine distyrylbenzene (pyridine-DSB) branches was constructed (see Figure 4). Ultrafast time resolved fluorescence anisotropy measurements turned out the excitation energy transport in this system is significant different from N(DSB)<sub>3</sub> system. Unlike nitrogen core, the benzene branching center acts as a weak excitonic coupler and the electronic delocalization across the branching center is hindered by the *meta* substitution of the chromophores. A depolarization time of ~800fs at room temperature was observed and we have explained the excitation energy transfer to the adjacent dipoles as Förster hopping mechanism. This is different from that we have observed for the nitrogen centered DSB system where the strong interaction of DSB chromophores resulted in a delocalized (coherent) excitation and subsequent fast energy migration process. As shown in Figure 4, the anisotropy residual value decreases with decreasing temperature. Also, the anisotropy decay curve can be fitted reasonably well with a two exponential decay function at room temperature while at 77K and 4K the curves are fitted with a three exponential decay function. At room temperature the average (initial component) decay time is approximately 800 fs while at 77K it is about 1700fs and the decay time is approximately 1100 fs at 4K temperatures. The additional component for the 77K and 4K decay curves was found to be approximately 280 fs and 110 fs respectively. The new fast anisotropy decay component in addition to slow (~1ps) component at low temperature suggests that energy transfer

dynamics approaches the intermediate (crossover) characteristics of incoherent and coherent regime. These important results have been published in Chem. Phys. Lett.



**Figure 4** Anisotropy decay of benzene center branching structure at room temperature, 77K and 4K.

## 2. Synthesis and optical properties of new materials

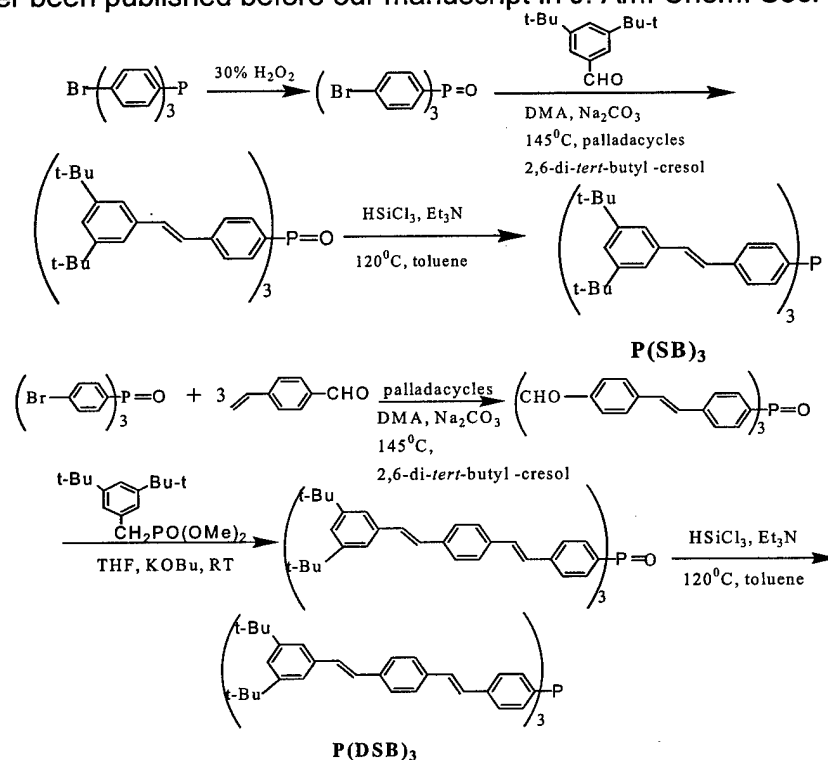
As reported previously, we have extensively investigated excitation energy transport processes in dendrimers and branching structures under the support of AFOSR. It was found that excitation energy transfer efficiency in certain light-harvesting dendrimers and branching structures can be as high as 99% and the energy migration has been characterized as a collective-coherent process. Another important discovery in the PI's group was that coherent energy migration process most frequently occurs in certain strong electronic coupling systems, for example, nitrogen cored dendrimers and branching structures. This implies that many chromophores participate in the excitation and emission process and this may lead to systems with enhanced transition dipole moments as well as improved light-harvesting capabilities. To understand the connection of a coherent energy transfer process with enhanced nonlinear properties in a series of nitrogen cored dendrimers and branching structures as well as to reveal new properties in new materials, we have carried out the synthetic methodologies to change some of the critical parameters of materials in order to focus on the origin of the enhanced optical properties. This has included the synthesis of phosphorous (P) and lanthanide ( $\text{Pr}^{3+}$ ) containing branching structures as well as

chromophore-functionalized dendrimers that incorporate transition metal nanoparticles.

## 2.1 Phosphorous cored branching structures

### 2.1.1 Synthesis of *tri*[4-(3',5'-di-*tert*-butylstyryl)phenyl]phosphine (*P*(*SB*)<sub>3</sub>) and *tri*[4-(3',5'-di-*tert*-butyldistyrylbenzenyl)phenyl]phosphine (*P*(*DSB*)<sub>3</sub>)

The synthesis of  $\pi$ -conjugated triarylphosphine was carried out in the PI's laboratory. The key step is to couple an oxidized phosphine  $\text{PO}(\text{C}_6\text{H}_4\text{Br})_3$  to aryl-aldehyde moieties. Then the oxidized tris(4'-formylstilbenyl)phosphine coupled with benzylphosphonate to give corresponding triarylphosphine (see Figure 5). The advantage of this strategy is subject to purification the product in comparison with the strategy that was used by the reaction of an aldehyde moiety at the dendron with bis(phosphonate) moiety at the core. Recently, functionalizations of these materials have been suggested for applications in nonlinear optics (Prof. John D. Protasiewicz, Case Western Reserve University) and sensors (Prof. Isabelle Leray, France). However, such phosphorous cored branching structures had never been published before our manuscript in *J. Am. Chem. Soc.*

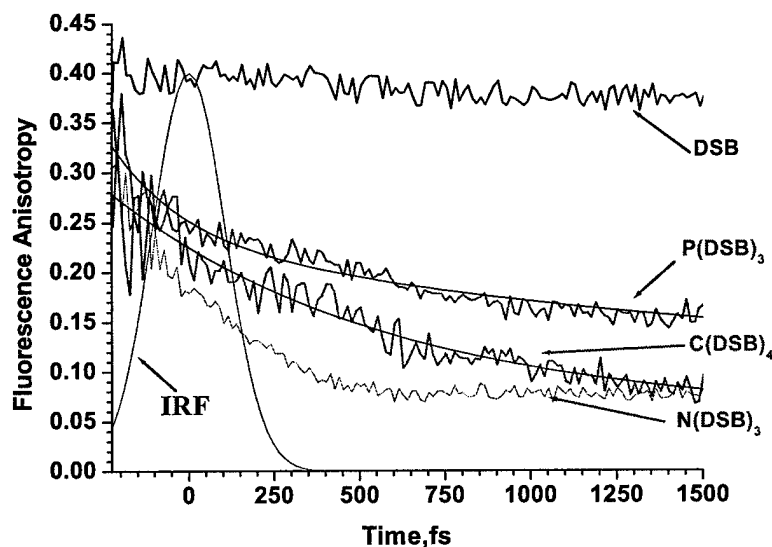


**Figure 5** Synthesis of phosphorous cored branching structures *P*(*SB*)<sub>3</sub> and *P*(*DSB*)<sub>3</sub>

### 2.1.2 Ultrafast dynamics of different cored branching structures

To explore an important role of the core element in intramolecular interactions and optical excitation energy transfer, we have investigated the ultrafast dynamics of *P*(*DSB*)<sub>3</sub> with the same building block, but different cored *N*(*DSB*)<sub>3</sub> and *C*(*DSB*)<sub>4</sub> systems. The measurements of ultrafast emission were

carried out by a graduate student (Mr. Mahinda Ranasinghe) and a postdoctoral assistant (Dr. Ying Wang) who synthesized these molecules. We have found that the anisotropy decay and residual value were very different for the four systems which were all composed of DSB branches (see Figure 6). The DSB chromophore itself has an expected rotational diffusion anisotropy profile that starts at 0.4 and decays very slowly (relatively) with a time constant on the order of  $\sim 100$  ps. the nitrogen cored system shows single exponential decay with the fastest anisotropy decay time of 57 fs and residual value close to 0.1. This implies that this system is very close to a planar geometry. The carbon system has a much longer decay time in comparison to the nitrogen system, and ultimately its residual value ( $\sim 0.075$ ) is much lower than that of nitrogen. Finally, the phosphorous system has a relatively high residual anisotropy value and the decay time is faster than that of carbon and slower than that of nitrogen cored systems. This suggests that the interaction and orientation of the chromophores for phosphorous branching structure is in between the nitrogen and carbon cored branching structures. Indeed, there is a special advantage for the nitrogen core due to the strong delocalization of unpaired electrons with the pi system.



**Figure 6** The fluorescence anisotropy decay of three branching structures and their linear counterpart

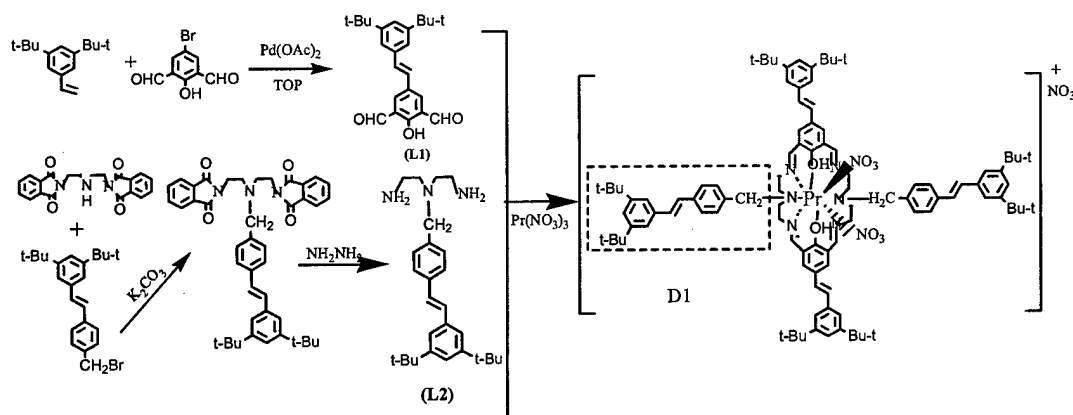
## 2.2 Lanthanide centered branching structures

### 2.2.1 Synthesis

Incorporation of lanthanide organic complexes into light-emitting and amplifier devices has inspired us to design and synthesis of new lanthanide based materials. Instead of non-conjugated chromophores that are frequently used in coordination with lanthanide, we have synthesized a system that lanthanide was encapsulated by four  $\pi$ -conjugated chromophores. This is also the first example of the ligands that participates as an integrated conjugation with

lanthanide. Indeed, we are using this material as a model system to investigate the roles of conjugation and excited state dynamics in novel  $\pi$ -conjugated polymer-based lanthanide materials.

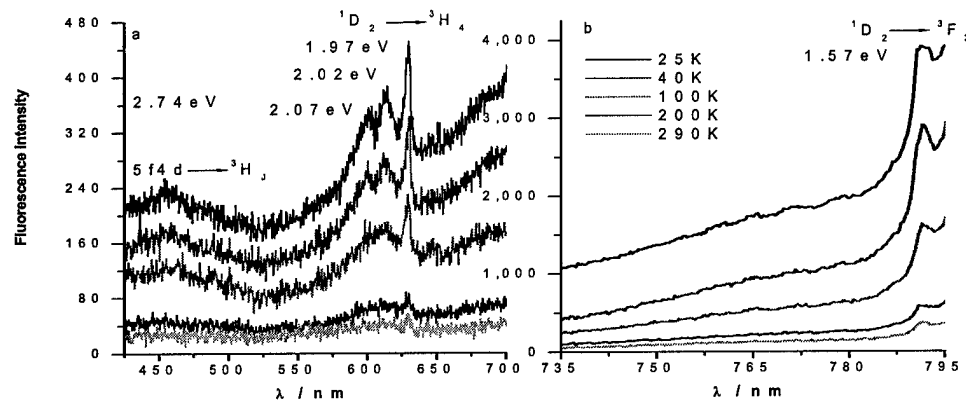
Using a lanthanide salt as a template, the branching structure was synthesized by the reaction of an aldehyde group of stilbene L1 with the amino group of stilbene L2 (see Figure 7). However, olefination of L1 and L2 is different. The L1 was synthesized by Heck coupling, while olefination of L2 was performed by Horner-Wadsworth-Emmons approach, which involved the aldehyde functionality of *p*-tolualdehyde and the anion of phosphonate 3,5-di-*tert*-butylbenzene. Our synthetic (structure) advantage for this molecule is to permit a facile manipulation of the ligands on the molecule level, which allows for the fulfillment of the design criteria for a given application.



**Figure 7** Synthesis of  $Pr^{3+}$  centered  $\pi$ -conjugated branching structures

### 2.2.2 Optical properties

We have investigated the photophysical properties of this novel lanthanide centered branching structures by steady-state absorption and emission spectroscopy. The line absorption originated from  $^3H_4 \rightarrow ^3P_0$  and  $^3H_4 \rightarrow ^1D_2$  transition is observed although other two absorption lines are shielded by the Schiff base. We have also observed narrow line shaped emission which results from the sensitization of stilbene and Schiff base functionality (see Figure 8). Complete or very efficient energy transfer takes place from the ligand to  $Pr^{3+}$ . The emission properties of  $Pr^{3+}$  provide new opportunities to apply this material in the near infrared (NIR) for optical communication and incorporate this material into device structure for light-emitting.

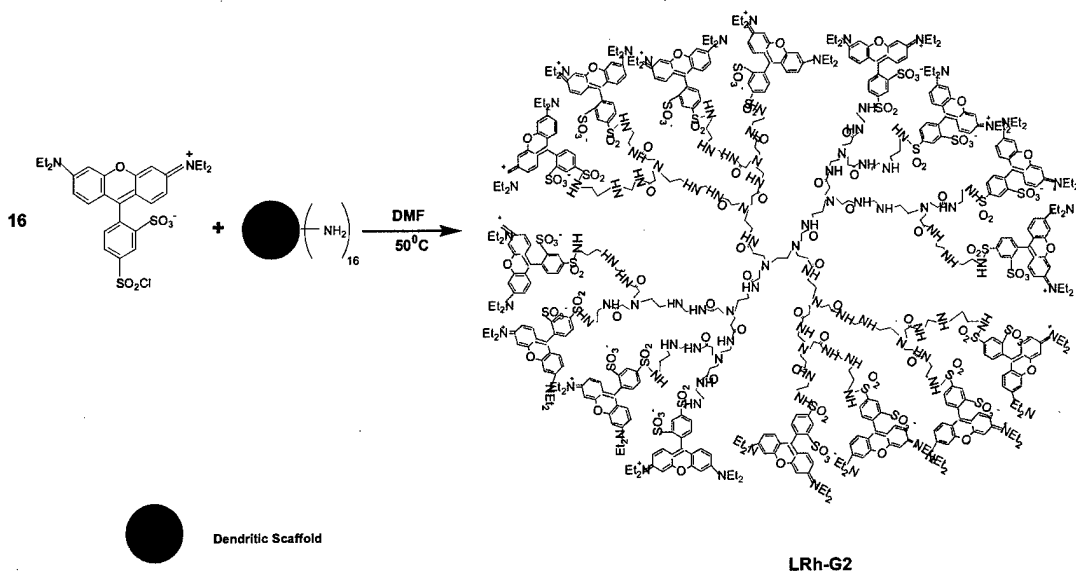


**Figure 8** The emission spectrum of the branching structure doped in PVB film, at various low temperatures upon laser excitation at 4.48 eV.

### 2.3 Photoactive dendrimers and dendrimer encapsulated metal nanoparticles

#### 2.3.1 Synthesis of chromophore-functionalized poly(amidoamine) dendrimers

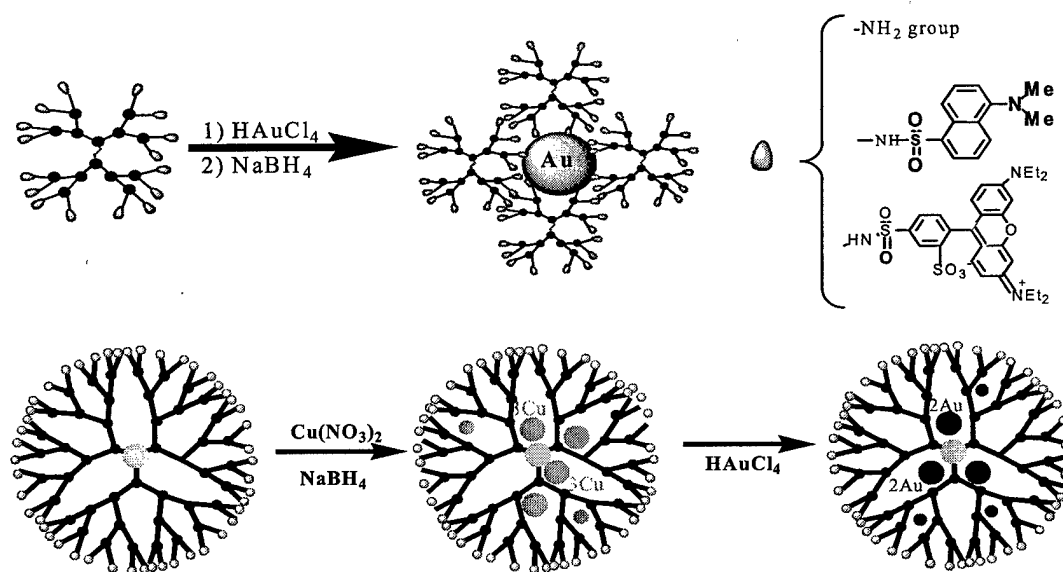
Functionalization of poly(amidoamine) (PAMAM) dendrimer by organic chromophores at the periphery provides the possibility to observe enhanced emission as well as two-photon absorption. Therefore, the synthesis and characterization of dansyl and rhodamine functionalized PAMAM dendrimer G2 was carried out in the PI's group. The sulfonamide PAMAM was prepared by common reaction between sulfonic acid chloride and primary amino groups (see Figure 9). The dansylated G2 (DNS-G2) was purified by flash chromatography and the product was confirmed by NMR, IR spectroscopy. Purification of rhodamine functionalized G2 (LRh-G2) is more difficult than that of DNS-G2. An exhaustive dialysis separation followed by a gel permeation filtration method was effective in separation of this macromolecule with free rhodamine and incompletely converted dendrimers. Characterization of LRh-G2 was carried out by MALDI-TOF, NMR, IR, UV as well as time-resolved fluorescence spectroscopy.



**Figure 9** Synthesis of rhodamine functionalized PAMAM dendrimer

### 2.3.2 Synthesis of dendrimer nanocomposites (DNCs)

We have used PAMAM dendrimers either as organic stabilizer or as a scaffolding agent to prepare DNCs. In general, gold nanoparticles were formed by reduction of gold-dendrimer complex using  $\text{NaBH}_4$ . The procedure in which the fabrication was carried out determined the overall topology of the nanocomposites. Depending on the topologies of dendrimers, gold nanoparticles can be surrounded by several dendrimers or encapsulated in the interior of dendrimers (see Figure 10). More specifically, gold nanoparticles in the size of 2~3 nm can be prepared by a ligand-exchange method.

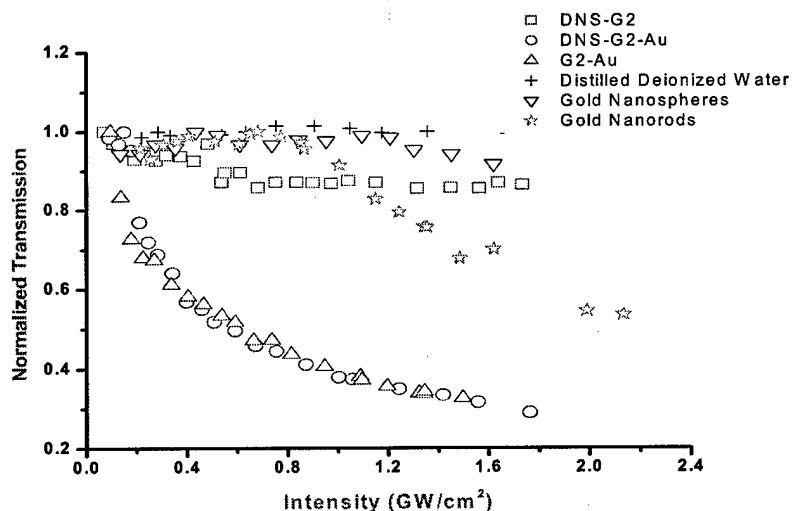


**Figure 10** Synthesis of dendrimer nanocomposites (DNCs) with different topologies

### 2.3.3 Optical properties of dendrimer nanocomposites (DNCs)

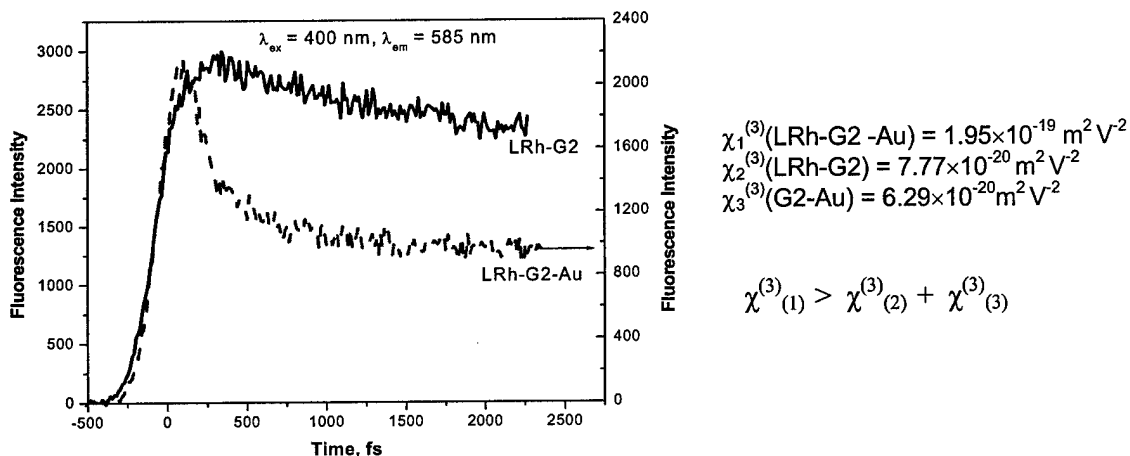
The optical properties of DNCs also including chromophore-functionalized dendrimer nanocomposites (DNS-G2-Au and LRh-G2-Au) were investigated for strong optical limiting and enhanced nonlinear effect. We have found that there is strong optical limiting effect in particular dendrimer nanocomposites and the nonlinear absorption is dependent of the geometry of these gold nanostructures as well as the morphology of dendrimers (see Figure 11). The two-photon absorption (TPA) coefficient for the gold nanorods is 5 orders of magnitude larger than gold nanospheres. As for the same morphology of G2-NH<sub>2</sub>-Au and DNS-G2-Au nanocomposites, the same NLT effect was observed.

We used ultrafast fluorescence spectroscopy to investigate intramolecular interactions of rhodamine-functionalized dendrimers (LRh-G2) and intermolecular interactions of dendrimers with gold nanoparticles (see Figure 12). A rise time followed by a fast decay component demonstrated this strong intramolecular interaction. In the presence of gold nanoparticles, the fast fluorescence decay dynamics and the enhancement of metal emission evidenced energy transfer from rhodamine to gold nanoparticles. In addition, we also used degenerated four wave mixing (DFWX) to investigate third-order nonlinear optical properties of this DNCs (LRh-G2-Au). It was found that LRh-G2-Au nanocomposites possess the enhanced nonlinear optical activity in comparison with LRh-G2 and G2-Au. This enhancement has been attributed to the local field effect that originates from strong dipole interactions between the excited chromophore molecules and gold nanoparticles. Further investigations of the enhancement of TPA in these novel chromophore-functionalized dendrimers and dendrimer encapsulated transition metal nanoparticles are being carried out in the PI's group.



**Figure 11** Nonlinear absorption of gold based nanostructures





**Figure 12** ultrafast emissions of rhodamine-functionalized dendrimer LRh-G2 and dendrimer nanocomposites LRh-G2-Au. LRh-G2-Au gives the enhanced nonlinear optical activity

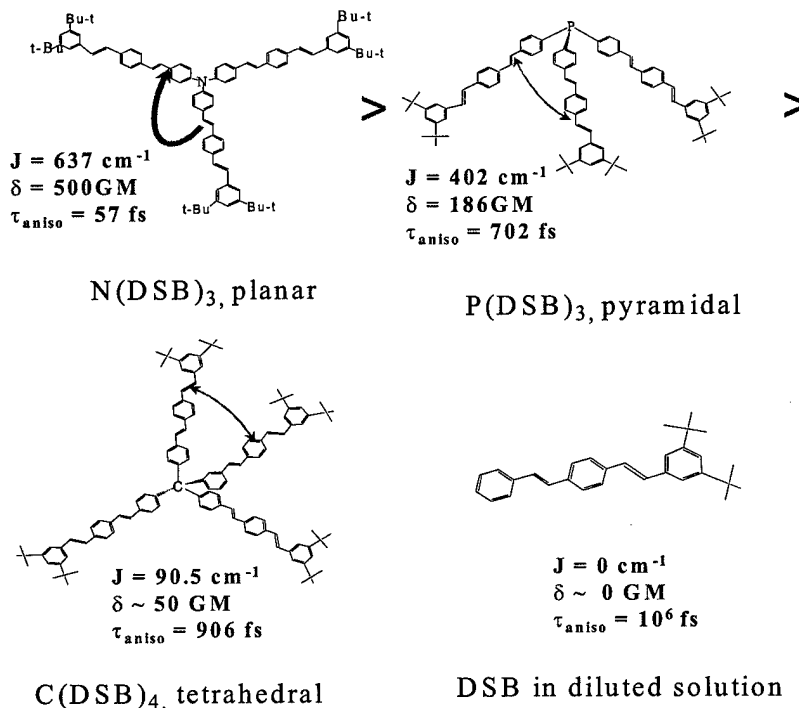
### 3. Novel two-photon absorption materials

The enhancement of two-photon absorption (TPA) continues to be an important issue related to many applications in material science and biological systems. Investigations of structure-property relationship of TPA chromophores have provided an insight into the design of molecules with large nonlinear optical effect. The common design criteria for large two-photon activity are the increasing conjugation length and interaction strength of donor-acceptor molecule as well as planarity and dimensionality of the molecules. However, until now, most known organic chromophores possess TPA cross sections ( $\delta$ ) on the order of  $10^3$  of GM (Göppert-Mayers,  $1\text{GM} = 10^{-50} \text{cm}^4\text{s}$  per photon per molecule) with fs pulses. Therefore, the search for enhanced TPA materials is challenging. Strong intramolecular or intermolecular interactions may perturb a two photon allowed  $A_g$  state and alter the reorientation of the transition dipoles. Thus, the enhanced TPA may occur in branching structures with strongly interacted chromophores. To test our hypothesis, we have carried out the measurements of  $\delta$  in a series of branching structures in order to focus on the origin of the enhanced TPA properties. The structures, TPA cross sections ( $\delta$ ), interaction strengths ( $J$ ) and fluorescence anisotropy decay times ( $\tau$ ) are shown below.

#### 3.1 Distyrylbenzene (DSB) based branching structures

Two photon excited fluorescence measurements were carried out for these systems with 75 fs pulses and excitation at 820 nm. In these branching structures,  $\delta$  is significant enhanced compared with their linear counterpart DSB. The magnitude of  $\delta$  is very sensitive to the molecular geometry that strongly relates to the interaction strength and exciton delocalization among branches (see Figure 13). The planar  $N(\text{DSB})_3$  shows the strongest interaction strength (or

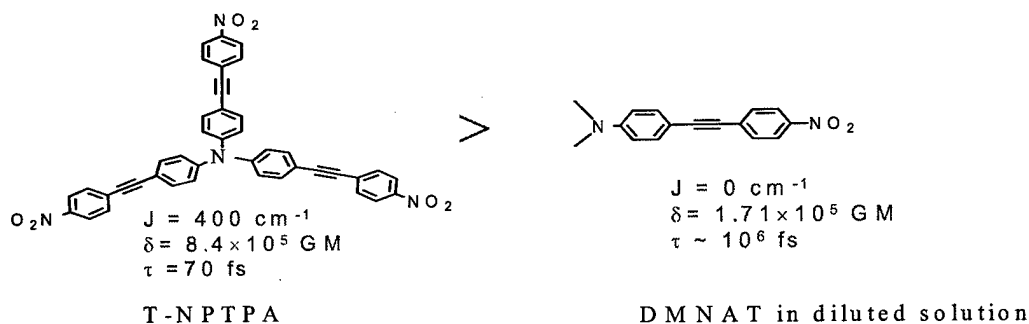
strongest exciton delocalization), the fastest fluorescence anisotropy decay and the largest enhancement of TPA, while the pyramidal P(DSB)<sub>3</sub> and tetrahedral C(DSB)<sub>4</sub> show weak intramolecular interaction and small enhancement of TPA.



**Figure 13** Enhanced TPA observed in these novel DSB branching structures. The enhancement corresponds to an increase in the strength of intramolecular interaction ( $J$ ) and a decrease in the time-resolved fluorescence anisotropy decay time ( $\tau_{\text{aniso}}$ ). This implies that Intramolecular interactions are important and should be taken in to account for enhanced NLO properties.

### 3.2 4-nitrophenylethynyl benzene based branching structure

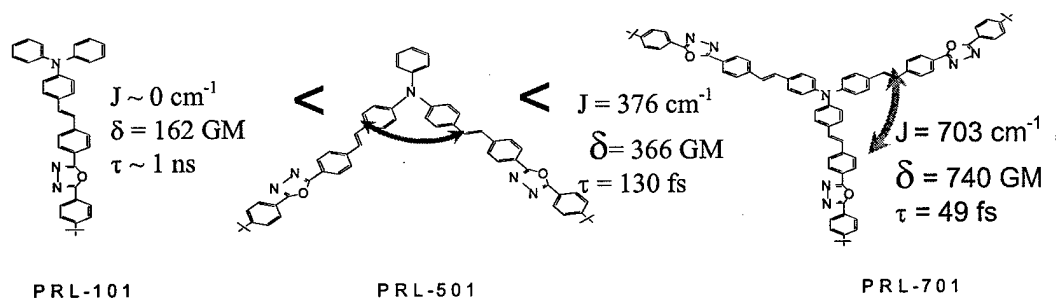
We used nonlinear transmission and degenerated four-wave-mixing methods to measure two-photon absorption coefficient from the following systems (see Figure 14). The samples were excited at 532 nm with 8 ns pulse. The enhanced  $\delta$  was observed in octopolar tris-4,4',4''-(4-nitrophenylethynyl)triphenylamine (T-NPTPA) system in comparison with 4-N,N-dimethylamino-4'-nitrotolane (DMNAT) monomer. Pump-probe and time-resolved fluorescence measurements have been carried out to investigate the origin of the enhancement. It was found that the initial electronic delocalization occurred in the time scale of femtosecond, while charge transfer stabilization taken place in the time scale of picosecond. We have attributed this enhancement to the strong coherent interactions among the arms. This interaction results in localized excited-states that strongly perturbed the two-photon allowed  $A_g$  states.



**Figure 14** The enhanced  $\delta$  observed in an octopolar system

### 3.3 [4-(*tert*-butyl)phenyl-1,3,4-oxadiazol-2-yl]phenyl-1-ethyl benzene based branching systems

In collaboration with Prof. P. N. Prasad in University of New York at Buffalo, we have carried out the measurements of  $\delta$  by two photon excited fluorescence method with 75 fs pulses and excitation at 820 nm. These branched architectures consist of the same TPA chromophores, but the number of chromophores is different. We observed significant enhancement of TPA for trimer system compared with monomer (see Figure 15). To illustrate excited-state dynamics, femtosecond pump-probe experiment was carried out in the PI's group. We have found that there is the fast anisotropy decay with time constant of 49 fs for the trimer and 139 fs for the dimer. These fast anisotropy decays signify the strong interactions among the branches. Specially, a trimer system showed the fast depolarization and the largest enhancement of TPA. This implies that intramolecular interaction and exciton delocalization should contribute to the enhancement of TPA.



**Figure 15** Enhancement of  $\delta$  observed in multi-branched donor- $\pi$ -acceptor systems

In summary, regardless of any types of multi-branched chromophore systems, significant enhancement of TPA was observed compared with its linear chromophore either by counting the effective number of  $\pi$ -electrons or the number of chromophores (Table 1). Importantly, we have found that N(DSB)<sub>3</sub> gives the same order of  $\delta$  as obtained from strong donors- $\pi$ -acceptor system (PRL-701). This implies that intramolecular interaction and exciton delocalization should take into account for the enhancement of TPA.

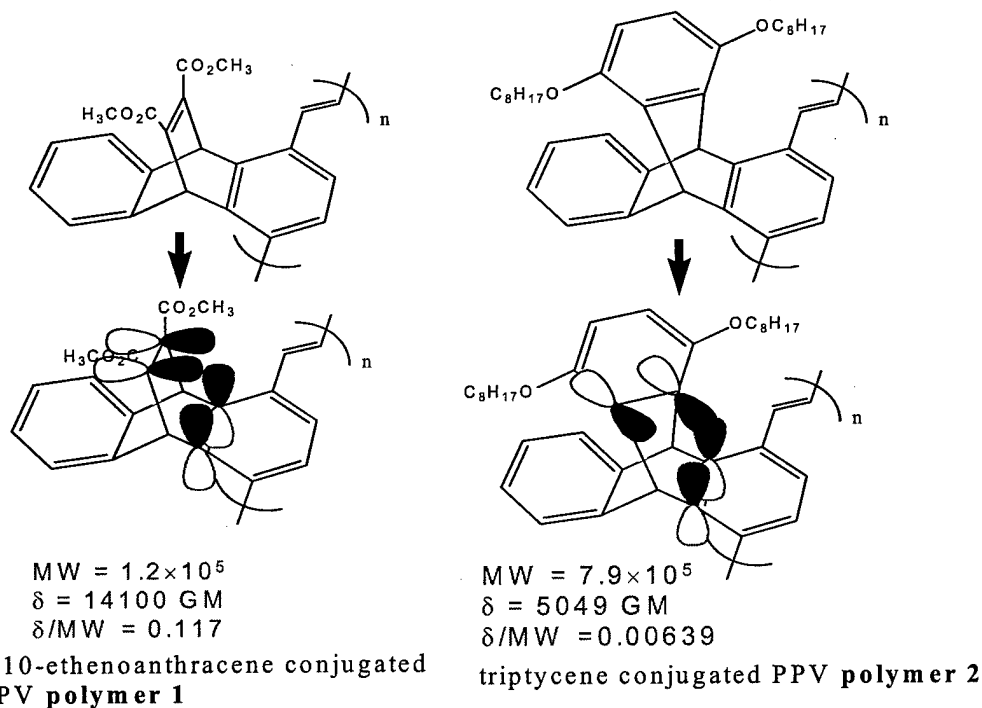
**Table 1** Relation between the enhanced TPA and the counting numbers

Compound	$\delta$ (GM)	Number of effective electrons ( $N_e$ )	Number of branched chromophores ( $N_c$ )	$\delta/N_e$	$\delta/N_c$	Comments
N(DSB) <sub>3</sub> P(DSB) <sub>3</sub> C(DSB) <sub>4</sub> DSB	500 186 50 0	38 38 44 22	3 3 4 1	13.16 4.89 1.14 0	166.67 62 1.14 0	Cooperative enhancement of TPA in all DSB branching structures. N(DSB) <sub>3</sub> gives the largest enhancement.
T-NPTPA DMNAT	* $8.4 \times 10^5$ * $1.71 \times 10^5$ *: nanosecond pulse	48 16	3 1	$1.75 \times 10^4$ $1.07 \times 10^4$	$2.8 \times 10^5$ $1.71 \times 10^5$	$\delta$ was enhanced to 1.63 times of monomer after normalization either by the number of electrons and chromophores
PRL-701 PRL-501 PRL-101	740 366 162	41.5 34.5 25.5	3 2 1	17.8 10.6 6.35	246.7 183 162	Largest enhancement of TPA observed in PRL-701 system

### 3.4 Novel hyperconjugated poly(p-phenylene vinylenes)

We have found that the branching structures, which have nitrogen as the central unit demonstrated good nonlinearity due to the persistence of planar geometry leading to strong electronic delocalization. Unfortunately, at much higher dendrimer generations (higher than the systems we have studied previously) this planarity in the nitrogen-centered systems will relax and subsequently the strong electronic delocalization will decay. Therefore, we are seeking for rigid, planar fused branching centers to enhance electronic coupling between the cores and branches.

The Investigations started from two polymers (synthesized by Timothy Swager's group) that have the same conjugated chains, but different fused cores (see Figure16). The measurement of TPA demonstrated that polymer 1 has much higher two-photon activity than polymer 2. The reason for this is due to the electron-deficient double bond in polymer 1 interacts strongly with polymer backbone in a hyperconjugated fashion than phenyl unit does in polymer 2. This result provided how the branching center can interact with long conjugated polymer chains. Indeed, the mode of interaction shown here are important in guiding to design multi-branched molecules without breaking the conjugation or the planarity of the molecules. Certainly, it is possible to design and synthesis dendrimer with highly conjugated, planar geometry by connection the branches with the rigid, planar fused cores as increasing dendrimer generation.



**Figure 16** Promising TPA materials with hyperconjugated architectures

#### 4. Correlation of enhanced TPA with anisotropy decay time

We have demonstrated the strong intramolecular interactions lead to cooperative enhancement of TPA in certain branching structures. Therefore, it is natural to ask how the coupled branches correlate with the enhanced TPA or how the excited state dynamics can be used to illustrate the enhanced nonlinear properties. Indeed, this is an unexplored area in which we are going to resolve. Initially, we only investigated the simplest branching structures, i.e. trimer systems, to find some relationship of structure-excited state dynamics-enhanced TPA. Understanding of this relationship would provide a new criterion to design molecules that combine large TPA with other useful chemical and optical properties for application in optoelectronics and biophotonics.

Ultrafast time-resolved fluorescence and pump-probe experiments have been carried out to investigate anisotropy decays in these particular multi-branching structures since the anisotropy decay can be used to illustrate excitation energy transfer processes that follow the reorientation of the transition dipole as a result of depolarization of emission dipole. Thus, the depolarization induced by energy transfer dynamics will reflect exciton-coupling strength, i.e. the strength of intramolecular interaction. As discussed previously, we have characterized the interaction strength by depolarization time and demonstrated the strong coherent electronic interaction occurred in  $N(\text{DSB})_3$ , PRL-701 and T-NPTPA systems.

In these three centrosymmetric branching structures, the nonpaired electrons of the nitrogen atom are participating in the conjugation with  $\pi$ -electrons in the neighboring chromophore units. Thus, excitations are extensively delocalized compared with other molecules investigated here. Ultrafast fluorescence anisotropy decay and pump-probe experiment demonstrated that the branches are communicated each other through strong coherent electronic interactions. The measurements of TPA give the largest enhancement of TPA in three trimer systems compared with their linear chromophores. This enhancement correlates the fastest depolarization of emission dipole. Also, strong coherent electronic interactions lead to exciton splitting at  $B_u$  states (defined as  ${}^1B_u$ ) in  $N(\text{DSB})_3$  system, while charge redistribution and coherent electronic interaction may perturb the excited states of PRL-701 and T-NPTPA, respectively. After two-photon excitation, one can expect high-lying  $A_g$  state could exist due to the transition dipole coupling between  $A_g$  and  $B_u$  state. Thus, strong interactions lead to substantial mixing between single and double excited states and finally enhance the dipole moment  $M_{ge}$ . In addition, a large number of excited states may also involve in the enhancement of TPA. Measurements of two-photon absorption spectrum at various wavelengths can reflect the involvement of different excited states. A theoretical and more experimental understanding of this correlation is currently underway in the PI's laboratory.

## 5. Publications

1. Ranasinghe, M.; Murphy, P.; Lu, Z., Huang, S. D.; Twieg, R.J. and Goodson, T. "Temperature Dependence of Excitation Energy Transport in Benzene Branching Molecular System" *Chem. Phys. Letts.*, **2004**, 383, 411.
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14. Ranasinghe, M.I.; Varnavski, O.P.; Pawlas, J.; Hauck, S.I.; Louie, J.; Hartwig, J.F.; Goodson, T., "Femtosecond Energy Transport in Triarylamine Dendrimers," *J. Am. Chem. Soc.* **2002**, 124, 6520.
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## **6. Participation/presentation at meeting, conference, seminars**

### **6.1 Invited papers presented at meetings**

- (1) Society of Physicists and Optical Engineers and Instrumentation (SPIE), Perth, "Quantum Optical Properties of Novel Organic Materials." Nov. **2003**.
- (2) Beckman Frontiers of Science Symposium, Irvine, "Novel Organic Branched Materials for Optical Applications, Nov. **2003**.
- (3) International Conference on Unconventional Spectroscopy, Leuven, "Ultrafast Dynamics of Novel Branched Macromolecules", Sept. **2003**.
- (4) International Conference on Optical Limiting Materials, Arizona, "Nonlinear Optical Properties of Metal Nanostructured Materials", Sept. **2003**.
- (5) American Chemical Society National Meeting, New Orleans, "Investigations of Electric Field Enhancement in Metal Nanotopologies" March **2003**.

- (6) International Wire and Cable Symposium-Defense Fiber Optical Applications, "Novel Macromolecular Materials for Optical Applications," Nov. **2002**.
- (7) Approaches to Combat Terrorism, Washington DC, Intelligence Community and National Science Foundation Workshop, Nov. **2002**.
- (8) International Conference on Organic Nanophotonics, France, "Optical Spectroscopy of Novel Dendrimer Metal Nanocomposites," Aug. **2002**.
- (9) Gordon Research Conference, Electron Donor and Acceptors, "Energy Migration in Organic Dendrimers," Aug. **2002**.
- (10) Gordon Research Conference, Electronic Processes in Organic Materials Conference, "Optical Excitations in Organic Dendrimers and Dendrimer Metal Nanocomposites," July, **2002**.
- (11) Society of Physicists and Optical Engineers and Instrumentation Conference (SPIE), Committee Director of Metal Nanostructured Materials Program, July, **2002**.
- (12) National meeting of Black Chemist and Chemical Engineers (NOBCCHE)  
Invited speaker at symposium held by Rohm and Haas Inc. "Organic Macromolecular Optical Applications," March, **2002**
- (13) International Conference on Organic Nonlinear Optics, "Optical Excitations in Organic Dendrimers and Dendrimer Metal Nanocomposites," Dec., **2001**.
- (14) International Conference on Dendrimers, "Optical Excitations in Organic Dendrimers Investigated by Ultrafast Spectroscopy," Japan, Oct. **2001**.
- (15) International Conference of Quantum Optical Advancements, "Generation of Squeezed States of Light in an Organic Polymer," July **2001**.
- (16) SPIE, "Ultrafast Investigations of Energy Transfer in Organic Dendrimers," July **2001**.
- (17) Army Research Laboratory Sensor Workshop, "Optical Limiting Properties of Dendrimer Metal Nanocomposites," March **2001**.
- (18) Optical Society of America, Ultrafast Phenomena, "Time-Resolved Spectroscopy of Dendrimers," July, **2000**.
- (19) National Science Foundation Materials Workshop, "Optical Properties of Dendrimers and Dendrimer Metal Nanocomposites," Oct., **2000**.

### **6.2 Papers contributed at meetings**

- (1) International Symposium on Dendrimers, "Optical Properties of Dendrimer and Dendrimer Metal Nanocomposites" Germany, Sept., **2003**.
- (2) Gordon Research Conference, "Ultrafast Excitations in Branched Molecules," Electron Donor and Acceptor Conference, July, **2000**.
- (3) Pacific Chemistry Meeting '00, American Chemical Society, "Time-resolved Luminescence in Dendrimers," Dec. **2000**.
- (4) American Physical Society Meeting, "Time-resolved Luminescence in Dendrimers," March, **2000**.

### **6.3 Invited talks at other institutions**

- (1) Bowling Green University, "Novel Organic Materials for Optical Applications", Nov. **2003**.
- (2) Wabash College, "Novel Organic Materials for Optical Applications" Oct. **2003**.



- (3) Grand Valley State University, "Novel Organic Materials for Optical Applications" August, **2003**.
- (4) University of Maryland-Laboratory of Physical Sciences, "Quantum Interference Effects in Organic Materials," May **2003**.
- (5) Massachusetts Institute of Technology, "Time-resolved Fluorescence and Nonlinear Optical Spectroscopy in Branched Macromolecules," May **2003**.
- (6) Georgia Institute of Technology, "Optical Excitations in Dendrimers," April, **2003**.
- (7) University of Texas, Austin, "Optical Excitations in Dendrimers," Feb. **2003**.
- (8) University of Miami, "Optical Excitations in Dendrimers," Feb. **2003**.
- (9) Central Michigan University/ Dendritic Nanotechnologies, "Optical Excitations in Dendrimers," Jan. **2003**.
- (10) Michigan Molecular Institute, "Nonlinear Optical Properties of Organic Dendrimer Metal Nanocomposites," Nov. **2002**.
- (11) North Carolina State University, "Optical Excitations in Dendrimer Light Harvesting Materials," Nov. **2002**.
- (12) University of Toronto, "Optical Excitations in Branched Macromolecules," Sept. **2002**.
- (13) University of Washington (Seattle), "Optical Excitations in Branched Macromolecules," Oct. **2002**.
- (14) University of Oregon, "Optical Excitations in Branched Macromolecules," Oct. **2002**.
- (15) Andrews University (Michigan), "Real World Applications of Macromolecules," Sept. **2002**.
- (16) Northwestern University, "Ultrafast Investigations of Energy Transfer in Organic Dendrimers," June **2002**.
- (17) Purdue University, "Ultrafast Investigations of Energy Transfer in Organic Dendrimers," April, **2002**.
- (18) Notre Dame University, "Ultrafast Investigations of Energy Transfer in Organic Dendrimers," April, **2002**.
- (19) Iowa State University, "Ultrafast Investigations of Energy Transfer in Organic Dendrimers," Feb. **2002**.
- (20) University of Colorado-Boulder, "Ultrafast Investigations of Energy Transfer in Organic Dendrimers," Sept., **2001**.
- (21) Veridian Research Corporation, "Quantum Applications of Organic Nanostructures," June **2001**.
- (22) Energy Conversion Devices, "Ultrafast Spectroscopy of Organic Nanostructures," July **2001**.
- (23) Air Force Research Laboratory, "Nonlinear Optical and Time-Resolved Properties of Dendrimers and Dendrimer Metal Nanocomposites," March **2001**.
- (24) Montana State University, "Nonlinear Optical and Time-Resolved Properties of Dendrimers and Dendrimer Metal Nanocomposites," March **2001**.
- (25) Ohio State University, "Nonlinear Optical and Time-Resolved Properties of Dendrimers and Dendrimer Metal Nanocomposites," March **2001**.
- (26) University of Michigan, "Nonlinear Optical and Time-Resolved Properties of Dendrimers and Dendrimer Metal Nanocomposites," March **2001**.

- (27) Kent State University, "Nonlinear Optical and Time-Resolved Properties of Dendrimers and Dendrimer Metal Nanocomposites," March **2001**.
- (28) University of Windsor, "Optical Properties of Dendrimers and Dendrimer Metal Nanocomposites," April, **2001**.
- (29) Oakland University, Department of Physics, "Nonlinear Optical and Time-Resolved Properties of Dendrimers and Dendrimer Metal Nanocomposites," Nov. **2000**.
- (30) University of Oxford, U.K., "Quantum Optical Applications of Organic Materials," July, **2000**.
- (31) University of Detroit-Michigan, "Ultrafast Investigations of Nonlinear Optical Materials," April, **2000**.
- (32) Oakland University, Department of Chemistry, "Quantum Optical Effects and Nonlinear Transmission in Organic Dendrimers," February, **2000**.

### **7. New discoveries**

Excitation energy transfer processes in large conjugated dendritic architectures and branching structures have been investigated in the PI's group. An important discovery is the strength of interactions among closely spaced chromophores dominated the mechanism of optical excitation and the mode of energy transport. The interaction length (dendrimer generation) and the relative conformation between adjacent branches (molecular geometry) are important factors that strongly effect the exciton coupling dynamics and energy migration processes. We also discovered a new synthetic strategy for the synthesis of different cored branching structures. Novel dendritic architectures that permit large cross-sections for energy transfer have been constructed for light-harvesting proposes. The creation of organic-inorganic nanohybrides was found to be very useful for enhanced nonlinear optical effect. In addition, we also found that the anisotropy decay time correlates with the enhancement of TPA in certain branching structures. Strong intersegmental interaction and extensive exciton delocalization are a new design criterion for large TPA materials.

### **8. Honors/Awards**

04/01	College of Science Teaching Award, Wayne State University
09/00	Army Research Office Young Investigator Award
04/00	Burroughs Welcome Fund Travel Award
05/02	The Camille and Henry Dreyfus Foundation Teacher-Scholar Award
01/02	National Science Foundation CAREER Award
03/03	Wayne State University Career Development Award
02/03	Lloyd Ferguson Young Scientist Award (NOBCCHE)
02/03	Alfred P. Sloan Foundation Fellow

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