Communication

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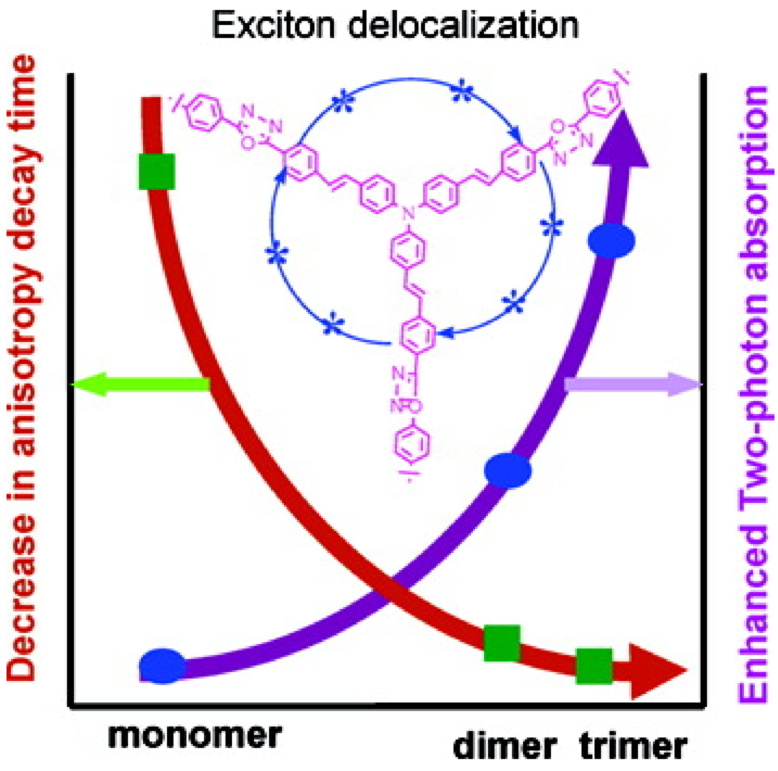

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Ultrafast Dynamics in Multibranched Structures with Enhanced Two-Photon Absorption

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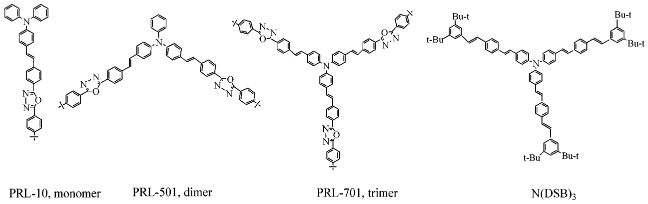
Organic materials with strong two-photon absorption (TPA) properties have motivated the creation of new photonic devices.[1] Significant enhancement of the TPA cross-section in multibranched structures has been reported.[2,3] The enhanced TPA properties have been theoretically investigated, and the importance of charge-transfer character and excitation delocalization has been shown.[4−6] Previously, time-resolved spectroscopic studies have been used to probe the mechanism of the enhancement.[7,8] However, the basic structure−function relationships regarding excited-state dynamics (transition moments, electronic coupling between levels, interaction with solvent) and enhanced TPA properties remain unclear. To further understand this important issue, a systematic set of branched chromophore systems that demonstrate the enhanced TPA properties were investigated using a combination of time-resolved spectroscopic techniques. The combined approach offers the capability of probing different dynamical processes in the excited states, such as population (T_1-process) and phase relaxation (T_2-process), which are ultimately related to the two-photon enhancement process. The description of ultrafast dynamics of these branched structures may provide a stronger basis for the suggestion of a mechanism of the enhancement based on excitonic coupling and delocalization.

The PRL branched structures and $N(DSB)_3$ are shown in Scheme 1. Table 1 summarizes the linear, two-photon absorption cross-section (δ) and time-resolved properties of the PRL series and $N(DSB)_3$. The maximum absorption and emission of the dimer and trimer (PRL chromophores) are red-shifted with respect to the monomer, suggesting that the lone pair electron on the central nitrogen atom is delocalized. Cooperative enhancement of the TPA cross-section was reported for the trimer and dimer as compared with the monomer, and this enhancement was partly attributed to the electronic coupling between the branches.[2] Theoretical studies have emphasized the importance of vibronic coupling,[9] as well as excitonic splitting,[5,6] which may provide more effective coupling channels and possibly enrich the TPA cross-section. To further understand the mechanism of the enhancement, the combined time-resolved spectroscopic measurements were carried out.

To probe the population decay (T_1-process) of the PRL series and to address the origin of the emission state, fluorescence lifetimes were measured, and the results are shown in Figure 1. From quantum yield and fluorescence lifetime measurements, the radiative decay time (τ_0) was calculated and showed a decrease with an increase in the number of branches (from 7.8 ns for monomer to 4.6 ns for trimer, Supporting Information). A decrease in the radiative lifetime implies that the emission of the trimer may stem from delocalized excitonic states,[6] which is also accompanied with the weak coupling of the trimer to the bath. This conclusion is also consistent with the larger three-pulse-photon-echo peak shift of the trimer as compared with the monomer and dimer (see Table 1). Indeed, the larger echo peak shift suggests a smaller total coupling of electronic transition frequency to the nuclear motions,[12] and this would correlate with the delocalization of excited state.[13]

Scheme 1. Structures of PRL Series and $N(DSB)_3$



To characterize the excitation delocalization and the mechanism of energy transfer in these branched structures, time-resolved fluorescence anisotropy measurements were carried out. Figure 2a shows the normalized anisotropy decays of the PRL series. The decays of the trimer and dimer are much faster than what is observed for the monomer. The monomer showed anisotropy decay similar to what is observed for rotational diffusion (∼50 ps). The fast anisotropy decay of trimer (deconvoluted with the instrumental response function) gave a decay time constant of ∼40 fs with a small residual anisotropy value. Our previous reports suggest that the fast anisotropy decay is a signature of strong intramolecular interactions.[10,11] For example, investigations with an amino−tolane trimer system showed a strong correlation of ultrafast anisotropy decay with intramolecular interaction strength and, subsequently, the enhanced nonlinear optical effect.[8] Similarly, the ultrafast dynamics (and related T_2-processes) that were observed in the PRL trimer system would suggest strong electronic coupling and a coherent energy transfer process due to strong intramolecular interactions. Thus, excitonic coupling may enrich the TPA properties.[5,6] However, recent calculations and experiments[14] have shown that in some cases the excitonic (Frenkel) model alone cannot explain the excited-state properties which are important to the understanding of the mechanism of the enhanced TPA. Beljonne et al.[5] have also suggested that an additional contribution from higher lying excited states may also be significant in similar systems.

To further probe these processes, pump−probe anisotropy measurements were carried out, and the results are shown in Figure 2b. Both dimer and trimer showed ultrafast anisotropy decays, while no decay was observed from monomer within the same decay time period. It is well-known that excited-state absorption (ESA)[15] can result in fast anisotropy decay in some cases and may contribute to the enhanced TPA cross-sections.[16] However, this does not seem to be the case for the trimer system investigated here. The similar anisotropy decay time (Table 1) that was measured by both pump−probe and fluorescence anisotropy suggests that both coherent excitations as well as coherent energy transfer primarily persist in this system. This trend observed in the PRL series (which showed the systematic enhancement of TPA) is consistent with what we have observed with similar N, P, and C centered branched

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Table 1. Linear, Nonlinear, and Time-Resolved Data of Multibranched Chromophore Systems

compound	Abs (λ_{max}, nm)	Flu (λ_{max}, nm)	δ (GM)	population decay time (ns)	echo peak shift (fs)	anisotropy decay time (upconversion) (fs)	anisotropy decay time (pump–probe) (fs)
PRL-101	398	458	87.5[a]	1.56 ± 0.1	0.6 ± 0.5	10^4	10^4
PRL-501	417	468	275[a]	1.77 ± 0.1	4.8 ± 0.2	50 ± 15	30 ± 15
PRL-701	420	472	600[a]	1.80 ± 0.1	6.0 ± 0.5	40 ± 10	40 ± 12
N(DSB)$_3$	419	468	500	1.80 ± 0.1	7.0 ± 0.3	57 ± 7[b]	40 ± 10

[a] From ref 2. [b] From refs 10 and 11.

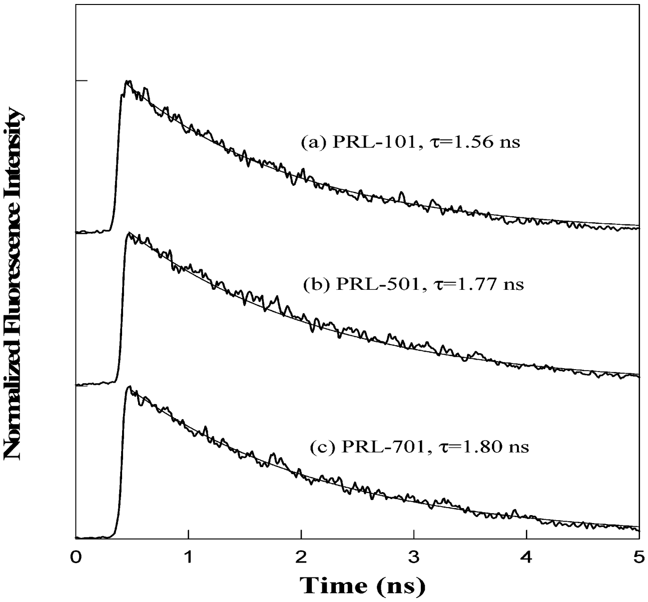

Figure 1. Fluorescence decays of PRL series.

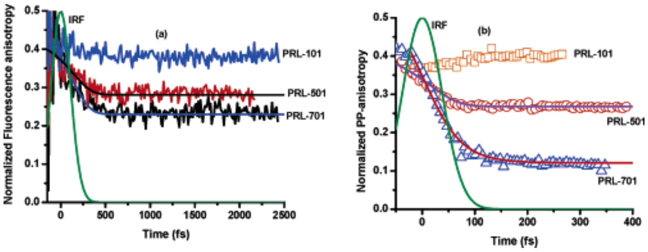

Figure 2. (a) Fluorescence anisotropy decay ($\lambda_{ex} = 410$ nm, $\lambda_{em} = 480$ nm) and (b) pump−probe anisotropy decays ($\lambda_{ex} = 415$ nm) of PRL series.

systems,[8,10,11] suggesting a correlation of ultrafast anisotropy decay (delocalization) with the mechanism of enhanced TPA properties. However, the mechanism of the enhanced TPA cross-sections reported for the PRL series may also extend beyond the exciton (Frenkel) model which has been used in the past to describe resonant nonlinear optical effects in J-aggregates.[17] Specifically, three-dimensional charge-transfer character may contribute to the enhanced TPA as well. It is also important to mention here that the covalently attached chromophore aggregates may show a degree of charge-correlation which is greater than that described for other chromophore aggregate systems. The charge-transfer character in these covalently attached chromophore aggregates may induce a coupling that cannot be accounted for by the Frenkel exciton model.

In conclusion, we have used a combined ultrafast time-resolved spectroscopic approach to probe the mechanism of the enhanced TPA properties in a dendritic model system as well as to provide a comparison to our previous ultrafast measurements of other trimer systems. Our results suggest that the optical excitation in the multibranched PRL chromophore systems is delocalized over several chromophores (branches) possessing weaker coupling with the bath, as suggested by the faster anisotropy decay (fluorescence upconversion and transition absorption), a larger initial photon echo peak shift values, and a longer population relaxation (fluorescence lifetime) dynamics. Indeed, these processes are sensitive to the degree of branching, and it is thus expected that the intramolecular interactions may persist beyond this situation of the trimer, but for larger dendrimer generations. The understanding of the mechanism and dynamics of a coherent delocalized state in an organic aggregate system and how this mechanism correlates with enhanced TPA properties is important in the particular design and applications of future nonlinear optical materials.

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Supporting Information Available: Experimental details, calculation of radiative decay times, complete ref 1b. This material is available free of charge via the Internet at http://pubs.acs.org.

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