

## ARTICLES

### Excited-State Deactivation of Branched Two-Photon Absorbing Chromophores: A Femtosecond Transient Absorption Investigation

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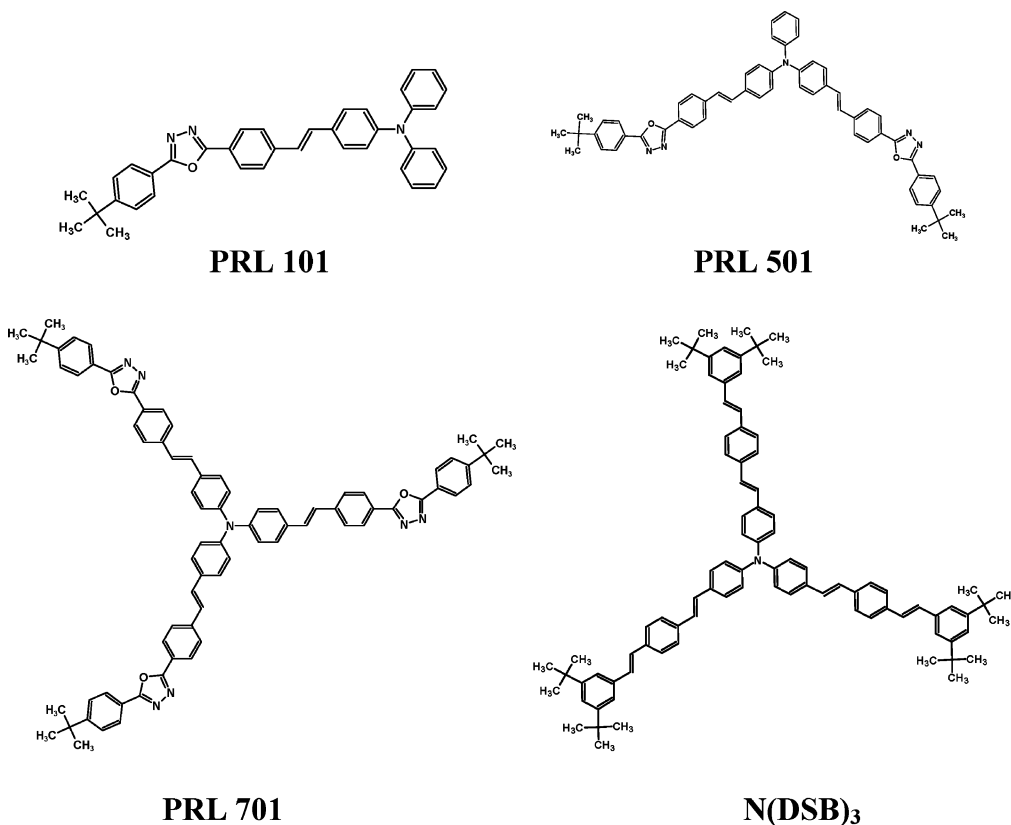
Branched macromolecular structures are now an important area of research for enhanced two-photon absorption (TPA) cross sections. The mechanism of this enhancement has been suggested as a complex interplay between intramolecular interactions and the extent of charge-transfer character in the branches. In order to probe these processes more clearly, excited-state dynamics of multibranching chromophores by means of femtosecond transient absorption spectroscopy are reported. Investigations have been carried out on the PRL dye series (PRL-101, PRL-501, PRL-701), which have shown cooperative enhancement of the TPA cross section. Upon photoexcitation, transient absorption measurements have shown the presence of a localized charge-transfer (intramolecular charge transfer, ICT) state independent of branching. The results point to ultrafast localization of charge in this particular system of chromophores. Pump–probe measurements in highly polar solvents have shown the presence of a nonemissive charge-transfer state which is a solvent stabilized and conformationally relaxed state. The population of this nonemissive state increases from monomer to trimer, and thus, it has been used as indicator of the polar nature of the Franck–Condon state. These results have shown an increase of charge-transfer character of the excited state with an increase in branching, and this explains the relative increase in the two-photon cross section of the PRL series.

#### Introduction

The development of organic molecular materials with large two-photon absorption (TPA) cross sections has recently been the focus of intense research interest.<sup>1,2</sup> Such molecules have potential applications in various fields such as two-photon laser scanning microscopy,<sup>3–6</sup> 3D microfabrication,<sup>7–10</sup> optical data storage,<sup>11–14</sup> optical limiting,<sup>15–16</sup> and photodynamic therapy.<sup>17</sup> For all of these applications, molecules with large TPA cross sections in the visible and near-infrared spectral region are desired. The discovery of new materials with improved TPA cross section has been focused on molecules with dipolar character.<sup>18–31</sup> Significant research has been carried out in

synthesizing novel materials with different donor–acceptor configurations to achieve higher two-photon absorption cross sections.<sup>1,21,23</sup> It has been shown that branched molecules can significantly enhance the TPA cross section by virtue of their increased chromophore density and cooperative interaction among the chromophores.<sup>32</sup> These results have stimulated research in the design and synthesis of several multiple branched chromophores with different configurations such as donor– $\pi$ -acceptor– $\pi$ -donor and acceptor– $\pi$ -donor– $\pi$ -acceptor.<sup>32–50</sup> Investigations intending to understand the mechanism of the enhancement have attributed it to interchromophore vibronic<sup>51</sup> and electronic coupling. Prasad and co-workers<sup>32</sup> have reported 7-fold enhancement for the tribranched chromophore compared to monomer in case of PRL series of dye molecules. It has been suggested by theoretical simulations that electronic coupling is

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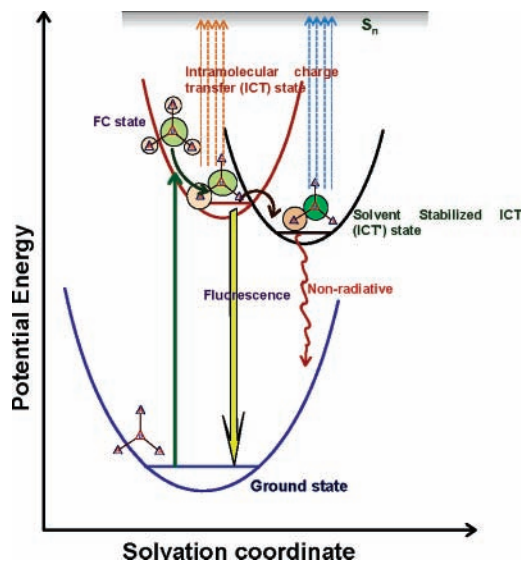


**Figure 1.** Chemical structures of the investigated chromophores.

nominal between the arms and vibronic coupling between the arms is significant in enhancing the TPA.<sup>51</sup> It has been shown theoretically and experimentally that, in amine-centered branched chromophores, the excitation is ultimately localized in one branch and the effective conjugation length is similar to that of monomer.<sup>40</sup> This process happens after a fast delocalization process.<sup>46a</sup> Indeed, understanding the intramolecular charge transfer (ICT) nature of the excited state with increased branching is crucial in the understanding of the TPA cross-section enhancement process.

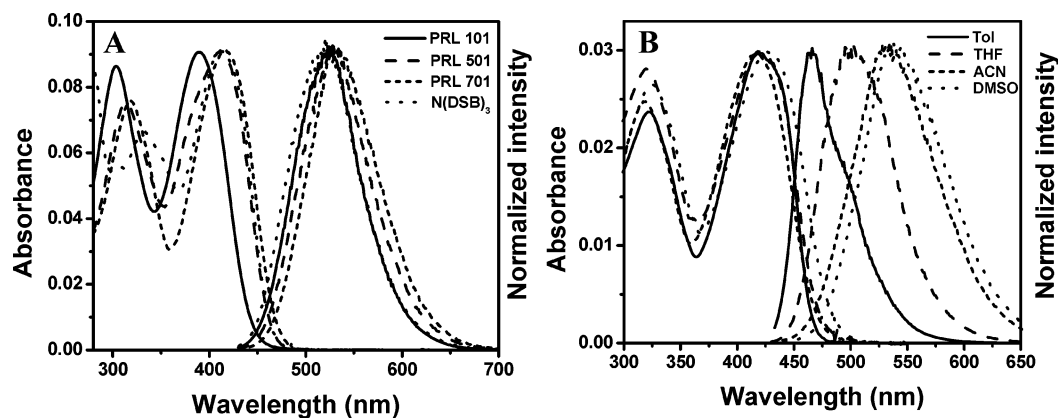
It has been well-established that the magnitude of TPA cross section in dipolar molecules depends on the degree of ICT upon excitation.<sup>1,52</sup> Thorough understanding of the structure–property relationships the design of molecules for larger TPA cross sections can be made by probing the mechanism behind the enhanced cross sections and by designing strategies to optimize the ICT character in donor– $\pi$ -acceptor systems. For a large number of donor– $\pi$ -acceptor systems, the degree of ICT state has been roughly estimated from the measurement of structural distortions associated with it, especially for the  $\pi$ -conjugated systems.<sup>18</sup> The bond length alternation (BLA) is considered to be a good measure of the degree of ICT character in ground state for many related  $\pi$ -conjugated systems.<sup>16,53–54</sup> The degree of ICT is varied by changing the donor–acceptor strength of substituents or nature of chemical bonding bridge. Although BLA is a good indicator of the CT nature of the systems, its applicability has been questioned in systems with aromatic rings as spacers.<sup>55</sup> Along with these, some other theoretical efforts have been made to evaluate the amount of ICT in  $\pi$ -conjugated push–pull molecules from the properties of electronegativity and polarizability of the substituents.<sup>56</sup> All the above indicators had a great degree of success in understanding several donor– $\pi$ -acceptor systems. However, it is not easy to evaluate the degree of ICT among the same set of donor–acceptors with an increase in branching. Most of the

**SCHEME 1: Mechanistic Diagram Showing the Excited-State Deactivation of the Investigated Chromophores<sup>a</sup>**



<sup>a</sup> FC represents the Franck–Condon state.

investigations aimed at understanding the charge-transfer nature of the TPA molecules have relied mainly on optical absorption and steady-state fluorescence. However, a clear understanding of the nature of the excited-state can be achieved with the aid of ultrafast spectroscopic investigations such as fluorescence upconversion and transient absorption. Although some investigations of this kind are available in the literature for the linear donor– $\pi$ -acceptor systems, the number of reports for the molecules with branching symmetry is limited. We have earlier observed that, in the series of PRL molecules, the initial state is a delocalized state with  $C_3$  symmetry which gets localized very fast.<sup>46</sup> We have also carried out fluorescence upconversion



**Figure 2.** (A) Optical absorption spectra of the monomer (PRL-101), dimer (PRL-501), trimer (PRL-701), and  $N(\text{DSB})_3$  in acetonitrile (ACN). The normalized emission spectra of the dyes in ACN are also given. (B) Optical absorption and steady-state emission spectra of PRL-701 in different solvents (toluene (Tol), tetrahydrofuran (THF), acetonitrile (ACN), and dimethyl sulfoxide (DMSO)).

measurements<sup>43–45</sup> on 4,4',4''-tris((4-nitrophenyl)ethynyl)triphenylamine (T-NPTPA) to understand the excited-state dynamics and have observed that the presence of an initial delocalized state followed by a charge separated state. Also, Rogers et al.<sup>47</sup> have carried out time-resolved investigations on a two-photon absorbing chromophore with donor- $\pi$ -donor system of AF-455 to correlate with TPA behavior. They have observed the presence of an ICT state on photoexcitation which gets solvated, but the spectral features of the transients have not been investigated. Similar investigations have also been carried out on a related chromophore of triazine by Li et al.<sup>48</sup> using fluorescence upconversion and transient absorption. They have observed a fast decay in the excited-state absorption after excitation at 400 nm and probing at 800 nm, which has been ascribed to the decay of population from higher energy level to a lower energy level in ICT state. Here, we have made a thorough investigation of the spectral features and associated excited-state dynamics in the multibranching chromophores.

In this investigation, we have carried out transient absorption measurements to understand the effect of branching on the excited-state dynamics and photophysics of  $N$ -[4-{2-(4-{5-[4-(*tert*-butyl)phenyl]-1,3,4-oxadiazol-2-yl}phenyl)-1-ethenyl}phenyl]- $N,N$ -diphenylamine (PRL-101),  $N,N$ -bis[4-{2-(4-{5-[4-(*tert*-butyl)phenyl]-1,3,4-oxadiazol-2-yl}phenyl)-1-ethenyl}phenyl]- $N$ -phenylamine (PRL-501), and  $N,N,N$ -tris[4-{2-(4-{5-[4-(*tert*-butyl)phenyl]-1,3,4-oxadiazol-2-yl}phenyl)-1-ethenyl}phenyl]amine (PRL-701) (abbreviated from now as the PRL series of dyes; molecular structures are shown in Figure 1), which consist of one, two, and three arms containing donor- $\pi$ -acceptor systems, respectively. In an effort to compare the acceptor strength, polar nature of the excited state, and their correlation to TPA cross sections, we have also carried out transient absorption measurements on tris[4-(3',5'-di-*tert*-butyldistyrylbenzenyl)phenyl]amine ( $N(\text{DSB})_3$ ) (Figure 1). Investigations have revealed interesting features in relation to the excited-state dynamics and amount of ICT character of the excited state with increase in branching, which are very important in elucidating the mechanism behind the TPA cross sections of the branched systems.

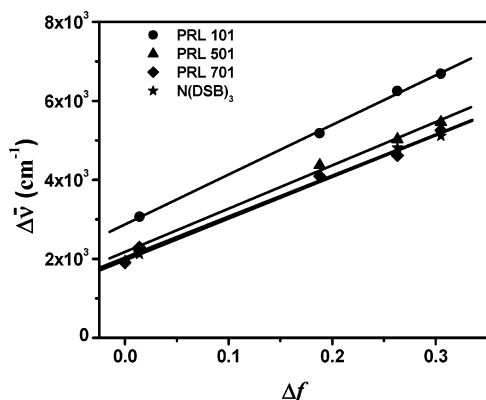
## 2. Experimental Details

**2.1. Materials.** The PRL series of dye molecules<sup>32</sup> and  $N(\text{DSB})_3$ <sup>46</sup> were synthesized by following the procedure reported earlier. Toluene (Tol), tetrahydrofuran (THF), acetonitrile (ACN), and dimethyl sulfoxide (DMSO) were from Aldrich (spectroscopic grade) and were used without further distillation.

**2.2. Methods.** Optical absorption measurements were carried out in Agilent 8432 UV-vis absorption spectrometer. Steady-state fluorescence measurements were carried out by use of a fluorescence spectrometer (Shimadzu). Femtosecond transient absorption investigations were carried out using an ultrafast pump-probe spectrometer detecting in the visible region. Briefly, 1 mJ, 100 fs pulses at 800 nm with a repetition rate of 1 kHz were obtained from a Nd:YLF (Evolution) pumped Ti:sapphire regenerative amplifier (Spectra Physics, Spitfire) with the input from Millennia pumped Ti:sapphire oscillator (Spectra Physics, Tsunami). The output of the laser beam was split to generate pump and probe beam pulses with a beam splitter (85% and 15%). The pump beam was produced by an optical parametric amplifier (OPA-800). The pump beam used in this investigation, i.e., 420 nm, was obtained from the fourth harmonic of the idler beam and was focused onto the sample cuvette. The probe beam was delayed with a computer-controlled motion controller and then focused into a 2 mm sapphire plate to generate a white light continuum. The white light was then overlapped with the pump beam in a 2 mm quartz cuvette containing the sample, and the change in absorbance for the signal was collected by a CCD detector (Ocean Optics). Data acquisition was controlled by the software from Ultrafast Systems, Inc. The typical power of probe beam was  $<0.1 \mu\text{J}$ , while the pump beam was around  $\sim 0.2\text{--}0.5 \mu\text{J/pulse}$ . Magic angle polarization was maintained between the pump and probe using a wave plate. The pulse duration was obtained from fitting of the solvent response, which was  $\sim 130$  fs. The sample was stirred by a rotating magnetic stirrer, and little degradation of the sample was observed during the experiments.

## 3. Results and Discussion

**3.1. Optical Absorption and Steady-State Fluorescence Measurements.** Figure 2A shows the optical absorption and normalized emission spectra of all the investigated chromophores in acetonitrile. It can be observed from Figure 2A that the optical absorption maximum has shifted to longer wavelengths with an increase in the branching. However, only a small red shift in the fluorescence has been observed with increase in branching. The red shifts in the optical absorption of trimer and dimer with respect to monomer are similar to what has been observed in earlier investigations<sup>32</sup> and have been ascribed to a greater degree of exciton delocalization between the chromophores. A closer look at the absorption and emission (Figure 2A) maxima indicate that the Stokes shift of the monomer is marginally higher than that of the dimer and trimer.



**Figure 3.** Plot of Stokes shift versus ( $\Delta\nu$ ) the solvent polarity function  $\Delta f$ .

This result suggests that significant reorganization is needed before emission for the monomer compared to the dimer and trimer indicating that the emitting state of the monomer may possess higher charge-transfer character than that of the trimer.

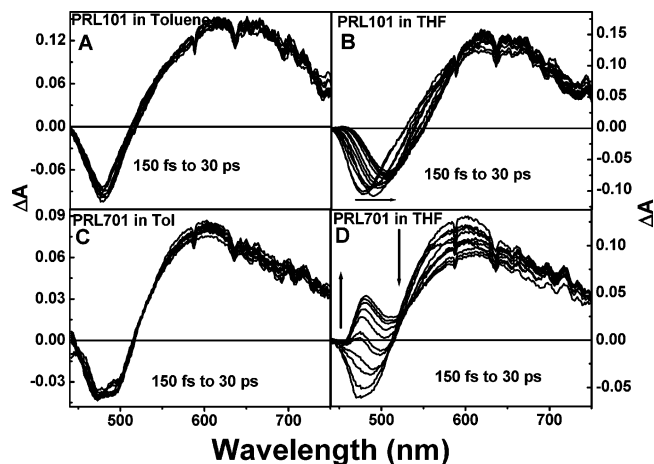
Optical absorption measurements with increase in polarity have been carried out. For the case of clarity, we have shown only the optical absorption of PRL 701 in different solvents of increasing polarity in Figure 2B. These dipolar molecules possess charge-transfer ground states, and it is well-known in the literature that solvent polarity can indeed shift these charge-transfer bands.<sup>57,58</sup> With increasing solvent polarity it is surprising to see that there is no appreciable shift in the absorption spectrum to longer wavelengths. By contrast, one observes a marginal blue shift in the absorption maximum. Similar solvent dependence on optical absorption features is observed for other donor–acceptor molecules.<sup>40,47</sup> However, the fluorescence of the molecule has shown significant positive solvatochromism (bathochromic shift with increase in polarity). It has been established in these branched molecules that the emission is arising from the state where the charge is localized in one of the arms of branched chromophores.<sup>40,46</sup> As the excited-state possesses a large charge separation, it is not surprising to observe such a large red shift in the fluorescence spectrum with an increase in polarity of the solvent. The above results present us with an interesting picture of increasing Stokes shift with solvent polarity. Such behavior is very consistent with the stabilization of a highly polar emitting state with an increase in polarity.<sup>58</sup> This solvatochromic nature can be explained using the standard Lippert–Mattaga relationship<sup>59,60</sup>

$$\Delta\bar{\nu}(\bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{em}}) = 2\Delta\mu^2\Delta f/hca^3 + \text{const} \quad (\text{eq 1})$$

where  $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{em}}$  are the absorption and fluorescence maximum in wave numbers,  $\Delta\mu$  is the difference between the excited-state and ground-state dipole moments,  $h$  is Planck's constant,  $c$  is the velocity of light, and  $a$  is the radius of the solute spherical cavity and solvent polarity parameter  $\Delta f$ , which describes the solvent polarity and polarizability is given by the following expression:

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (\text{eq 2})$$

Here,  $\epsilon$  is the dielectric constant and  $n$  is the refractive index of the solvent. The solvatochromic plots for all the chromophores are presented in Figure 3.

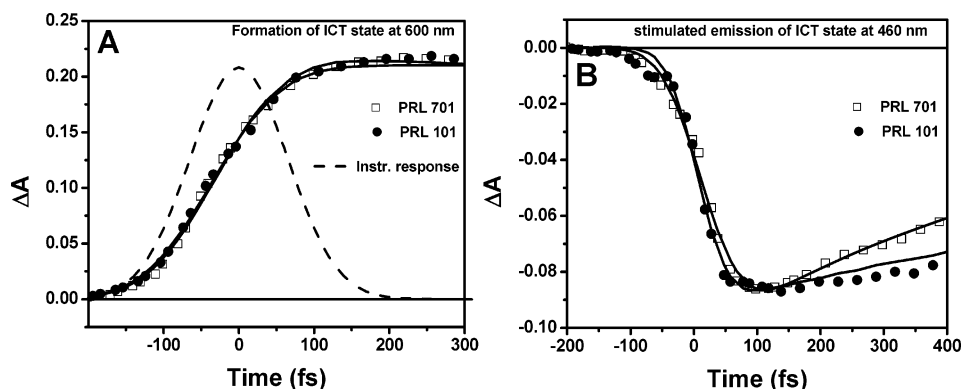


**Figure 4.** Femtosecond transient absorption spectra of PRL 101 in (A) toluene and (B) THF (B) and of PRL 701 in (A) toluene and (B) THF at different solvents at time delays between 150 fs and 30 ps. A clear presence of localized ICT state is observed within the time resolution of the measurements, and also a striking evolution of the solvent-stabilized ICT state is observed with a concomitant decay of ESA in THF.

The good and linear fit of the Lippert–Mattaga plots suggest that the emitting state is similar for all the three chromophores and most likely arises from the charge localized on one branch. Similar localization of the emitting state on one branch has been shown both theoretically and experimentally for other triarylamine-branched systems<sup>40</sup> and also for similar nitrogen-cored multibranch structures with the aid of fluorescence anisotropy measurements.<sup>42a</sup> As the emitting state is localized on one arm for all the molecules, it would be interesting to see if there is any change in dipole moment as branching is increased from monomer to trimer. It can be observed from Figure 3 that the slopes of all the plots are found to be linear and almost parallel with respect to each other. Since the emitting states are same for all the chromophores independent of branching, one can assume same cavity radius for all of them. In such a situation, a similar slope of Lippert–Mattaga plot irrespective of branching indicate that the effective dipole moment change ( $\Delta\mu$ ) is almost equivalent for all the molecules. An analogous trend in change in dipole moments is also theoretically predicted for triphenylamine-cored branched molecules.<sup>40</sup> This indicates that the amount of charge transfer is nearly equal for monomer, dimer, and trimer and hence its effect on TPA cross section with increase in branching will be comparable. Thus, the steady-state measurements of low Stokes shift of the trimer in comparison to the monomer and similar change in dipole moments from the Lippert–Mattaga plot and theoretical calculations<sup>40</sup> suggest that there is negligible effect of charge transfer on the TPA cross sections with increase in branching. It would be interesting to see if ultrafast transient measurements can provide new information on the amount of charge transfer in the excited states with increase in branching.

### 3.2. Femtosecond Transient Absorption Measurements.

Our earlier work<sup>46</sup> has demonstrated that optical excitation of the multibranch PRL chromophore systems is delocalized over several chromophores (branches) possessing a relatively weaker coupling with the bath. This was suggested by measurements of the faster anisotropy (fluorescence upconversion and degenerate pump–probe) and a larger initial photon echo shift.<sup>46</sup> For a detailed understanding of the excitation delocalization, charge localization, and nature of ICT in these PRL series of dye molecules, femtosecond transient absorption measurements have been carried out. Figure 4 shows the transient absorption spectra



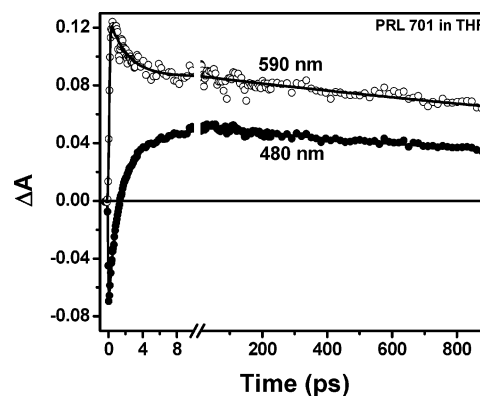
**Figure 5.** (A) Kinetics of formation of ICT state of monomer and trimer in THF at 600 nm and also the curve representing the instrument response of 130 fs. (B) Growth of stimulate emission of ICT state of monomer and trimer at 480 nm. It is interesting to note that both of them follow each other and also instrument response is limited.

at different time delays from 150 fs to 30 ps for monomer (PRL 101) and trimer (PRL 701) in toluene and THF.

While we have carried out the transient measurements up to 1 ns, for clarity we have only shown up to 30 ps since the spectrum at 30 ps time delay represent the final relaxed excited state. It can be observed from Figure 4 that the transient absorption features at the initial time delay of monomer and trimer look similar in both the solvents with bleach in the region of 450 to 530 nm with a positive absorption beyond 530 nm and a maximum around 600 nm. The bleach in the 450–530 nm region with a maximum around 480 nm can be ascribed to the stimulated emission arising from the ICT state. The positive absorption is due to the excited singlet state ( $S_1$  to  $S_n$ ) absorption (ESA). It is evident from the transient absorption spectra of the monomer (Figure 3A) and the trimer (Figure 3B) in toluene that there is no additional evolution of transients other than what is observed at early time delay.

In contrast to the measurements in toluene (Figure 4A,C), interesting transient absorption features are observed for the monomer and trimer in THF (Figure 4B,D). At the initial time delay the transient absorption features of the monomer and trimer in THF are similar to what was observed in toluene. To have a closer look at the initial time transient absorption features of monomer and trimer, the kinetic traces depicting the growth of ESA at 590 nm and stimulated emission at 480 nm are shown in Figure 5A,B respectively. Also, shown is the Gaussian curve representing the instrument response function of the transient absorption spectrometer. It can be observed from Figure 4 that the kinetic traces of monomer and trimer follow each other and are limited by the instrument response. The fast excited-state formation for both the monomer and trimer suggests that in the trimer system (PRL 701) the localization of the charge is very fast (less than 100 fs).

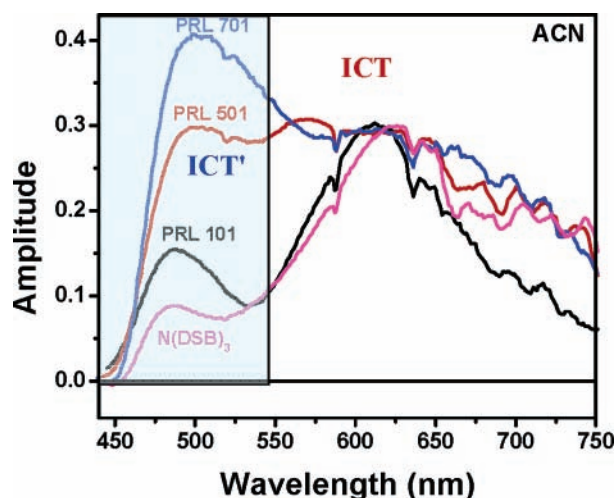
The results described above give support to the process of localization of charge in higher branched chromophores on an ultrafast time scale. Also, this would suggest that the time scale of internal conversion from a delocalized state to a localized state is even faster than 100 fs. While the spectral features of the PRL-701 trimer are similar in THF and toluene at the initial time delay period, quite different spectral characteristics are observed when the time delay is increased. With an increase in time delay from 150 fs to 30 ps, a new transient started to appear in the region of 450–500 nm with a simultaneous decay of ESA around 600 nm. It can be observed from Figure 4B,D that the population of the new transient is quite large for trimer compared to monomer. Similar transient measurements have been carried out for all the dye molecules and also in solvents of increasing polarity (shown in Supporting Information). The



**Figure 6.** Kinetic decay traces along with the fitting curves for all the molecules in THF in two different wavelengths, one at 480 nm signifying the growth of ICT' state and another at 590 nm, the maximum of ESA. The decay of ESA has matched the growth of the ICT' state.

results have shown a clear trend of increased population of the new transient with increase in branching and also with increase in polarity of the solvent. Kinetic analysis of the new transient has shown that the growth of the transient is both solvation and viscosity dependent (see Supporting Information). Hence, we can attribute the new transient to a solvent-stabilized and conformational relaxed ICT (designated as ICT') state. At this point, it has to be emphasized that the fluorescence quantum yields of the dyes decrease with increase in polarity of the solvent (see table in the Supporting Information). Correlation has been found with the appearance of ICT' state and the decrease in fluorescence quantum yields of the dye molecules. Thus, we ascribe ICT' state to be nonemissive, which is the reason behind the low quantum yields of the investigated chromophores in high-polarity solvents. A similar presence of solvent-stabilized and conformationally relaxed state (nonemissive) has been observed for several dipolar molecules<sup>61,62</sup> containing diphenyl- or dialkylamine as donors. To understand the dynamics of excited-state deactivation, we have analyzed the kinetic traces at different wavelengths. Shown in Figure 6 are the kinetic traces of the PRL-701 in THF showing the decay of ESA at 590 nm and the growth of ICT' at 480 nm. It can be seen from the Figure 6 that the growth of the ICT' state is following the decay of ESA of the ICT state. The final state thus formed is decaying with the lifetime of the excited state of the chromophore.

**3.3. Mechanism of Excited-State Deactivation.** It has been well established in linear push pull molecules that photoexcitation drives the molecule into the charge-transfer state.<sup>18</sup> It has been shown recently both theoretically and experimentally by



**Figure 7.** Species-associated spectra (normalized with respect to the ICT state) of relaxed states of the investigated chromophores illustrating the ratio of ICT' to ICT states.

Blanchard-Desce and co-workers<sup>40</sup> that, in branched molecules with triphenyl amine as the core group, the photoexcitation produces a charge-transfer state which is emissive, wherein the emission is localized on one of the chromophores. Similar excitation localization on one of the chromophore has been observed for several multiple branched chromophores,<sup>40,43,46–48</sup> and our steady-state measurements on PRL series of dye molecules are consistent with the same phenomenon. In this investigation, we have studied the excited-state deactivation of the PRL series monomer to trimer and it can be suggested from our results that there is an ultrafast pathway by which there is a localization of the charge in the PRL-701-branched chromophore. Interestingly, in highly polar solvents one more state designated as an ICT' state (nonemissive) is derived from the ICT state with the solvation time of the solvent. The population of this state is highly dependent on solvent polarity and also on the viscosity of the solvent. All the presented transient measurements of the chromophores have unambiguously verified the mechanism (Scheme 1) of the excited-state deactivation of all the investigated triphenylamine-cored branched molecular systems.

Although similar excited-state deactivation has been observed for all the molecules independent of branching, there is very interesting trend in the population of the ICT' state with increase in branching. From the optical absorption and steady-state fluorescence measurements (section 3.1), it has been observed that the Stokes shift of the monomer is higher than that of the dimer and trimer, which suggests that the amount of charge transfer in the monomer might be larger than in the dimer and trimer. A strikingly different trend has been observed from transient absorption measurements with regard to the degree of charge transfer of the ICT state with increase in branching. Figure 7 shows the population of ICT' and ICT states (after the normalization of population of the ICT state) with increase in branching in acetonitrile. In a solvent of same polarity, the population of the ICT' state is higher for the trimer than dimer, which in turn is higher than the monomer. As the ICT' state is a solvent-stabilized state derived from the ICT state, its population indicates the amount of charge transfer in the ICT state. Thus, the transient measurements have unambiguously shown that the amount of charge-transfer character increases with increase in branching, which was very difficult to be predicted by steady-state measurements. The differences observed in the steady-state measurements with respect to charge

transfer (Stokes shifts) can be explained if one considers that the red shift in the absorption spectrum with increase in branching has arisen due to the interaction between the branches, which is not prominent in the emission spectrum.

Also, one interesting point to note here is that the population of the ICT' state within the similar trimer systems of PRL-701 and N(DSB)<sub>3</sub> is higher for PRL-701 when compared to N(DSB)<sub>3</sub> suggesting that the acceptor strength in the case of PRL-701 is higher, and thereby higher is the amount of excited-state charge transfer.

**3.4. Correlation of the Polar Nature of the Excited-State and Two-Photon Absorption Cross Section.** Having understood the excited-state dynamics of the PRL series of dye molecules within the context of evaluating the ICT character, one is able to correlate this information with the TPA cross sections. Within the framework of the exciton model,<sup>35</sup> octupolar molecules such as the PRL series of dye molecules with C<sub>3</sub> or C<sub>3h</sub> symmetry can be regarded as three dipolar-like arms and associated low-lying charge-transfer excited states with a characteristic transition dipole moment ( $M_{ge}$ ) and a difference in dipole moment ( $\Delta\mu_{ge}$ ) with respect to the ground state. Important aspects for this transition are that the TPA cross section relates primarily to the amount or degree of photoinduced charge transfer along the arms<sup>35</sup> as well as electron delocalization.

However, it has to be noted here that the TPA process is an instantaneous process and it is mainly influenced by the Franck–Condon (FC) excited state. So, the nature of FC state should be understood to explain the enhanced cross section for the case of multibranch structures. One-photon excited-state dynamics measurements can give an insight into such states. In a previous report,<sup>46</sup> combined time-resolved measurements of fluorescence depolarization and pump–probe anisotropy measurements have been used to show that the anisotropy of an immediate excited state decays very fast with a time scale of around 50 fs to a residual anisotropy of around 0.1 (consistent with the anisotropy of a planar compound). This ultrafast anisotropy has been ascribed to strong intrachromophore electronic coupling between the arms.<sup>46</sup> Also, the 3 pulse photon-echo spectroscopy measurements on the same series of dye molecules have shown that there is a strong coupling of excited state to solvent bath (by virtue of small initial photon echo shift of the PRL series of trimers in comparison to nitro trimers).

The extent to which the excited states are delocalized over the entire molecular framework of multibranch chromophores is an important phenomenon to monitor. Present transient measurements have shown that the delocalized state has a very short lifetime, and localization on one of the chromophores happens much faster than 100 fs. The results indicate that the barrier of the FC to ICT state is relatively small and there is effective vibronic coupling with the localized ICT state (almost like a same potential energy surface with a same reaction coordinate, Scheme 1). In such a scenario, the nature of relaxed or localized ICT state does have substantial influence on the FC state. Similar sub 100 fs S<sub>2</sub> and ICT state internal conversion has been observed for the case of peridinin by Premvardhan et al.,<sup>63</sup> and it has been suggested that S<sub>2</sub> and ICT states are intimately linked via a structural coordinate<sup>64,65</sup> and thereby possess similar excited-state character. Even though it is not easy to monitor the FC state, one can trace back its characteristics by following the nature of the ICT state. The excited-state dynamics measurements described above have shown the presence of an immediate ICT state followed by a solvent polarity dependent ICT' state (nonemissive). The population of

**TABLE 1: Ratio of ICT' State to ICT State Population of the Chromophores in Various Media**

molecule	toluene	$\Delta A_{ICT'}/\Delta A_{ICT}$		
		THF	ACN	DMSO
PRL-101	~0	~0.05	0.51	0.42
PRL-501	~0	~0.15	1.01	1.32
PRL-701	~0	~0.32	1.39	1.43
N(DSB) <sub>3</sub>	~0	~0.05	0.3	0.35

such a dark state can be taken as a measure of strength of ICT character of the immediate excited state. With an assumption that the extinction coefficients for the ESA of the ICT state and ICT' state are similar for all the chromophores, the  $\Delta A_{ICT'}/\Delta A_{ICT}$  ratio can give the ratio of population of ICT' state to ICT state. Such ratios of  $\Delta A_{ICT'}/\Delta A_{ICT}$  for all the compounds in different solvents are given in Table 1.

It can be seen in Table 1 that the population of the ICT' state (which is dependent on the solvent polarity) is higher in the case of the trimer and dimer when compared to monomer in the same solvent. It can be argued that the ICT' state is a conformationally relaxed state and as the trimer is bulkier than monomer, it can give a higher population of the ICT' state. In such a case, steric interaction would be the main contributing factor and a similar or higher population of the ICT' state for N(DSB)<sub>3</sub> compared to the PRL-701 system should have been observed. To the contrary, we have observed a decrease in the population for N(DSB)<sub>3</sub> of ICT' when compared to PRL-701, and thus, it appears that it is the acceptor strength and degree of CT character that are crucial in determining the population of the ICT' state and hence a good measure of the ICT strength. These results thus confirm a monotonous increase in strength of ICT with increase in branching. From PRL-101 to PRL-701, the strength of ICT in the excited state has increased with increase in branching which was *not* predicted by steady-state Stokes shift measurements. A greater amount of charge transfer observed in the case of the trimer when compared to the monomer suggest that there is more to the molecular picture of the emitting state than just the charges localized on one arm of the branch as predicted by theoretical calculations<sup>40</sup> and steady-state measurements. It can be suggested that because of dominant electronic interactions between various arms of the trimer, the effective electron-donating ability of the triphenylamine core is enhanced in the trimer thereby increasing the amount of charge transfer from donor to acceptor in the ICT state. Similar increase (by more than a factor of 2) in the donor to acceptor charge transfer/arm has been observed when switching from a dipolar compound to an octupolar compound based on an amine as the core donor and cyano benzene as the acceptor.<sup>35</sup> As discussed above, the FC state and ICT state are coupled very strongly and hence the charge-transfer nature of ICT state can be directly extrapolated to the FC state. Thus, the present ultrafast transient measurements have shown that the amount of charge transfer in the FC state increases with increase in branching and contributes significantly to the enhanced TPA cross sections in multibranching chromophores. Enhanced amounts of charge transfer in the excited state and strong coupling between the arms are the crucial mechanisms behind the enhanced TPA cross sections of the PRL series with increase in dimensionality.

A question can be asked if this trend is universal for all the trimers or multibranching chromophores. The answer is not straightforward because of the fact that the nature of immediate excited (FC state) state varies for different branched compounds. It should be mentioned here that the excitation is localized very fast in case of PRL series of dyes and others,<sup>40,47</sup> but it may

not be the case for all the trimers. If the charge is shared in all the arms of the chromophore in the excited state, then it cannot be directly correlated with the degree of ICT of the monomer.<sup>42b</sup> In that case, the conjugation length of the chromophore may be the main reason for the cooperative enhancement as has been observed in the case of two-dimensional charge transfer containing cumulene molecules.<sup>66</sup> Thus, the present result gives an insight that if we can understand the one-photon photo physics of the chromophore, then one can be able to predict the two-photon behavior especially in case of donor- $\pi$ -acceptor chromophores with branching. Further if the increase of charge-transfer character with branching can be extrapolated for large dendrimers, then very large TPA cross sections may be obtained.

#### 4. Conclusions

Excited-state dynamics of two-photon absorbing chromophores belonging to PRL series of dye molecules along with N(DSB)<sub>3</sub> has been investigated by ultrafast transient absorption spectroscopy to correlate the enhancement of the two-photon absorption properties with excited-state dynamics. In view of the fact that the absorbing state is a delocalized state, ultrafast transient measurements have shown that the initial delocalized excited state (FC state) with coherent interaction among arms relaxes very fast to an ICT state with a time scale of sub 100 fs. Steady-state measurements by virtue of Stokes shift measurements suggested that there is little to no difference in the amount of charge transfer with increase in branching and thereby it has negligible effect on the enhancement of observed TPA cross section. However, ultrafast transient measurements have shown interesting trend with respect to the amount of the charge-transfer character with increase in branching. Pump-probe measurements have shown the presence of a solvent-stabilized and conformationally relaxed ICT (ICT') state with increase in polarity. The population of this ICT' state has been used as an indicator of the amount of charge transfer in the ICT state, and it is observed that it is greater for the case of trimer than dimer, which in turn is higher than the monomer. Since the internal conversion of FC to the ICT state occurs on an ultrafast time scale, they can be intimately linked by the same reaction coordinate and one can expect similar charge correlations for the FC and the ICT states. Thus, these results suggest that there is a higher amount of charge transfer in FC configuration for the molecules with increase in branching, which strongly contribute for the enhanced TPA cross sections. Here, we have demonstrated that, along with the coherent coupling between the arms, charge transfers in the excited states of the branched structures do play a vital role in understanding the enhanced TPA cross sections. Judicious synthesis of the advanced branched structures (for examples particular organic dendrimers) with a larger degree of ICT character can serve the purposes of creating materials with large TPA cross sections.

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**Supporting Information Available:** Complete photophysical properties and transient absorption spectra of all the molecules in different solvents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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