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Static and Ultrafast Transient Photophysics of Mono- and Dual-Branched Triarylamines *

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Mono- and dual-branched molecules, {4-[2-(4-benzothiazol-2-yl-phenyl)-vinyl]-phenyl}-(4-methoxy-phenyl)-phenyl-amine (BS1) and bis-{4-[2- (4-benzothiazol-2-yl-phenyl)-vinyl]-phenyl}-(4-methoxy-phenyl)-phenyl-amine (BS2), are investigated with one- and two-photon static spectroscopy, and the femtosecond fluorescence up-conversion technique. The molecules show branch-based fluorescence emission at low quantum yield. Ultrafast non-radiative decay on a picosecond time scale is found and is attributed to intramolecular charge-transfer bridged by the central triphenylamine. The two-photon absorption cross-sections of BS1 and BS2 are 19.1 and 19.4 GM, respectively.

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In recent years the materials with strong two-photon absorption (TPA) properties have attracted much attention in science research and practical applications, e.g. three-dimensional micro-fabrication, information technology, laser technology, and biological system imaging.[1−3] For these materials, the electron donor and acceptor group were connected symmetrically or unsymmetrically by a π-conjugated bridge to form D-π-A structures (or containing auxiliary donors and acceptors) along the conjugated backbone.[4,5] The building of the multiple branched chromophores and co-polymers has been reported as a significant way to form new materials with better TPA properties.[6] The dynamics of their exited state and relaxation process is very attractive for uncovering their photophysical mechanism. Many different experimental methods, such as transient absorption, time-resolved fluorescence, Z-scan, and three-pulse photon-echo peak shift techniques, have been used to visualize the ultrafast evolution from the initially excited state to the final relaxed state.[7−10] Experimental and computational studies investigated the excitation migration between the localized excited states on one branch and neighboring branches via a ping mechanism.[11−13] Varnavski suggested that at lower generations the Förster model might be suitable for describing the mechanism of the energy transfer from dendrons to the core by calculating the energy-transfer efficiency and the rate from time-resolved experiments.[10]

Because of the electron-donating nature of the nitrogen atom, triarylamines keep attracting considerable interest as hole-transport materials in various applications like organic light emitting diodes (OLEDs), solar cells, and other photonic devices.[14−16] It has also been found that molecules with larger TPA cross-sections can be developed based on the triphenylamine molecular platform.[16,17] Recently, these multi-branched molecules were investigated by Goodson Ⅲ etc. in series, with ultrafast transient absorption and photon echo spectroscopy.[18] They found that though the correlation of TPA enhancement with intramolecular charge transfer (ICT) is not clear by static spectra, ultrafast spectroscopy reveals a solvent-stablized and conformationally relaxed ICT state, in which the charge-transfer increases with the branches at the initial Frank–Condon (FC) state. Then they concluded that the ICT plays a vital role in understanding the TPA properties of branched molecules. In this Letter, we study the femtosecond fluorescence dynamics of mono- and dual- branched BS1 and BS2 in dimethyl sulfoxide (DMSO), whose molecular structures are shown in Fig. 1. These molecules are designed to have charge transfer properties between branches, which is different from the normal symmetric structure with all-the-same branches.

The sample molecules BS1 and BS2 are shown in Fig. 1. The concentrations of BS1 and BS2 in *n*-hexane, $CHCl_3$ and DMSO solutions are 10^{-4} M. The absorption spectra were recorded with a UVIKON-810 UV–visible spectrophotometer. The fluorescence spectra were recorded with a Hitachi F3000 fluorescence spectrometer. The technique of femtosecond time-resolved fluorescence up-conversion was employed to obtain the transient dynamics of the fluores-

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cence of the samples. The ultrafast laser pulse train was delivered from a Ti:sapphire system (Mira900F, Coherent, USA) with 820 nm central wavelength. A frequency doubled 410 nm pulse was used to excite the sample. The generated fluorescence from the sample solution was collected and focused together with the 820 nm gating pulses into another type I β-BBO crystal to produce the sum-frequency signal. The generated up-conversion UV signal finally entered the slit of a monochromator, after which a Hamamatsu R585 photomultiplier was placed at the exit slit. A Hamamatsu C5410 photon counter recorded the UV photons and sent the signal to a computer.

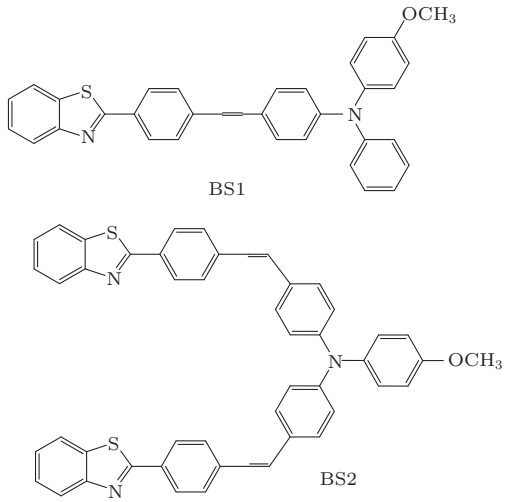

Fig. 1. The mono- and dual- branched molecules of BS1 and BS2.

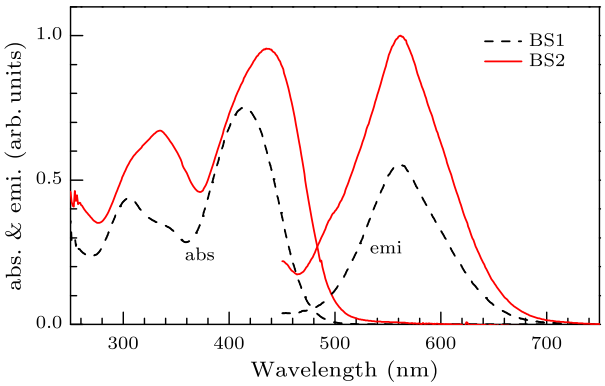

Fig. 2. Absorption and steady state fluorescence spectra of BS1 and BS2 at 0.25×10^{-4} M in DMSO. The excitation wavelength is 410 nm.

The steady state absorption spectra of BS1 and BS2 solutions in DMSO are shown in Fig. 2. The BS1 has two peaks at 306 nm and 414 nm, while a shoulder exists at about 335 nm. The BS2 shows similar structures with three distinct structures. However, the blue-most one in BS1 becomes a shoulder with similar intensity while the former shoulder increases nearly one time in absorbance. The red-most peak shifts to 435 nm for BS2. The maximum molar extinction coefficients of the two molecules are 4.4×10^4 and 6.0×10^4 cm^{-1}M^{-1}, respectively. Compared with similar structures containing triphenylamine and stilbenzene,[6,19–21] the shoulder at 335 nm corresponds to the $n-\pi^*$ transition of the benzothiazole group, while the 306 nm peak comes from the localized excitation of triphenylamine. The red-most absorption band is attributed to π-conjugation excitation at the charge-transfer band of the molecules.[22] The emission spectrum in Fig. 2 shows that their emission spectra have different behavior to the absorption. The emission peak does not show a clear shift on the number of branches or the overall conjugation. This phenomenon was found in several molecule systems and is regarded as the localization of the excited state into branches.[18]

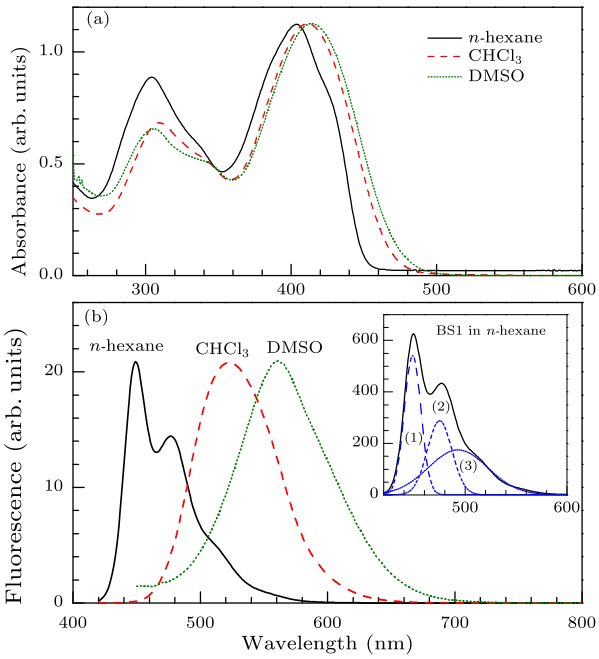

Fig. 3. Polarity dependent spectra of BS1. (a) Absorption of BS1 in n-hexane, CH_3Cl, and in DMSO. (b) The emission of BS1 in three solvents. Inset: the multiple Gaussian peak analysis of emission in n-hexane.

The ground state absorption spectra of these conjugated molecules are solvent dependent. The solvents were n-hexane, $CHCl_3$, and DMSO, with increasing dipoles of 0.27, 3.84 and 14.8 (10^{-30} C·m), respectively. Figure 3(a) shows the solvent polarity dependence. The red-most peak at 400 nm in n-hexane shifts to longer wavelengths with increasing solvent polarity. The shoulder at 335 nm also follows this sequence both in BS1 and BS2. As shown in Fig. 3(b), the emissions of sample molecules are much more environmentally sensitive. In n-hexane, the emission spectra have sub-structure inside the emission band, which is absent in other solvents. Multi-peak analysis fitting with a Gaussian function indicates three possible bands, as listed in Table 1. Peaks 1 and 2 shift

to red when the system changes from mono- to dual-branch. Peak 3 stays at the same position for both the molecules. Peak 3 is similar to the emission of BS1 and BS2 in the polar solvent. We suggest that peak 3 is from the same origin with emission from the polar solvent.

Table 1. Emission peak allocation of BS1 and BS2 (units: nm).

	n-hexane			$CHCl_3$	DMSO
	peak(1)	peak(2)	peak(3)		
BS1	449	476	484	522	561
BS2	465	495	490	523	562

Peak 3 in *n*-hexane and the corresponding single emission band in polar solvents shows an intensity change, depending on the quantity of branches, instead of overall conjugation. Stronger emission from BS2 is also expected and observed. This phenomenon indicates that the final excited states are based on a single branch. Peaks 1 and 2 show the full-molecule framework conjugation dependence (red shift as the amount of branches increases) and disappear in polar solvent. The quantitative analysis gives the result that when normalized with the absorbance at 410 nm, the photon yield from peak 3 is very similar to the fluorescence peak in chloroform. This suggests that from static spectra, though peaks 1 and 2 disappear, their energy decays through the non-radiative way have little effect on the energy deposit to peak 3 in polar solvents. All this information indicates a polar solvent induced, very efficient non-fluorescent deactivation channel. This channel is usually regarded as a non-radiative twisted intramolecular charge-transfer (TICT) state. The low quantum yield results support this suggestion. They show that BS2 has a larger fluorescence quantum yield (2.5%) than BS1 (1.5%).

Excited with the femtosecond laser pulses at 800 nm, two-photon fluorescence (TPF) spectra of BS1 and BS2 were obtained. The peaks of TPF are similar compared to the single-photon fluorescence spectrum. In principle, one-photon and two-photon excitation follow different excitation pathways. For the one-photon excitation process, the excitation happens directly between ground and excited states 1^1B_u, while a short-lived virtual state exists for two-photon excitation between the ground and excited states 2^1A_g. However, the finally reached excited state by both types of excitation are the same in many cases.[23,24] By using Rhodamine 6 G as the reference ($\sigma_2 = 16.2$ GM),[25] the TPA cross-sections σ_2 of BS1 and BS2 were calculated to be 19.1 and 19.4 GM. From our results and other reports,[6,16,20] we found that the TPA cross sections of the dual-branched molecule that exhibits the C_{2v} symmetry structure are comparable to those of the mono-branched molecule, whereas the TPA cross section of the three-branch molecule that exhibits C_{3v} symmetry structure is about 4 times larger than that of the mono-branched molecule.

As indicated from static spectra, a non-radiative species formed after the excitation, which should be on an ultrafast time-scale. To validate this, we performed a fluorescence up-conversion experiment with a time resolution of 120 fs to reveal the detail ultrafast excited state dynamics in DMSO. Figures 4(a) and 4(b) show the time-resolved fluorescence decay curves at wavelengths of 520, 560, and 600 nm. It is evident that the decaying processes are wavelength dependent. At the blue side of the static fluorescent band, 520 nm, the fast decay process dominates the emission decays. The slower components become significant at longer wavelengths. With the detected wavelength increasing, the fast decay becomes slower. At 600 nm, all the emission components become much longer compared with those in the blue side.

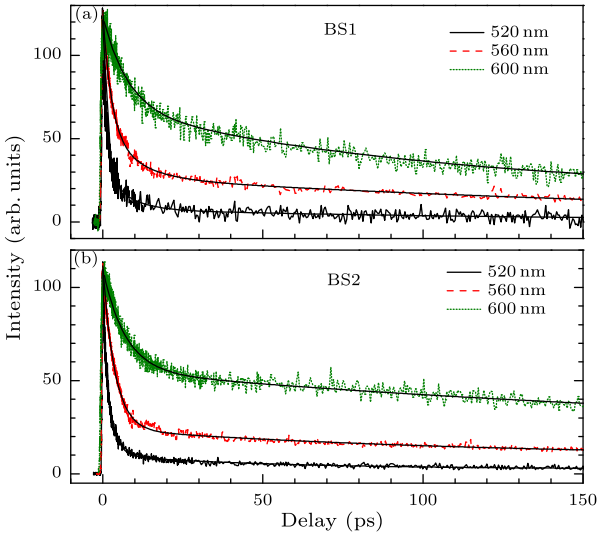

Fig. 4. Ultrafast time-resolved fluorescence decay curves of BS1 (a) and BS2 (b) at a concentration of 10^{-4} M in DMSO.

Table 2. Multi-exponential fitting to the fluorescence decay curves by fluorescence up-conversion. Here τ is the decay time, and α is the normalized contribution.

	Wavelength(nm)	τ_1(ps)	(α1)	τ_2(ps)	(α2)	τ_3(ps)	(α3)
	520	1.24	(0.73)	6.8	(0.21)	122	(0.06)
BS1	560	2.80	(0.56)	8.1	(0.21)	174	(0.23)
	600			8.3	(0.46)	180	(0.54)
	520	0.98	(0.57)	3.9	(0.36)	193	(0.07)
BS2	560			3.9	(0.80)	307	(0.20)
	600			7.3	(0.52)	447	(0.48)

In this work, all decay curves were fitted by a multi-exponential function. The results are listed in Table 2 for each detecting wavelength. It indicates that three possible decay channels exist in the blue side, while only two relaxation channels exist in the red side of the emission spectra. The quickest process happens during only 1–2 ps for both the molecules in the blue side of 520 nm. BS2 shows faster decay and a lower portion than that for BS1. For the secondary

decay component, BS2 is still quicker than BS1, but reaches a similar time scale of 10 ps at the longer wavelength of 600 nm. The longest component is the lifetime of local emission species, as mentioned in the static spectra section.

From our analysis and work by Ramakrishna and Goodson[18] using transient absorption spectra on their PRL series, the excitation finally localized in branches. The initial process of localization of the excitation is the key to understanding their photophysics including TPA. From their transient absorption, it is found that the solvent stabilized and conformationally relaxed ICT process couples to the FC state, which is fast and less than 100 fs. This extremely fast process participates in the TPA process and its amplitude increases with the number of branches around the central atom. However, in our ultrafast fluorescence decay experiment, the quickest component is about 1 ps. Considering the structural difference and similar TPA cross-section for BS1 and BS2, we suggest that the faster twisting process here happens between the triarylamine plane and branch moieties. As is known from the experiment, this twisting is related to full molecule conjugation and branch independence. The result of twisting leads to non-radiative decay through overall conjugation. Then the emissive behaviors have a single-branch basis in polar solvents. It should be also noticed that the solvent plays an important role in the process. The TICT is induced and stabilized by the solvent.[26]

It should be noticed that several other ultrafast processes such as fast vibrational decay also happen in this system. These dynamics mix together and then become environment dependent. The second few-picosecond process exists at all wavelengths, which increases gradually because of the local relaxation. Though it is hard to figure out what exactly happens in the branch group, it can still be suggested that this decay process might be bond twisting towards trans-cis isomerization within the branch moieties, or, say, another local TICT. This is supported by the semi-empirical calculation in a hemicyanine dye.[27]

In summary, we have investigated the one- and two-photon and ultrafast excited state dynamics of two TPA molecules, BS1 and BS2. The experiment indicates that this system shows both a localized excited state and a solvent induced TICT state. A non-emissive process happens when the molecule is in polar solvents. At the same time, the local branch behavior is dominant in the emission spectra. The ultrafast dynamics reveals that the fast TICT happens in 1–2 ps while the local branch relaxation takes place in a few picoseconds.

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