

The Ultrafast Dynamics and Nonlinear Optical Properties of Tribranched Styryl Derivatives Based on 1,3,5-Triazine

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By using the femtosecond laser spectroscopic techniques, we have studied the ultrafast response and the nonlinear optical properties of three molecules with donor–acceptor structure (denoted as T01, T02, and T03). Two-photon absorption (2PA) cross sections measured by the open aperture Z-scan technique were determined to be 77, 90, and 410 GM for T01, T02, and T03, respectively. The relaxation dynamics of the excited states were measured by two-color femtosecond pump–probe and time-resolved photoluminescence (PL) experiments. By changing the solvent from chloroform (CHCl₃) to dimethyl sulfoxide (DMSO), the transient dynamics was found changed significantly and the decay time of PL emission decreased dramatically because DMSO with large dipole moment accelerates the cross-transfer process and the nonradiative process in the molecules.

1. Introduction

The recent studies about the special characteristics of the materials with intense two-photon absorption (2PA) have shown that these materials have a variety of potential applications, including three-dimensional microfabrication,^{1,2} information technology,³ laser technology,⁴ biological system imaging,⁵ and so forth. The significant issue is how to synthesize the materials with large 2PA cross section. Several design strategies were proposed to improve 2PA response,^{6–10} such as the connection of donor and acceptor symmetrically or unsymmetrically by π -conjugated bridge to form D– π –D, A– π –A, or D– π –A structures and the building of the multibranch molecules^{9,10} which can significantly enhance 2PA cross sections because of the increased chromophore density of the molecules and the cooperative enhancement effect among the chromophores. It was found that the ratio of 2PA cross sections of the tribranched molecules to the monomer was near the value 6.8 reported in Chung's work.¹¹ Theoretical calculations have shown that the three-coordinated octupolar complex is a better kind of 2PA material than the two-coordinated one.¹²

Meanwhile, as there arises the basic interest in the details of the excited-state formation in donor–acceptor systems, especially in those systems with multibranch structures, the dynamics of this kind of molecules have been measured by different methods. Varnavski and co-workers reported that by means of the time-resolved photoluminescence (TRPL), pump–probe, and three-pulse photon echo measurements, the presence of an intermediate C_3 symmetry state in the trimer showed a very high depolarization rate, with an evolution into a polar state localized on one branch within a few picoseconds (ps).¹³ They suggested that at lower generations the Förster model may be suitable in 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. Also, the very fast anisotropy decay, facilitating the core branched geometry, may play a large role in the intermolecular interaction in the similar dendrimer systems.¹⁴ Transient absorption, as well as time-resolved microwave conductivity techniques, has also been used to investigate the dynamic feature of 2PA materials. It was suggested that the bath-equilibrated polar excited state was localized on one branch in C_3 symmetry amino-substituted triphenylbenzene derivatives.¹⁵

In the molecules with unsymmetrically D– π –A structure, a locally excited state (LE) is populated upon photoexcitation, from which an intramolecular charge transfer (ICT) state with a large dipole moment is produced. For the multibranch molecules, the dipole moment may not change a lot because of the C_3 symmetric structure. This result indicates that the multibranch molecules will show different solvation compared with single-branched D– π –A structure molecules. The solvation has been widely studied as it has great influence on the chemical and physical properties of the solutes, such as absorption and photoluminescence spectra. The effect of the solvation on the excited-state relaxation processes of coumarin has been reported recently.^{16,17} It is still a challenging topic to investigate the solution effect on the optical properties and ultrafast response of the compounds with different molecular structures, monomer or multibranch structures.

In this paper, we present the research results on the optical properties and the excited-state dynamics of three new compounds T01, T02, and T03, whose molecular structures are given in Figure 1. The structures for T02 and T03 almost possess C_{2v} and C_{3v} symmetry, respectively. The excited-state dynamics were probed by the femtosecond (fs) pump–probe and time-resolved photoluminescence measurements. The transient response of the compounds was explained by relaxation and energy-transfer processes between the LE state, the ICT state, and the triplet state. Two solvents with quite different polarities, CHCl₃ and DMSO, were used in our experiment to study the

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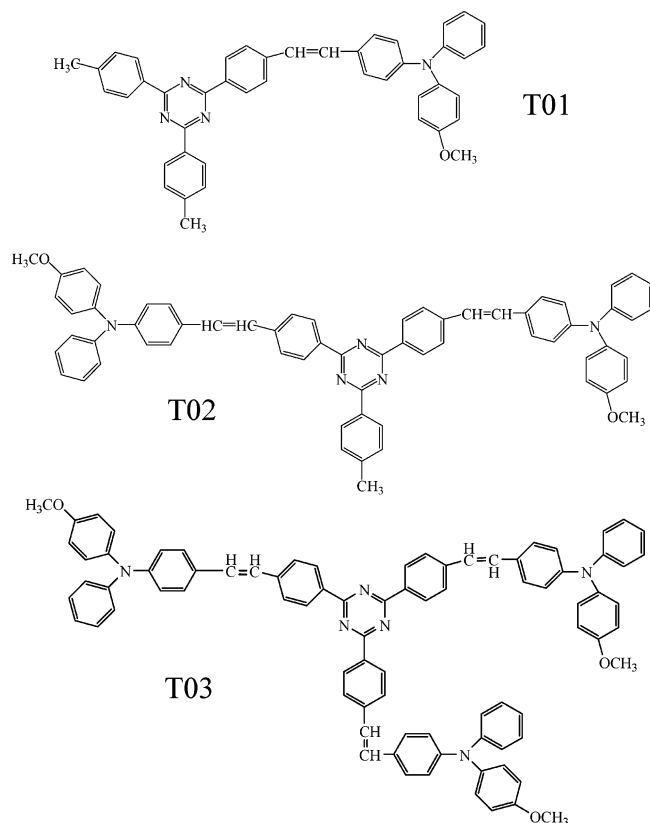


Figure 1. Molecular structures of T01, T02, and T03.

solvation on the ultrafast optical response and the excited-state dynamics. It was found that the solvent has a significant impact on the relaxation dynamics of the excited states and on the temporal behavior of the photoluminescence of these compounds with different structures. In comparison to CHCl_3 solution, the relaxation processes of the excitation in DMSO solution were dramatically speeded up for three compounds.

2. Materials and Experiment

The compounds T01, T02, and T03 were synthesized from 2,4,6-tris(*p*-methylphenyl)-1,3,5-triazine and 4-[(2-chlorophenyl)imino]methyl-*N*-(*p*-methoxyphenyl)-*N*-phenyl-benzenamine with stoichiometric ratio of 1:1, 1:2, and 1:3, respectively. The final products were characterized with ^1H NMR, ^{13}C NMR, and TOF-MS. The detailed synthetic procedure and characterization of the compounds were reported elsewhere in detail.¹⁸ In these compounds, triphenylamine serves as an electron donor, 1,3,5-triazine as an electron acceptor, and styryl as a chromophore. T01 and T02 form D- π -A and D- π -A- π -D linear structures, respectively, while T03 forms octupolar tribranched structure containing three D- π -A subunits. The molecular weight of T01, T02, and T03 are 636, 921, and 1206, respectively. The solutions of these molecules in both CHCl_3 and DMSO were used in the experiment.

Steady-state absorption spectra were recorded with a UV-vis spectrophotometer (UV-3101PC, SHIMADZU) and the PL spectra were measured with a fluorescence spectrophotometer (F-2500, HITACHI). For the study on the nonlinear optical properties and the ultrafast response of these new materials, we employed a femtosecond laser system consisting of a mode-locked Ti:sapphire oscillator (Tsunami, Spectra-Physics) and a regenerative amplifier (Spitfire, Spectra-Physics). The average output power was about 300 mW with the repetition rate of 1 kHz, the pulse duration of 140 fs, and the wavelength at 800

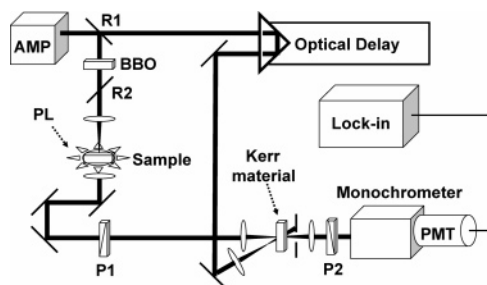


Figure 2. Experimental setup for the OKG method. R1: beam splitter; R2: high reflective mirror at 800 nm; P1: polarizers; P2: analyzer; Kerr material: CS_2 ; PMT: photomultiplier tube.

nm. We used the open aperture Z-scan technique to measure the 2PA cross section. The laser beam with 0.5 μJ pulse energy was focused on the solution in 1-mm cell by a lens of 10-cm focal length and the transmitted light, after the sample was collected by a photodiode detector connected with a Boxcar integrator.

In the two-color pump-probe experiment, the fs laser beam at 800 nm was divided into two beams by a beam splitter. One was frequency doubled via a nonlinear optical crystal BBO to generate 400-nm second-harmonic beam serving as the pump beam, while the other beam at 800 nm was used as the probe beam. After the pump beam passed through an optical delay line, two beams were focused onto the same spot of the sample. Behind the sample, the pump beam was blocked, while the transmitted probe beam was detected by a photodiode together with a lock-in amplifier (SR830, Stanford Research Systems). The temporal resolution in this experiment was about 150 fs.

TRPL dynamics of the samples were investigated by the optical Kerr-gate (OKG) method.¹⁹ Figure 2 illustrates the schematic diagram of our TRPL experiment setup. The fundamental beam generated by the regenerative amplifier was divided into two beams by a splitter (R1). The intense transmitted beam was used as the gating beam to generate the birefringence in the Kerr medium after passing through an optical delay line, while the reflected beam was frequency doubled to 400-nm beam by a BBO crystal, which was used to excite the molecules in the solution filled in a 1-mm cell. The PL emission from the solution was collected by a lens and passed through a polarizer (P1), whose polarization was set to be 45° with that of the gate beam. Then, the polarized PL emission and the gating beam were focused onto the same point in the Kerr medium which was CS_2 filled in a 5-mm thick cell. After the polarized PL emission passed through an analyzer (P2) with the cross-polarization to the polarizer (P1) and a monochromator, TRPL signals were detected by a photomultiplier (Hamamatsu R1104) in conjunction with a lock-in amplifier (SR830, Stanford Research Systems). The total response time was about 1.5 ps.

3. Results and Discussions

Linear and Nonlinear Optical Properties. The one-photon absorption and the normalized one-photon PL spectra of T01, T02, and T03 are shown in Figure 3 a and b for solvent CHCl_3 and DMSO, respectively, and some measured data are given in Table 1. The absorption peak in the long wavelength range corresponding to the π - π^* excitation is at 418 nm for T01 in CHCl_3 solution, while those for T02 and T03 solutions are red-shifted to 423 and 428 nm, respectively. This red shift may be presumably due to the delocalized electrons and the interaction among the chromophores. The absorption band at about 300 nm is attributed to the excitation of the higher excited state. All three compounds emit intense PL under the excitation at

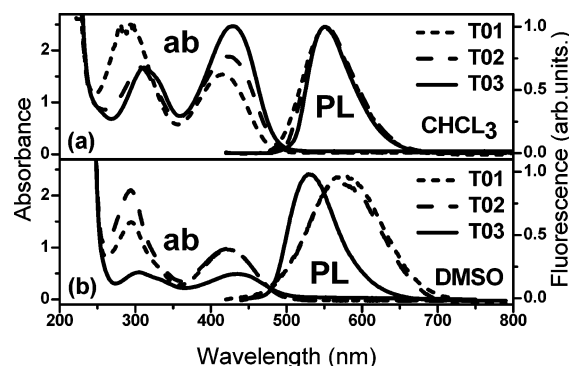


Figure 3. One-photon absorption spectra (ab), normalized one-photon photoluminescence (PL) of T01, T02, and T03 in (a) chloroform solutions and (b) DMSO solutions.

415 nm. PL emission spectra of the three compounds, extending from 500 to 700 nm, are similar and the PL peak wavelengths for T01, T02, and T03 are 550, 553, and 550 nm, respectively. When the solvent was changed from CHCl_3 to DMSO, the peaks in both the absorption and the PL emission spectra were shifted. The shift in the absorption spectra can be explained by a model proposed in ref 20. The ground-state S_0 and the excited-state S_1 are both lowered in a polar solvent and the change of the energy position of S_0 and S_1 is related to their dipole moments. If the dipole moment of S_0 is smaller than that of S_1 , S_1 will be more lowered than S_0 by the polarity of the solvent. In that case, the energy gap between S_0 and S_1 is reduced, resulting in a red-shift of the absorption band. On the contrary, the blue-shift occurs when the dipole moment of S_0 is larger than that of S_1 . In comparison with the CHCl_3 solution, the shift of the absorption peak in DMSO solutions is caused by the fact that the dipole moment of DMSO is larger than that of CHCl_3 and the influences of the solvent on the dipole moment of the molecules are different. The PL spectra for T01 and T02 in DMSO, shown in Figure 3b, are similar, but for T03, the peak wavelength of PL band shows a significant blue-shift relative to those of T01 and T02. Because triphenylamine serves as an electron donor, 1,3,5-triazine as an electron acceptor, and styryl as a chromophore in these compounds, the ICT effect should be considered. In the molecules with D- π -A structures, the ICT state has the high PL emission ability;²¹ hence, the single peak in the PL emission spectra shows that the state responsible for the PL emission is not the localized excited state but the ICT state. So, the different dipole moments of the ICT and the ground state lead to the shift in PL spectra.

The open aperture Z-scan results are shown in Figure 4a. The values of two-photon absorption coefficient (β) were determined by fitting the experiment results with self-compiled programs. 2PA cross section σ_2 can be calculated from the formula $\sigma_2 = h\nu\beta/N_0 = 10^3 h\nu\beta/N_A C$, where N_0 is the number density of absorption centers, N_A is the Avogadro constant, and C represents the solute molar concentration. The 2PA cross section of T01, T02, and T03 were calculated to be 77, 90, and 410 GM, respectively. By using the nonlinear transmission

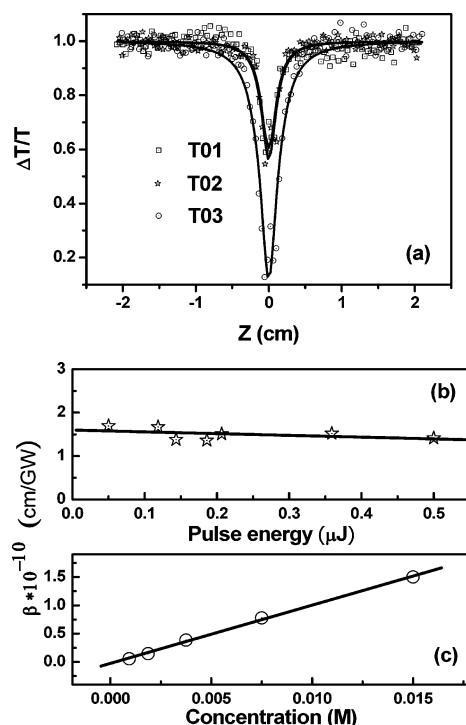


Figure 4. (a) The experimental (dot) and fitting (solid line) results of open-aperture Z-scan experiments for T01, T02, and T03 solutions. The values of β for T03 versus (b) pulse energy and (c) concentration.

measurement with nanosecond laser pulse, Lee and co-workers obtained the result that the σ_2 of their sample SSEH3 was about 9400 GM.²² Because of the different pulse durations and the experiment methods, the values of 2PA cross section measured from many experiments cannot be directly compared. The factor, defined as the ratio of 2PA cross sections of the tribranched molecule to that of the monomer, was found to be about 5 for T03 to T01. This result demonstrates that the cooperative effect on the branches in T03 certainly results in a large 2PA cross section. We also measured the values of β for these three compounds with different pulse energies and different concentrations of the sample. The results of the three compounds are similar and the typical results for T03 are given in Figure 4b and c, respectively. It can be seen that the values of β are independent of the pulse energy and it has a linear relationship with the concentration, which further proves that the dip signals in Z-scan result are caused by the 2PA process.

Excited-State Dynamics. In the two-color fs pump-probe experiment, the pump beam at 400 nm can effectively excite the molecules via linear absorption, while the probe beam was at 800 nm. Figure 5 shows the results obtained from the two-color pump-probe experiment, in which the left three figures are for CHCl_3 solutions and the right figures are for DMSO solutions. It can be clearly seen that the samples in DMSO solutions have much faster response than those in CHCl_3 solutions, demonstrating a large solvation. After fitting the experimental results by biexponential processes with the de-

TABLE 1: The Summary of the Data for Three Samples^a

	$\lambda_{\text{max}}^{\text{ab}}$ (nm)		$\lambda_{\text{max}}^{\text{pl}}$ (nm)		σ_2 (GM)	decay time (ps)			
	CHCl_3	DMSO	CHCl_3	DMSO		τ_1		τ_2	
						CHCl_3	DMSO	CHCl_3	DMSO
T01	290, 415	295, 423	550	575	77	6.7	1	135	2
T02	307, 423	294, 423	553	566	90	6.0	1.8	44	143
T03	312, 428	305, 435	550	530	410	5.3	1	43	28

^a In the table, the value of the slow decay time for T02 in DMSO is for the photobleaching signal.

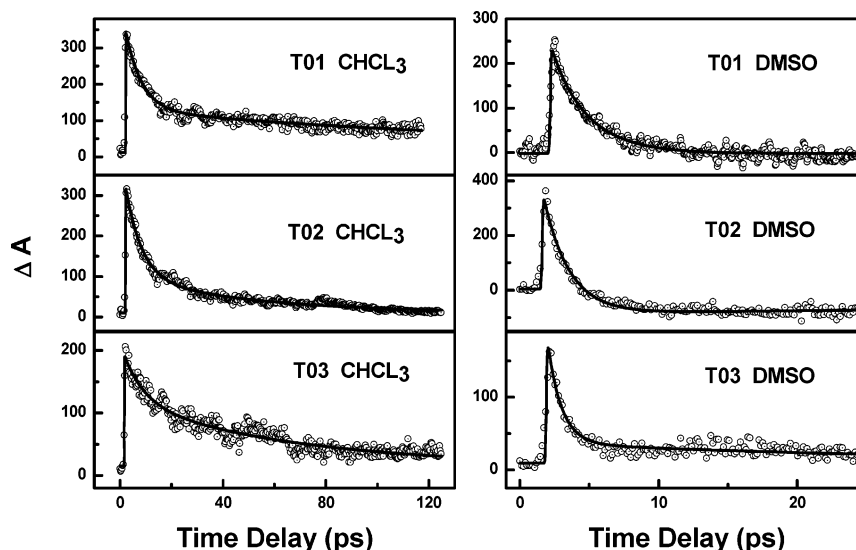


Figure 5. Two-color pump–probe dynamics with 400-nm pump and 800-nm probe for T01, T02, and T03 in different solutions: chloroform (left) and DMSO (right).

convolution of the instrumental response function, we obtained the values of two decay times τ_1 and τ_2 , which are shown in Table 1. The fast decay process may correspond to the relaxation from the localized excited state to the ICT state. When the CHCl_3 was used as the solvent, the fast decay time for T01, T02, and T03 are 6.7, 6.0, and 5.3 ps, respectively. In DMSO, τ_1 for these three samples are all decreased to about 1 ps because the larger dipole moment of DMSO speeds up this relaxation process. The slow decay time τ_2 for T01, T02, and T03 in CHCl_3 were determined to be 135, 44, and 43 ps, respectively, which were larger than those in DMSO solutions, except for T02 solution with a long-lasting bleaching signal. We suggest that this large variation comes from the different properties between the ICT states formed in two kinds of solutions. The solvent DMSO with larger dipole moment than CHCl_3 results in the faster energy transfer from LE state to ICT state and the shorter decay time in pump–probe dynamics in DMSO solutions.

As the photoabsorption (PA) effect is caused by the fact that the absorption cross section σ_e of the excited state is larger than σ_g of the ground state, the observed PA behavior reflects that the excited state of these molecules has larger absorption cross section than that of the ground state. However, the observed photobleaching (PB) signal occurring in the long delay scale for T02 in DMSO should come from the effects, such as saturated absorption, where the excited state with distinct population has smaller absorption cross section than that of the ground state. We tentatively attribute this PB behavior to the very weak absorption in the triplet state in T02 compound. In the following TRPL section, we will give further explanation to this phenomenon.

Figure 6a, b, and c shows the TRPL dynamics pumped by 400-nm fs pulses and detected at different wavelengths for T01, T02, and T03 in CHCl_3 solution, respectively. The fitting results are also shown in the figure, and the rising time (the time delay from the emergence of the signal to its maximum value) and the decay time (fit by monoexponential) are given in Table 2. We can see that when the detected wavelength was tuned from 510 to 570 nm both the rising time and the decay time increased, which indicated that the ICT state responsible for PL emission was a broad band with different energy levels. The level with higher energy has two relaxation channels: one is the relaxation to a lower energy level and the other is the PL emission process. As the intraband relaxation is a fast process via the electron–

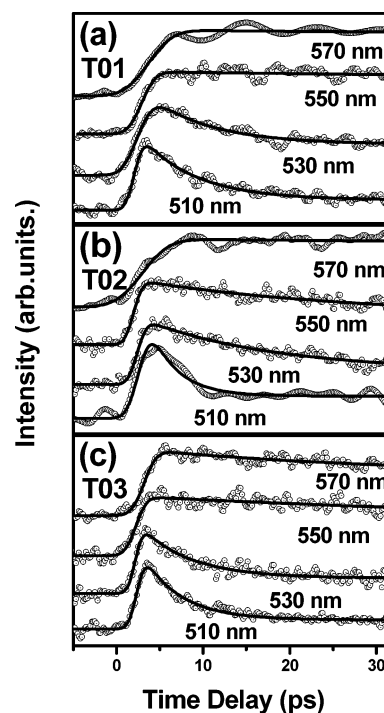


Figure 6. TRPL results at different detection wavelength in 30 ps scale: (a) T01, (b) T02, and (c) T03 in chloroform solutions. The dynamic traces are vertically shifted for clarity.

TABLE 2: The Summary of the TRPL Data for Three Samples

wavelength (nm)	T01		T02		T03	
	time (ps)		time (ps)		time (ps)	
	rise	decay	rise	decay	rise	decay
510	3.5	6.3	4	3.2	3	4.4
530	5	7	4.5	15	3.5	5.7
550	6		5	24	5	22
570	10		10		6	
CHCl_3		48		64		18
DMSO		2.5		2.9		3.2

phonon interaction, TRPL dynamics has a shorter rising time and a faster decay of PL emission at shorter detected wavelengths. At longer detection wavelengths, the longer rising time

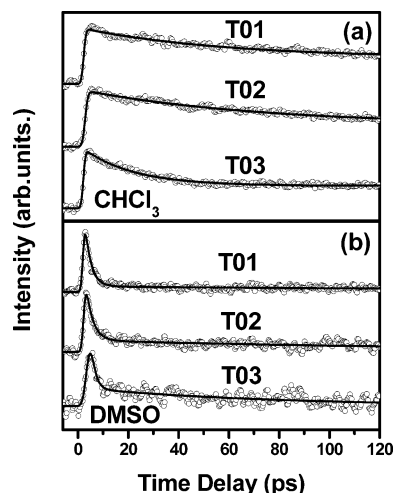


Figure 7. TRPL results of T01, T02, and T03 detected at the peak wavelength of PL emission in 120 ps time scale; (a) chloroform and (b) DMSO.

of the PL emission reflects the slower accumulation of the population in the lower levels coming from the higher levels, and the longer decay time shows the longer lifetime in the lower level. For example, at 510 nm, the rising time and the decay time of PL emission are 3.5 and 6.3 ps, respectively, much shorter than those at 570 nm with a rising time of 10 ps and a decay time too long to be obtained from the fitting process. In some papers,^{14,23} either the solvent rearrangement or the photoinduced solute conformational changes were used to explain the observed TRPL behaviors. As T02 and T03 almost exhibit C_{2v} and C_{3v} symmetry, respectively, the ICT state should also have this symmetry. It means that the character of the dipole moment for the ICT states should be different. If it is true, the solvation in these samples would also be different. T01 and T02 have similar characters at the same detected wavelength, but T03 solution has faster rising and decay features than T01 and T02.

To gain more information of the solvent effect, we studied the TRPL dynamics for these samples dissolved in the two kinds of solvent in 120 ps time scale and used the peak of the PL emission spectra as the detected wavelength. The experimental and the fitting results for the molecules in CHCl_3 and DMSO are shown in Figure 7a and b, respectively. The decay curve was fitted reasonably well with a biexponential decay function and the results are listed in Table 2. In CHCl_3 solution, the longer decay time related to the lifetime of the ICT state is too long to be fitted. TRPL features of DMSO solutions are quite different from those of CHCl_3 solutions. Both the rising time and the decay time in TRPL traces are much shorter than those in CHCl_3 solutions; they are in agreement with the results of transient pump-probe measurement. The decay time of the fast component was decreased to about 2 ps. Taking the viscosity coefficient into account, if the origin of the fast decay process in the TRPL dynamics was the conformational change, this fast decay time related to the molecule torsion would increase in the solution with DMSO which has a higher viscosity coefficient than CHCl_3 . The decrease of the first decay time indicates that the conformational change is not the main reason for the change of the rising and decay components. The shortening of the slow decay time can be explained by using the twisted intramolecular charge-transfer (TICT) model.²¹ Because of the space resistance in the ground state of the D- π -A structure molecules, the donor, π -bridge, and acceptor are not in the same plane. When the molecules were excited with the laser pulses, the intramo-

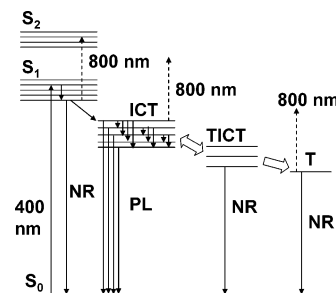


Figure 8. Energy level diagram. NR: nonradiative process; T: triplet state.

lecular charge-transfer state tends to be a planar structure, but it is not the stable state. The donor and the acceptor can twist vertically to the π -bridge plane. This twist will lower the energy of the state and form a more stable structure which is denoted as the TICT state. The TICT state is characteristic of high polarity and nonradiation, and it can be easily relaxed to the triplet state T_1 through cross-transfer which will be accelerated in the solution with a solvent of large dipole moment. Consequently, the lifetime of PL emission of the solutions in DMSO with large dipole moment is much shorter than that in the CHCl_3 solution.

The decay times of the fast component for T01 and T02 in DMSO solutions are 2.5 and 2.9 ps, respectively, slightly shorter than that for T03. After 5-ps delay, the PL emission from the two solutions nearly disappeared, while the PL emission from T03 solution still lasted long. This result reveals that after 5-ps delay, for T01 and T02, there is nearly no population in ICT state via the relaxation to the TICT state and the triplet state. For T02 compound, the triplet state would have a smaller absorption cross section than that of the ground state, leading to a PB effect. As the triplet state has a long lifetime, the population in this state would generate a long-lasting PB signal in T02 solutions, but the T03/DMSO solution still maintains PA feature.

For illustrating the processes happening in the compound solution, we propose an energy level diagram which is shown in Figure 8. The excitation of 400-nm beam excites the compound to the high-lying level in the S_1 state, from which the molecule relaxes rapidly to the lowest level via the electron-phonon coupling. Then, the excitation in the molecule transfers to ICT state and subsequently to TICT state which finally relaxes to the triplet state via the cross-transfer process.

In two-color fs pump-probe experiment, the molecules in S_1 state have a larger absorption at 800 nm than in the ground state, and they induce a transient absorption signal. The excitation-transfer processes, including the nonradiative process from S_1 state directly to the ground state and the energy transfer between S_1 state and ICT, happens in few ps scale, leading to the fast decay component in pump-probe dynamics. The slow decay component corresponds to the evolution of the excitation within ICT state. The shortening of the fast decay in DMSO solution reflects the rapid relaxation of the energy transfer from S_1 to ICT state because of intense coupling.

In TRPL experiment, the transient signal should mainly reflect the excitation and the relaxation of ICT state. In that case, the signal appears when the excitation starts to transfer to the ICT state and the population in ICT state increases. The rising time of TRPL signal corresponds to the accumulation time of the population in ICT state, where the lower levels would have longer accumulation time. The decay of the PL emission reveals the relaxation of the excitation in ICT state. The very fast decay of PL emission in DMSO solution is caused by the very efficient

energy transfer from the ICT state to the TICT state and the triplet state, resulting in the weak PL emission and the short decay time. The longer wavelength of the PL emission peak for T01 and T02 solutions in DMSO demonstrates that there would be a smaller energy gap between the ICT state, the TICT state, and the triplet state, leading to a more efficient cross-transfer to the triplet state and the faster decay of PL emission, while the slow decay component in T03/DMSO solution just demonstrates the long lifetime in this ICT state.

4. Conclusions

In summary, we have measured the ultrafast dynamics and the nonlinear optical properties of newly synthesized three compounds by means of the fs laser techniques. The values of 2PA cross section for these compounds were measured to be 77, 90, and 410 GM, respectively. The dynamics of the transient absorption and TRPL show dramatic differences between the CHCl_3 solutions and the DMSO solutions for three compounds. We suggest that the fast decay component in the pump–probe experiment is caused by the relaxation process from the excited state to the ICT state. Compared with the CHCl_3 solution, the decay time of the fast component for the three samples in DMSO solutions is greatly decreased because the solvent DMSO with the larger dipole moment will accelerate this relaxation process. In the time-resolved photoluminescence dynamics, the fast decay process is attributed to relaxation process from the high-energy level to the low-energy level in the ICT state. The long decay time is attributed to the lifetime of the lowest energy level in ICT state. The shortening of the decay time in DMSO solution was explained by the twisted intramolecular charge-transfer (TICT) model.

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