

Symmetric, Asymmetric Charge Transfer Process of Substituted Stilbene or Its Analogues and the One-Photon-/Two-Photons-Excited Emission

Xiaomei Wang,[#] Yufang Zhou, Guangyong Zhou, Wanli Jiang, and Minhua Jiang*

State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

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The luminescence behaviors of a series of symmetrically and asymmetrically substituted stilbene or its analogues on one-photon excitation (OPE) and two-photons excitation (TPE) have been investigated and compared. To understand the influence of intramolecular charge transfer upon the fluorescence properties, steady-state and time-resolved fluorescence spectra on one-photon-/two-photons-excitation, the solvent effect and the linear absorption spectra as well as the relative fluorescence quantum yields were examined. Based on the quantum chemical calculations of the charge density and the twisted intramolecular charge transfer (TICT) model, the luminescence properties have been interpreted. The results obtained have shown that the OPE and the TPE fluorescence behaviors are both strongly influenced by the intramolecular charge transfer process and by the planarity of effective fluorophore under the excited state. On the other hand, for a given dye, its luminescence behaviors on one-photon- and two-photons-excitation are very much alike, which means that the knowledge of two-photon fluorescence properties can be obtained by understanding the one-photon fluorescence behaviors.

Two-photons-excited (TPE) fluorescence has been of fast-growing interest for a wide variety of applications including two-photons-excited up-converted lasing,[1] optical data storage,[2,3] and two-photons photodynamic therapy.[4] Applications that specifically require excited state fluorescence include TPE fluorescence microcopy,[5] which has gained widespread popularity in the biology community, owing to its ability to image at an increased penetration depth in tissue with reduced photodamage. Due to the quadratic dependence of fluorescence intensity on the excitation intensity, the photobleaching occurs only in the vicinity of the focal point, and this also makes it possible to achieve depth discrimination even without a confocal aperture in front of the photon-detector.[6] In addition, the use of long-wave-wavelength light minimizes autofluorescence of the sample; cells are also more viable under the infrared excitations, thus permitting the imaging of living tissue. Moreover, use of IR excitation opens up the entire visible spectrum for multiple detection channels. So, the research in molecules with efficient TPE fluorescence recently has been of interest from the application point of view.

Generally, the key ingredients for efficient molecular TPE fluorescence are a large two-photon absorption cross section and a high fluorescence quantum yield. In most cases, TPE fluorescence applications have relied on molecules originally designed for one-photon-excited (OPE) fluorescence.[7] However, the structure-property relationships of molecules with high either OPE fluorescence or TPE fluorescence have not been well understood yet. It is known that the OPE luminescence properties (especially, solvent effect) for asymmetric molecules can be well interpreted by the "TICT" (the twisted intramolecular charge transfer) model[14–16] that plays an important role in the present study. However, there is no report yet which gives a comparative study on the relationships between the intramolecular charge transfer process for the symmetric/asymmetric molecules and the resultant OPE/TPE fluorescence behaviors using the "TICT" model.

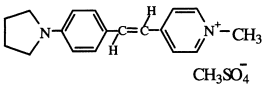
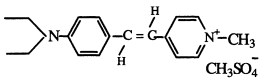
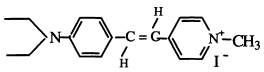
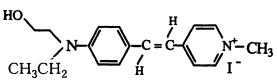
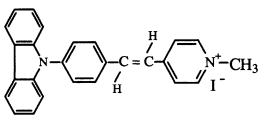
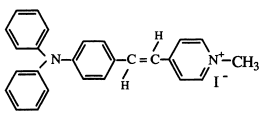
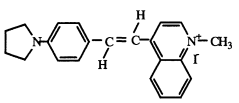
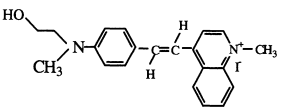
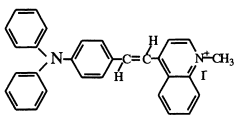
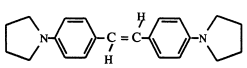
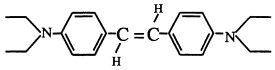
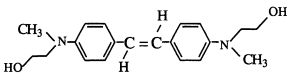
Recently, we reported a series of substituted stilbene-type derivatives with symmetric and asymmetric intra-molecular charge transfers and investigated their two-photons absorptivities.[9–10] The results have shown that substituted stilbenes with symmetric intra-molecular charge transfer have larger two-photons absorption (TPA) cross-sections than those of the counterparts with the asymmetric charge transfer.[9] Also, we examined briefly the OPE spectra for symmetrically and asymmetrically substituted stilbenes and found that the one-photon fluorescence intensity for the asymmetric molecules is dramatically decreased, in comparison with their symmetric counterparts.[9] Here, we investigate in detail the relationships between the intra-molecular symmetric/asymmetric charge transfer way and the resultant OPE/TPE luminescence properties based on the quantum chemical calculations and the "TICT" model. The results of this work are as follows: (i) A comparative study on OPE fluorescence behavior has been done for understanding the relationship between symmetric and asymmetric intramolecular charge transfer process and photoluminescence behavior. (ii) The TPE fluorescence spectra, temporal behavior and solvent effect were compared with the corresponding results obtained for OPE fluorescence in order to understand the relationship between OPE fluorescence and TPE fluorescence behavior.

Experimental

Materials and Characterizations. Table 1 presents the mo-

College of Material Science and Engineering, Soochow University, Suzhou 215021, China

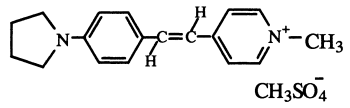
Table 1. Molecular Structures, Linear Absorption, Extinction Coefficients (ε), One-Photon-Excited Fluorescence and the Corresponding Fluorescence Intensity (I_{em}) in DMF*

Dyes	Molecular structures	λ_{max}^{ab}/nm (ε/l mol^{-1} cm^{-1})	λ_{max}^{em}/nm (Intensity)
PSPS 4-[*trans*-4-(1-Pyrrolidinyl)styryl]-1-methylpyridinium methylsulfate		479 (31,000)	592 (100)
DEASPS 4-[*trans*-4-(Diethylamino)styryl]-1-methylpyridinium methylsulfate		482 (32,000)	597 (200)
DEASPI 4-[*trans*-4-(Diethylamino)styryl]-1-methylpyridinium iodide		483 (36,000)	597 (120)
HEASPI 4-{*trans*-4-[Ethyl(2-hydroxyethyl)amino]-styryl}-1-methylpyridinium iodide		478 (33,000)	597 (120)
CSPI *trans*-4-(9-Carbazolyl)styryl-1-methylpyridinium iodide		400 (17,000)	597 (10)
DPASPI 4-[*trans*-4-(Diphenylamino)styryl]-1-methylpyridinium iodide		458 (31,000)	597 (10)
PSQI *trans*-4-(1-Pyrrolidinyl)styryl-1-methylquinolinium iodide		554 (18,000)	no fluo
HMASQI 4-{*trans*-4-[(2-Hydroxyethyl)-methylamino]styryl-1-methylquinolinium iodide		551 (5,900)	no fluo
DPASQI 4-(*trans*-4-Diphenylaminostyryl)-1-methylquinolinium iodide		514 (26,000)	no fluo
DPS *trans*-4,4′-Di(1-pyrrolidinyl)stilbene		376 (20,000)	425 (550)
BDEAS *trans*-4,4′-Bis(diethylamino)stilbene		374 (55,000)	435 (600)
BHMAS *trans*-4,4′-Bis[*N*-(2-hydroxyethyl)-methylamino]stilbene		374 (44,000)	406 (500)

*The concentrations for all dyes are 1×10^{-5} M in the measurement of linear absorption, while the concentrations are 1×10^{-5} M for asymmetric dyes and 1×10^{-8} M for symmetric dyes in the measurement of one-photon excited fluorescence.

lecular structures discussed in this paper. Here, the new dyes 4-[*trans*-4-(1-pyrrolidinyl)styryl]-1-methyl pyridinium methyl sulfate (PSPS) and 4-[*trans*-4-(diethylamino)styryl]-1-methyl pyridinium methyl sulfate (DEASPS), as shown in Fig. 1, were firstly synthesized according to the similar methods reported previously;[10] the synthesis procedure of other samples was reported in our

PSPS:



DEASPS:

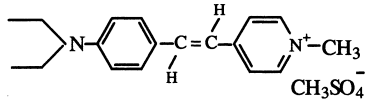


Fig. 1. Molecular structures for newly synthesized dye PSPS and DEASPS.

other work.[9,11] These dyes are a series of stilbene-type derivatives with either asymmetric substituents (i.e. D-π-A structural type) or symmetric substituents (i.e. D-π-D structural type). Most of them were crystallizable in suitable solvent and have been solved on a Bruker P4 four-cycle diffractometer.

Linear absorption spectra of all samples at $c = 1.00 \times 10^{-5}$ M (1 M = 1 mol dm^{-3}) have been measured with a Hitachi U-3500 recording spectro-photometer from quartz curettes of 10 mm path. The extinction coefficients (ε) were determined from the absorption measurement with a concentration of 1×10^{-5} M. The influences from the quartz liquid cell and the solvent DMF have been subtracted.

One-photon-excited (OPE) fluorescence spectra including steady-state fluorescence and the time-resolved emission spectra were measured on a Schimadzu RF5000U fluoro-photometer or an Edinburgh FLS 920 fluorophotometer in a 10-mm path length cell. The concentrations of symmetric dyes are at 1.0×10^{-8} M, and of asymmetric dyes are at 1.0×10^{-5} M. Different solvents including toluene, chlorobenzene, benzyl alcohol, chloroform, DMF, acetone, acetonitrile, and water were employed to study the solvent effect. The relative fluorescence quantum yield (Φ_f) were calculated by the equation: $F = 2.303(\varepsilon cl)\Phi_f I_0$. Here F is the relative fluorescence intensity; ε, c, and l are the extinction coefficient, the sample concentration and the thick of sample cell, respectively. I_0 is the incident intensity on excitation.

Two-photons-excited (TPE) emission spectra were made in a 10-mm path length cell. An optical parameter amplifier pumped by a mode-locked Nd:YAG laser (operating at 1064 nm, pulse duration of 40-ps and pulse repetition of 10 per second) was used as the pump source; the laser is tuned between 500-1100 nm in our measurements. The TPE fluorescence collection was taken at a right angle to the incident radiation using a streak camera C5680-01 with a 2-ps resolution, and the time-decay curves were also recorded with a similar method. TPE super-emission spectra were determined in front-face configuration by the streak camera; a double-detector energy-meter (EPM 2000, Molectron) was used in the measurement of the super-emission efficiencies.

Computations. Semi-empirical quantum chemical method (PM3) was used to determine the charge density distribution on each atom in molecule under the ground state (S_0) and the excited state (S_1); while ZINDO program was used to calculate the molecular dipole moment change ($\Delta\mu_{ge}$) between S_0 and S_1 states.

Results and Discussion

Symmetric, Asymmetric Charge Transfer Process and the OPE Fluorescence. Table 1 shows the maximum peak of the linear absorption (λ_{max}^{ab}) and the corresponding extinction coefficients (ε), and the maximum peak of the OPE fluorescence spectra (λ_{max}^{em}) as well as the relative fluorescence intensity (F). It can be seen that the asymmetric dyes show electronic absorption at relatively obvious bathochromic shift from 400–483 nm (ε = 17,000–36,000) for pyridinium derivatives to 514–554 nm (ε = 5,900–26,000) for quinolinium derivatives. On replacing the terminal acceptor group of asymmetric dyes with a donor group, a blue-shift occurs to the maximum absorption peak of about 374 nm (ε = 20,000–55,000). On the excitation of their respective absorption wavelength light, dyes emit fluorescence except for all quinolinium derivatives.

Calculated relative fluorescence quantum yields for symmetric and asymmetric dyes are quite different. As presented in Table 2, the relative fluorescence quantum yields (denoted as $\Phi_f I_0$) are 4.7×10^5–1.2×10^6 for symmetric dyes, and 1.4×10^1–1.4×10^3 for asymmetric pyridinium derivatives. When the donor group is fixed to a diethylamino group, the relative fluorescence quantum yields in DMF solvent vary from 4.9×10^5 for BDEAS (D-π-D), to 2.7×10^2 for DEASPS (D-π-A), and 1.4×10^2 for DEASPI (D-π-A). Evidently, the relative fluorescence quantum yields in DMF sol-

Table 2. Charge Distribution on "D", π-Center and "A"/"D" for Asymmetric Dyes (D-π-A) and Symmetric Dyes (D-π-D), Dipole Moment Change ($\Delta\mu_{ge}$), and the quantum yield in DMF at the Concentration of 1×10^{-5} M

Compounds	$\Delta\mu_{ge}$/D	Quantum yield ($\Phi_f I_0$)	S_0 state			S_1 state		
			Q_{amino}	Q_π	Q_{pyrid}/Q_{amino} (e)	Q'_{amino}	Q'_π	Q'_{pyrid}/Q'_{amino} (e)
D-π-A								
PSPS	3.4	1.4×10^2	+0.2150	+0.0428	−0.2573	+0.6269	+0.1927	−0.8228
DEASPS	8.1	1.4×10^3 ($CHCl_3$) 2.7×10^2 (DMF)	+0.2325	+0.0478	−0.2611	+0.6670	+0.1695	−0.8365
HEASPI	8.2	1.6×10^2	+0.1954	+0.0528	−0.2611	+0.6162	+0.2024	−0.8365
DEASPI	8.1	1.4×10^2	+0.2325	+0.0478	−0.2640	+0.6670	+0.1695	−0.8798
DPASPI	11.8	1.4×10^1	+0.2141	+0.0409	−0.2481	+0.9309	+0.0498	−0.8138
CSPI	7.4	2.5×10^1	+0.1286	+0.0709	−0.2295	+0.4138	+0.0040	−0.4734
D-π-D								
BHMAS	0.03	4.7×10^5	−0.0287	+0.0577	−0.0287	+0.0267	−0.0534	+0.0267
DPS	0.02	1.2×10^6	−0.0255	+0.0510	−0.0255	+0.0312	−0.0623	+0.0312
BDEAS	0.04	4.9×10^5	−0.0271	+0.0543	−0.0271	+0.0417	−0.0834	+0.0417

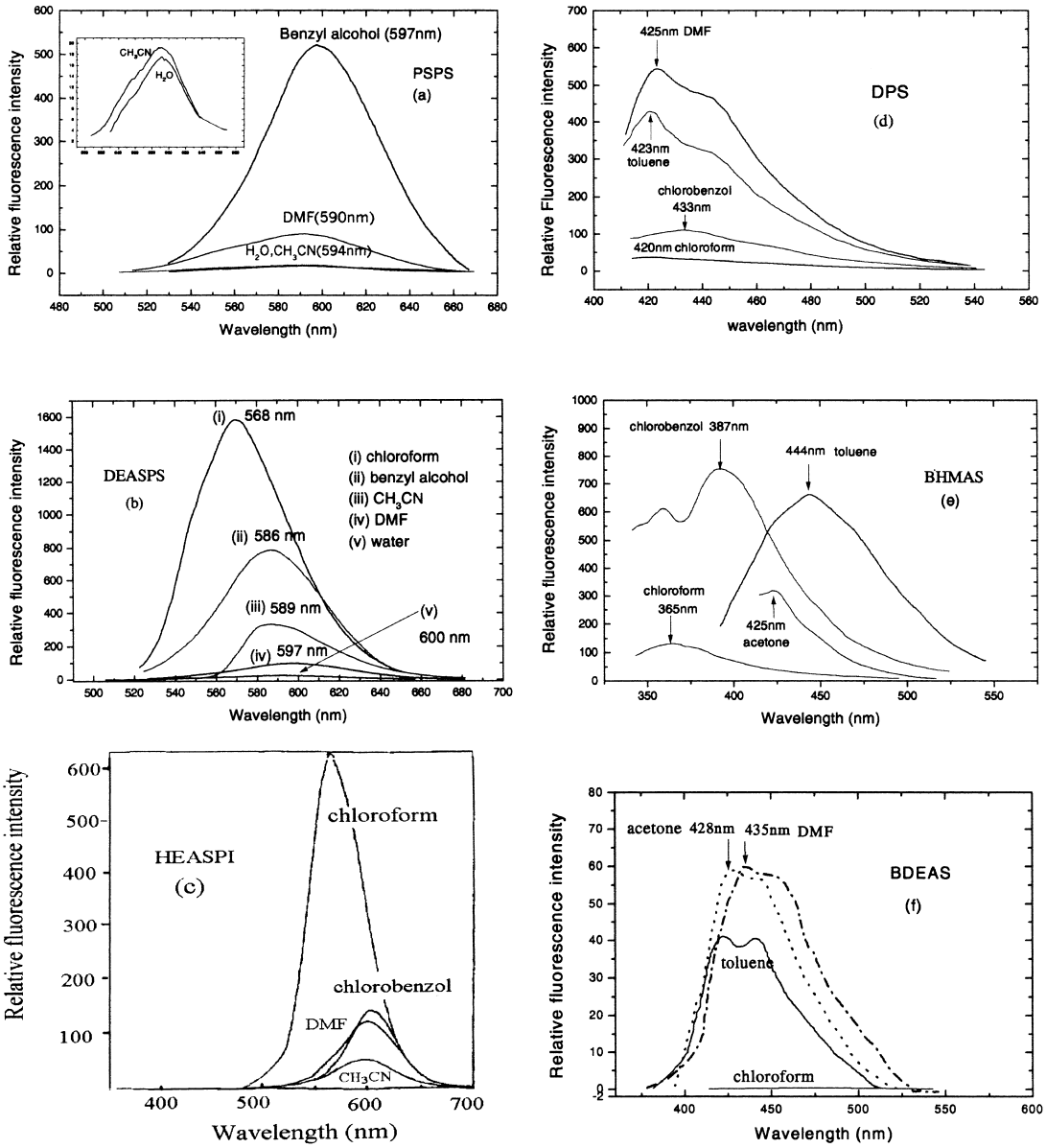


Fig. 2. OPE fluorescence for asymmetric ($c = 1 \times 10^{-5}$ mol dm^{-3}) and symmetric dyes ($c = 1 \times 10^{-8}$ mol dm^{-3}) in different solvents. The curve of DPS in toluene is obtained by reduced the original measured data 6 times in the intensity scale.
*Combination with solvent polarity parameter $E_T(30)$[12] and the dipole moments in the gas phase (μ_0),[13] the polarity sequence of some solvents is obtained as follows: water, CH_3CN, DMF, acetone, benzyl alcohol, chlorobenzol, $CHCl_3$, and toluene.

vent for symmetric dyes are much larger than those for their asymmetric counterparts.

Figure 2 shows there are quite different solvent effects for symmetric and for asymmetric dyes. For asymmetric pyridinium derivatives, the luminescence behaviors are very sensitive to the solvent polarity, but for symmetric dyes the luminescence behaviors are not sensitive to the solvent polarity. From Fig. 2a, Fig. 2b, and Fig. 2c, one can observe that PSPS, DEASPS and HEASPI give a bathochromic shift of the long-wave fluorescence spectra with increases in solvent polarity. For example, the maximum shifts of DEASPS (see Fig. 2b) are from 568 nm in chloroform, 586 nm in benzyl alcohol, 589 nm in acetonitrile, 597 nm in DMF, to 600 nm in water. Along with the red-shift, the relative fluorescence intensity obviously lowers. Similar behaviors are also observed for PSPS and HEASPI in Fig. 2a and Fig. 2c, which are as same as that for PSPI reported previously.[9]

On the contrary, the luminescence behaviors for symmetric dyes, DPS, BHMAS and BDEAS, seem to not be correlated with the solvent polarity. From Fig. 2d, Fig. 2e and Fig. 2f, it can be seen that the relative fluorescence intensities are all strong both in a nonpolar solvent such as toluene and in a polar solvent such as DMF. Identical observations are obtained for other symmetric stilbene dyes BDPAS.[9]

It is interesting to find that symmetric dyes in chloroform gave the weakest emission intensity, while asymmetric pyri-

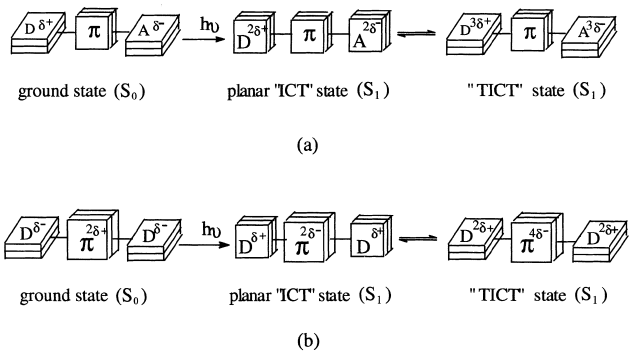


Fig. 3. "TICT" model of asymmetric charge transfer for pyridinium and quinolinium derivatives (a) and symmetric charge transfer for bis-donor substituted stilbenes (b).

dinium derivatives in chloroform gave the strongest emission. The latter fluorescence quantum yield is increased by almost one order of magnitude, compared with the corresponding quantum yield in DMF (see Table 2). These results indicate that the emission behaviors depend on not only the molecular structure-type but also the solvent effect.

To explain the intrinsic elements that influence the fluorescence properties of symmetric and asymmetric dyes, it is necessary to examine the π-electron redistribution between the ground state (called S_0 state) and the excited state (called S_1 state), since the luminescence behavior is generally correlated with these two states. An illustration of the changes about charge density based on our calculations and about geometry based on "TICT" model[14] is shown in Fig. 3a and Fig. 3b.

Calculated results have shown that asymmetric dyes experience the asymmetric intramolecular charge transfer from donor end to acceptor end both in S_0 and S_1 states, as the arrow shows in Fig. 3a. One can also see from Table 2 that the charge density distribution of PSPS in S_0 state is as follows: $Q_{\text{amino}} = +0.2150\ e$, $Q_{\pi} = +0.0428\ e$ and $Q_{\text{pyrid}} = -0.2573\ e$, an obvious asymmetric polar distribution. Once in S_1 state, a larger asymmetric charge transfer occurs further from donor to acceptor along the molecular axis, and the resultant charge distribution is $Q'_{\text{amino}} = +0.6269\ e$, $Q'_{\pi} = +0.1927\ e$ and $Q'_{\text{pyrid}} = -0.8228\ e$. Similar results of the other asymmetric dyes in Table 2 can be expected. In contrast, symmetric dyes possess the symmetric intramolecular charge transfer, just as the arrow direction in Fig. 3b denotes. In S_0 state, charge transfer in the symmetric molecule shifts from central stilbene-unit to the terminal substituted amino groups. And in the S_1 state, the interaction of the π-orbits between the two terminal substituted amino and the stilbene-center gives rise to an efficient charge reverse, i.e., charge transferring from two donating groups to the stilbene center. For example, charge distribution of BHMAS is $Q_{\text{amino}} = -0.0287$e, $Q_{\pi} = +0.0577\ e$ in S_0 state, and $Q'_{\text{amino}} = +0.0267\ e$, $Q'_{\pi} = -0.0534\ e$ in S_1 state. Same charge transfer behaviors of other symmetric dyes can also be observed in Table 2.

From Fig. 3a–3b, one can see that, in the course of the excitation from S_0 state to S_1 state (concluding "ICT" and "TICT" states), the molecule with twisted configuration initially undergoes an intra-molecular asymmetric or symmetric charge transfer and forms a planar intra-molecular charge transfer excited state (abbreviated "ICT" state). And then, it becomes a twisted configuration, called twisted intra-molecular charge transfer excited state (abbreviated "TICT" state), as a result of further symmetric or asymmetric intra-molecular charge transfer.

For asymmetric molecules such as pyridinium and quinolinium derivatives, the planar "ICT" state is the emissive one and the twisted "TICT" state is nonradiative.[15] We consider that, for asymmetric dyes ("D-π-A") such as substituted styryl-pyridinium dyes, the effective fluorophore group is "styryl-pyridinium" moiety (i.e. "π-A"), while the "D" moiety just acts as the fluorochrome group based on our spectral experiments. The "TICT" state is less emissive in the range of near IR wavelengths because the planarity of the effective fluorophore has been distorted or twisted. Since the charge density is gradually increased on the acceptor end from S_0 state, "ICT" state to "TICT" state (as shown in Fig. 3a), we deduce that the dipole moment in the "ICT" state is larger than that in the ground state, and becomes even larger in the "TICT" state. Calculations have confirmed that the dipole moment for asymmetric dyes in the excited state is greater than that in the ground state by 3.4–11.8 D, as shown in Table 2. Based on this consideration, the experimental results shown in Fig. 2a, Fig. 2b, and Fig. 2c can be explained. Solvation of asymmetric dyes under the excited state is more effective than that of the ground state, which effectively lowers the energy level of the excited state. Generally, the larger solvent polarity, the more obvious solvation for the non-emissive "TICT" state, and a much lower energy level between S_0 and S_1 ("TICT") state will be formed, as shown in Fig. 7. As a result, in a more highly polar solvent such as water, CH_3CN and DMF, asymmetric dyes give very low fluorescence intensity accompanied with a red-shifted peak position. In relatively lower polar solvents such as $CHCl_3$ and benzyl alcohol, asymmetric dyes will give relatively high fluorescence intensity, owing to more effective solvation of the planar emissive "ICT" state, and accompanied with a blue-shifted peak position. But a very low polar solvent, such as toluene, has been demonstrated to be a hindrance to forming polar "ICT" state and the fluorescence intensity decreased very much.

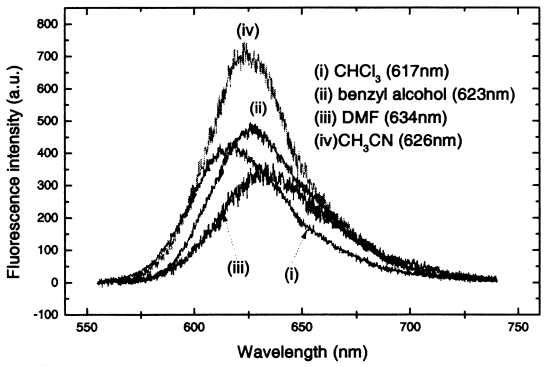
In addition, the fact that there exists no detectable fluorescence for quinolinium derivatives, as presented in Table 1, can be also explained. Since the fused aromatic heterocycle in the substituted styryl-quinolinium derivatives such as PSQI, HMASQI, and DPASQI has much more tendency to form a nonradiative "TICT" state, this may have quenched the fluorescence completely. Similarly, the terminal aromatic (hetero) rings in CSPI and DPASPI have also much more tendency to form "TICT" state, so the resultant fluorescence yields are markedly decreased as shown in Table 2.

As for symmetric dye, it is our opinion that the stilbene-center (here "π" moiety) is the effective fluorophore group, while the two terminal donors act as fluorochromes based on our spectral experiments. From Fig. 3b, it can be seen that on the excitation when the electron density surrounding the stilbene-center becomes much more abundant (see Table 2), the resultant planarity of the stilbene-center is generally increased. Moreover, such an intra-molecular symmetric charge transfer does not lead to a change in molecule dipole moment ($\Delta\mu_{\text{ge}}$).

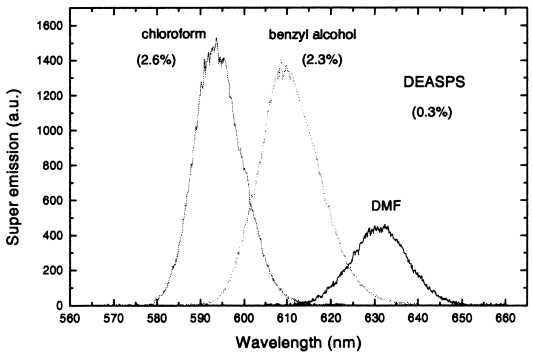
PM3 calculations have confirmed that the difference in dipole moment ($\Delta\mu_{ge}$) for symmetric molecules is almost negligible (see Table 2). In other words, during a symmetric charge transfer, not only the polarity but also the planarity of the fluorophore in both "ICT" and "TICT" states are generally unchanged. Therefore, there will be two aspects that are quite different from their asymmetric counterparts in fluorescence behaviors. One is that symmetric dyes are less sensitive to the solvent polarity, which has been confirmed by our experiments shown in Fig. 2d, Fig. 2e, and Fig. 2f. The other is that both "ICT" and "TICT" states for symmetric dyes are emissive due to the planarity of effective fluorophore in the two states being almost equal. The proof is that the fluorescence spectra for all symmetric dyes exhibit dual fluorescence (see Fig. 2d, Fig. 2e, and Fig. 2f), and the measured time-resolved emission spectra give the lifetime values for "ICT" and "TICT" states which are nearly the same. For example, the lifetimes of these two states for DPS are 2.09 ns and 2.44 ns in toluene; and 1.69 ns and 1.57 ns in chlorobenzene. In contrast, for asymmetric dyes, the emission spectra just display single fluorescence (see Fig. 2a, Fig. 2b, and Fig. 2c.), showing that only "ICT" state is emissive. For this reason, the relative fluorescence quantum yield of symmetric dyes is much larger than that of their asymmetric counterparts.

As for the quite different luminescence behaviors in chloroform for symmetric and asymmetric dyes, one hypothesis is that a chloroform molecule exhibits withdrawing electron property. The solvation of symmetric dyes in chloroform hinders the intramolecular symmetric charge transfer since the charge transfer direction is from two-terminal donors to the stilbene-center on the excitation (see Fig. 3b). That is, the solvation in chloroform has the disadvantage of forming either "ICT" or "TICT" state. So, the fluorescence in chloroform for symmetric molecules is quenched heavily. On the other hand, owing to intramolecular asymmetric charge transfer, the solvation of asymmetric dyes in chloroform may stabilize the excited state; it would especially stabilize the emissive "ICT" because the relatively small polarity of chloroform would restrain the solvation of "TICT" state. So the fluorescence in chloroform for asymmetric dyes would strengthen dramatically.

OPE Fluorescence and TPE Fluorescence Behaviors. To explore the relationship of luminescence behavior for one-photon- and two-photons-excitation, a series of comparative experiments about OPE fluorescence and TPE fluorescence behaviors were systematically conducted. It is interesting to note that the TPE fluorescence behaviors are very similar to the OPE fluorescence behaviors. Firstly, the solvent effect behaviors on the OPE- and TPE-fluorescence are very much alike. Figures 4a and 4b show TPE fluorescence and super-emission spectra for DEASPS, respectively. Comparing Fig. 4a with Fig. 2b, one can see that the peak positions for both OPE and TPE fluorescence spectra are blue-shifted generally with the decrease of the polarity of the solvents. For example, one can see from Fig. 4a that the peak position is at 634 nm in DMF, 626 nm in CH_3CN, 623 m in benzyl alcohol and 617 nm in chloroform, which is in agreement with the solvent effect of OPE (see Fig. 2b). The identical blue-shift sequence for super-emission spectra with the decrease of solvent polarity can be observed in Fig. 4b. From Fig. 4b, it can be also seen that the



(a)



(b)

Fig. 4. TPE fluorescence (a), super-emission spectra (b) for DEASPS.

efficiency of TPE super-emission is in the sequence: 2.6% (in chloroform) $>$ 2.3% (in benzyl alcohol) $>$ 0.3% (in DMF), while in water there is no emission. This sequence is the same as the sequence of OPE relative fluorescence intensity, as shown in Fig. 2b.

Secondly, the TPE- and OPE-fluorescence spectra are very much alike in shape. Figure 5 shows the TPE fluorescence spectra for symmetric molecules DPS, BHMAS, and BDEAS in DMF solvent at $c = 0.005$ M. If one compares these spectra shapes with their OPE fluorescence spectra shapes, as presented in Fig. 2d, Fig. 2e, and Fig. 2f, one can observe the obvious dual fluorescence for both of two-photons excitation and one-photon excitation. The explanation is the presence of both emissive "ICT" and emissive "TICT" state when a symmetric charge transfer occurs on the excitation.

Finally, time-resolved TPE fluorescence for DEASPS shows that the fluorescence lifetime decreases with the increase of solvent polarity, which is in agreement with the change effect on the OPE fluorescence lifetime in different solvents. The TPE fluorescence decay curves, as presented in Fig. 6, exhibit the lifetime of 231.1 ps in chloroform, while in the polar solvent such as DMF and acetonitrile, the fluorescence decay rate is much faster, i.e. 78.33 ps in DMF, and 37.93 ps in acetonitrile. Correspondingly, the measured lifetime of OPE fluorescence for DEASPS is 2.09 ns in chloroform, 2.01 ns in benzyl

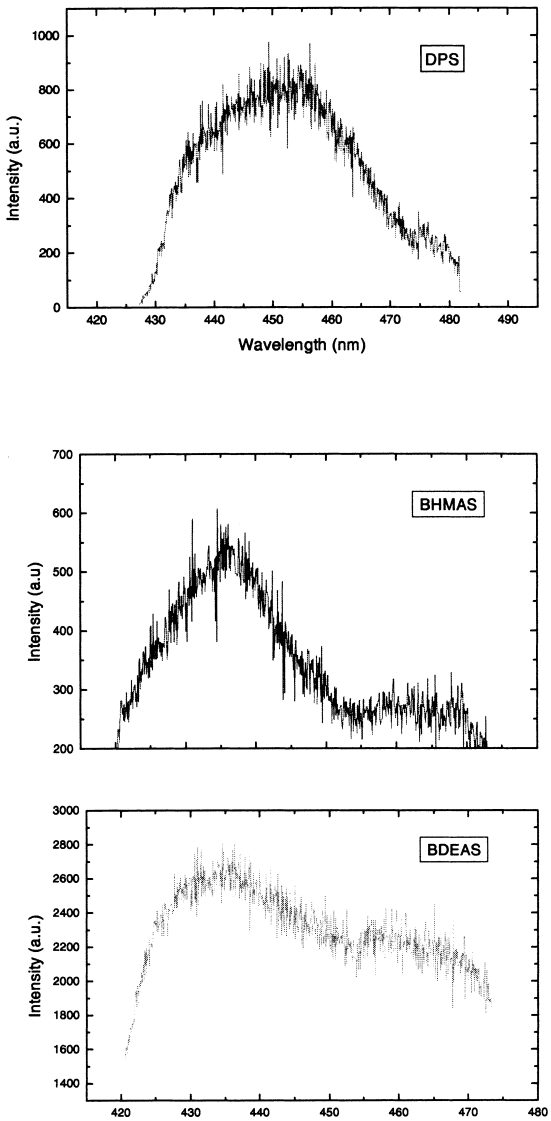


Fig. 5. TPE fluorescence spectra of symmetric dyes in DMF at $c_0 = 0.005$ mol dm^{-3}, using 740 nm laser pulse.

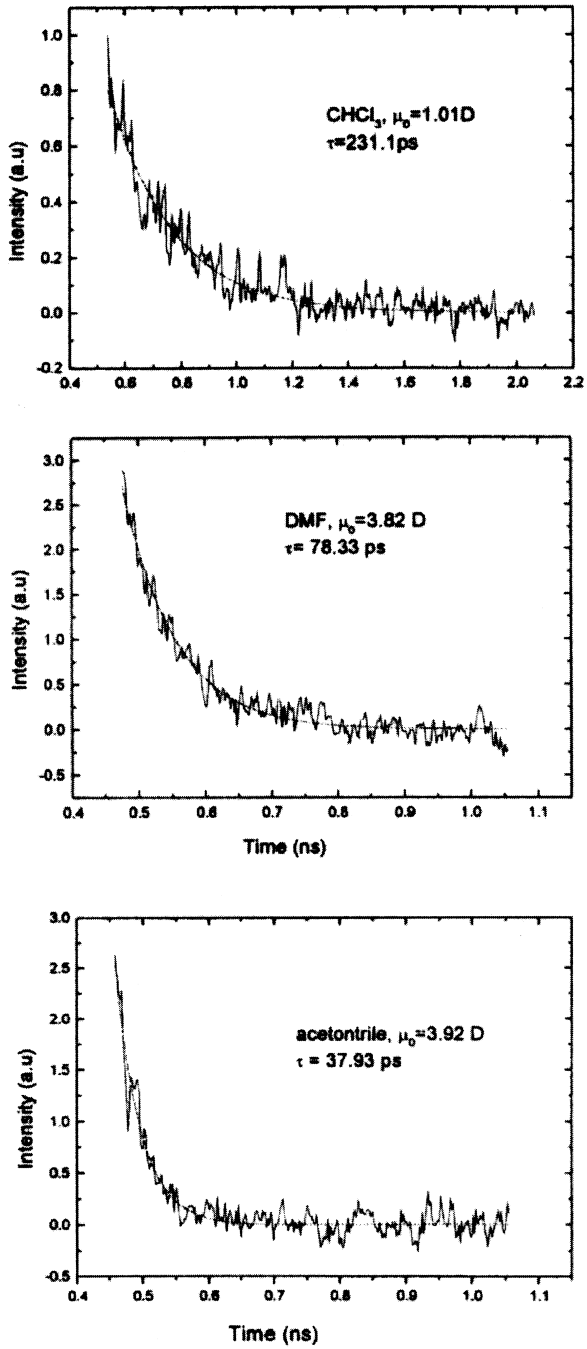


Fig. 6. Two-photon fluorescent decay curves of DEASPS (0.005 mol dm^{-3}) in different solvents, in which solid lines are the fitting results at 1064 nm laser pumping.

alcohol, and $<$ 1.58 ns in DMF; showing there exists an identical change effect on the lifetimes of both OPE and TPE fluorescence.

From such analyses, one can deduce that the fluorescence emission on both one-photon- and two-photons-excitation is predominantly from the transition of the same state, i.e. from S_1 to S_0 state. From Fig. 7, one can observe that the main difference between OPE and TPE fluorescence is their excitation processes; one is one-photon excitation (OPE), and the other is two-photons excitation (TPE) in which a molecule is excited from S_0 state to the S_1 state by simultaneous absorption of two photons. In both cases, the initially excited molecule relaxes to the excited state from the up-lying vibration energy level, then either emits the fluorescence or follows a nonradiating way to the ground state. From Fig. 7, it can be also deduced that molecular two-photons-excited fluorescence behavior can be predicted using the "TICT" model and that the one-photon fluorescence behaviors offer a simple way to help understanding the two-photons fluorescence properties, which accords with the conclusions reported by J. W. Baur and co-workers.[8] Having investigated the relationship between the solvent effect and the optical properties for some asymmetric molecules, J. W. Baur and co-workers have also confirmed that the one-photon luminescence and two-photon luminescence have some similarity.

Conclusions

The relationships between the symmetric/asymmetric charge transfer and molecular one-photon-/two-photons-excit-

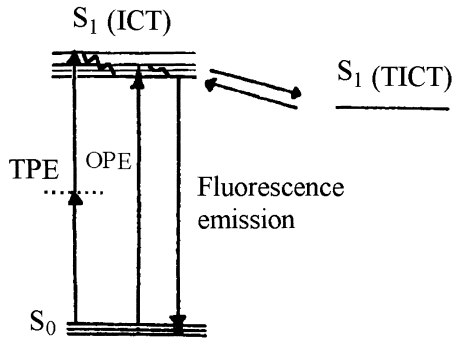


Fig. 7. The micro-process of the one-photon- and two-photon-excited emission.

ed fluorescence properties of a series of substituted stilbene-type derivatives have been reported. The results have shown that intramolecular charge transfer way and the planarity of the effective fluorophore in the excited state are the main elements that result in variations in the corresponding luminescence properties on both one-photon- and two-photons-excitation.

The reason why symmetric and asymmetric dyes in chloroform show opposite fluorescence behaviors is that the solvation of chloroform hinders the symmetric intramolecular charge transfer from two-terminal donor-ends to the stilbene-center, while it hastens asymmetric intramolecular charge transfer that helps to stabilize the emissive "ICT" state for asymmetric moleculaes. As a result, asymmetric pyridinium derivatives show the strongest fluorescence emission and symmetric dyes exhibit the weakest, and in one case even quench fluorescence completely.

The experiments have shown that "ICT" and "TICT" states for symmetric dyes are emissive since the planarity of the effective fluorophore in "ICT" and "TICT" states is better than that in the ground state. On the other hand, for asymmetric dyes, only "ICT" state is emissive due to its fluorophore in "TICT" state being distorted heavily. The resultant relative fluorescence quantum yield decreases dramatically from symmetric molecules to asymmetric counterparts. Quantum chemical calculations have shown that on the excitation the polar moment change of the symmetric dyes is almost negligible, while that of the symmetric dyes is much larger owing to their different charge transfer way. Therefore, for symmetric dyes the fluorescence behaviors seems to be less influenced by solvent polarity, but for asymmetric dyes the fluorescence behaviors are very sensitive to solvent polarity.

For each given molecule, the two-photons-excited fluorescence behaviors are similar to those of the one-photon fluorescence in shape, solvent effect and lifetime. It is deduced that molecular two-photons-excited fluorescence properties can be predicted based on either the "TICT" models or the corresponding one-photon-excited fluorescence behaviors.

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