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Two-photon fluorescence properties of a styrylpyridinium derivative organic chromophore in different solvents

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ABSTRACT The fluorescence properties of a new two-photon absorption chromophore in dimethyl formamide, methanol, acetone, benzyl alcohol, methylene chloride and chloroform are reported. The lifetime, intensity and central wavelength of the fluorescence signal vary significantly in different solvents. The fluorescence properties are explained by using the twisted intramolecular charge-transfer model, the viscosity of the solvents and the formation of the hydrogen bond. For the dye in all solvents, the longer the fluorescence lifetime, the higher the fluorescence intensity. Generally, the higher the dipole moments, the longer the central wavelengths of the dye.

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1 Introduction

Two-photon absorption (TPA)-induced frequency up-conversion lasing has become increasingly interesting and promising in recent years [1–8]. Its main advantages are the elimination of phase-matching requirements, high wavelength tunability and the capability of adopting waveguide and fiber configurations. The lifetime of the excited state affects the formation of lasing oscillation directly. In general, the longer the lifetime of the excited state, the easier the lasing oscillation. Some pyridiniums with 'donor–π–acceptor' structures have a large TPA cross section and an excellent up-conversion efficiency [7–11]. Trans-4-[p-(N-n-propyl-N-n-propylamino)-styryl]-N-methyl-pyridinium p-toluene sulfonate is a new organic dye synthesized by Y.P. Tian's group. The dye has excellent solubility in some low polar solvents such as benzyl alcohol, methylene chloride and dimethyl chloroform, as well as some high polar solvents such as formamide (DMF), acetone and methanol. But the lifetimes and intensities of the TPA fluorescence vary with different solvents. In this paper the TPA fluorescence properties and mechanisms for the variation of the properties in different solvents are reported.

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2 Experimental methods

The concentration of the dye for each solvent was kept constant (0.01 mol/l) and all experiments were performed using a 1-cm-path cuvette. Figure 1 shows the experimental arrangement for the measurement of the spectral and temporal properties of the TPA-induced fluorescence of the dye. The incident 1064-nm laser beam came from a mode-locked Nd : YAG laser (Continuum, PY61C-10). The beam size, pulse duration, repetition rate and angular divergence were 3 mm, 42 ps, 10 Hz and 0.4 mrad, respectively. The pump laser beam was focused onto the sample through an $f = 15$ cm lens. The focus point of the lens was outside of the sample to avoid the generation of TPA amplified spontaneous emission (ASE). In order to minimize the reabsorption of the fluorescence, the laser beam was as close as possible to the cuvette wall from which the fluorescence was collected. The TPA-induced fluorescence was collected from one side of the sample by two lenses. The spectral and temporal profiles of the TPA fluorescence were measured with a streak camera (Hamamatsu, C5680-01) in conjunction with an imaging spectrograph (Hamamatsu, C5094). A beam splitter was used to split off ∼ 5% of the pump laser to the detector of the delayer, which was
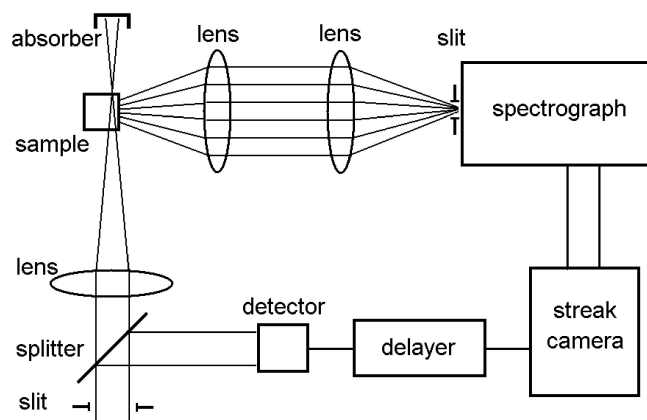
FIGURE 1 The experimental arrangement used for the measurement of the temporal and spectral profiles of the TPA fluorescence of the dye
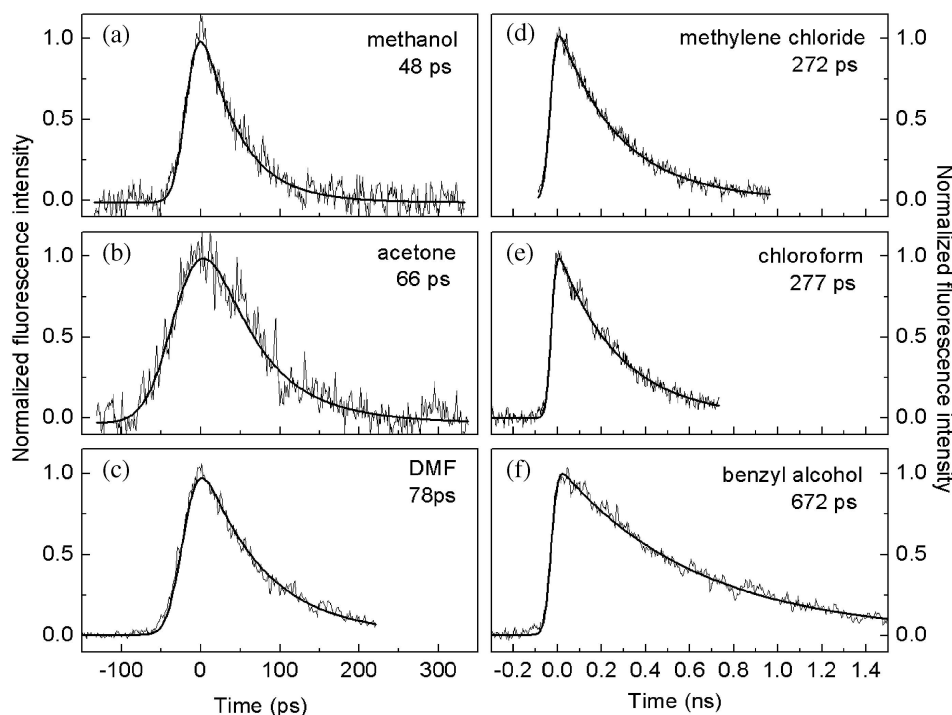
FIGURE 2 The temporal profiles of the TPA-induced fluorescence of the dye in different solvents
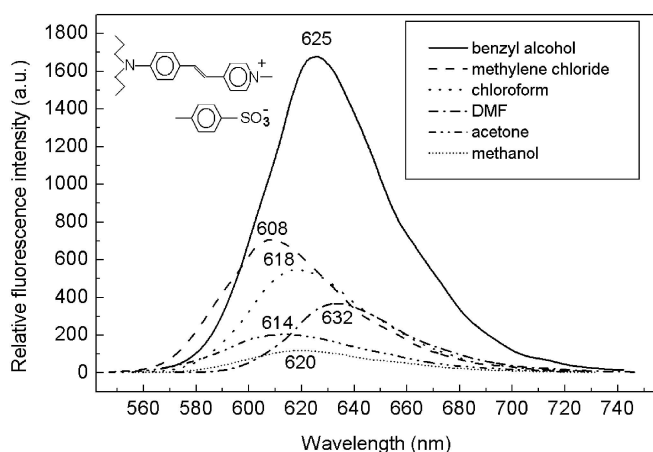
used to trigger the streak camera in the measurement of the temporal properties.

3   Results

Figure 2 shows the temporal profiles of the TPA-induced fluorescence of the dye in different solvents. The fluorescence lifetime of the dye varies significantly for each solvent. The fluorescence lifetimes of the dye were measured to be 48 ps, 66 ps and 78 ps in three high polar solvents (methanol, acetone and DMF) and 272 ps, 277 ps and 672 ps in three low polar solvents (methylene chloride, chloroform and benzyl alcohol), respectively. Figure 3 shows the spectral profiles of the dye in different solvents. One can see that the intensity and the peak wavelength vary significantly in differ-

ent solvents. By comparing Figs. 2 and 3, it can be seen that the longer the lifetime of the fluorescence, the higher the intensity of the fluorescence. For example, in benzyl alcohol, the dye has the highest intensity and the longest fluorescence lifetime. In methanol, the dye has the lowest fluorescence intensity and the shortest fluorescence lifetime.

From Fig. 3 one can also see that the central wavelengths of TPA fluorescence are different in different solvents. For the solvents methylene chloride, chloroform, methanol, benzyl alcohol and DMF, the larger the dipole moments, the longer the central wavelengths. This is because the lowest-energy state of the first excited state is lowered in a polar solvent. The larger the dipole moment, the lower the excited state [14]. However, acetone does not obey this rule. For methanol and benzyl alcohol, the dipole moments are almost the same, but the central wavelengths are different.

4   Discussion

4.1   *The effect of the polarity of the solvents on the lifetimes*

The polarity of the solvents may affect the fluorescence lifetime of the dye. Table 1 shows the polarity (dipole moment) and viscosity coefficients of the solvents [12] as well as lifetimes, central wavelengths and intensities of TPA-induced fluorescence. In general, the smaller the dipole moment, the longer the lifetime. The properties can be explained by using the 'twisted intra-molecular charge-transfer (abbreviated as TICT)' model [13]. The schematic diagram is shown in Fig. 4a. There is a space resistance in the ground state (S_0) of the molecules with 'D–π–A' structure. The amido-cyanogen (donor, D), styrene group and pyridyl (acceptor, A) are not in the same plane. The structure on the left-hand side in Fig. 4a is a typical structure of a molecule in ground state S_0. When the molecule was excited to the first excited

FIGURE 3 The spectral profiles of the dye in several different solvents at the concentration of 0.01 mol/l. The *upper-left corner* shows the chemical structure of the dye

	Benzyl alcohol	Methylene chloride	Chloroform	DMF	Acetone	Methanol
Dipole moment (10^{-30} C m)	5.54	3.8	3.84	12.88	8.97	5.55
Viscosity coefficient (mPa s)	7.76	0.425	0.563	0.802	0.316	0.595
Lifetime (ps)	672	272	277	78	66	48
Central wavelength (nm)	625	608	618	632	614	620
Peak intensity (a.u.)	1681	711	553	370	205	121

TABLE 1   The dipole moments and the viscosity coefficients of the different solvents as well as the central wavelengths and intensities of TPA-induced fluorescence of the dye in different solvents
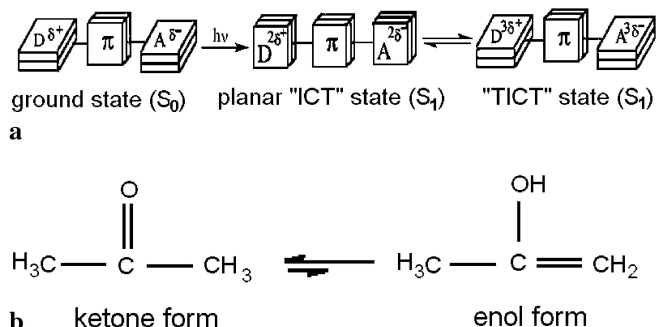
FIGURE 4   The twisted intra-molecular charge-transfer (TICT) model of the pyridinium compounds with a D–π–A structure (**a**) and chemical structures of two resonant structures of the acetone: ketone-form acetone and enol-form acetone (**b**)

state S_1 by light, the electrons transfer from the donor to the acceptor. The positive charge at the donor and the negative charge at the acceptor both increase. The molecule tends to be in a plane and forms an intra-molecular charge-transfer (ICT) state. This state has high fluorescence-emission ability. But, in view of the energy, the ICT state is not the most stable state. As the electrons transfer from the donor to the acceptor, the amidocyanogen twists to almost vertical to the styrene-group plane and the acceptor also twists away from the styrene-group plane. This twist of the molecule lowers the energy and the molecule becomes more stable than before. This state is called the twisted intra-molecular charge-transfer (TICT) state. The molecule in the TICT state has high polarity, bad planarity and is more stable than in the ICT state. But the molecule in the TICT state can easily transfer to the non-radiative triplet state T_1 through cross-transfer. So, the TICT state is a non-radiative state. The destruction of the planarity of styrene pyridinium in the chromophore is the main property of the TICT state. The solvent with a large dipole moment will accelerate the cross-transfer process. So, the fluorescence lifetime in the solvent with a large dipole moment is shorter than that in the solvent with a small dipole moment. The fluorescence properties of the dye in methylene chloride, chloroform and DMF can be explained by using the TICT model.

4.2   *The effect of the viscosity of the solvents on the lifetime*

The TICT model cannot explain the fluorescence properties in all solvents used in this work. For example, the dipole moment of benzyl alcohol is 5.54×10^{-30} C m, which is bigger than those of methylene chloride and chloroform; the lifetime should be shorter than those of methylene chloride and chloroform if only the TICT model was considered.

However, the lifetime is much longer than those in methylene chloride and chloroform. From Table 1 one can see that the viscosity coefficient is 7.76 mPa s, which is more than one order larger than those of the other solvents. We assumed that the high viscosity of benzyl alcohol results in the long lifetime. Because of the restriction of the collision between the dye molecules and solvent molecules, it is not easy for a molecule in an excited state to transfer from the radiative ICT state to the non-radiative TICT state. As a result, the fluorescence lifetime in benzyl alcohol is much longer than that in the other solvents. Another pyridinium dye HESAPS with a similar structure doped in a solid polymer has a fluorescence lifetime as long as 4.14 ns as the result of the complete restriction of the molecule torsion [7].

4.3   *The effect of the hydrogen bond on the lifetimes*

The dipole moment of methanol is smaller than that of DMF and the difference of viscosity coefficients is not big, but the fluorescence lifetime of the dye in methanol is much shorter. This is due to the formation of the H bond between the hydrogen in the hydroxyl of the methanol and the nitrogen in the pyridyl of the dye. In the ground state, there are always negative charges on the methanol–pyridinium of the dye. In the excited state, due to the transfer of the electrons from the donor to the acceptor, there are more negative charges on the methanol–pyridinium. Because of the formation of the hydrogen bond, the methanol can be considered as a new function group added to the dye. So, the energy structure of the dye was changed and the planarity of the dye was destroyed. The benzyl alcohol molecule also has the hydroxyl. It is not easy to form a hydrogen bond due to the existence of the large phenyl. So, the hydroxyl in benzyl alcohol does not affect the dye very much.

4.4   *The existence of the enol form in acetone*

Comparing acetone with DMF, one can see that the dipole moment of acetone is smaller than that of DMF. However, the lifetime in acetone is much shorter than that in DMF. This phenomenon can be explained as follows. (1) The viscosity coefficient of DMF is 2.5 times larger than that of acetone. As discussed above, the high viscosity of the solvent will help to increase the lifetime of the fluorescence. (2) The polarity of acetone is relatively high (8.97×10^{-30} C m). The high polarity will lead to a short fluorescence lifetime. (3) The possibility of the existence of enol-form acetone. In general, we consider acetone as a pure compound with the chemical structure shown on the left-hand side in Fig. 4b. This kind of structure is called ketone-form acetone. In fact, there is another resonant form in acetone with the chemical structure

shown on the right in Fig. 4b. There is equilibrium between these two structures and the ratio of them is a constant at a certain condition in pure acetone. In general the proportion of the enol form is extremely small and in most cases it can be ignored. But the hydroxyl group in enol-form acetone may form a hydrogen bond with the dye, just like methanol. The equilibrium between ketone-form acetone and enol-form acetone will be destroyed and move to the side of enol-form acetone. This process will continue until a new equilibrium is established. The proportion of enol-form acetone will be much larger in the new equilibrium than that in pure acetone. In total, the high polarity, the low viscosity and the existence of enol-form acetone together lead to the short fluorescence lifetime of the dye in acetone.

5   Conclusion

The temporal and spectral properties of TPA fluorescence of a dye in different solvents were studied. The lifetime, intensity and central wavelength vary significantly in different solvents. For the solvents methylene chloride, chloroform and DMF, the larger the dipole moments, the shorter the fluorescence lifetimes. For the solvent benzyl alcohol, it is the high viscosity that leads to the long lifetime. The possible existence of the hydrogen bond between the methanol and the dye leads to the short lifetime in methanol. The existence of enol-form acetone, the relatively large dipole moment and the relatively low viscosity coefficient lead to the very short fluorescence lifetime of the dye in acetone. For all solvents used in our experiments, the longer the fluorescence lifetime, the higher the fluorescence intensity. In general, the larger the dipole moment, the longer the central wavelength of the TPA fluorescence. From our results we know that benzyl alcohol is the best solvent to use for this dye in achieving TPA cavity lasing because the dye has long fluorescence lifetime, high fluorescence intensity as well as high boiling point, and methylene chloride is the best candidate to achieve cavity lasing at short wavelength.

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