Investigation of energy transfer from pyrromethene dye to cresyl violet 670 in ethanol*

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In this paper, radiative and nonradiative energy transfer from laser dye pyrromethene 567 (PM567) and pyrromethene 580 (PM580) as donors to cresyl violet 670 (CV670) as acceptor in ethanol are investigated by using the steady-state emission measurement and the second harmonic generation (532 nm, $\sim$ 13 ns) of a Q-switched Nd:YAG laser as the pumping source. The fluorescence intensity of the acceptor is improved due to the introduction of the donors, and the largest enhancement is obtained to be 128% in the PM567:CV670 dye mixture system. Energy transfer parameters, including the radiative and nonradiative energy transfer rate constants (K_R and K_{NR}), critical distance (R_0), and half quenching concentration ($[A]_{1/2}$) are investigated using the Stern–Volmer plots, and the acceptor concentration dependencies of radiative and nonradiative transfer efficiencies are also obtained. The values of K_R for PM567:CV670 and PM580:CV670 systems are 2032.0×10^9 L·mol^{-1}·s^{-1} and 2790.4×10^9 L·mol^{-1}·s^{-1}, respectively, and the values of corresponding K_{NR} are 3.3×10^9 L·mol^{-1}·s^{-1} and 4.2×10^9 L·mol^{-1}·s^{-1}, respectively. The results indicate that the dominant mechanism responsible for the energy transfer in the dye mixture systems is of the radiative type.

Keywords: energy transfer, dye mixture, Stern–Volmer plot, steady-state emission

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1. Introduction

The energy transfer between laser dyes has been widely investigated by researchers[1–15] since it demonstrated that it was able to expand the lasing wavelength range[16,17] and enhance the efficiency[7,18,19] of dye laser. This process is of great importance for laser dyes with low efficiencies when directly excited with the commercial lasers. By introducing the donor dye molecules into the lasing matrices, the pumping energy can be effectively coupled to the acceptor dye molecules through the energy transfer process, thus resulting in enhanced laser efficiency.

The energy transfer between laser dyes has been reported both in liquid solutions and solid state matrices. Kumar and Unnikrishnan[5] investigated the energy transfer between FDS and rhodamine B (RhB) in methanol using an Ar ion laser as the pumping source. They concluded that the dominant energy transfer mechanism was of the radiative type using the Stern–Volmer plots and the acceptor concentration dependencies of radiative and nonradiative transfer efficiencies. Sahare *et al.*[7] investigated the effect of acceptor concentration on the energy transfer in acriflavine:rhodamine 6G (Rh6G) and acriflavine:RhB binary dye solutions in methanol. They determined that the dominant mechanism responsible for the energy transfer was of nonradiative type due to long-range dipole–dipole interaction. The energy transfer between dye mixtures has also been reported in solid state matrices to improve the laser properties of solid state dye lasers. By doping dye mixture Rh6G:RhB into PMMA matrix, Kumar *et al.*[6] demonstrated an enhancement of the fluorescence intensity of RhB by 226%. Nhung *et al.*[8] realized the tuning band position control and increased efficiency with the energy transfer between RhB and Perylene red (P-red) in xerogel matrices. Yang *et al.*[9] obtained enhanced laser performances based on energy transfer of several coumarin dyes and PM567 as the donors with P-red as the acceptor. They obtained a two-fold enhancement in laser efficiency and a tunable range of 80 nm.

The main mechanisms for the intermolecular energy transfer in dye mixtures include:[1,3–5,18,20] (i) radiative energy transfer in which the emission of the donor is absorbed by the acceptor; and (ii) nonradiative energy transfer due to the interaction between the donor and the acceptor during the excitation lifetime of the donor. This mechanism can be divided into two types, i.e., 1) diffusion-controlled energy transfer, which occurs over intermolecular distances of the order of molecular distances and is dependent on the viscosity and temperature of the solvents; 2) resonance energy transfer due to long-range dipole–dipole interaction, and the process occurs with the donor–acceptor separation much greater than the collisional diameters. The two mechanisms can be distinguished by measuring the donor fluorescence lifetime as a function of the acceptor concentration. If the donor lifetime is little affected by the acceptor concentration, then the mechanism (i)

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can be considered to be dominant.[18]

Pyrromethene (PM) dyes have been widely used in recent years due to their high efficiency and good chemical stability.[21–24] Cresyl violet 670 (CV670) is a kind of dye emitting in the red region of the spectrum,[13,18] which has many potential applications in biology and medical care. However its lasing efficiency is usually very low. In this paper, two PM dyes, i.e. PM567 and PM580 as energy donors are dissolved into ethanol with CV670 as energy acceptor, and different relative concentrations are used to improve the efficiency of CV670. The fluorescence spectra of the dye mixtures are investigated by measuring the steady-state emission and using the second harmonic generation (SHG) of a Q-switched Nd:YAG laser as the pumping source. The energy transfer parameters, including the radiative rate constant ($K_{\rm R}$), nonradiative rate constant ($K_{\rm NR}$), critical distance (R_0), and half quenching concentration ($[A]_{1/2}$) are obtained using the Stern–Volmer plots and the acceptor concentration dependencies of the radiative and nonradiative transfer efficiencies are also investigated.

2. Experiment

PM567, PM580, and CV670 (Exciton Inc.) were directly used without further purification. Ethanol (spectroscopic grade, $> 99.9\%$) was used to prepare the dye mixtures with the specific concentration ratios in a rectangular quartz cell of dimensions 2 mm×20 mm. The dye mixtures were pumped with the SHG (532 nm, $\sim$ 13 ns) of a home-made Q-switched Nd:YAG laser, and the steady-state emission spectra were measured at the right angle with a high resolution portable spectrometer (HR4000, Ocean Optics). The absorption spectra of the dye solutions were measured using a Shimadzu UV-3010PC spectrophotometer. The fluorescence lifetime of the donors was measured using the 530 nm, $\sim$ 50 fs output of a femtosecond optical parameter amplifier (OPA, TOPAS, Coherent) as the pumping source. A combination of fast silicon PIN detector (DET210, Thorlabs) and a 1-GHz digital storage oscilloscope (DPO7104, Tektronix) was used as the detection system.

3. Theory

The energy transfer rate constants for the radiative and nonradiative energy transfer mechanisms can be obtained from the Stern–Volmer plots given by the following equations[3–5,18]

$$\frac{I_{0\rm d}}{I_{\rm d}} = 1 + K_{\rm SV}[A] = 1 + K_{\rm T}\tau_{0\rm d}[A], \tag{1}$$

$$\frac{\phi_{0\rm d}}{\phi_{\rm d}} = 1 + K_{\rm NR}\tau_{0\rm d}[A], \tag{2}$$

where $I_{0\rm d}$ and I_d are the fluorescence intensities of the donor in the absence and presence of the acceptor, respectively, $\phi_{0\rm d}$ and $\phi_{\rm d}$ are the corresponding quantum yields, $[A]$ is the acceptor concentration, $\tau_{0\rm d}$ is the fluorescence lifetime of the donor in the absence of the acceptor, $K_{\rm SV}$ is the quenching rate constant, $K_{\rm T}$ and $K_{\rm NR}$ are the total and nonradiative energy transfer rate constants, respectively.

The radiative energy transfer rate constant $K_{\rm R}$ can be obtained as

$$K_{\rm R} = K_{\rm T} - K_{\rm NR}. \tag{3}$$

Another important parameter for the energy transfer is the critical transfer distance R_0, which is the average distance between the donor and the acceptor, at which the probability of intermolecular energy transfer is just equal to the sum of probabilities for all the de-excitation processes of the excited state donor.[10] The R_0 can be calculated by[10,18]

$$R_0 = 7.35/([A]_{1/2})^{1/3}, \tag{4}$$

where $[A]_{1/2}$ is the half-quenching concentration, which can be obtained under the condition

$$I_{0\rm d}/I_{\rm d} = 2. \tag{5}$$

The energy transfer efficiencies can be calculated by measuring the fluorescence intensities and quantum yields of the donor with and without acceptor. The total energy transfer efficiency $\eta_{\rm T}$ can be obtained as

$$\eta_{\rm T} = 1 - \frac{I_{\rm d}}{I_{0\rm d}}. \tag{6}$$

The nonradiative energy transfer efficiency $\eta_{\rm nr}$ can be expressed in the form of

$$\eta_{\rm nr} = 1 - \frac{\phi_{\rm d}}{\phi_{0\rm d}}. \tag{7}$$

Then the radiative energy transfer efficiency $\eta_{\rm r}$ can be obtained as

$$\eta_{\rm r} = \eta_{\rm T} - \eta_{\rm nr}. \tag{8}$$

The $\eta_{\rm nr}$ can also be calculated theoretically.[2] For nonradiative energy transfer of diffusion controlled mechanism

$$\eta_{\rm nr} = \frac{K_{\rm diff}[A]}{K_{\rm diff}[A] + \tau_{0\rm d} - 1}, \tag{9}$$

where $K_{\rm diff} = 2 \times 10^5 T/\eta$ with T being the temperature, and η the coefficient of viscosity of the medium. For nonradiative energy transfer due to long range dipole–dipole interaction, we have

$$\eta_{\rm nr} = \pi^{1/2} X \exp(X^2)(1 - {\rm erf}X), \tag{10}$$

where $X = [A]/[A]_0$ is the molar concentration of the acceptor, $[A]_0 = 3000/(2\pi^{3/2} N R_0)$, and

$${\rm erf}X = \frac{2}{\pi^{1/2}} \int_0^X \exp(-t^2)\,{\rm d}t.$$

Another expression for the nonradiative transfer efficiency η_{nr} is[3]

$$\eta_{nr} = 1 - \frac{\tau_d}{\tau_{0d}}. \tag{11}$$

Combining Eq. (7) and Eq. (11), we have

$$\tau_d/\tau_{0d} = \phi_d/\phi_{0d}. \tag{12}$$

4. Results and discussion

The spectral overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor is the prerequisite for the energy transfer process. Figure 1 shows the overlap between the fluorescence spectra of the donors of 1×10^{-4} mol/L and the absorption spectrum of the acceptor of 5×10^{-5} mol/L in ethanol. It is shown that there is a large area of overlapping between the fluorescence spectra of the donors and the absorption spectrum of the acceptor, indicating that the energy transfer should be possible.

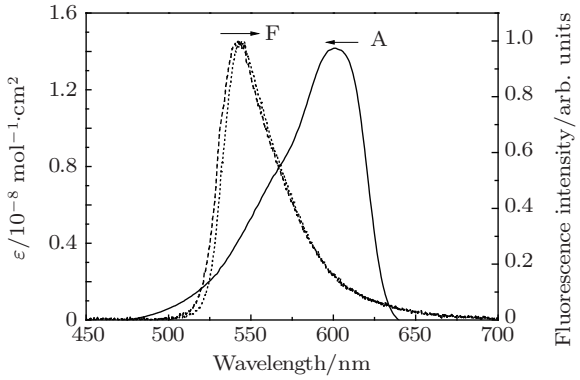


Fig. 1. Absorption spectrum of CV670 of 5×10^{-5} mol/L (solid) and fluorescence spectra of PM567 (dash) and PM580 (dot) of 1×10^{-4} mol/L.

Shown in Figs. 2 and 3 are the fluorescence spectra of PM567:CV670 dye mixtures with the donor concentration fixed to be 1×10^{-4} mol/L and varying acceptor concentrations, and with the acceptor concentration fixed to be 1×10^{-4} mol/L and varying donor concentrations, respectively. The corresponding fluorescence spectra of PM580:CV670 dye mixtures are presented in Figs. 4 and 5, respectively. For both dye-mixture systems, with the donor concentration fixed and increasing the acceptor concentration, the fluorescence intensity of the donor decreases gradually, while the fluorescence intensity of the acceptor increases accordingly (see Figs. 2 and 4). The results confirm the existence of energy transfer in the dye mixtures. For the case of fixing acceptor concentration and increasing donor concentration, the fluorescence intensities of the acceptor are increased by different orders of magnitude due to the introduction of donors. The highest enhancement is obtained to be 128% in the PM567:CV670 dye-mixture system.

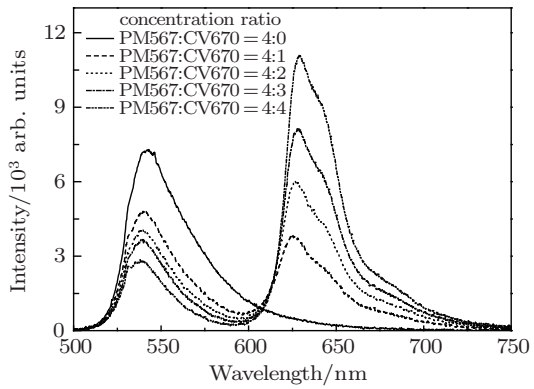


Fig. 2. Fluorescence spectra of PM567:CV670 dye mixtures with fixed donor concentration and varying acceptor concentrations. The concentration of PM567 is 1×10^{-4} mol/L.

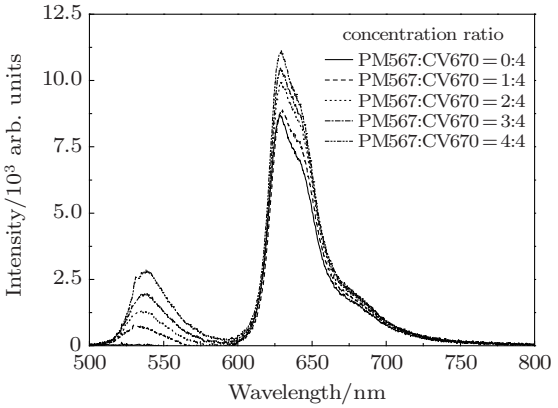


Fig. 3. Fluorescence spectra of PM567:CV670 dye mixtures with fixed acceptor concentration and varying donor concentrations. The concentration of CV670 is 1×10^{-4} mol/L.

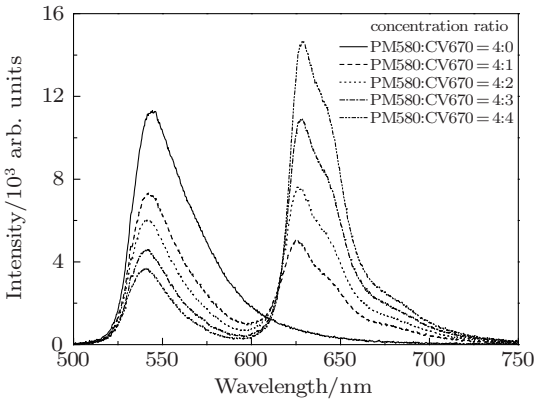


Fig. 4. Fluorescence spectra of PM580:CV670 dye mixtures with fixed donor concentration and varying acceptor concentrations. The concentration of PM580 is 1×10^{-4} mol/L.

The variations of I_{0d}/I_d with the acceptor concentration for the two dye-mixture systems are presented in Fig. 6. The quenching rate constant K_{SV} and critical transfer distance R_0 are obtained with Eq. (1) and Eq. (5).

The fluorescence lifetime of the donor in the absence of the acceptor τ_{0d} is measured with the 530 nm, $\sim$ 50 fs OPA output as the pumping source, and τ_{0d} is determined to be 7.91 ns and 8.23 ns for the PM567 and PM580, respectively. Then the total energy transfer rate constant K_T is obtained using Eq. (1). The measured K_{SV}, K_T, and R_0 are presented in

Table 1.

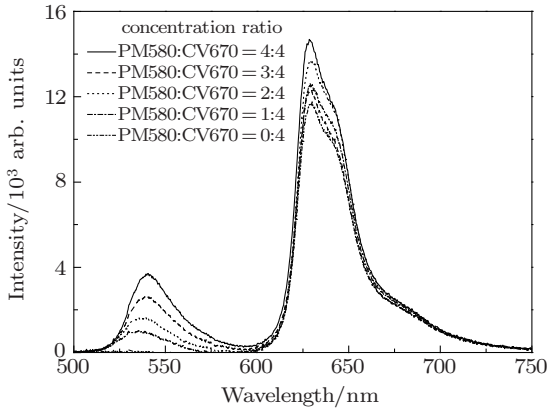


Fig. 5. Fluorescence spectra of PM580:CV670 dye mixtures with fixed acceptor concentration and varying donor concentrations. The concentration of CV670 is 1×10^{-4} mol/L.

The large values of R_0 indicate that the nonradiative energy transfer is of the long range dipole–dipole type. Therefore Eq. (10) is used for the calculation of η_{nr}, since the diffusion cannot play an important role in the system with such large intermolecular distances.[2] The dependencies of η_{nr} on the acceptor concentration $[A]$ are shown in Fig. 7. It is shown that the η_{nr} increases linearly with acceptor concentration increasing.

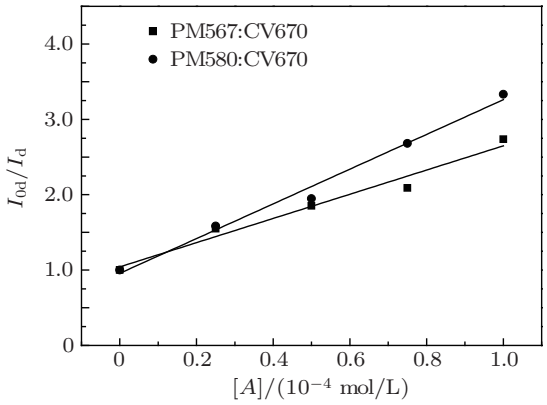


Fig. 6. Stern–Volmer plots for relative fluorescence intensity of PM567:CV670 and PM580:CV670 dye-mixtures

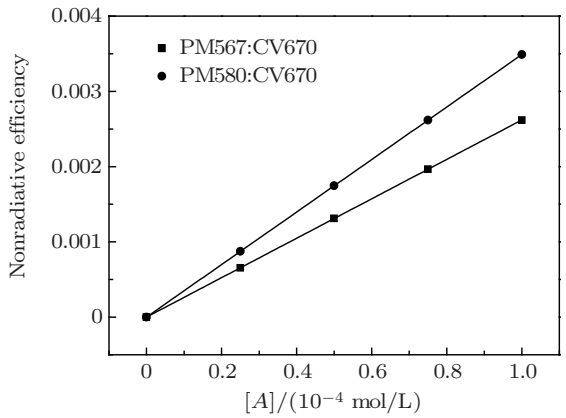


Fig. 7. Acceptor concentration dependencies of nonradiative energy transfer efficiencies of PM567:CV670 and PM580:CV670 dye-mixtures.

The total transfer efficiency η_T is calculated with Eq. (6), and the results are presented in Fig. 8. It is shown that the η_T increases gradually with the increase of acceptor concentration. The radiative transfer efficiency η_r is obtained using Eq. (8). The variations of η_r/η_{nr} with acceptor concentration is presented in Fig. 9. It is shown that the η_r/η_{nr} decreases gradually with the increase of acceptor concentration, and seems to be saturated when the acceptor concentration is higher than 0.7×10^4 mol/L. However, the η_r/η_{nr} is always higher than 200 for the acceptor concentrations investigated in this paper.

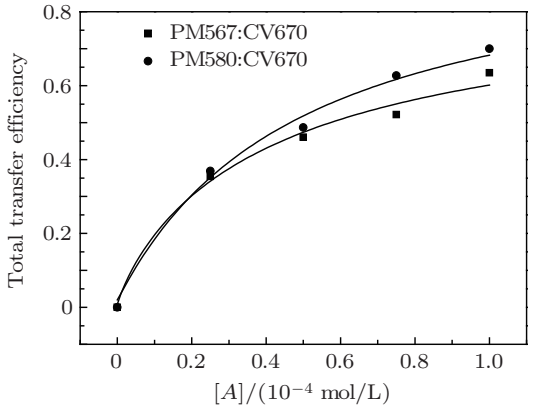


Fig. 8. Acceptor concentration dependencies of total energy transfer efficiencies of PM567:CV670 and PM580:CV670 dye-mixtures.

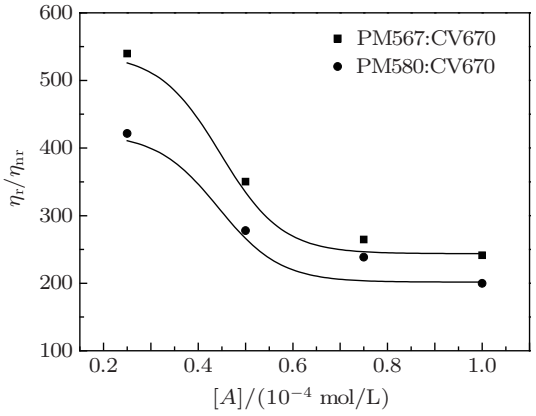


Fig. 9. Acceptor concentration dependencies of η_r/η_{nr} for PM567:CV670 and PM580:CV670 dye-mixtures.

The values of ϕ_{0d}/ϕ_d with various acceptor concentrations are obtained using Eq. (7) with the calculated η_{nr}. Shown in Fig. 10 are the variations of ϕ_{0d}/ϕ_d with acceptor concentration for the two dye-mixture systems. The nonradiative energy transfer rate constant K_{NR} is calculated from the slopes of the Stern–Volmer plots in Fig. 10. Then the radiative energy transfer rate constant K_R is calculated using Eq. (3).

The values of K_T, K_{NR}, and K_R for the two dye-mixture systems are listed in Table 1. It is shown that the value of K_R is three orders of magnitude higher than that of K_{NR}, thus the dominant mechanism responsible for the energy transfer in the present systems is of the radiative type.

Table 1. Calculated energy transfer parameters of the dye-mixtures dissolved in ethanol.

Compound	$[A]_{1/2}/10^{-4}$ mol·L^{-1}	R_0/Å	$K_{SV}/10^4$ L·mol^{-1}	$K_T/10^9$ L·mol^{-1}·s^{-1}	$K_R/10^9$ L·mol^{-1}·s^{-1}	$K_{NR}/10^9$ L·mol^{-1}·s^{-1}
PM567:CV670	0.60	187.8	1.61	2035.3	2032.0	3.3
PM580:CV670	0.45	206.6	2.30	2794.6	2790.4	4.2

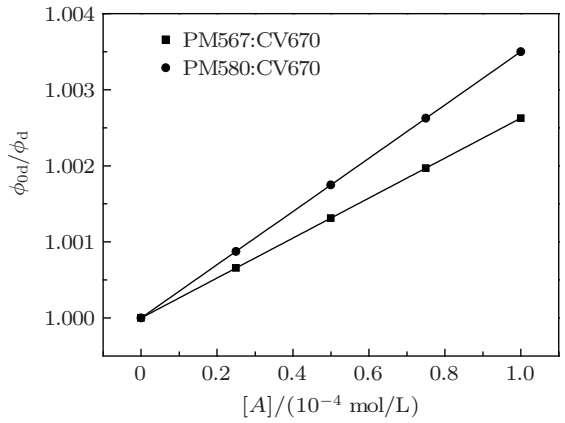


Fig. 10. Stern–Volmer plots for relative quantum yields of PM567:CV670 and PM580:CV670 dye-mixtures.

The fluorescence lifetime of the donor in the presence of acceptor τ_d was then calculated with Eq. (12). The value of τ_d at an acceptor concentration of 1×10^{-4} mol/L are 7.89 ns and 8.20 ns for PM567:CV670 and PM580:CV670 system, respectively, which are almost identical with the values of corresponding τ_{0d} 7.91 ns and 8.23 ns. The little difference between the fluorescence lifetime of the donor in the absence and that in the presence of acceptor also indicates that the radiative energy transfer mechanism is the dominant mechanism in the present dye-mixture systems.[18]

5. Conclusion

We investigated the energy transfer from two pyrromethene dyes PM567 and PM580 as the energy donors to CV670 as the energy acceptor in ethanol using the steady-state emission measurement. The intensities of the acceptor were improved by up to 128% through the energy transfer between the donor and acceptor. The radiative energy transfer constant K_R is three orders of magnitude higher than the nonradiative energy transfer constant K_{NR}, indicating that the dominant mechanisms for the energy transfer in the present systems are both of the radiative type. The energy transfer between dye mixtures can be used to improve the efficiency of dyes lasing with low efficiencies when directly pumped by the commercial lasers. This will help to expand the tuning range of the dye lasers and to promote the relevant applications.

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