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Novel Trichromophoric Rhodamine Dyes and Their Fluorescence Properties

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ABSTRACT

Trichromophoric laser dyes containing two 1,8-naphthalimide derivatives as antennas and Rhodamine 6G or Rhodamine DR-21 as lasing moiety linked via an ethylene bridge, have been investigated by means of absorption and fluorescence spectra. The fluorescence of the antennas in these trichromophoric dyes was partly quenched. Energy transfer from antenna to rhodamine was observed and the fluorescence quantum yield of the trichromophoric dyes can be increased by this energy transfer to the rhodamine moiety. For comparison, mixture systems of rhodamine dyes (Rh 6G or DR21) and 1,8-naphthalimide derivatives were also studied. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Some bichromophoric laser dyes, consisting of 1,8-naphthalimide derivatives as an antenna and Rhodamine 101 or Rhodamine B as lasing moiety linked via an ethylene and ester bridge, have been synthesized and investigated by measurements of absorption and fluorescence spectra.[1] As a result of effective singlet–singlet intramolecular energy transfer in these bichromophoric rhodamine dyes, the fluorescence quantum efficiency is increased. Since 1,8-naphthalimides have strong absorption in the UV region, the bichromophoric rhodamine dyes containing 1,8-naphthalimide moieties also have strong absorption in the UV region and this results in the bichro-

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mophoric rhodamine dyes absorbing effectively the UV pump energy. Thus, a relatively low concentration of the rhodamine dye solution can be used in a transverse pump system and this will reduce resonator loss due to rhodamine ground state reabsorption in its emission spectra region.[2] For efficient dye laser operation, a high value of the fluorescence quantum yield is generally useful. However, absorption by dye molecules in the lowest excited singlet and triplet states may cause a severe loss of pump and dye laser radiation. On the other hand, in order to absorb efficiently UV pump energy (e.g. XeCl excimer laser, 308 nm), a high concentration of the rhodamine dye solution must be used in a transverse pump system since the rhodamines have only a small extinction coefficient in the near UV. Thus, dye laser radiation is partly reabsorbed by the dye in its ground state, because the emission of the dyes overlaps the low energy tail of the absorption band. This loss is especially high if high dye concentration is required in order to absorb the pump light; this is a frequent situation in pumping. Linking the laser dye with one or more chromophores that absorb strongly at the pump wavelength has been suggested, and energy is efficiently absorbed by these antennas [e.g. 2,5-diphenyloxazole (PPO)] and then transferred to the laser chromophore.

In this paper some new trichromophoric rhodamine laser dyes, consisting of two 1,8-naphthalimide derivatives and one rhodamine lasing moiety, have been synthesized. The structures of the dyes are shown in Fig. 1. Since 1,8-naphthalimides have strong absorption in the UV region, the trichro-

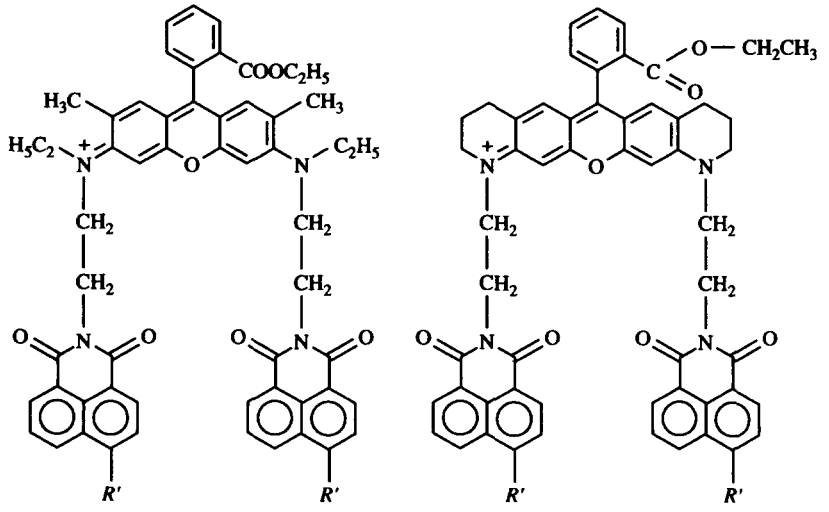

Fig. 1. Structures of the trichromophoric dyes synthesized in this study.

mophoric rhodamine dyes shown in Fig. 1 also have strong absorption in UV region due to two 1,8-naphthalimides antennas, which could effectively transfer UV pump energy to the rhodamine moiety by intramolecular singlet–singlet energy transfer. This will obviously reduce resonator loss[2] due to rhodamine ground state reabsorption in its emission spectra region.

EXPERIMENTAL

Synthesis of the compounds

The structures of the new trichromophoric rhodamine dyes are shown in Fig. 1. The synthesis of the 1,8-naphthalimide derivative intermediates has been previously described.[3] Rhodamine 6G chloride (Merck) was used for synthesis without further purification. Rhodamine DR-21 perchloride was prepared by Prof. Dr K. H. Drexhage (Siegen University, Germany) and his co-workers. Condensation of the rhodamines (Rh 6G or DR-21) and *N*-(2-bromoethyl)-1,8-naphthalimides (BEN or BEBrN in Fig. 1) produced the trichromphoric rhodamine dyes: **TCR-1**, **TCR-2**, **TCR-3**, **TCR-4**. The structures and purities of these dyes were confirmed by ^{1}H NMR, mass spectra and IR spectra.

TCR-1: ^{1}H NMR (in CF_3COOD): 0·86(t, 3H), 1·24 (t, 6H), 2·08 (s, 6H), 3·60 (m, 8H), 3·84 (m, 2H), 4·41 (t, 4H), 6·97 (s, 2H), 7·28 (s, 2H), 7·57 (m, 6H), 8·10 (m, 6H), 8·42 (m, 4H).

TCR-2: ^{1}H NMR (in CF_3COOD): 0·60 (t, 3H), 0·98 (t, 3H), 1·83 (s, 6H), 3·24 (m, 8H), 3·63 (m, 2H), 4·53 (m, 4H), 6·72 (s, 2H), 7·07 (s, 2H), 7·48 (m, 6H), 8·20 (m, 8H).

TCR-3: ^{1}H NMR (in CF_3COOD): 0·52 (t, 3H), 1·60 (d, 4H), 2·32 (m, 4H), 3·28 (m, 4H), 3·60 (m, 2H), 4·14 (m, 8H), 6·58 (s, 2H), 6·81 (s, 2H), 7·32 (m, 6H), 7·87 (m, 6H), 8·16 (m, 4H).

TCR-4: ^{1}H NMR (in CF_3COOD): 0·50 (t, 3H), 1·48 (d, 4H), 2·12 (m, 4H), 3·02 (m, 4H), 3·55 (m, 2H), 4·05 (m, 8H), 6·32 (s, 2H), 6·70 (s, 2H), 7·40 (m, 5H), 7·72 (m, 5H), 8·12 (m, 4H).

Measurements

Absorption spectra were recorded on a Shimadzu- UV-260 spectrophotometer with spectral bandwidth of 1 nm. Fluorescence spectra were measured on a Hitachi-850 fluorometer with a 1 nm bandwidth for emission. Solutions (the concentration of samples measured was 10^{-5} M) were generally prepared in absolute ethanol. In the comparative systems (rhodamines

mixed with BEN or BEBrN) the concentration of the rhodamine was 10^{-5} M and that of the 1,8-naphthalimides is 2×10^{-5} M (since in the trichromophoric rhodamine dyes there are two 1,8-naphthalimides residues). The measurements were performed at room temperature (*c.* 20°C).

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of the dyes are shown in Figs 2 and 3. The new trichromophoric rhodamines have absorption spectra that agree to a first approximation with the superposition of the spectra of one rhodamine and two 1,8-naphthalimide moieties, and the absorption in the UV region is then quite strong (Fig. 2, Table 1). The absorption spectrum of the trichromophoric dyes is the exact sum of the spectra of the constituent chromophores indicating little or no interaction between them, so that their individual characteristics should be maintained in the trichromophoric dyes. On excitation at 342 nm, the fluorescence of the 1,8-naphthalimide antennas (BEN in **TCR-1**) is partly quenched in the trichromophoric dyes (Fig. 3(a)). On excitation in the UV region, the fluorescence of BEN or BEBrN in other trichromophoric rhodamine dyes are also partly quenched to different degrees. However, in the mixture solutions of two antenna

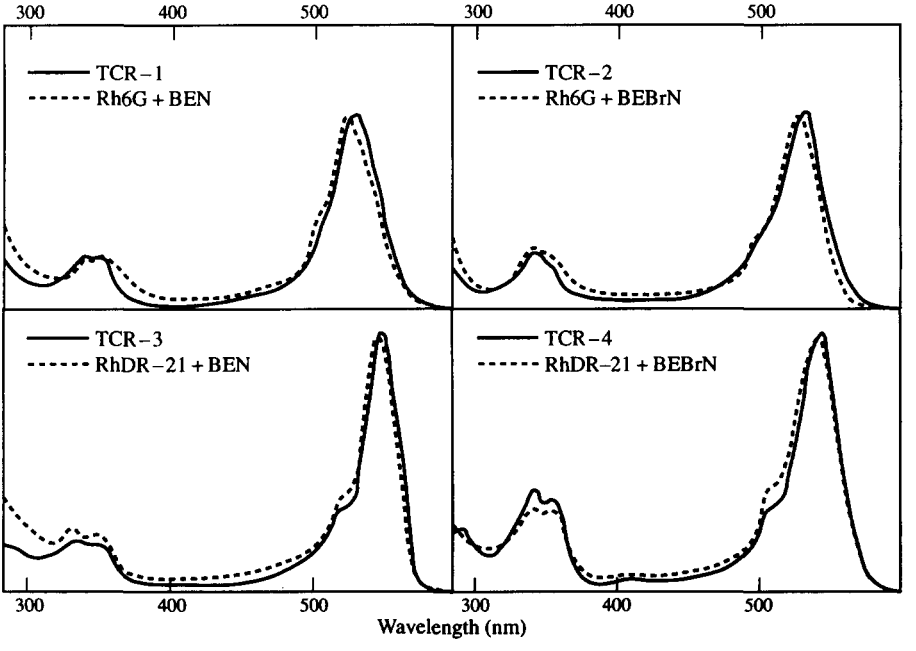

Fig. 2. Absorption spectra of trichromophoric dyes in ethanol solution (10^{-5} M).

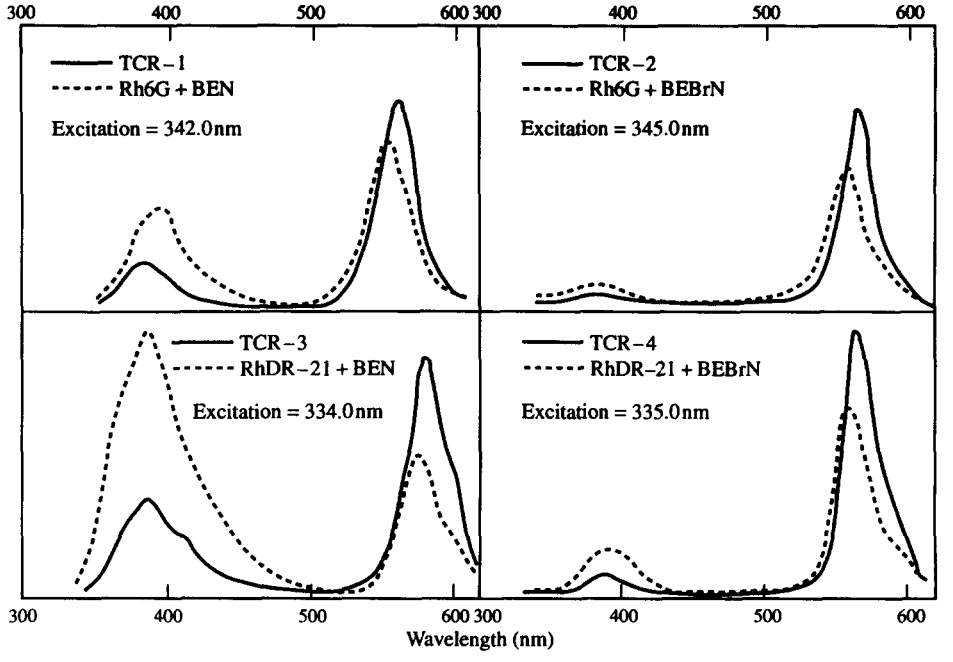

Fig. 3. Fluorescence spectra of the dyes.

molecules and one rhodamine fluorescence emission of the antenna and rhodamine both appear on excitation in the UV region. For instance, the 1,8-naphthalimide derivative (BEN, 2×10^{-5} M) mixed with Rh 6G in ethanol solution (10^{-5} M) emits the fluorescence of the antenna at 350–450 nm on excitation at 342 nm (Fig. 3(a)). In this case, no (or below the monitor sensitivity at least) energy transfer takes place from the 1,8-naphthalimide derivative to the rhodamine. This intermolecular interaction should depend strongly on the distance and interaction between the donor and acceptor systems, and therefore the energy transfer is inefficient in the BEN

TABLE 1

Absorption Maximum (λ_{max}^{ab}) and Fluorescence Maximum Wavelengths (λ_{max}^{fl}) of the Dyes in Ethanol Solution (10^{-5} M)

Dye	λ_{max}^{ab}/nm ($\epsilon/10^4$ cm^{-1} mol^{-1} litre)	λ_{max}^{fl}/nm
TCR-1	347 (2·70); 532 (10·41)	565
TCR-2	345 (2·72); 531 (10·32)	561
TCR-3	334 (2·69); 547 (13·83)	575
TCR-4	342 (3·22); 547 (13·66)	573
BEN	332 (1·26)	385
BEBrN	343 (1·40)	391

TABLE 2
Fluorescence Quantum Yield of Trichromophoric Rhodamine (ϕ^{TCR}) Relative to that of the Corresponding Equal Molar Mixture System (ϕ^{mix}) on Excitation at 342 n for **TCR-1**, 345 nm for **TCR-2**, 334 nm for **TCR-3** and 335 nm for **TCR-4**

	TCR-1	*TCR-2*	*TCR-3*	*TCR-4*
	Rh 6G + BEN	*Rh 6G + BEBrN*	*Rh DR-21 + BEN*	*Rh DR-21 + BEBrN*
$\frac{\phi^{TCR}}{\phi^{mix}}$	1·21	1·435	1·01	1·332

plus Rh 6G mixture system. Similarly, in other antennas and rhodamine mixture systems, the fluorescence of the antennas was not quenched. When comparing systems, in the trichromophoric rhodamines intramolecular energy transfer takes place from the antennas to the rhodamine moiety due to the partial fluorescence quenching of the antennas. This is confirmed by the experimental results, i.e. the fluorescence quantum yield of the trichromophoric rhodamines is higher than for the corresponding mixture systems (Table 2).

On the other hand, the fluorescence integration (from 450 to 650 nm) of the mixture Rh 6G + BEN is almost equal to that of Rh 6G at the same solution concentration on excitation at 342 nm. The also indicates that no intermolecular energy transfer from BEN molecules to Rh 6G takes place in the mixture system.

Compared with Rh 6G or DR-21, the new trichromophoric rhodamines show relative high fluorescence quantum yield on excitation in the UV region (Table 3). As seen in Table 3, at the same concentration of rhodamine moiety and excitation wavelengths, the new trichromophoric dyes synthesized exhibit higher fluorescence emission than that of Rh 6G or DR-21 alone. We attribute this to a partial energy transfer from antenna to rhodamine in these trichromophoric dyes. For efficient dye laser operation, a

TABLE 3
Ratio of Fluorescence Integration (from 450 to 650 nm) between Trichromophoric Dyes ($\int I_{fl}^{TCR} d\lambda$) and Rhodamine ($\int I_{fl}^{rh} d\lambda$); Excitation at 342 nm for **TCR-1**, 345 nm for **TCR-2**, 334 nm for **TCR-3** and 335 nm for **TCR-4**

	TCR-1	*TCR-2*	*TCR-3*	*TCR-4*
	Rh 6G	*Rh 6G*	*Rh DR-21*	*Rh DR-21*
$\frac{\int I_{fl}^{TCR} d\lambda}{\int I_{fl}^{rh} d\lambda}$	1·165	1·53	1·113	1·315

high value of fluorescence quantum yield is useful. However, in order to absorb 90% of UV pump light in a depth of 1 mm, concentrations of about 10^{-3} mol litre^{-1} are needed for Rh 6G due to its rather low absorption in the UV region. Such a high concentration in turn causes a high absorbance in the long-wavelength tail of the main absorption band, where the stimulated emission occurs. This reabsorption may cause a severe loss of pump and dye laser radiation. Therefore efficient laser dyes are only those compounds in which the excited state absorption coefficients are small in the pertinent wavelength regions. The loss due to T-T absorption also depends on the S-T intersystem crossing rate and the triplet decay rate. In rhodamines, these quantities, taken together, have values very favourable for dye laser operation.[4] For the trichromophoric rhodamines synthesized in this work, the absorption of the dyes in the UV region is quite strong, so that a lower concentration is enough to absorb the UV pump light. Thus, the loss of pump and dye laser radiation due to reabsorption at high concentration will be reduced in the trichromophoric dyes.

At the same concentration, and when the excitation is at wavelengths at which the extinction coefficients of the trichromophoric dyes is the same as that of the corresponding antennas alone (BEN or BEBrN), the resulting fluorescence quantum yield ratios (integration in the region below 450 nm) of the dyes are as listed in Table 4. For example, on excitation at 342 nm **TCR-1**, emission in the region 350–450 nm (in fact, that is fluorescence of the antennas) is less than that of BEN alone. In Table 4 the excitation wavelength for **TCR-2** is 345 nm, for **TCR-3** 334 nm and for **TCR-4** 335 nm, where the extinction coefficients of the trichromophoric dyes are the same as those of the corresponding antennas molecules alone (BEN or BEBrN). As shown in Table 4, the trichromophoric dyes have lower fluorescence quantum yield relative to their antennas' chromophore. This is because there exists a partial energy transfer from antennas, to rhodamine chromopore in the trichromophoric dyes, which show a higher fluorescence efficiency relative to their lasing chromophores as shown in Table 3.

TABLE 4.

Quantum Yield of the Antennas (ϕ^{An}, Integration Below 450 nm) in Trichromophoric Dyes Relative to the Quantum Yield of Antennas. Excitation at 342 nm for **TCR-1**, 345 nm for **TCR-2**, 334 nm for **TCR-3** and 335 nm for **TCR-4**

Dyes	*TCR-1*	*TCR-2*	*TCR-3*	*TCR-4*
	BEN	*BEBrN*	*BEN*	*BEBrN*
ϕ^{An}	0·331	0·446	0·554	0·463

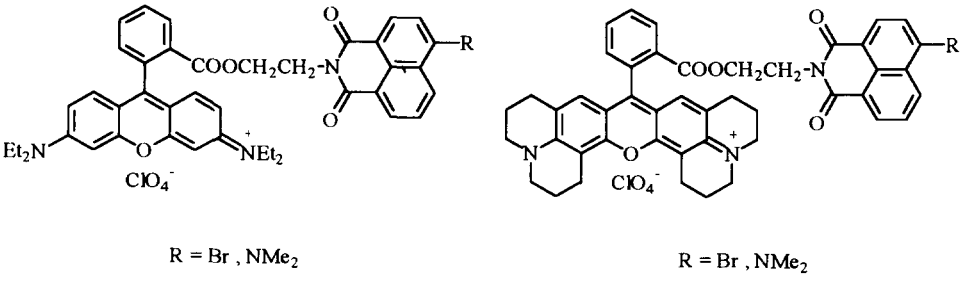

Fig. 4. Structures of bichromophoric rhodamine dyes.

However, in the bichromophoric rhodamine dyes synthesized previously by us (Fig. 4), the relative fluorescence quantum yields are higher than those of corresponding equimolar mixture systems (Table 2 in Ref. 1). Compared with Rh 101 and Rh B, the bichromophoric rhodamines show fluorescence integration about three times that of Rh 101 and Rh B alone (Table 3 in Ref. 1). We attributed this to an efficient energy transfer from antenna to rhodamine in the bichromophoric dyes. Compared with the trichromophoric dyes in this study, the intramolecular energy transfer from antennas to rhodamine is less efficient than that in bichromophoric dyes. The molecular structure of the bichromophoric compounds, as far as the relative arrangement of the donor and acceptor moieties is concerned, is largely determined by the carboxylated phenyl group of the constituent rhodamine part. The antenna (TN-1 or TN-2 shown in Ref. 1) is chemically linked via two methylene groups to the ester oxygen of the carboxyl group in an ortho position of the phenyl ring. It can be concluded that energy transfer between two large chromophores linked by two methylene groups in the bichromophoric compound is still adequately described by the basic Forster equation, although the separation of the chromophores is comparable to their size.[5,6] In the trichromophoric dyes in this study, with two antennas connected via two CH_2-groups to the N-atoms of the rhodamine, the fluorescence quantum yields were reduced compared with bichromophoric dyes. This is similar to the phenomena observed in PPO-rhodamine-PPO trichromophoric dyes.[2,7] We attribute these phenomena again to a strong interaction of the π-electron systems of the antenna and rhodamine moieties. We conclude that these trichromophoric dyes exist in a folded conformation, such that the π-electron systems of the individual chromophores come into close contact. The rhodamine chromophore may interact with the antennas in an undesirable manner, leading to a reduced fluorescence efficiency.

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