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Bichromophoric Rhodamine Dyes and their Fluorescence Properties

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ABSTRACT

Bichromophoric laser dyes, consisting of 1,8-naphthalimide derivatives as an antenna and Rhodamine 101 or Rhodamine B as a lasing moiety linked via an ethylene and ester bridge, have been investigated by measurements of absorption and fluorescence spectra. The fluorescence of the antenna in these bichromophoric dyes was quenched. Complete energy transfer from antenna to rhodamine was observed and the fluorescence quantum yield of the bichromophoric dyes can be increased by this energy transfer to the rhodamine. For comparison, mixtures of the rhodamine dyes and the 1,8-naphthalimide derivatives were also studied.

INTRODUCTION

Rhodamines and related oxazine dyes are an important class of laser dyes in the spectral range 550–800 nm. For efficient dye laser operation, a high fluorescence quantum yield is necessary. 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 efficiently absorb 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 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 emission of the dyes overlaps the low energy tail of the absorption band. This loss is especially high if a

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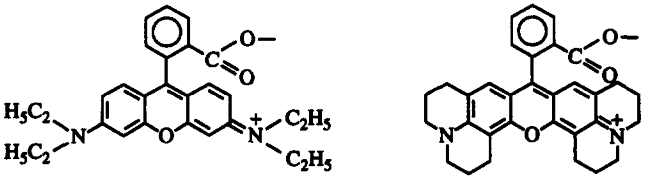
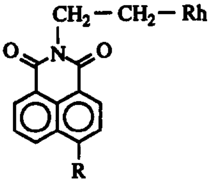
high dye concentration is required in order to absorb the pump light which is a frequent situation in pumping. In order to reduce resonator loss by ground state absorption, multichromophoric rhodamine dyes with UV-absorbing antennas have been synthesized.[1,2] Connection of the laser dye with one or more chromophores that absorb strongly at the pump wavelength has been suggested and energy is efficiently absorbed by such antenna (e.g. 2,5-diphenyloxazole (PPO)) and then transferred to the laser chromophore. In this paper, we have applied this concept to Rhodamine 101 (**Rh101**) and Rhodamine B (**RhB**), and we report on several bichromophoric rhodamines. It is interesting that the rigidized **Rh101**, in spite of its high fluorescence efficiency, is markedly less efficient in most pumping configurations;[3] these differences are not yet fully understood. We have therefore prepared bichromophoric dyes consisting of 1,8-naphthalimide derivatives as an antenna, and **Rh101** or **RhB** as a lasing moiety, linked via an ethylene and ester bridge. The absorption of 1,8-naphthalimide in the UV region is quite strong.

EXPERIMENTAL

The structures of the new rhodamine dyes are shown in Fig. 1. The synthesis of the 1,8-naphthalimide intermediates has been previously described.[4] **RhB** chloride was used for synthesis without further purification. **Rh101** perchloride was prepared by the method given in Ref. 5; synthesis of the bichromophoric rhodamine dyes is similar to that described in Ref. 6. The structures of these dyes were confirmed by ^{1}H NMR, mass spectra and elemental analysis. Further details of dye preparation will be published separately.



RhB **Rh101**



Dyes	Rh	R
TR-1	Rh101	NMe_2
TR-2	Rh101	Br
TR-3	RhB	NMe_2
TR-4	RhB	Br
TN-1	OH	NMe_2
TN-2	OH	Br

Fig. 1. Structures of the bichromophoric rhodamine dyes.

TABLE 1

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

Dyes	λ_{max}^{abs}/(*nm*) ($\varepsilon/10^4$ cm^{-1} mol^{-1} *litre*)	λ_{max}^{fl} (*nm*)
TR-1	429 (0·95); 577 (5·15)	603
TR-2	355 (2·43); 577 (5·69)	601
TR-3	421 (1·51); 556 (11·24)	584
TR-4	355 (2·14); 557 (11·36)	584·4
TN-2	342 (1·66)	390
TN-1	419 (1·21)	519·4

Fluorescence data were measured by excitation at 325 nm.

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 (concentration 10^{-5} M) were prepared in absolute ethanol; measurements were performed at room temperature (ca. 20°C).

RESULTS AND DISCUSSION

The absorption maxima (λ_{max}^{abs}) and fluorescence maxima (λ_{max}^{fl}) of the dyes in this study are listed in Table 1. The new bichromophoric rhodamines have absorption spectra that allow a first approximation with the superposition of the spectra of one rhodamine and one 1,8-naphthalimide derivative, and the absorption in the UV region is quite strong (Fig. 2).

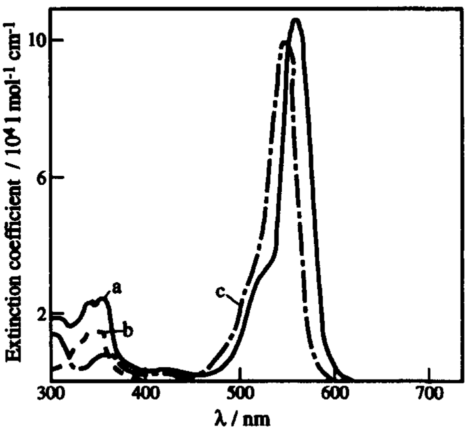


Fig. 2. Absorption spectra of compounds: (a) **TR-4**; (b) TN-2; (c) **RhB**.

The absorption spectrum of the bichromophoric dyes is a summation of the spectra of the constituent chromophores, indicating little or weak interaction between them, i.e. their individual character should be maintained in the bichromophoric dyes. On excitation at 325 nm, fluorescence of the 1,8-naphthalimide is quenched in the bichromophoric dyes (Fig. 2). If one applies Forster's theory[7] to such a system of donors and acceptors, a very efficient energy transfer from the 1,8-naphthalimide antenna to the rhodamine is expected. However, in a mixture of equimolar solutions of the antenna molecule and rhodamine, both fluorescence emission of the antenna and of the rhodamine appear on excitation at 325 nm. For instance, the 1,8-naphthalimide derivative **TN-2** mixed with an equimolar solution of **RhB** in ethanol emits fluorescence at 350–480 nm on excitation at 325 nm (Fig. 3). In this case, no energy transfer takes place from the 1,8-naphthalimide derivative to the rhodamine. This intermolecular interaction should depend, to a large extent, on the distance and collision between donor and acceptor systems, and, therefore, the energy transfer is inefficient in the **TN-2**–Rhodamine B mixture. Similarly, in other antenna and rhodamine mixture systems, the fluorescence of the antenna was not quenched. When comparing systems, the bichromophoric rhodamines show intramolecular energy transfer from the antenna to the rhodamine moiety very efficiently, due to complete fluorescence quenching of the antenna (Figs 3 and 4). This is confirmed by our experiments: the fluorescence quantum yields of the bichromophoric rhodamines are higher than those of corresponding equimolar mixture systems (Table 2).

On the other hand, fluorescence integration of the mixture **Rh101** +

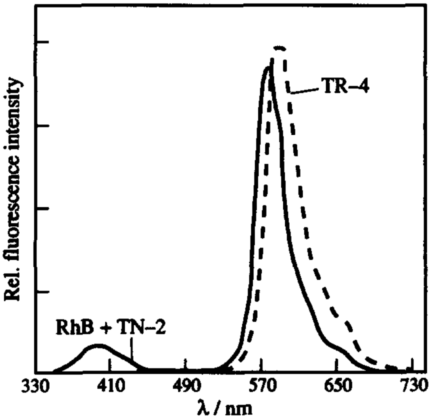


Fig. 3. Fluorescence spectra of dyes (bichromophoric dye **TR-4**: dashed line; the mixture system of **RhB** and **TN-2**: solid line).

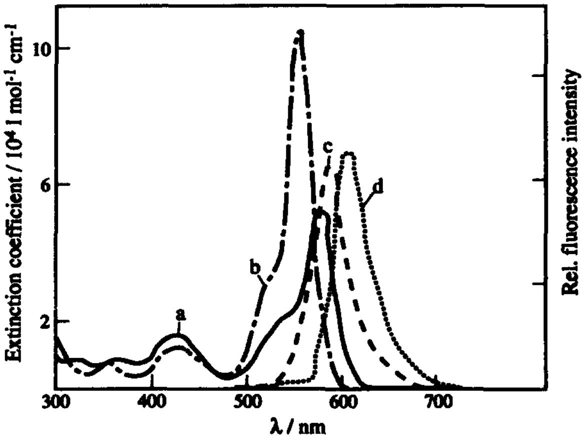


Fig. 4. Absorption and fluorescence spectra of bichromophoric rhodamines (**TR-1**: (a) absorption; (d) fluorescence; and **TR-3**: (b) absorption; (c) fluorescence. Fluorescence was measured on excitation at 415 nm.

TN-2 is almost equal to that of **Rh101** at the same solution concentration on excitation at 325 nm. This indicates that no intermolecular energy transfer from **TN-2** molecules to **Rh101** takes place in the mixture system. The fluorescence integration of the bichromophoric dye **TR-2** is about three times that of the **Rh101** + **TN-2** system and energy transfer from antenna to rhodamine in the bichromophoric rhodamines is, as anticipated, very efficient.

Compared with **Rh101** or **RhB**, the new bichromophoric rhodamines show relatively high fluorescence quantum yields on excitation at 325 nm (Table 3). Since the concentrations of the samples measured are the same (10^{-5} M), the extinction coefficients at 325 nm for the bichromophoric dyes and **Rh101** (or **RhB**) are quite different. For convenient comparison, the relative fluorescence quantum yields can be replaced by the ratio of fluorescence integration (Table 3). As seen in Table 3, at the same concentration and excitation wavelengths, the new bichromophoric dyes synthesized exhibit a higher fluorescence emission than that of **Rh101** or

TABLE 2

Fluorescence Quantum Yield of Bichromophoric Rhodamine ϕ^{bc} Relative to that of the Corresponding Equimolar Mixture System ϕ^{mix} on Excitation at 325 nm

	$\frac{\textit{TR-1}}{\textit{Rh101 + TN-1}}$	$\frac{\textit{TR-2}}{\textit{Rh101 + TN-2}}$	$\frac{\textit{TR-3}}{\textit{RhB + TN-1}}$	$\frac{\textit{TR-4}}{\textit{RhB + TN-2}}$
$\frac{\phi^{bc}}{\phi^{mix}}$	1·18	2·93	1·17	2·70

TABLE 3
Ratio of Fluorescence Integration (Excitation at 325 nm) Between Bichromophoric Dyes $\int I_{fl}^{bc}\,d\lambda$ and Rhodamine $\int I_{fl}^{rh}\,d\lambda$

	$\frac{TR\text{-}1}{Rh101}$	$\frac{TR\text{-}2}{Rh101}$	$\frac{TR\text{-}3}{RhB}$	$\frac{TR\text{-}4}{RhB}$
$\frac{\int I_{fl}^{bc}}{\int I_{fl}^{rh}}$	1·10	2·96	1·24	2·90

RhB alone. We attribute this to an efficient energy transfer from antenna to rhodamine in the bichromophoric dyes. For efficient dye laser operation, a high value of fluorescence quantum yield is useful. However, in order to absorb 90% of UV pump light over 1 mm, concentrations of about 10^{-3} mol/litre are necessary for **Rh101** or **RhB**, due to their relatively 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 favorable for dye laser operation.[8] For the bichromophoric rhodamines synthesized in this study, the absorption of the dyes in the UV region is quite strong (Fig. 4), so that a lower concentration is sufficient to absorb the UV pump light. Thus, the loss of pump and dye laser radiation due to absorption at high concentration will be reduced in the bichromophoric dyes.

At the same concentration, when excitation at wavelengths where the extinction coefficiency of the bichromophoric dyes is the same as that of the corresponding rhodamine alone (**Rh101** or **RhB**), the fluorescence quantum yield ratios of the dyes are listed in Table 4. The excitation wavelengths for **TR-1**, **TR-2** and **Rh101** are 560 nm, and their extinction coefficients are the same. At 540 nm the extinction coefficients of **TR-3**, **TR-4** and **RhB** are also the same, and therefore their fluorescence quantum yields on excitation at 540 nm can be compared (Table 4). Because **Rh101**-antenna dyes and **RhB**-antenna dyes also have maximum absorption near 560 and 540 nm, respectively, the fluorescence quantum yield on excitation at these wavelengths is the maximum value for **Rh101**-antenna and **RhB**-antenna, respectively. The data listed in Table 4 are, in fact, the ratio of the maximum quantum yield between rhodamine-antenna and rhodamine. As shown in Table 4, the bichromophoric dyes

TABLE 4
Maximum Quantum Yield (ϕ^{bc}_{max}) of Bichromophoric Dyes Relative to the Maximum Quantum Yield (ϕ^{rh}_{max}) of Rhodamine (**Rh101** or **RhB**)

Dyes	***TR-1***	***TR-2***	***TR-3***	***TR-4***
$\frac{\phi^{bc}_{max}}{\phi^{rh}_{max}}$	1·025	1·028	1·01	1·311

TR-1 and **TR-2** were measured by excitation at 560 nm; **TR-3** and **TR-4** were measured by excitation at 540 nm.

have a higher fluorescence quantum yield relative to their lasing chromophore. They show a fluorescence efficiency close to unity. It can thus be considered that a very effective method of improving the properties of laser dyes is that antenna chromophores, which absorb the light of pump and emit in the region of the lasing chromophore absorption, are linked to the lasing chromophore by an unconjugated chemical bridge.

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