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ABSTRACT

In this study, we synthesized two asymmetric rhodamine laser dyes based on 1-naphthol (Dye-1 and Dye-2) and investigated their photophysical and laser performances. It was found that the fluorescence emission wavelengths of the two dyes are successfully extended to the deep red region. Compared with Dye-1, the esterification product Dye-2 displays a redshift of ~8 nm in the maximum absorption wavelength (λ_{abs}) and fluorescence emission wavelength (λ_{em}). In aprotic solvents, both λ_{abs} and λ_{em} of Dye-2 red-shift with the increase of solvent polarity, while its fluorescence quantum yield always decreases with the increase of solvent polarity, no matter in protic solvents or aprotic solvents. The results of laser tests indicated that both Dye-1 and Dye-2 have wide laser tuning range and strong laser conversion efficiency in the red region. The laser conversion efficiency is closely relative to the dye concentration and linearly increases with the increase of pump laser energy.

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1. Introduction

ournal Pre-sulfonic acid to get Dye-1. Finally, Dye-2 was obtained by the esterification reaction between Dye-1 and methanol.

Organic fluorescent dyes are considered to the most competent laser medium materials, due to their wide tunable spectrum, high fluorescence quantum yield and wide frequency band. In 1966, for the first time phthalocyanine dye was used as a laser dye [1]. Later, rhodamine 6G dye was successfully applied in the dye laser and realized the output of dye laser [2]. Up to now, hundreds of laser dyes including coumarin [3, 4], rhodamine [5-7], BODIPY [8-14], and cyanine dyes [15-19], have been developed. Since the output wavelength range of these laser dyes can cover the waveband from ultraviolet region of 300 nm to the near infrared region of 1200 nm, they also have a promising prospect in the applications of biology, medicine, physics and spectral analysis [20-27].

As a type of laser dyes, rhodamine laser dye has received much attention owing to their high laser conversion efficiency and laser stability. However, the absorption wavelengths of traditional rhodamine laser dyes are generally shorter than 580 nm, and the fluorescence emission wavelengths are no longer than 600 nm [28]. In some special cases, it is necessary to use the red laser dyes with emission wavelengths longer than 600 nm. For instance, in the medicine field, the short wavelength laser with higher energy not only easily damages the biological tissue but also cannot reach the deep tissue. Therefore, it is very necessary to develop some rhodamine laser dyes in red (or deep red) region. One way of obtaining red (or deep red) laser dyes is to modify the structure of traditional rhodamine dyes. For example, a useful strategy to obtain red (or deep red) laser dyes is to increase the conjugated structure of rhodamine molecules.

Herein, two asymmetric rhodamine laser dyes Dye-1 and Dye-2 containing only one nitrogen atom were synthesized by replacing the aniline structure at one end of rhodamine molecule with naphthalene ring. The results showed that both Dye-1 and Dye-2 exhibited two fluorescence emission peaks, one of which appeared in the deep red region (646 nm for Dye-1 and 655 nm for Dye-2). On this basis, we further tested the laser emission spectra and photo-stability of Dye-1 and Dye-2, and investigated the effects of solvent type, concentration and pump power on their laser performances.

2. Results/Discussion

2.1. Synthesis of Dye-1 and Dye-2



Scheme1. Synthetic routes of Dye-1 and Dye-2

Scheme1 illustrates the synthetic routes of Dye-1 and Dye-2: Firstly, the intermediate M2 was synthesized by the Friedel-Crafts reaction between 8-hydroxyjulolidine (M-1) and phthalic anhydride. Then, it reacted with 1-naphthol in methane 2.2. Absorption and fluorescence emission spectra



Figure 1. (a) Normalized absorption and (b) fluorescence emission spectra of Dye-1 and Dye-2 in ethanol solution (1 × 10^{-5} mol/L). The fluorescence emission spectra were measured by using the 530 nm line of Xenon lamp as the excitation source ($\lambda_{ex} = 530$ nm).

Figure 1 shows the absorption and fluorescence emission spectra of Dye-1 and Dye-2 in ethanol solution with a concentration of 1.0×10^{-5} mol/L. As shown in Figure 1a, both Dye-1 and Dye-2 have two absorption peaks in the range of 450-600 nm, ascribed to the S₀-S₁ electron transition and vibrational transition, respectively [29, 30]. In addition, both of the two dyes possess another peak at 400 nm, which is from the S₀-S₂ electron transition [29, 30]. The maximum absorption wavelengths (λ_{abs}) of Dye-1 and Dye-2 in ethanol solution are 519 nm and 527 nm, respectively, while their maximum fluorescence emission wavelength (λ_{em}) are 593 nm and 602 nm, respectively (Figure 1b). As the dye was esterified from carboxylic acid Dye-1 to methyl Dye-2, its λ_{abs} and λ_{em} are red-shifted by 8 nm and 9 nm, respectively. Additionally, Dye-1 and Dye-2 display two strong fluorescence emission peaks at 646 nm and 655 nm, respectively.

2.3. Effect of solvents on the absorption and fluorescence spectra



Figure 2. (a) Absorption and (b) fluorescence emission spectra of Dye-2 in different solvents $(1.0 \times 10^{-5} \text{ mol/L})$. For all the fluorescence measurements, λ_{ex} is 530 nm.

Table 1. Absorption and fluorescence characteristics of Dye-2 in different solvents.

Solvent	Polarity	λ_{abs} (nm)	$\begin{array}{ll} \lambda_{abs} & \epsilon_{max} \\ (nm) & (\times \ 10^4 \ M^{-1} \ cm^{-1} \) \end{array}$		$\Phi_{\rm F}{}^{\rm a}$	
CH ₂ Cl ₂	3.40	526	1.58	599	0.52	
CHCl ₃	4.40	528	1.18	601	0.36	
CH ₃ CN	6.20	529	0.85	612	0.22	
DMSO	7.20	532	0.35	619	0.10	
C_2H_5OH	4.30	527	1.48	606	0.49	
$\rm CH_3OH$	6.60	527	1.34	605	0.41	
H_2O	10.20	527	0.70	610	0.19	

^a The values of fluorescence quantum yields (Φ_F) were determined by using rhodamine 101 as standard (Φ_F of rhodamine 101 in ethanol is 0.96).

Figure 2 displays the absorption and fluorescence emission spectra of Dye-2 in different solvents. Table 1 lists the solvent polarity, λ_{abs} , molar extinction coefficient (ϵ_{max}), λ_{em} , and fluorescence quantum yield (Φ_F). From Figure 2 and table 1, it can be seen that in aprotic solvents (CH₂Cl₂, CHCl₃, CH₃CN and DMSO), both λ_{abs} and λ_{em} of Dye-2 red-shift with the increase of solvent polarity. However, both λ_{abs} and λ_{em} have no evident difference in protic solvents (C₂H₃OH, CH₃OH and H₂O). No matter in protic solvents or aprotic solvents, all of the molar extinction coefficient (ϵ_{max}), fluorescence intensity, and fluorescence quantum yield (Φ_F) of Dye-2 gradually decrease with the increase of solvent polarity. This is because the strong interaction between the excited state molecule and the polar solvent would increase the probability of non-radiative transition [31].

2.4. Effect of dye concentration on fluorescence characteristics



Figure 3. Fluorescence spectra of Dye-2 with different concentrations in ethanol solution. The dye concentration is $C \times 10^{-5}$ mol/L (C is the value of the inset). For all the fluorescence measurements, λ_{ex} is 530 nm.

To ivestigate the effect of dye concentration on its fluorescence characteristics, we measured the fluorescence emission spectra of Dye-2 in different concentrations of ethanol solution $(1.0 \times 10^{-6} - 1.0 \times 10^{-3} \text{ mol/L})$. As shown in Figure 3, when the dye concentration is 1.0×10^{-6} mol/L, the fluorescence spectrum of Dye-2 consists of a strong peak at 600 nm and a weak shoulder peak at ~ 650 nm. With the increase of dye concentration, the intensity of the second peak in the range of 648-665 nm increases gradually at the beginning, and then reaches a maximum when the dye concentration is 7.5×10^{-6} mol/L. According to the previous reports [32, 33], the intensity increase of the second peak should be ascribed to the increase of stacked dye aggregates. When the dye concentration is higher than 7.5×10^{-6} mol/L, the intensity of the second peak begins to decrease with further increasing the dye concentration, which is because the high dye concentration would result in fluorescence quenching. When the concentration of dye reaches 1.0×10^{-3} mol/L, the fluorescence seems to be completely quenched. We further analyzed the influence of dye concentration on its maximum fluorescence wavelength (λ_{em}). As summarized in table 2, the maximum fluorescence wavelengths of peak 1 and peak 2 gradually red-shift with increasing the dye concentration. For instance, as the dye concentration increases from 1.0 $\times 10^{-6}$ mol/L to 1.0 $\times 10^{-4}$ mol/L, the corresponding λ_{em}

redshifts from 600 nm to 611 nm. The variation of fluorescence emission wavelength is probably relative to its existence state in solvent: At high concentration, the dye molecules would assemble into J-aggregates, leading to the red-shift of absorption and fluorescence wavelengths [34, 35].

Table 2. The relationship between the maximum fluorescence wavelengths (λ_{em}) of Dye-2 and its concentrations.

$\begin{array}{c} \text{Concentration} \\ \times 10^{-5} \text{ mol/L} \end{array}$	0.1	1.0	2.5	5.0	7.5	10.0	25	50	75	100
Peak 1 (nm)	600	604	605	607	608	611	612	612	613	613
Peak 2 (nm)		649	652	652	652	654	655	659	662	664

2.5. Laser performances



Figure 4. (a) Laser emission spectra of Dye-1 and Dye-2 in ethanol $(0.56 \times 10^{-3} \text{ mol/L})$. (b) Laser efficiencies of the second peak of Dye-1 and Dye-2 in different concentrations of ethanol solutions. The output energy of pump laser for the above tests was fixed at 13 mJ.

Figure 4 a shows the laser emission spectra of Dye-1 and Dye-2 in ethanol solution, in which X-axis is the detection wavelength and the Y-axis is the corresponding laser conversion efficiency. As can be seen, the laser tuning range of Dye-1 is from 594 nm to 680 nm, and it has two peaks at 608 nm and 654 nm, corresponding to the maximum laser conversion efficiencies of 11.6% and 12.4%, respectively. The laser tuning range of Dye-2 is in the range of 600–670 nm, and the maximum laser efficiencies at 608 nm and 654 nm are 11.8% and 14.4%, respectively. By comparing the fluorescence and laser emission spectra of Dye-2, it can be found that the maximum laser emission wavelength of Dye-2 is consistent with its maximun fluorescence emission wavelength.

Since the laser conversion efficiency of a laser dye is closely relative to its concentration in solvent [9, 36], here we measured the laser conversion efficiencies of Dye-1 and Dye-2 at 654 nm and 660 nm, respectively. As shown in Figure 4 b, when the dye concentration is less than 0.2×10^{-3} mol/L, no laser is generated, due to the self-absorption of dye to light. When the dye concentration is increased to 0.56×10^{-3} mol/L, Dye-1 and Dye-2 have the maximum laser conversion efficiencies of 11.8% and 14.4%, respectively. However, when the dye concentration is higher than 0.56×10^{-3} mol/L, the laser conversion efficiency begins to decrease with the increase of dye concentration, which is due to the reabsorption/reemission processes as well as the generation of non-fluorescent aggregates [37, 38].

To study the influence of pump laser energy on the laser conversion efficiency, we tested the laser conversion efficiencies of Dye-2 at 660 nm by tuning the pump laser energy from 1 mJ to 20 mJ. When the pump laser energy is lower than 4 mJ, no laser emission can be detected, indicating that the threshold of Dye-2 for laser emission is about 4 mJ. According to the

principle of laser [38], during laser production, energy gain and loss take place simultaneously in the optical cavity. The threshold of laser refers to the condition when the gain energy is equal to the loss energy. Only when the energy of pump laser is higher than the threshold, can the laser emit. As shown in Figure 5, the laser conversion efficiency increases linearly with the increase of pump laser energy. The laser conversion efficiency (Y) can be estimated by the equation Y = 0.3209x + 0.1097 (*x* is pump laser energy).



Figure 5. Variation of Dye-2 laser efficiency as a function of laser pumped energy. The dye concentration in ethanol is 0.56×10^{-3} mol/L and the detection wavelength is 660 nm.



Figure 6. Photo-stability of Dye-1 and Dye-2 measured in ethanol solution $(0.56 \times 10^{-3} \text{ mol/L})$ under pump laser irradiation. The output energy of pump laser was fixed at 13 mJ.

Since the photo-stability of laser dye is very important to a laser dye for its practical application, here we investigated the variation of output laser efficiency as a function of pump laser irradiation time. As can be seen in Figure 6, the decline rate of the output laser efficiency of Dye-2 is much slower than that of Dye-1. The half-lives of output laser efficiency for Dye-1 and Dye-2 are 120 min and 320 min, respectively. The above results mean that the photo-stability of Dye-2 is much higher than that of Dye-1. The huge difference of Dye-1 and Dye-2 in photo-stability can be interpreted by their difference in electrophilicity index (w). As a kind of global reactivity descriptor similar to the chemical hardness and chemical potential, ω has been used to evaluate the photostability of some fluorescent dyes [39]. As the increase of ω , the molecule would become more stable, leading to better light fastness and photo-stability [40, 41]. The electrophilicity index (ω) of two dyes were calculated by Eq. (1):

$$\omega = \mu^2 / 2\eta \tag{1}$$

Where chemical potential (μ) and chemical hardness (η) were determined using the energies of frontier molecular orbitals E_{HOMO} , E_{LUMO} and given by Eqs. (2-3):

$$\mu = -1/2 \left(E_{\text{HOMO}} + E_{\text{LUMO}} \right) \tag{2}$$

$$\eta = 1/2 \left(E_{\text{LUMO}} - E_{\text{HOMO}} \right) \tag{3}$$

The electrophilicity indexes of Dye-1 and Dye-2 in different solvents (dichloromethane, DMSO, propanol, ethanol and methanol) were calculated at B3LYP/6-311G(d) level. As shown in Table 3, the ω values of Dye-2 in different solvents are higher than those of Dye-1, implying that Dye-2 has higher photo-stability than Dye-1.



Figure 7. (a) Laser conversion efficiency and (b) Laser stability of Dye-1 and Dye-2 in different solvents $(0.56 \times 10^{-3} \text{ mol/L})$. The detection wavelengths for Dye-1 and Dye-2 are 645 nm and 660 nm, respectively. The output power of pump laser is 13 mJ.

The laser properties of a laser dye is relative to not only its structure but also the property of the used solvent. Herein, we further investigated the influences of different solvents (dichloromethane, DMSO, propanol, ethanol, methanol and

Table3. The electrophilicity indexes (ω) of Dye-1 and Dye-2 in different solvents.										
solvents	Dye-1				Dye-2					
	E _{LUMO} (eV)	E _{HOMO} (eV)	μ (eV)	η (eV)	ω (eV)	E _{LUMO} (eV)	E _{HOMO} (eV)	μ (eV)	η (eV)	ω (eV)
CH_2Cl_2	-3.4450	-6.3022	4.8736	1.4286	8.3130	-3.4695	-6.3103	4.8899	1.4204	8.4170
DMSO	-3.2436	-6.0845	4.6641	1.4205	7.6572	-3.2545	-6.0899	4.6722	1.4177	7.6989
PrOH	-3.3062	-6.1498	4.7280	1.4218	7.8612	-3.3198	-6.1579	4.7389	1.4191	7.9126
C_2H_5OH	-3.2871	-6.1307	4.7089	1.4218	7.7978	-3.2980	-6.1362	4.7171	1.4191	7.8398
CH₃OH	-3.2654	-6.1062	4.6858	1.4204	7.7291	-3.2763	-6.1144	4.6954	1.4191	7.7680

water) on the laser conversion efficiency and laser stability of Dye-1 and Dye-2. From Figure 7 a, it can be seen that the laser conversion efficiencies of Dye-2 are very different in the above solvents. For instance, the laser conversion efficiencies of Dye-1 and Dye-2 in dichloromethane are 11.8% and 15.0%, respectively, but they are less than 10% in DMSO. Strangely, both Dye-1 and Dye-2 almost have no laser emission in water, which is probably due to their very low solubility in water. Figure 7 b shows the laser stability of Dye-1 and Dye-2 in different solvents. In a same solvent, the laser stability of Dye-2 is higher than that of Dye-1. The laser stability of Dye-1 and Dye-2 varies in different solvents, which may be relative to the difference of solvent characteristics such as polarity, viscosity, oxygen content, dissolving ability to dye, and so on [42].

We further tested the laser performances of the commercial dye rhodamine B (Figure S9 and Figure S10) and compared them with those of Dye 1 and Dye 2 (Table S1). It can been that the laser emission wavelength and laser tuning range of these two dyes are larger than rhodamine B, but their laser conversion efficiency and laser stability is lower that of rhodamine B.

3. Conclusion

In this work, for the first time we synthesized two asymmetric rhodamine laser dyes based on 1-naphthol (Dye-1 and Dye-2) and systematically investigated their light absorption, fluorescence emission, and laser performances. It was found that the fluorescence emission wavelengths of Dye-1 and Dye-2 were successfully extended to the deep red region (646 nm for Dye-1 and 655 nm for Dye-2). Due to the effect of esterification, the absorption and fluorescence emission wavelengths of Dye-2 red-shift ~8 nm compared with those of Dye-1. In aprotic solvents, both λ_{abs} and λ_{em} of Dye-2 red-shift with the increase of solvent polarity, but they have no evident difference in protic solvents. No matter in protic solvents or aprotic solvents, the fluorescence quantum yield of Dye-2 gradually decreases with the increase of solvent polarity. The results of laser tests indicate that both Dye-1 and Dye-2 have a wide laser tuning range and a strong laser conversion efficiency in the red region. The laser conversion efficiency is closely relative to the dye concentration and the optimized concentration of Dye-1 and Dye-2 in ethanol is 0.56×10^{-3} mol/L. The laser conversion efficiency increases linearly with the increase of pump laser energy. Since the effect of esterification, Dye-2 exhibits much higher laser stability than Dye-1. Moreover, it was found that the solvents have a vital influence on both the laser conversion efficiency and laser stability. We believe that this study provides a reference for the synthesis and application of deep red laser with high efficiency and photo-stability.

4. Experimental section

4.1. Instruments and test methods

¹HNMR and ¹³CNMR spectra were recorded on a Bruker AM400 NMR spectrometer, using TMS as the internal standard. The mass spectra of the samples were determined by an Agilent G2577A electron bombardment mass spectrometer. UV–Vis absorption spectra were measured with a Shimadzu UV-2450 spectrophotometer at room temperature. The fluorescence spectra and fluorescence quantum yield were determined on an Edinburgh Instruments FLS 980 fluorescence spectrophotometer and the 530 nm line of Xenon lamp was used as the excitation source ($\lambda_{ex} = 530$ nm).

4.2. Laser performance measurement

Dr The laser performances of Dye-1 and Dye-2 were measured by a home-made laser testing system, in which a 532 nm Nd:YAG pulsed laser with a frequency of 10 Hz and pulse duration time of 8 ns was employed as the excitation light source. Before the measurements, the solid-state laser was lightened for 30 min to make the outputted laser become stable. For each measurement, 1.5 mL dye solution was injected into the cuvette fixed in the light path and excited by the Nd:YAG pulsed laser. At different output wavelengths, the output powers of dye solution were measured with an optical power meter and the output powers were recorded at the intervals of 2 nm.

4.3. Calculation details

The optimization and frequency calculations of Dye 1 and Dye 2 were performed by using the DFT-B3LYP method implemented with the 6-31G(d) basis set. The results confirm that there is no imaginary frequency in the optimized geometry, thus, the molecules are in the minimum energy state. The calculations of the frontier molecular orbitals (HOMO: highest occupied molecular orbital and LUMO: lowest unoccupied molecular orbital) were fulfilled at DFT-B3LYP/6-311G(d) level. The chemical potential (μ) , chemical hardness (η) were calculated using the energies of frontier molecular orbitals, which are further used for the calculation of electrophilicity index (ω) of the two dyes. In addition, the polarizable continuum model (PCM) was adopted as a solvation model as implemented in Gaussian 09 software to simulate the solvent effects. All of the calculations have been carried out with Gaussian 09. GaussView05 was used for visualization of the results from the output file.

2-[(2,3,6,7-tetrahydro-10-hydroxy-1H,5H-benzo[ij]quinolizin-9-yl)carbonyl] (M-2)

Under argon protection, 1.89 g (10 mmol) 8-hydroxyjulolidine (M-1) and 1.60 g (10.8 mmol) phthalic anhydride were added to 100 mL toluene. Then, the mixture was refluxed under 120 °C for 24 h. After the mixture was cooled to room temperature, the precipitate was filtered and washed with water. Finally, the crude product was purified by column chromatography using dichloromethane/methanol = 100/2 (v/v) as the eluent to give a yellow crystal (M-2) (2.35g, 69.7%). ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 12.83$ (s, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 6.45 (s, 1H), 3.24 (q, J = 7.2 Hz, 4H), 2.74 (t, J = 6.4 Hz, 2H), 2.47 (t, J = 6.1 Hz, 2H), 1.95 (m, 2H), 1.85 (m, 2H).(Figure S1) ¹³C NMR (400 MHz, CDCl₃, ppm): δ = 197.77, 170.56, 160.75, 149.34, 141.42, 132.56, 131.11, 130.32, 128.96, 128.26, 127.88, 112.79, 109.02, 105.54, 50.17, 49.79, 27.27, 21.63, 20.66, 19.89. (Figure S2)

Synthesis of Dye-1

Under argon protection, 337 mg (1.0 mmol) **M-2** and 144 mg (1.0 mmol) 1-naphthol were added into a 100 mL round-bottom flask containing 10 mL methane sulfonic acid. After stirred overnight at 70°C, the reaction mixture was poured into a saturated sodium perchlorate solution and stirred at 80°C for 1 h. Then, the resulting precipitate was filtered, dried in vacuum, and purified by column chromatography. Finally, the product **Dye-1**. Yield: 380 mg, 70.0%. ¹H NMR (400 MHz, DMSO-d6): $\delta = 8.72$ (d, J = 7.9 Hz, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 7.0 Hz, 1H), 7.90 (d, J = 15.4, 7.6 Hz, 5H), 7.49 (d, J = 7.2 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.91 (s, 1H), 3.68 (d, J = 16.6 Hz, 4H), 3.17 (t, J = 6.0 Hz, 2H), 2.78 (m, 2H), 2.10 (m, 2H), 1.93 (m, 2H). (Figure S3) ¹³C NMR (101 MHz, DMSO): $\delta = 166.40$, 160.23,

149.95, 139.23, 135.36, 133.19, 130.88, 130.47, 130.00, 128.41, 125.98, 125.86, 122.67, 122.55, 122.22, 119.99, 117.99, 117.16, 114.45, 105.57, 105.28, 100.51, 98.94, 97.16, 51.33, 50.83, 26.75, 19.69, 19.12, 18.78. (Figure S4) **HRMS (ESI)**: Calcd. For $[C_{30}H_{24}NO_3]^+$ 446.1751; found 446.1761. (Figure S5)

Synthesis of Dye-2

1.00 g (2.17 mmol) Dye-1, 3 mL concentrated sulfuric acid, and 100 mL absolute methanol were added into a 250 mL round bottom bottle with condensing tube and drying tube. Subsequently, the mixture solution was refluxed for 36 h. When the reaction solution was cooled to room temperature, it was dropped into a 10% NaClO₄ solution to obtain precipitation. Then, the crude product was purified by SiO₂ column chromatography using the mixed solution of dichloromethane and methanol with a volume ratio of 100/4. Finally, the product was recrystallized in ethanol to obtain the target product Dye-2. Yield: 940 mg, 92.2%. ¹**H NMR** (400 MHz, DMSO-d6); $\delta = 8.77$ (m, 1H), 8.35 (d, J = 7.9 Hz, 1H), 8.14 (d, J = 6.8 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.97 (s, 1H), 7.92 (s, 1H), 7.91 (d, J = 3.9 Hz, 2H), 7.88 (s, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.03 (d, J = 8.9 Hz, 1H), 6.94 (s, 1H), 3.75 (t, J = 5.3 Hz, 2H), 3.70 (t, J = 5.4 Hz, 2H), 3.57 (s, 3H), 3.22 (t, J = 6.1 Hz, 2H), 2.78 (m, 2H), 2.11 (dd, J = 11.2, 5.3 Hz, 2H), 1.92 (m, 2H). (Figure S6) 13 C NMR (101 MHz, DMSO): $\delta = 165.04$, 156.14, 154.05, 152.12, 150.24, 135.50, 133.67, 133.58, 131.14, 130.99, 130.65, 130.59, 129.57, 129.14, 128.54, 128.50, 126.10, 125.98, 122.79, 122.32, 122.16, 118.27, 117.30, 105.57, 52.40, 51.48, 51.02, 26.72, 19.58, 19.03, 18.66. (Figure S7) **HRMS** (ESI): Calcd. For $[C_{31}H_{26}NO_3]^+$ 460.1907; found 460.1919. (Figure S8)

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Supplementary Material

Supplementary data (Figures S1-S10 and Table S1) to this article can be found online at https://doi.org/.

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Highlights

- Two rhodamine laser dyes based on 1-naphthol were synthesized for the first time. \triangleright
- Both of the two dyes display a wide laser tuning range. \triangleright
- Both of the two dyes exhibit a strong laser conversion efficiency in the deep red region. \geq
- Solvents have a vital influence on both the laser conversion efficiency and laser stability. \triangleright

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Jinlong Zhang

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