

Spectroscopic and lasing characteristics of 1,3,5,7-tetramethyl-8-ethyl-pyrromethene-BF₂ complex

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The basic optical properties of the newly synthesized pyrromethene-BF₂ derivative (Compound 1) were investigated systematically by its ultraviolet to visible (UV-visible) absorption, fluorescence and triplet-triplet absorption. Its lasing characteristics were measured on a dye laser system pumped by a continuous wave Ar ion laser. The results suggest that, compared with the typical pyrromethene-BF₂ dye such as P-546, Compound 1 possesses stronger fluorescence and lower triplet-triplet absorption over its fluorescence spectral region. Excellent laser properties were also observed for Compound 1. It outperforms the commercially available benchmark laser dye rhodamine 6G in laser wavelength tuning range, which proves that Compound 1 is probably a potential candidate to be developed as the all-solid-state laser material.

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In recent years, intensive interests in all-solid-state dye lasers have been stimulated because of their unique features including wide wavelength-tunability, low threshold output, a compact and maintenance-free system, and a low cost gain medium^[1]. Different kinds of dyes have also been considered for developing all-solid-state laser materials, of which coumarins and rhodamines are most commonly employed because of their high lasing efficiency and photostability^[2-5].

Since they were synthesized for the first time by E. Vos de Wael in 1977^[6], 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (pyrromethene-BF₂) derivatives have been proved to be excellent fluorescent materials, which have found numerous applications in various fields such as all-solid-state dye lasers^[1,7,8], fluorescent probes for DNA sequencing^[9,10], photodynamic therapy for cancer^[11], and molecular optoelectronic devices^[12,13]. In particular, as efficient active media of tunable dye lasers, some of them outperform coumarins and rhodamines in visible spectral region, owing to their superior photostability, excellent solubility, higher fluorescence quantum yields and lower triplet-triplet absorption over their fluorescence spectral regions^[14-20]. For example, 4,4-difluoro-1,3,5,7,8-pentamethyl-3a,4a-diaza-4-bora-s-indacene (P-546) has a similar photostability as rhodamine 6G (R6G) and lases about 300% more efficiently than coumarin 545 when excited by flashlamp at 546 nm^[15]. Noteworthy, it is the dye with the lowest triplet extinction coefficient among any laser dyes known, with $\epsilon_t = 1 \times 10^{-3}$ l/(mol-cm) over the laser action spectral region^[15].

Although laser properties of many pyrromethene-BF₂ complexes have been extensively investigated both in liquid^[14-20] and solid solutions^[21-24], to the best of our knowledge, only a few systematic studies on their photophysical behaviors, especially triplet-triplet absorption properties, have been carried out. To obtain a clearer understanding of the correlation between molecular structure and spectroscopic (laser) properties of

pyrromethene-BF₂ complexes, a derivative of P-546, 4,4-difluoro-1,3,5,7-tetramethyl-8-ethyl-3a,4a-diaza-4-bora-s-indacene (Compound 1), was synthesized, and its photophysical properties, including ultraviolet to visible (UV-visible) absorption, fluorescence and triplet-triplet absorption, were studied in detail by comparison with P-546. By operating a Coherent 599-21 dye laser system pumped by a continuous wave (CW) Ar ion laser, the lasing tunability of Compound 1 and R6G was also examined.

The chemical structures of Compound 1 and P-546 are shown in Fig. 1. They were synthesized according to the procedure described in Ref. [25]. Their structures were confirmed by mass spectra, ¹H nuclear magnetic resonance (NMR), infrared (IR) and elemental analysis. Ethanol and ethylene glycol, employed for UV-visible absorption, fluorescence, triplet-triplet absorption and laser action measurements, were commercial spectrophotometric grade solvents.

In order to obtain the intrinsic photophysical characteristics of Compound 1 and P-546 in solution, the re-absorption and re-emission effects (probability of absorbing a previously emitted photon) should be minimized. Therefore, a comparatively diluted solution (2.5×10^{-5} mol/l in ethanol) of Compound 1 and P-546 was chosen to register their absorption and fluorescence spectra and the corresponding spectra were collected at room temperature on Shimadzu UV-260 UV-visible spectrometer. Their shapes are shown in Fig. 2. From Fig. 2, it can be clearly seen that Compound 1 and P-546 exhibit strong absorption in the visible regions centered at 495.4 and 496.6 nm, with the full-width at half-maximum (FWHM) of 51.2 and 39.3 nm, respectively. The absorption bands of the two compounds are very similar to those of rhodamine dyes, indicating both dye families share similar absorption characteristics at wavelength between 400 and 600 nm. Moreover, there also exists a shoulder (located at about 470 nm) on the short-wavelength side of the central peak of Compound 1 and P-546. This structure

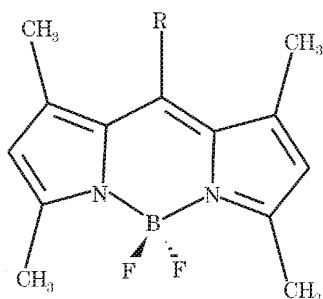


Fig. 1. Chemical structures of P-546 ($R = \text{CH}_3$) and Compound 1 ($R = \text{CH}_2\text{CH}_3$).

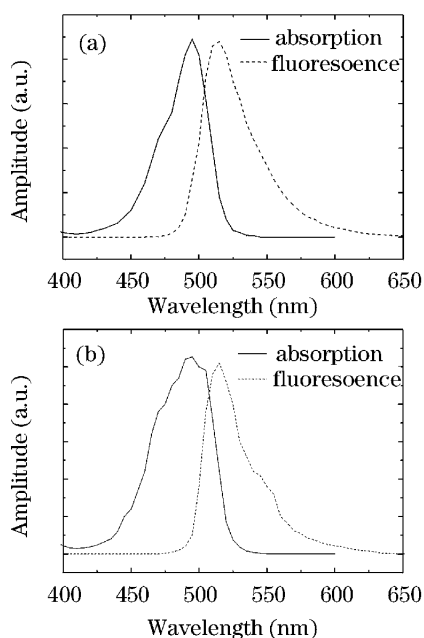


Fig. 2. Absorption and fluorescence spectra of (a) P-546 and (b) Compound 1.

reflects the vibronic splitting of the S_1 excited singlet state, which is typical of vibrational bending modes of the pyrromethene- BF_2 chromophore.

As expected, the fluorescence spectra of Compound 1 and P-546 are basically in agreement with their mirror image UV-visible absorption features except that the tails on the long-wavelength side, corresponding to the image of the shoulders in the absorption spectra, are not so pronounced. The fluorescence patterns of the two compounds are nearly identical. They all show significant emission around 515 nm, with FWHM of 33.4 and 39.1 nm and Stokes shift of about 19.6 and 18.4 nm, respectively. This observation suggests that, compared with P-546, the introduction of ethyl to the eight-position imposes little influence on the fluorescence properties of the pyrromethene- BF_2 chromophore due to the weak electron-donating capability of alkyl. Another noteworthy fact is that the profiles of their spectra are independent on the excitation wavelength, which implies that the fluorescence emission is from the lowest vibrational level of the S_1 excited singlet state.

Triplet-state dye molecules, generated from excited singlet state S_1 to excited triplet state T_1 through inter-

system crossing, have strikingly negative effects on laser efficiency because they reduce the population of S_1 to undergo stimulated emission and, most importantly, because they strongly absorb laser radiation. Thus, it is of great importance to decrease triplet-triplet absorption for the development of laser dye with high efficiency.

To obtain triplet-triplet absorption parameters of Compound 1 and P-546, pump-probe experiments (McClure's method^[26]) were adopted in our experiment. The experimental setup is shown schematically in Fig. 3. By the use of CW lasers (Ar ion laser beam at 514 nm, with the power of 41 mW) as pump sources, high population of triplet state molecules can be easily generated. The probe beam was the light derived from a monochromator controlled by a step motor. These two beams were chopped with the frequencies of $f_1 = 373$ and $f_2 = 310$ Hz, respectively. The chopped tungsten lamp pulse was detected by photodiode (PD) as reference signal. In order to prevent the distortion during absorption, the probe beam was arranged at a right angle to the pump beam in the sample cell, which contained the ethanol solution of Compound 1 or P-546 with the concentration of 3×10^{-5} mol/l. The transmission intensity of the probe beam was detected by a photomultiplier (PMT), magnified by the sum reference frequency $f_1 + f_2$ mode of a lock-in amplifier with 100- μV sensitivity and 100-ms time constant, and then sent to a computer. By scanning the wavelength of the probe beam between 350 and 650 nm, the triplet-triplet absorption spectra can be recorded successfully. In Fig. 4, the relative triplet extinction coefficients of Compound 1 and P-546 are depicted. It follows obviously from Fig. 4 that they all feature very weak triplet-triplet absorption intensity over their fluorescence (laser action) spectral region and Compound 1 presents a little higher triplet extinction coefficient than that of P-546. The triplet-triplet absorption dips are located near 503.5 nm, with a FWHM ~ 59 nm for Compound 1, and 496.4 nm, with a FWHM ~ 40 nm for P-546, respectively.

The intensity of triplet-triplet absorption in fluorescent dyes depends mainly on π electron distribution as described by a simple rule found by Drexhage^[27]. The rule suggests that in a dye where the non-localized π system of the chromophore can make a loop when oscillating between the end groups, the triplet yield will be higher than that in a related compound where this loop is

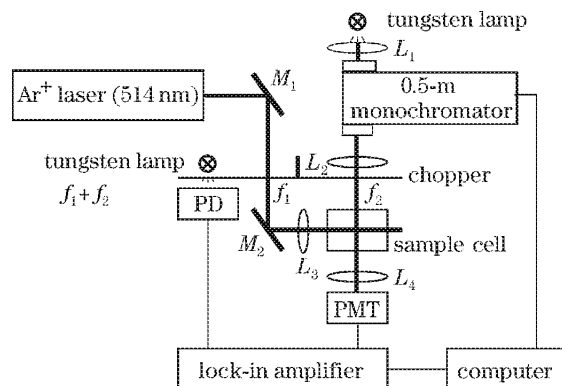


Fig. 3. Experimental setup to measure the triplet-triplet absorption spectra.

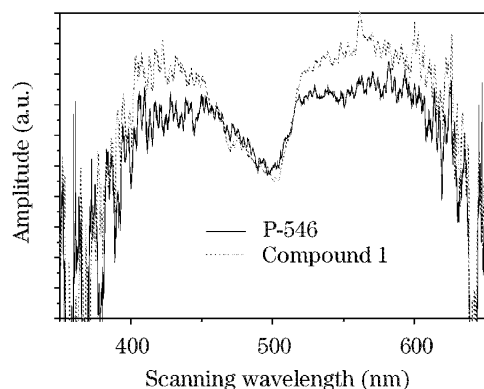


Fig. 4. Triplet-triplet absorption spectra of P-546 and Compound 1.

blocked. Due to the unique structure of pyrromethene-BF₂ chromophore, the circulating of π -electrons is restricted seriously by the tetrahedral configuration formed by N, B and F atoms, and consequently the probability for inter-coupling of electron spin and orbital moment is rather low. This decreases spin-orbit coupling, and consequently reduces the rate of inter-system crossing, therefore giving rise to a low triplet-triplet absorption of Compound 1 and P-546, as presented by our experiment.

The lasing characteristics of Compound 1 and R6G were obtained from a CW Coherent 599-21 dye laser system, the schematic layout of which is shown in Fig. 5. This system was pumped by the 514-nm line of Ar ion laser with the power of 3.5 W. A dye circulation setup (average flow speed 10 m/s) was employed to avoid

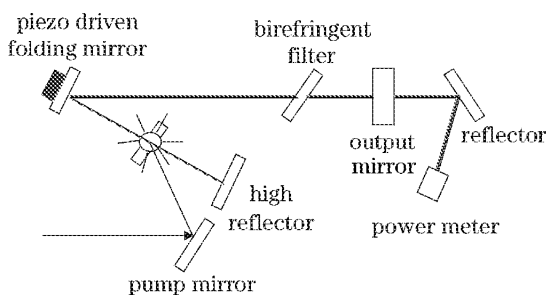


Fig. 5. Schematic layout of the dye laser system.

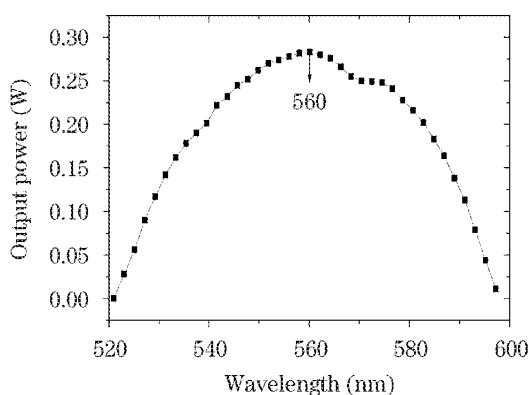


Fig. 6. Laser tuning curve of Compound 1.

photodecomposition of dye molecule and observable fluctuation of the output laser intensity. During the experiment, Compound 1 and R6G were dissolved in ethylene glycol with a concentration of 4.5×10^{-3} mol/l.

As depicted in Fig. 5, the pump laser beam is firstly reflected to the dye plate by a pump mirror, then, because of the intense interaction between the pump photons and ground state dye molecules, the excited state population inversion comes into being and the excited state dye molecules begin to emit fluorescence. The stimulated dye laser photons undergo resonance among the high reflector, piezo-electrically driven folding mirror, and output reflector, the corresponding laser output can be easily carried out. By tuning the birefringent filter, the laser tuning spectrum of Compound 1 was obtained, which is given in Fig. 6. From Fig. 6, it can be clearly seen that Compound 1 exhibits a very broad wavelength tunability, the lasing in the range of 522 – 596 nm, centered at ~ 560 nm, for a dye concentration of 4.5×10^{-3} mol/l. The wavelength tuning curves of R6G were also obtained under the same condition, which only ranges from 569 to 591 nm.

In conclusion, 4,4-difluoro-1,3,5,7-tetramethyl-8-ethyl-3a,4a-diaza-4-bora-s-indacene (Compound 1) was synthesized and its structure was confirmed in detail by mass spectral, ¹H NMR, IR, and elemental analysis. Its photophysical behaviors such as ground state absorption, fluorescence and triplet-triplet absorption were studied systematically, indicating that Compound 1 exhibits broader band of absorption, more intense fluorescence emission, and rather low triplet-triplet absorption in visible spectral region. Compared with R6G, Compound 1 features broader tunability when running on a Coherent 599-21 dye laser system pumped by a CW Ar ion laser at 514 nm, which implies that Compound 1 is likely a promising candidate to be developed as the all-solid-state laser material. All these results provide valuable basis for further studies on the quantitative relationship between structure and activity of pyrromethene-BF₂ complexes.

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