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Solid-state laser with newly synthesized pigment

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Abstract

A yellow laser oscillation was obtained using a newly synthesized pigment. The compound used in this study is a derivative of 3,6-diphenylpyrrolo(3,4-c)pyrrole-1,4-dione. In the compound used, the phenyl groups are substituted by *p*-methylphenyl groups and the hydrogen atoms attached to the nitrogens by allyl groups. We prepared a 10-μm-thick thin polymethyl methacrylate (PMMA) film, into which we incorporated the pigment, around a 3-mm-diameter quartz rod. In this study we adopted the thin-film ring laser system in order to examine the laser action with the pigment. We pumped the pigment-doped PMMA thin film with the third-harmonic-generation (THG) produced by a pulsed Nd:YAG laser. The center wavelength of the laser oscillation was 575 nm. The threshold pump energy density was approximately 0.55 mJ/cm^2.

Keywords: Solid-state dye laser; Pigment; PMMA; Yellow laser; Thin-film ring resonator

1. Introduction

Dye lasers have been commonly used as coherent light sources since 1966 [1]. Organic dyes have wide wavelength range tunability, and by choosing appropriate dye compounds, dye lasers can cover the wavelength range from ultra violet to infrared. However, as the dye molecules are dissolved with organic solvent and circulated in a dye laser system, the handling and maintenance of the dye laser system is troublesome. Therefore, a solid-state dye laser [2–4] with a simple structure and allowing easy maintenance is hoped to be realized. Three approaches have been made toward the realization of a practical solid-state dye laser; (1) to adopt dye or pigment molecules with high quantum yield and high photo stability, (2) to solidify the dye or pigment, (3) to adopt a simple and appropriate structure for a solid-state dye laser. Thus far we have studied several kinds of solid-state dye lasers and achieved blue, yellow, and red lasers. For example, we solidified stilbene 3 into a silica gel thin film using the sol-gel method and constructed a thin-film ring laser system [5,6]. A pulsed blue laser beam was obtained at a wavelength of 433 nm. This laser has a simple structure and the system does not require tuning to start the laser oscillation. Another example is a photo-induced DFB (distributed feed back) solid-state

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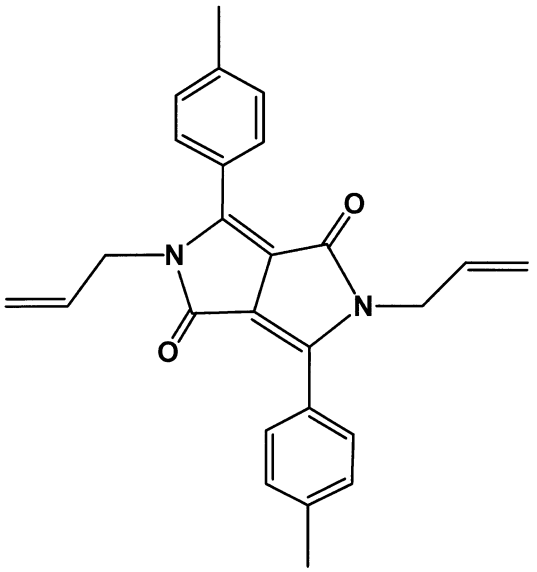
dye laser [7]. We fabricated a rhodamine-B-doped xerogel monolith and exited it with THG of a pulsed Nd:YAG laser. By means of the two-beam interference, a photo-induced DFB resonator was formed and laser oscillation was achieved. The FWHM (full width at half maximum) of the laser spectrum was approximately 1 nm.

In this study, we tried to use a newly synthesized pigment as a laser medium. We doped the pigment into PMMA (polymethyl methacrylate) and formed a 10 μm-thick thin film and used it as a laser medium. We adopted the thin-film ring laser system and obtained a yellow laser beam at a wavelength of 575 nm. This report presents the characteristics of the new pigment as a laser medium.

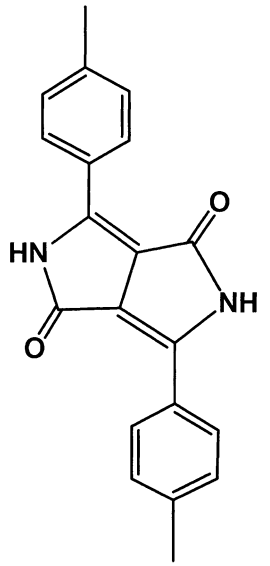
2. Experiment

Fig. 1 shows the chemical structure of the pigment. The pigment was newly synthesized as a derivative of 3,6-diphenylpyrrolo(3,4-c)pyrrole-1,4-dione. We prepared the pigment as follows: 0.73 g (2.3 mM) 1,4-diketo-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole, whose chemical structure is shown in Fig. 2, was slurred in dry 1-methyl-2-pyrrrolidinone (15 ml) for 2 h at room temperature and 0.35 g of sodium hydride (60–72% dispersion in mineral oil) was added to the slurry under nitrogen. After stirring for 2 h, 0.80 g (6.6 mM) of allyl bromide was added to the reaction mixture and the mixture was stirred additionally for 2 h. The mixture was poured into 50 ml of water and the precipitate was collected by filtration. The obtained red solid was purified by column chromatography (silica gel, dichloromethane as eluent). After being dried, 0.72 g of red fluorescent solid was obtained. Its yield was 75%. The molecular weight of the pigment is 396.48. Fig. 3 shows the ^{1}H and ^{13}C NMR spectrum of the new pigment. The spectra were recorded with 400 MHz NMR system (JEOL JNM-ECP 400). Fig. 4



C26H24N2O2
Exact Mass: 396.18
Mol. Wt.: 396.48
C, 78.76; H, 6.10; N, 7.07; O, 8.07

Fig. 1. Structural formula of the pigment.



$C_{20}H_{16}N_2O_2$
Exact Mass: 316.12
Mol. Wt.: 316.35
C, 75.93; H, 5.10; N, 8.86; O, 10.11

Fig. 2. Structural formula of 1,4-diketo-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole.

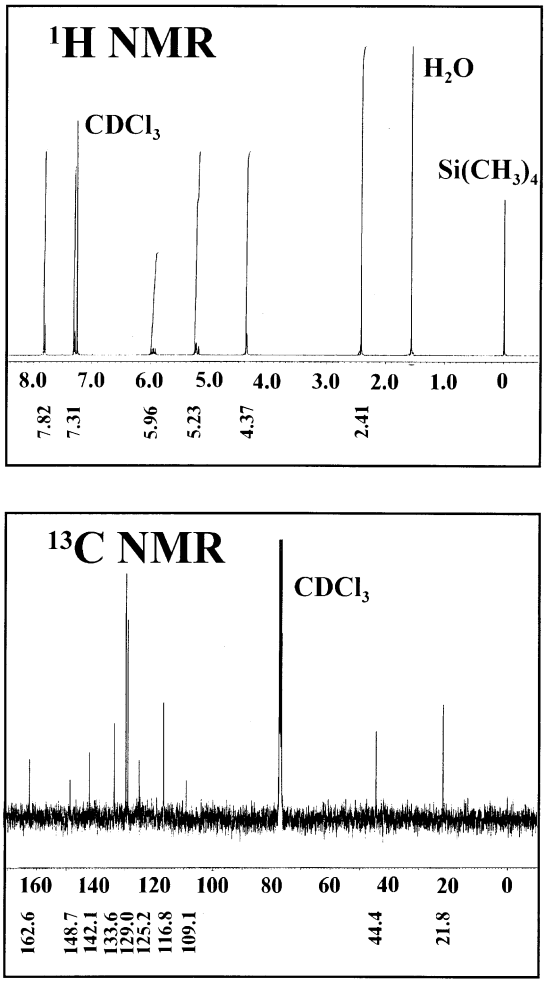


Fig. 3. ^{1}H and ^{13}C NMR spectra of the pigment.

shows the correspondence between the NMR spectra and the new pigment synthesized, which clearly demonstrates the designed pigment was synthesized. These data identified the structure of the pigment. Table 1 shows the data of the new pigment, Φ is the fluorescent quantum yield, and Table 1 shows that Φ is 0.97 of the new compound. Therefore, a strong fluorescent emission was expected. The data of rhodamine B is listed in comparison with the new pigment. We dissolved PMMA and the pigment in acetone. We dipped a 3-mm-diameter quartz rod into the pigment-doped PMMA solvent and formed a thin film around the quartz rod. The sample was dried in a drying oven

Table 1
The λ_{max} is the wavelength at which the absorbance is maximum and F_{max} is the wavelength at which the fluorescence spectrum is maximum. Φ is the fluorescent quantum yield

Samples	λ_{max} (nm)	F_{max} (nm)	Quantum yield Φ in aerated NMP[a]
Pigment	474	531	0.97
Rhodamine B	542	568	0.40

[a] NMP, *N*-methylpyrrolidone.

for 6 h. The concentration of the pigment was 2 mM/l. We used the quartz rod as a ring resonator and the light amplifier of the thin-film ring laser system.

The thin film ring laser employed in this study is shown schematically in Fig. 5. This device is composed of two components. One is a quartz rod coated with a pigment-doped PMMA thin film. The thin film fabricated by the dip coating method works as a ring resonator. The other of the device is a planar waveguide. This waveguide is also a PMMA thin film that was prepared by spin-coating on a flat quartz substrate. The pumping source is a third-harmonic genenation of a pulsed Nd:YAG laser; its wavelength is 355 nm and its pulse width is 7 ns. The pumping laser beam is turned into a 0.2-mm-width line with three cylindrical lenses to excite the active media. A part of the pumping beam was reflected by the mirror and excites the pigment molecules on the opposite side of the ring resonator. Fluorescence, which is the seed of the laser, is then emitted from the excited pigment molecules. Part of the fluorescence satisfying the conditions of propagation can wind around the quartz rod and is amplified by the pumped pigment molecules. At the contact point of the thin film ring resonator and the planar waveguide, the amplified light wave separates into two parts; one is the light wave transferred onto the planar waveguide by the evanescent coupling, and the other remains in the thin film ring resonator. The light that remains in the ring resonator is amplified again and propagates along the circumference of the thin film ring waveguide. The planar waveguide conducts the light wave transferred from the ring resonator, and the light wave is outputted through the waveguide as a laser

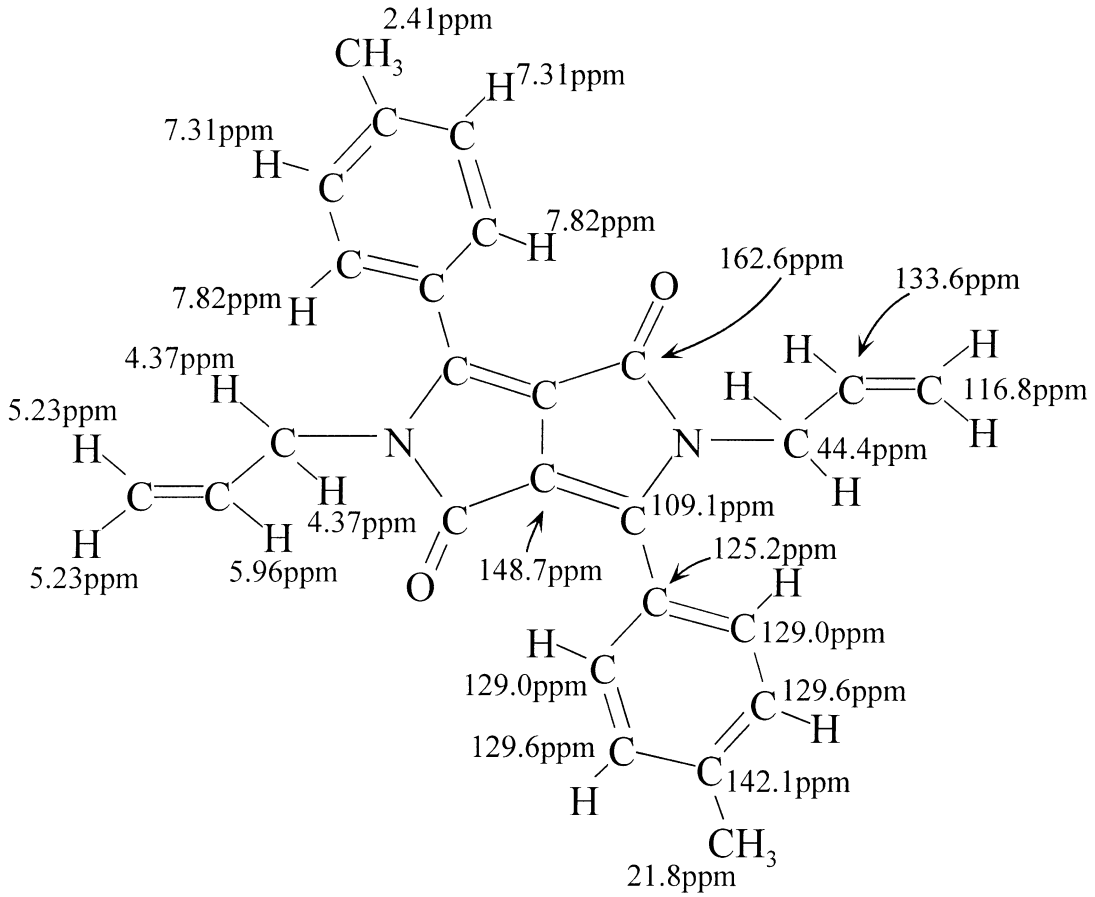


Fig. 4. Correspondence between the NMR spectra and the synthesized pigment.

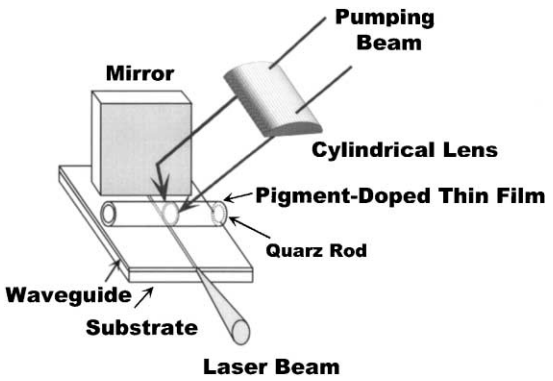


Fig. 5. Thin-film ring laser.

beam. Fig. 6 is a schematic view of a typical experimental setup of the thin-film ring laser system for measurement. The spectrum of the thin-film ring laser was measured using a CCD (charge coupled device)-based spectrometer, and the input-output characteristic of the thin-film ring laser was measured using pyroelectric detectors.

3. Results and discussion

Fig. 7 shows the absorbance characteristic and the fluorescent spectrum of the new pigment diluted by acetone. The wavelength at the peak of the absorbance spectrum was 468nm and that of the fluorescent spectrum was 521 nm. The Stokes shift of the compound was 53 nm. Fluorescent materials, which have larger Stokes shift generally, exhibit stable laser oscillation due to smaller absorption loss. Stokes shifts of typical laser dyes are 50 nm

for rhodamine B and 80 nm for stilbene 3, for example. The shift of the present compound is comparable to that of rhodamine B. Therefore, the compound is expected to be one of the laser media. Fig. 7 also shows that the bandwidth of the fluorescent spectrum was approximately 51 nm, which is larger than that of rhodamine B. Fig. 8 shows the narrow banded laser spectrum of the thin-film ring laser with the new pigment. We achieved yellow laser oscillation, with a center wavelength of the laser of 575 nm. The energy density of the pumping beam was 0.83 mJ/cm^2. It was 1.5 times the laser threshold energy density. The FWHM of the thin-film ring laser spectrum was reduced to 1/4 that of the fluorescent spectrum.

As we did not insert external resonators, such as etalon or diffraction grating, into the thin film ring laser, a multimode oscillation is assumed. However, the CCD-based spectrometer used in this study was unable to resolve the fine longitude modes. Fig. 9 shows the input-output characteristics of the

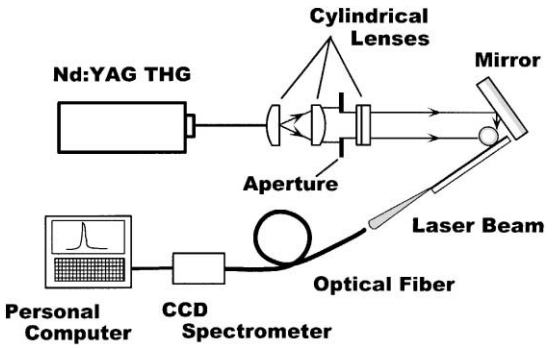


Fig. 6. Experimental setup; THG (third harmonic generation) produced by a pulsed Nd:YAG laser (continuum minilite I) was used as the pump source.

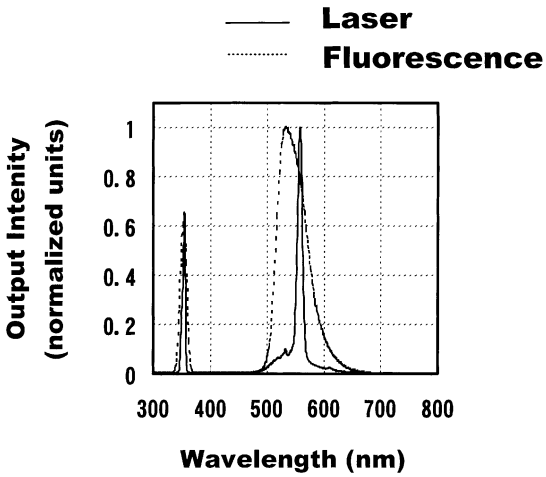


Fig. 8. Laser spectrum.

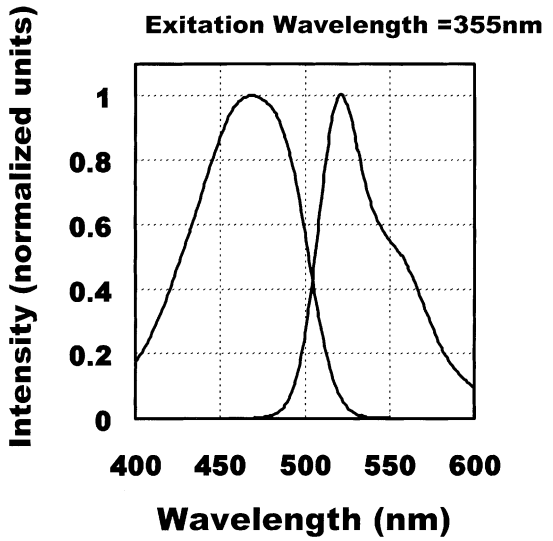


Fig. 7. Absorption and fluorescent spectrum of the pigment.

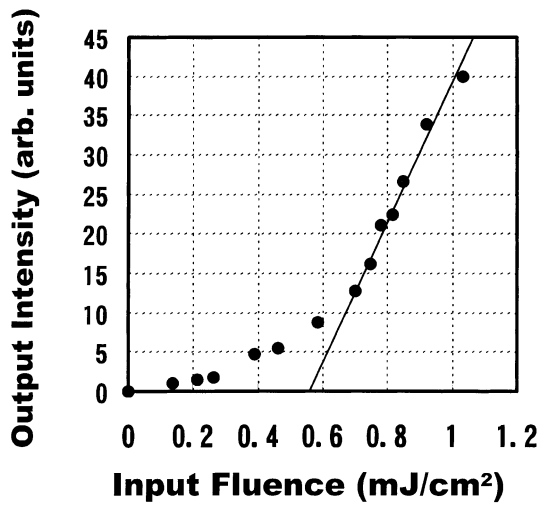


Fig. 9. Output–input characteristics of the thin-film ring laser.

thin-film ring laser. The threshold at which the laser gain exceeds the optical loss was observed. The threshold input energy density was approximately 0.55 mJ/cm^2.

4. Conclusion

Yellow laser oscillation was obtained using a newly synthesized pigment which is a derivative of 3,6-diphenylpyrrolo(3,4-c)pyrrole-1,4-dione. We doped the pigment into PMMA and prepared active laser media for the thin-film ring laser. The center wavelength of the laser oscillation was 575 nm.

Acknowledgements

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