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Dyes and Pigments 63 (2004) 115–125

DYES and PIGMENTS

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Evaluation of new organic pigments as laser-active media for a solid-state dye laser

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Received 10 October 2003; received in revised form 4 February 2004; accepted 15 February 2004

Abstract

Solid-state dye lasers are small, low-cost, simple, and coherent light sources. These lasers can output a laser beam at many wavelengths by changing the organic dyes or pigments. Photodegradation of the laser-active medium, however, is difficult with this type of laser. Research regarding new fluorescent materials that are not easily degraded by exposure to the pump light is therefore important in developing practical applications for solid-state dye lasers. In the present study, six new organic pigments were synthesized and evaluated as the active medium of the solid-state dye laser. The issues evaluated were: (1) whether the pigments can oscillate as laser medium or not; and (2) degradation by exposure to UV light. As a result of the evaluation, each of the six pigments oscillated as laser medium and green and yellow laser oscillations were obtained. The pigments were also found to have degradation characteristics similar to those of Rhodamine B.

Keywords: Solid-state dye laser; Organic pigments; Photo bleach; Thin-film ring laser

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1. Introduction

Since the first report of the laser oscillation of a dye laser confirmed by Sorokin and Lankard [1] in 1966, dye lasers have been widely used as pulsed or continuous wave lasers in many fields. Dye lasers can oscillate at wavelengths from the ultra violet to infrared region by changing the dyes or pigments. We are studying solid-state dye lasers, which have a small simple structure and can also be easily operated. Many trials regarding solidification of organic dyes have been conducted since the first report by Soffer and McFarland in 1967 [2]. In 1984, Avnir et al. [3] reported the application of a dye-doped silica gel synthesized by the sol–gel method. Heretofore, we have fabricated many types of solid-state dye lasers [4–6] with simple structures using many organic dyes and pigments such as stilbene, rhodamine, perylene, and newly synthesized pigment [7]. We have

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doi:10.1016/j.dyepig.2004.02.002

also demonstrated that laser oscillations can be obtained in many colors. We are now developing these solid-state dye lasers for more practical coherent light-source systems. The main problem of solid-state dye lasers for practical use is photobleaching of the organic dyes by exposure to the pump beam. Overcoming this problem is an important theme of current research. One method of overcoming the photobleaching problem is to have the bleached laser medium easily replaced with new medium. To achieve this, a device must be designed that is both simple and low-cost. Secondly, in order to prolong the longevity of the device, we must search for new organic dyes or pigments that are not easily photobleached. The above two approaches are both needed to achieve a practical solid-state dye laser system. We therefore have synthesized six new organic pigments and fabricated a thin-film ring solid-state dye laser with these six pigments. We achieved laser oscillations with all of the pigments and evaluated their longevities.

2. Synthesis of pigments

In the previous work [7], light stability of the two compounds mentioned was insufficient for practical use because the dyes were decomposed by exposure to the pump light. It was supposed that the bond cleavage would take place between the allyl group and the nitrogen atom on the pyrrolopyrrole skeleton. In an attempt to improve the bond strength thermodynamically, the alkyl group was employed in place of the allyl group. On top of that, several aromatic groups were incorporated to investigate the effect on the laser properties. On the basis of that, and in order to create a practical solid-state dye laser, we synthesized six new compounds as laser-active media. Tables 1–6 show the chemical structure and physical data for compounds A–F. Table 7 shows the apparatuses used for the measurements of the physical data of the pigments. Table 8 shows the yield of each compound and Table 9 shows the mass spectra of these compounds. Syntheses of the pigments were carried out as follows.

2.1. Preparation of compound A

To synthesize compound A, 53 g (0.47 mol) of potassium *t*-butoxide, 50 g (0.38 mol) of 3-methoxybenzonitrile, and 250 ml of *tert*-amyl alcohol were heated to 100 °C under a nitrogen atmosphere. As soon as this temperature was reached, a solution of 50.6 g (0.22 mol) of di-*n*-butyl succinate and 50 ml of *tert*-amyl alcohol was added over 1 h using a dropping funnel. When the addition was completed, the reaction mixture was kept at 100 °C for 20 h, then cooled to 65 °C, neutralized with 35 ml of glacial acetic acid, and boiled briefly at the reflux temperature. The resulting pigment suspension was filtered at room temperature. The filter cake was suspended in 500 ml of water, and the pigment was isolated again by filtration, and then finally washed with methanol and water until the washings ran colorless. After being dried at 100 °C in vacuo, 42.3 g (65% in

Table 1
Compound A

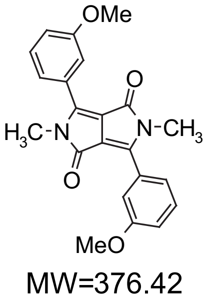
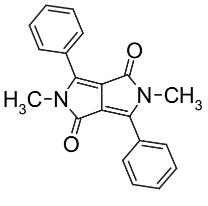
	mp: 210–211 °C IR(KBr): ν = 1674 cm^{-1} (s, C=O), 1614 cm^{-1} (m), 1597 cm^{-1} (m), 1578 cm^{-1} (m), 1490 cm^{-1} (m), 1475 cm^{-1} (m), 1456 cm^{-1} (m), 1437 cm^{-1} (m), 1368 cm^{-1} (m), 1301 cm^{-1} (w), 1244 cm^{-1} (m), 1244 cm^{-1} (w), 1214 cm^{-1} (w), 1189 cm^{-1} (w), 1098 cm^{-1} (w), 1076 cm^{-1} (w), 1037 cm^{-1} (m), 905 cm^{-1} (w), 867 cm^{-1} (m), 789 cm^{-1} (w), 768 cm^{-1} (m), 729 cm^{-1} (m), 686 cm^{-1} (m), 639 cm^{-1} (w) ^{1}H NMR ($CDCl_3$): δ 3.36 (s, 6H), 3.91 (s, 6H), 7.01–7.08 (m, 2H), 7.35–7.44 (m, 4H), 7.55–7.58 (m, 2H)

Table 2
Compound **B**



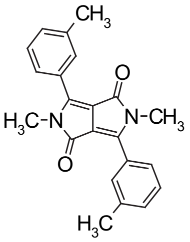
MW=316.36

mp: 230–233 °C

IR(KBr): $\nu = 1667$ cm^{-1} (s, C=O), 1602 cm^{-1} (m), 1591 cm^{-1} (m), 1562 cm^{-1} (m), 1496 cm^{-1} (m), 1446 cm^{-1} (m), 1421 cm^{-1} (m), 1365 cm^{-1} (m), 1225 cm^{-1} (w), 1093 cm^{-1} (m), 1049 cm^{-1} (m), 1022 cm^{-1} (m), 800 cm^{-1} (w), 784 cm^{-1} (m), 749 cm^{-1} (w), 726 cm^{-1} (m), 696 cm^{-1} (m), 640 cm^{-1} (m)

^{1}H NMR (CDCl$_3$): δ 3.34 (s, 6H), 7.49–7.56 (m, 6H), 7.85–7.90 (m, 4H)

Table 3
Compound C



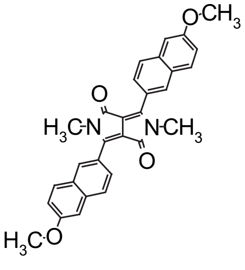
MW=344.42

mp: 187–189 °C

IR(KBr): $\nu = 1673$ cm^{-1} (s, C=O), 1612 cm^{-1} (m), 1588 cm^{-1} (m), 1581 cm^{-1} (m), 1488 cm^{-1} (w), 1427 cm^{-1} (m), 1376 cm^{-1} (m), 1227 cm^{-1} (w), 1090 cm^{-1} (m), 1047 cm^{-1} (m), 1040 cm^{-1} (m), 882 cm^{-1} (w), 810 cm^{-1} (w), 732 cm^{-1} (m), 694 cm^{-1} (w), 644 cm^{-1} (w)

^{1}H NMR (CDCl$_3$): δ 2.41 (s, 6H), 3.29 (s, 6H), 7.26–7.40 (m, 4H), 7.58–7.62 (m, 2H), 7.68 (s, 2H)

Table 4
Compound D



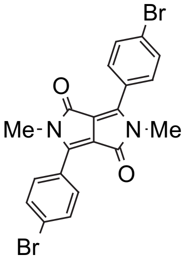
MW=476.54

mp: 331–332 °C

IR(KBr): $\nu = 1684$ cm^{-1} (s, C=O), 1627 cm^{-1} (m), 1592 cm^{-1} (s), 1561 cm^{-1} (w), 1500 cm^{-1} (w), 1486 cm^{-1} (m), 1394 cm^{-1} (m), 1275 cm^{-1} (m), 1230 cm^{-1} (m), 1207 cm^{-1} (m), 1166 cm^{-1} (m), 1083 cm^{-1} (s), 1028 cm^{-1} (m), 854 cm^{-1} (m), 806 cm^{-1} (w), 731 cm^{-1} (m), 456 cm^{-1} (m)

^{1}H NMR (CDCl$_3$): δ 3.45 (s, 6H), 3.96 (s, 6H), 7.12–7.22 (m, 4H), 7.80–7.97 (m, 6H), 8.38 (s, 2H)

Table 5
Compound E



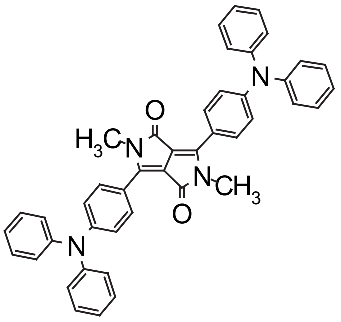
MW=474.15

mp: 338–339 °C

IR(KBr): $\nu = 1667$ cm^{-1} (s, C=O), 1612 cm^{-1} (m), 1488 cm^{-1} (m), 1426 cm^{-1} (w), 1399 cm^{-1} (w), 1365 cm^{-1} (w), 1090 cm^{-1} (m), 1071 cm^{-1} (m), 1042 cm^{-1} (w), 1006 cm^{-1} (m), 845 cm^{-1} (w), 763 cm^{-1} (w), 736 cm^{-1} (w), 674 cm^{-1} (w)

^{1}H NMR (CDCl$_3$): δ 3.32 (s, 6H), 7.64–7.76 (dd, 8H)

Table 6
Compound F



MW=650.79

mp: 323–325 °C

IR(KBr): $\nu = 1670\ \text{cm}^{-1}$ (s, C=O), $1505\ \text{cm}^{-1}$ (s), $1583\ \text{cm}^{-1}$ (s), $1489\ \text{cm}^{-1}$ (s), $1431\ \text{cm}^{-1}$ (w), $1336\ \text{cm}^{-1}$ (m), $1321\ \text{cm}^{-1}$ (m), $1300\ \text{cm}^{-1}$ (m), $1197\ \text{cm}^{-1}$ (w), $1082\ \text{cm}^{-1}$ (m), $836\ \text{cm}^{-1}$ (w), $753\ \text{cm}^{-1}$ (w), $741\ \text{cm}^{-1}$ (w), $696\ \text{cm}^{-1}$ (m), $521\ \text{cm}^{-1}$ (w)

^{1}H NMR ($CDCl_3$): δ 3.38 (s, 6H), 7.06–7.36 (m, 24H), 7.82–7.86 (d, 4H)

theory, based on dibutyl succinate) of 3,6-bis-(3-methoxylphenyl)-pyrrolo-(3,4-*c*)-pyrrole-1,4-dione was obtained. The product was used in the next step without further purification.

Next, 2.0 g (5.74 mmol) of 3,6-bis-(3-methoxylphenyl)-pyrrolo-(3,4-*c*)-pyrrole-1,4-dione was slushed in 20 ml of 1-methyl-2-pyrrolidinone for 2 h at room temperature, and 1.61 g (14.35 mmol) of potassium *t*-butoxide was added to the slurry under nitrogen. After stirring for 2 h, 5.0 g (35.2 mmol) of methyl iodide was added to the reaction mixture and stirred additionally for 4 h. The reaction mixture was poured into 50 ml of water, and the red solid was filtered off and purified by column chromatography (silica gel, dichloromethane–hexane as eluent). After drying, 1.85 g (86%) of orange solid was obtained.

Table 7
Apparatuses used for the measurements and comments

mp (Melting point)	BUCHI Melting Point B-540 Melting points data are uncorrected
IR (Infrared spectrum)	PERKIN ELMER 1600 Series FTIR Absorption intensity: s = strong, m = middle, w = weak
NMR: Varian UNITY Plus (400 MHz)	Proton chemical shifts are reported in δ (ppm) downfield from an internal tetramethylsilane standard for solutions in $CDCl_3$ s = singlet, d = doublet, dd = doublet of doublet, m = multiplet

2.2. Preparation of compounds B, C, D, E, and F

The procedure for the preparation of compound A is repeated using the corresponding nitrile compounds to prepare compounds B–F:

Compound	Used nitrile
B	Benzonitrile
C	3-Methylbenzonitrile
D	6-Methoxy-2-naphthonitrile
E	4-Bromobenzonitrile
F	4-(Diphenylamino)benzonitrile

In this way, we obtained six new organic pigments as laser-active media for a solid-state dye laser.

Table 8
Yield of each compound

Compound	Yield	
	1st step/pigment	2nd step/alkylation
A	65%	86%
B	IRGAZIN DPP Scarlet EK[a]	96%
C	42%	76%
D	35%	24%
E	43%	28%
F	15%	63%

[a] Commercial products of Ciba Specialty Chemicals.

Table 9
Mass spectra of each compound

Compound	Mass
	m/z (%)
A	377 [M + H$^+$] (100)
B	317 [M + H$^+$] (100)
C	345 [M + H$^+$] (100)
D	477 [M + H$^+$] (100)
E	473 [M + H$^+$] (62), 475 [M + 2 + H$^+$] (100), 477 [M + 4 + H$^+$] (43)
F	651 [M + H$^+$] (100)

Apparatus: ZQ-micromass produced by Waters.
Method: LC–APCI method (LC = Liquid chromatography, APCI = Atmospheric Pressure Chemical Ionization).
By the method, amino type compounds like DPP usually give protonated peak (M + 1) as a main peak. As for compound E, three main peaks can be explained by the existence of two bromine atoms in the structure and the ratio of their isotopes, i.e. ^{79}Br and ^{81}Br. In conclusion, every data of compound A–F agrees to the expected structure.

3. Experiment

3.1. Thin-film ring laser [4,7]

The thin-film ring laser used in this study is shown schematically in Fig. 1 as a cross-sectional view. This device consists of two components. One is a quartz rod coated with pigment-doped polymethylmethacrylate (PMMA) thin film. The thin film fabricated around the quartz rod functions as a ring resonator and light amplifier. The other component is a planar waveguide. This waveguide conducts the laser beam transferred from the ring resonator, and the laser beam is output from the edge of the waveguide. We prepared the thin-film ring resonator by the dipping method shown in Fig. 2. We first dissolved PMMA in dichloromethane, and placed the pigment in the solvated PMMA. A quartz rod with a size of 3 mm in diameter and 40 mm in length was dipped in the pigment-doped PMMA. We then pulled out the quartz rod and dried the PMMA film. We repeated this process a few times until approximately 50 μm-thickness film was coated around the quartz rod. We prepared one sample for each compound. Next, we tried laser oscillation with each sample. The pumping source was a pulsed Nd:YAG laser third-harmonic generation (THG); its wavelength was 355 nm and the pulse duration approximately 7 ns. In this system, the laser oscillates when the optical gain along the circumference of the ring resonator exceeds the total loss of the system. We examined whether the six pigments are capable of lasing with the thin-film ring laser.

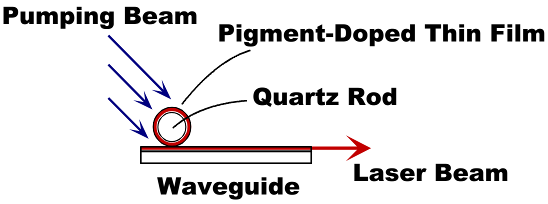


Fig. 1. Structure of the thin-film ring laser.

3.2. Evaluation of photodegradation

The photobleaching characteristic is one of the important factors relating to laser dyes or pigments. Fig. 3 schematically shows a block diagram of the photodegradation measurement we used in this study. The method of evaluation was as follows. We prepared spin-coated pigment-doped PMMA thin film on a slide glass. The samples were pumped by the THG of Nd:YAG laser. The wavelength of the pump beam was 355 nm. The pump beam was linearly concentrated by a pair of

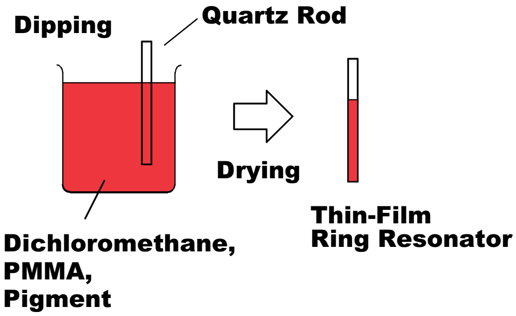


Fig. 2. Fabrication of the thin-film ring resonator by the dip-coating method.

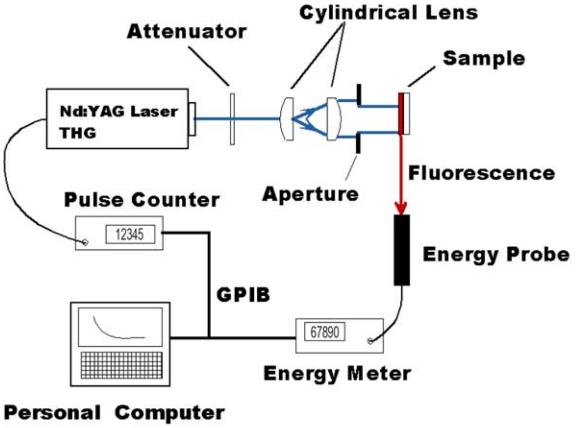


Fig. 3. Block diagram of photodegradation measurement.

cylinder lenses. The energy density of the pump beam was 0.5 mJ/cm^2. The fluorescence from the pigment was input into an energy probe (RjP-765 Silicon Probe, Laser Probe Inc.), and the measured value of the fluorescence energy was displayed on the energy meter (Rj-7610, Laser Probe Inc.). At the same time, the number of pump shots was counted by the pulse counter (TC110, Yokogawa Electric Corp.). The results of the measurements by the energy meter and the pulse counter were downloaded to a personal computer via GPIB (General Purpose Interface Bus) and plotted on a graph (x-axis: number of pump shots, y-axis: output energy), as is schematically shown in Fig. 4. To compare the characteristics of photobleaching for each pigment, we normalized the measurement for each graph. We first removed the offset of the data. Because part of the pumping beam enters into the energy probe, the value corresponding to the pumping beam must be subtracted. Next, the output energy, which corresponds to the intensity of the fluorescence, is normalized.

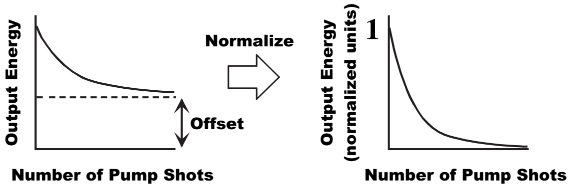


Fig. 4. Normalizing method for the measured photodegrading data.

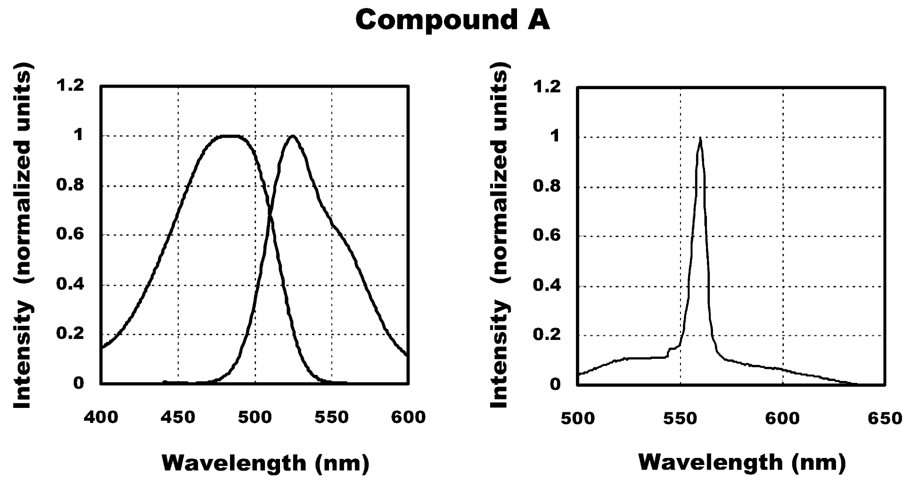
4. Results and discussion

Figs. 5–10 show the measured absorption and fluorescent spectra (left side of the graph), and laser spectra (right side of the graph) for each of the pigments, respectively. These graphs show that we achieved a narrow-banded laser oscillation in a 500-nm wavelength band with every compound. We obtained yellow laser with compound A, and green laser with compounds B–F. The graphs show that the laser spectra have approximately 3–6 nm of full width at half maximum. As the laser we adopted in this study has a ring resonator, a multimode oscillation is expected. Therefore the measured laser spectra curves show the envelope, and have the width of 3–6 nm.

Fig. 11 shows the results of the evaluation of photobleaching characteristics obtained by the above method. As a reference for the photobleaching, a photodegrading curve of Rhodamine B is superposed onto each graph. It can be seen in the graphs that each compound exhibits a photobleaching characteristic similar to that of Rhodamine B. We therefore can conclude from the experiments described above that the six new pigments synthesized in this study function well as laser-active media in the solid-state dye laser.

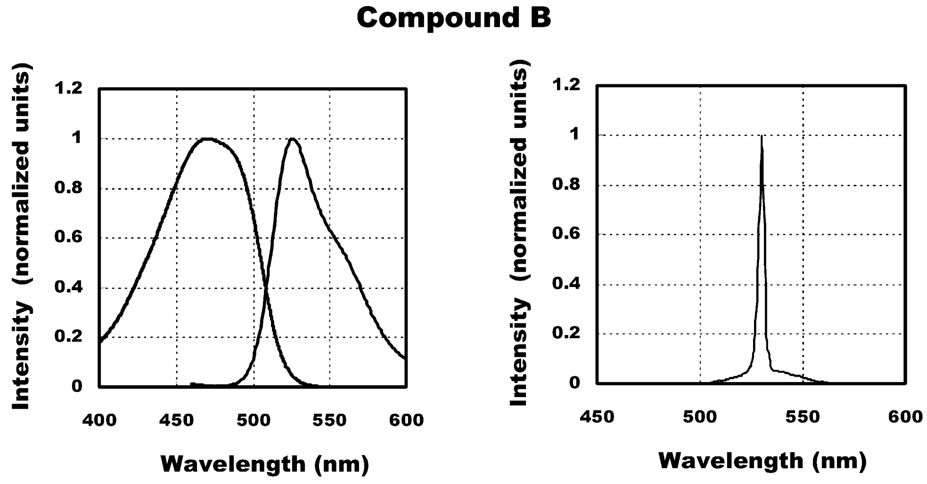
5. Conclusion

Six pigments were synthesized and found to give laser oscillations with a thin-film ring laser. The colors of the lasers were green or yellow. We also measured the photodegrading characteristics. The pigments showed a photodegrading characteristic similar to that of Rhodamine B. As such, the pigments can function well as laser-active media in the solid-state dye laser.



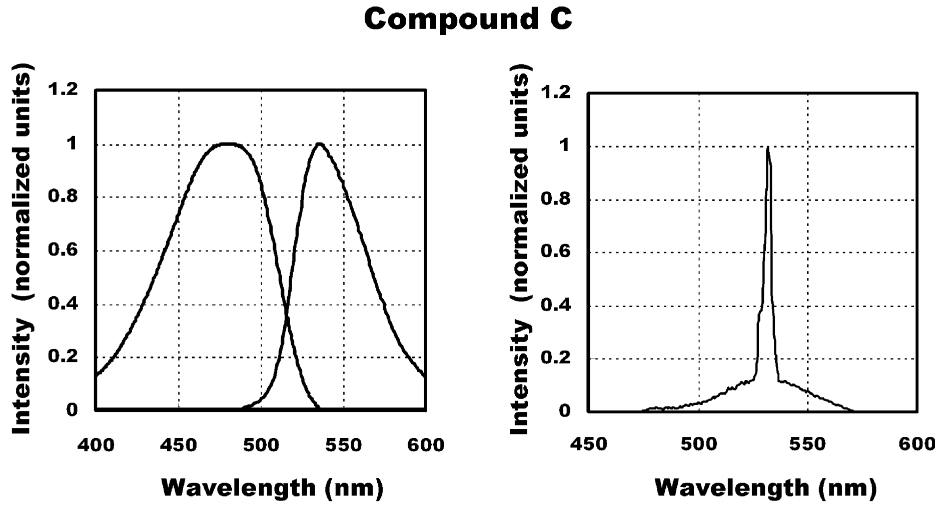
(a) Absorption and fluorescent spectrum **(b) Laser spectrum**

Fig. 5. (a) Absorption and fluorescent characteristics and (b) laser spectrum of compound A.



(a) Absorption and fluorescent spectrum **(b) Laser spectrum**

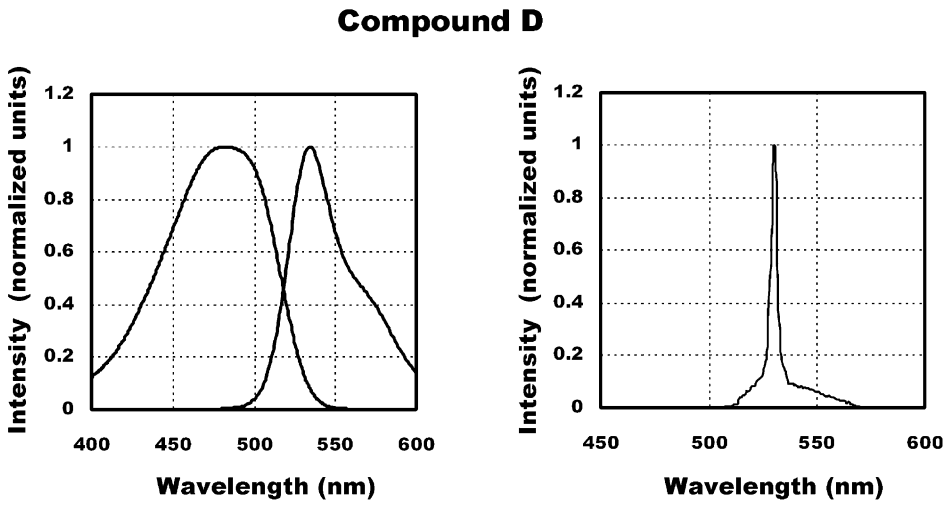
Fig. 6. (a) Absorption and fluorescent characteristics and (b) laser spectrum of compound B.



Compound C

(a) Absorption and fluorescent spectrum **(b) Laser spectrum**

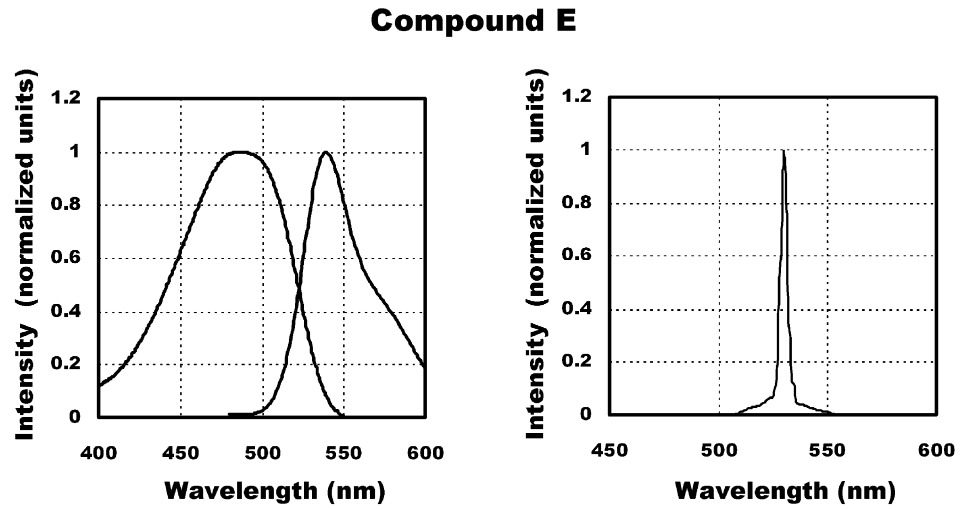
Fig. 7. (a) Absorption and fluorescent characteristics and (b) laser spectrum of compound C.



Compound D

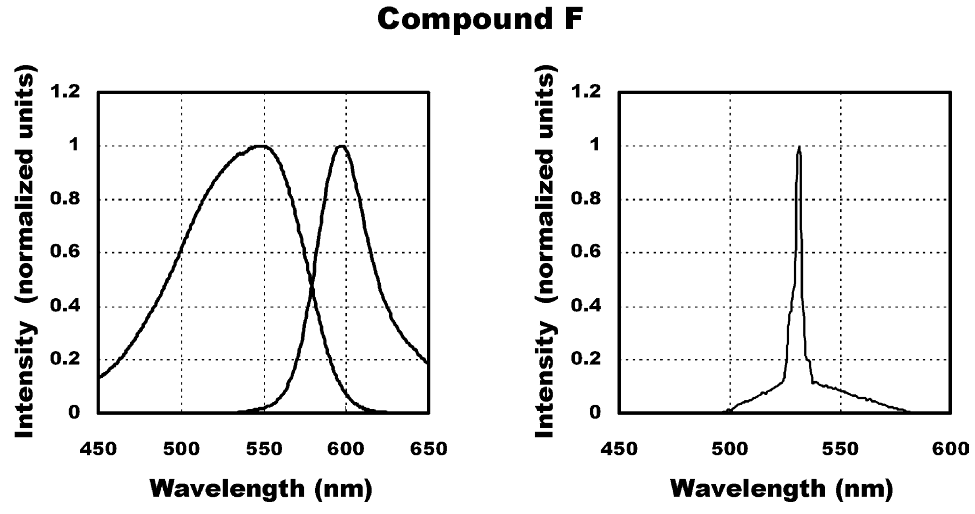
(a) Absorption and fluorescent spectrum **(b) Laser spectrum**

Fig. 8. (a) Absorption and fluorescent characteristics and (b) laser spectrum of compound D.



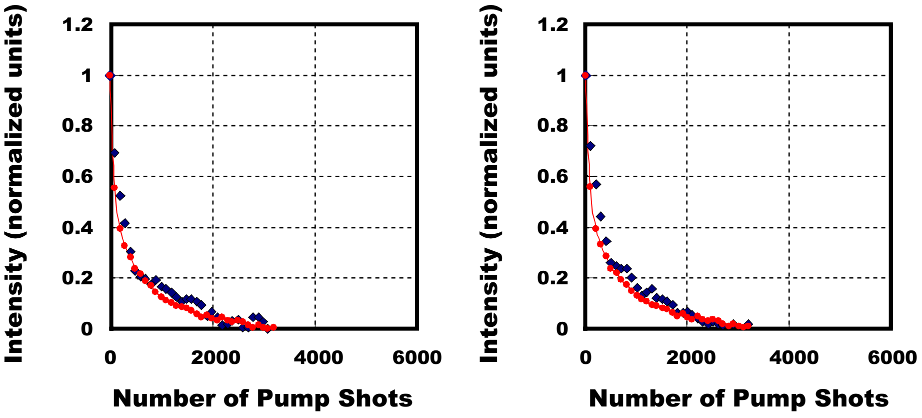
(a) Absorption and fluorescent spectrum **(b) Laser spectrum**

Fig. 9. (a) Absorption and fluorescent characteristics and (b) laser spectrum of compound E.



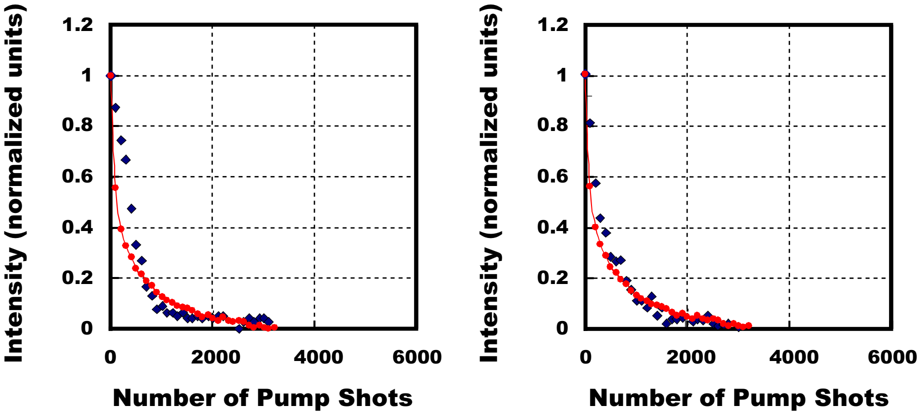
(a) Absorption and fluorescent spectrum **(b) Laser spectrum**

Fig. 10. (a) Absorption and fluorescent characteristics and (b) laser spectrum of compound F.



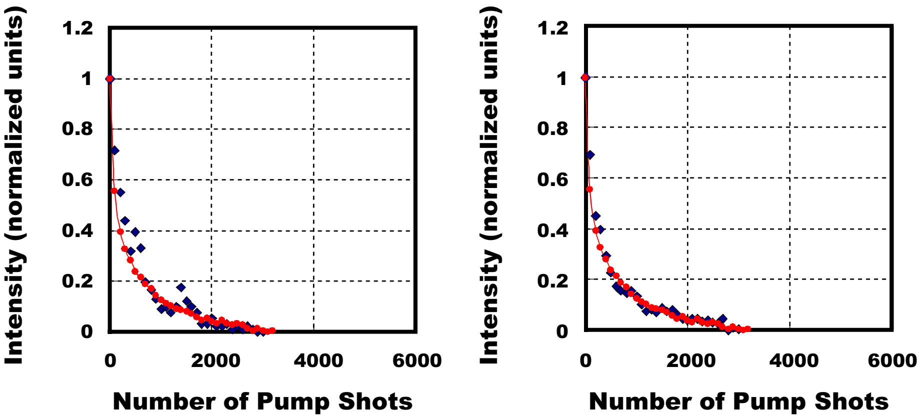
(a) compound A

(b) compound B



(c) compound C

(d) compound D



(e) compound E

(f) compound F

Fig. 11. Photodegrading results: ♦, measured data for each compound; ●, data for Rhodamine B.

Acknowledgements

This work was supported in part by the Takahashi Industrial and Economic Research Foundation.

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