

Newly Synthesized Dyes and Their Polymer/Glass Composites for One- and Two-Photon Pumped Solid-State Cavity Lasing

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A newly synthesized laser dye, *trans*-4-[*p*-(*N*-ethyl-*N*-(hydroxyethyl)amino)styryl]-*N*-methylpyridinium tetraphenylborate (ASPT or dye I) has high thermal stability and photostability. To modify the solubility of dye I, a series of dyes has been synthesized. Using dye I doped polymer film with a refractive index less than that of the glass substrate, a leaky waveguide device has been investigated. Under pump conditions of 532 nm wavelength, 10 ns pulse width, and 5 Hz repetition rate, one-photon cavity lasing was obtained at 590 nm, with a lasing efficiency of 12%, and lasing lifetime $>3 \times 10^4$ pulses. Utilizing dye I doped bulk polymer rods, two-photon pumped frequency up-converted cavity lasing has also been accomplished using a Q-switched Nd:YAG laser as the pump source. The new dyes possess a much greater two-photon-absorption cross section and much stronger up-converted fluorescence emission than that exhibited by common organic dyes (such as rhodamine). The cavity lasing wavelength and pulse duration were 600 nm and 3–6 ns obtained with a pump wavelength of 1.06 μm and pump pulses of 10 ns. Lasing lifetime, in terms of pulse numbers, was more than 4×10^4 pulses at 2 Hz repetition rate. By impregnating these dyes into a sol-gel glass:poly(methyl methacrylate) (PMMA) and Vycor glass:PMMA composite glasses, two-photon pumped cavity lasing properties have also been studied.

I. Introduction

The newly emerging technology of photonics has drawn a great deal of interest in searching for new optical materials. One of these interests is in the development of solid-state dye lasers.^{1–3} The applications of solid-state lasers in optical data storage and photoresist are well documented.⁴ A solid dye laser is an attractive alternative to a liquid-state dye laser with obvious technical advantages, such as compactness, absence of toxic solutions, the suppression of flow fluctuation, and no problem due to solvent evaporation (environmental safety, etc.). In particular, polymeric materials would facilitate the design of solid laser systems because they are inexpensive and easy to fabricate. However, up to now these polymer-based lasers have suffered a number of shortcomings, mainly due to low laser-damage resistance. Many researchers have reported^{5–12} that photodegradation of polymer host dye lasers was due to direct photolysis of the polymer

matrix; another explanation was that the dye was thermally converted into a nonemissive species.

To understand the photochemical mechanism of thermal bleaching and photobleaching of polymeric dye lasers and to find possible ways for enhancing their photostability and lasing efficiency, we synthesized a new dye, *trans*-4-[*p*-(*N*-ethyl-*N*-(hydroxyethyl)amino)styryl]-*N*-methylpyridinium tetraphenylborate (dye I) with a high thermal stability and photostability. By doping dye I in polyepoxy, we investigated a dye film leaky waveguide laser.

In addition, we discovered that this dye had very strong two-photon absorption (TPA) and could be used for up-conversion lasing. Frequency up-converted lasing is an important area of research and is becoming more interesting and promising in recent years. To date, two major technical approaches have been used to achieve frequency up-conversion lasing: one is based on direct two-photon excitation of a gain medium (two-photon pumped), the other is based on sequential stepwise multiphoton excitation (stepwise multiphoton pumped). Since 1970s, there were several reported experimental results of two-photon pumped (TPP) lasing behavior in organic dye solutions.^{13–18} The solutes used in the past

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were commercial dyes such as rhodamine 6G, rhodamine B, DMP, and PYC. Recently, TPP up-conversion simulated emission was reported in a DCM dye doped PMMA channel waveguide configuration.¹⁹ Compared to other coherent frequency up-conversion techniques, such as optical harmonic generation, the main advantages of up-conversion lasing techniques are feasibility of using semiconductor lasers as pumped sources and capability of adopting waveguide/fiber configuration. With the view to limit the motion of the dye gain medium and increase the rigidity of the system, we also impregnated dye molecules into a sol-gel glass and a Vycor glass matrix.

In this paper, we report the molecular design, synthesis, and characterization of the new dye (dye I) and its polymer and glass composites for one- and two-photon cavity lasing behavior. To modify the solubility of dye I in different solutions, we also synthesized a series of dyes (dyes II–IV). The synthesis of these dyes along with the characterization techniques are described in section IIA. In section IIB, the sample preparations and measurement are presented. Results show that our samples have high lasing efficiency and lasing lifetime for both one- and two-photon lasing. The results also show that our samples possess a much greater two-photon absorption cross section and a much stronger up-converted fluorescence emission than common organic dyes (such as rhodamine).

II. Experimental Section

A. Synthesis. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Polyscience, Inc. It was recrystallized twice from methanol. All other chemicals were bought from the Aldrich Chemical Co. and were used as received unless stated otherwise. The synthetic schemes of dyes I–IV are shown in Scheme 1.

Decomposition temperatures of the four dyes were measured by differential scanning calorimetry (DSC) thermograms with Shimadzu DSC-50GPC under nitrogen. Proton NMR and UV-visible absorption spectra were recorded by a Varian Gemini-300 300MHz spectrometer and with a Shimadzu UV-3101 PC spectrophotometer, respectively.

Dyes I and II are soluble in polar organic solvents, such as DMF and cyclopentanone, while dyes III and IV are soluble in a water and DMF mixture. All dyes have limited solubility in ethanol. Good optical-quality films can be cast from a dye-doped polymer solution. Figure 1 shows the UV-visible absorption spectra of all these dyes in DMF. The decomposition temperature of all the dyes are shown in Table 1. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA.

4-(N-Ethyl-N-(hydroxyethyl)amino)benzaldehyde (1).²⁰ Following ref 20, compound 1 was obtained as a pale yellow oil, yield 65%. ¹H NMR (CDCl₃) δ 1.18 (t, 3H), 2.3 (s, 1H), 3.62 (m, 2H), 3.66 (t, 2H), 3.8 (t, 2H), 6.7 (d, 2H), 7.68 (d, 2H), 9.62 (s, 1H) ppm.

4-Methyl-N-methylpyridinium Iodide (2). Using a 500-mL three-neck flask fitted with a stirrer, thermometer, and condenser, 9.3 g (0.1 mol) of 4-picoline and 21.6 g (0.11 mol) of methyl iodide were mixed in toluene. The solution was stirred at room temperature for 4 h and then refluxed for 30 min. After cooling, the solution was filtered and the solid was washed with ethyl ether. The pale yellow solid was dried

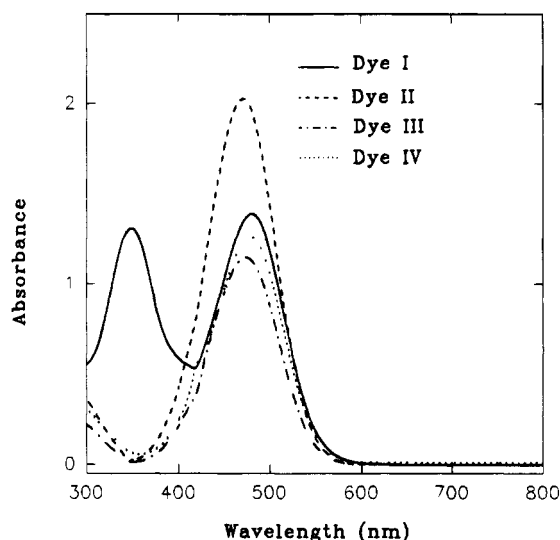


Figure 1. UV-visible absorption spectra of all dyes in DMF.

Scheme 1

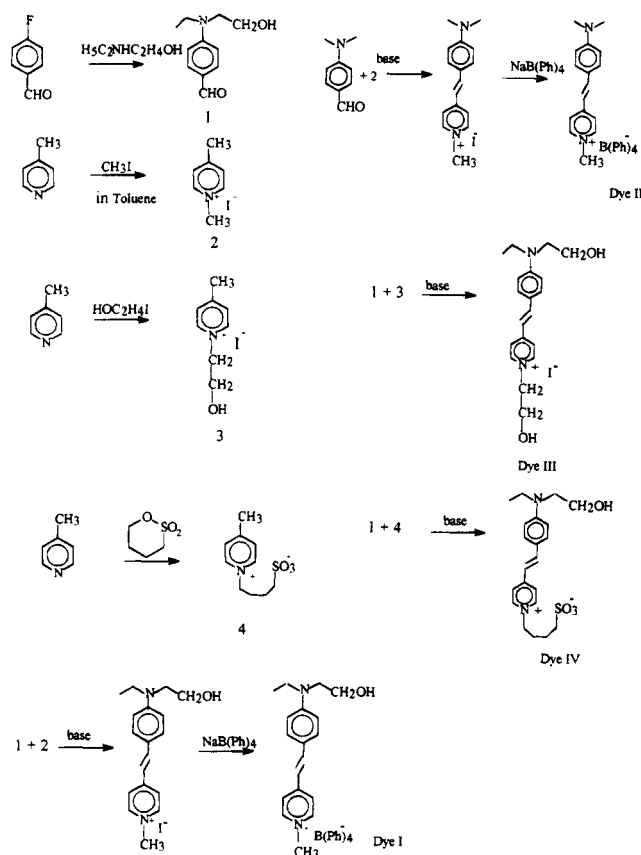


Table 1. Decomposition Temperature of Dyes (Heating Rate 10 °C/min, under Nitrogen)

	dye I	dye II	dye III	dye IV
T_d , °C	264	266	270	241

under vacuum, yield 21.2 g (90%). ¹H NMR (DMSO-*d*₆) δ 2.56 (s, 3H), 4.20 (s, 3H), 7.0 (d, 2H), 8.90 (d, 2H) ppm.

4-Methyl-N-(2-hydroxyethyl)pyridinium Iodide (3). Using the same method as above, by reaction of 9.3 g (0.1 mol) of 4-picoline and 19.0 g (0.11 mol) of 2-hydroxyethyl iodide, 23.9 g of yellow solid was obtained (yield 90%). ¹H NMR (DMSO-*d*₆) δ 2.56 (s, 3H), 3.70 (q, 2H), 4.40 (t, 2H), 5.2 (t, 1H), 7.95 (d, 2H), 8.90 (d, 2H) ppm.

4-Methylpyridinium-N-butanefulfone (4). Using a 500-mL three-neck flask fitted with a stirrer, a thermometer, and a

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condenser, 9.3 g (0.1 mol) of 4-picoline, 13.6 g (0.1 mol) of butanesulfone, and 150 mL of toluene were mixed. The solution was heated to 100 °C for 2 h. After cooling, the solution was filtered and the solid was washed with ethyl ether. The yellow solid was dried under vacuum, yield 13.7 g (60%). ¹H NMR (D₂O) δ 1.60 (m, 2H), 1.90 (m, 2H), 2.56 (s, 3H), 2.75 (t, 2H), 4.1 (t, 2H), 7.60 (d, 2H), 8.2 (d, 2H) ppm.

trans-4-[p-(N-Ethyl-N-(hydroxyethyl)amino)styryl]-N-methylpyridinium Tetraphenylborate (Dye I). Using a 500-mL one-neck flask fitted with a stirrer and a condenser, 2.5 g (0.013 mol) of compound 1, 3.1 g (0.013 mol) of compound 2, and 30 mL of absolute ethanol were mixed. Five drops of piperidine was added into the mixture. Then the solution was heated to reflux overnight. After cooling, 4.5 g (0.013 mol) of sodium tetraphenylborate was added into the solution. The solution again was heated to reflux for 10 min. A red solid formed after cooling. The solution was filtered, and the solid was washed with ethanol and water each two times, yield 4.7 g (60%). ¹H NMR (DMSO-*d*₆) δ 1.0 (t, 3H), 3.30 (q, 2H), 3.4 (t, 2H), 3.80 (q, 2H), 4.10 (s, 3H), 4.80 (t, 1H), 6.70 (t, 4H), 6.8 (t, 8H), 7.02 (d, 1H), 7.10 (d, 8H), 7.5 (d, 2H), 7.8 (d, 2H), 7.9 (d, 1H), 8.0 (d, 2H), 8.62 (d, 2H) ppm. Elemental Anal. Calcd for C₄₂H₄₃BN₂O: C, 83.7; H, 7.0; B, 1.8; N, 4.7; O 2.8. Found: C, 83.8; H, 6.8.

trans-4-[p-(N,N-Dimethylamino)styryl]-N-methylpyridinium Tetraphenylborate (Dye II). The above process was followed by reaction of 14.9 g (0.1 mol) of 4-(*N,N*-dimethylamino)-benzaldehyde, 23.6 g (0.1 mol) of compound 2 and 34.6 g (0.1 mol) of sodium tetraphenylborate. The red dye II was made with a yield of 70% ¹H NMR (DMSO-*d*₆) δ 3.00 (s, 6H), 4.1 (s, 3H), 6.70 (t, 4H), 6.8 (t, d, 2H), 6.9 (t, 8H), 7.02 (d, 1H), 7.10 (d, 8H) 7.50 (d, 2H), 7.9 (d, 1H), 8.0 (d, 2H), 8.62 (d, 2H) ppm. Elemental Anal. Calcd for C₄₀H₃₅BN₂: 86.0; H, 7.0; B, 1.8; N, 5.0. Found: C, 86.0; H, 7.1; N, 4.9.

trans-4-[p-(N-Ethyl-N-(hydroxyethyl)amino)styryl]-N-hydroxyethylpyridinium Iodide (Dye III). The above process was followed by reaction of compounds 1 and 3. The red dye III was made with a yield of 67%. ¹H NMR (DMSO-*d*₆) δ 1.0 (t, 3H), 3.3 (q, 2H), 3.40 (q, 2H), 3.50 (t, 2H), 3.80 (q, 2H), 4.40 (t, 2H), 4.70 (t, 1H), 5.2 (t, 1H), 6.7 (d, 2H), 7.1 (d, 1H), 7.80 (d, 2H), 7.90 (d, 1H), 8.10 (d, 2H), 8.70 (d, 2H) ppm. Element Anal. Calcd for C₁₉H₂₅IN₂O₂: C, 51.8; H, 5.7; I, 28.8; N, 6.4; O, 7.3. Found: C, 51.5; H, 5.3; N, 7.0.

trans-4-[p-(N-Ethyl-N-(hydroxyethyl)amino)styryl]-N-butanesulfonepyridinium (Dye IV). The above process was followed by reaction of compound 1 and compound 4. The red dye IV was made with a yield of 50%. ¹H NMR (D₂O) δ 1.60 (m, 2H), 1.90 (m, 2H), 2.80 (t, 2H), 2.90 (s, 3H), 3.40 (t, 2H), 3.60 (q, 2H), 4.10 (t, 2H), 4.70 (t, 1H), 6.70 (d, 2H), 6.75 (d, 1H), 7.35 (d, 2H), 7.40 (d, 1H), 7.60 (d, 2H), 8.20 (d, 2H) ppm. Elemental Anal. Calcd for C₂₀H₂₆N₂O₄S: C, 61.5; H, 6.7; N, 7.2; O, 16.4; S, 8.2. Found: C, 61.6; H, 6.7; N, 7.1; S, 8.3.

B. Sample Preparation and Measurement. 1. *One-Photon-Pumped Cavity Lasing. Dye film leaky waveguide laser:* The film was prepared by the following method: Dye I was added into an epoxy precursor (9653-2 from Epoxylite), and then the solution was cast to make a film. After drying, the film contained dye I, 1.5×10^{-3} M, and the film thickness was 50 μm. Figure 2 shows the absorption and fluorescence spectrum of the film.

The experiment setup is shown in a previous paper.²¹ In our experiment the pump source is a Q-switched and frequency-doubled Nd:YAG laser with a 10 ns pulse width and 5 Hz repetition rate. The lasing lifetime was measured when the output laser pulse energy dropped to one-third of the initial value.

2. *Two-Photon Pumped Cavity Lasing. (a) Dye-doped polymer rod for two-photon pumped lasing:* The polymer rod was made by doping 5 mg of dye I (8×10^{-3} M) in 1.2 g of 2-hydroxyethyl methacrylate (HEMA) and then adding 1% mol ratio AIBN to polymerize HEMA at 40 °C for a week. The two end faces of the sample were polished. The polymer rod

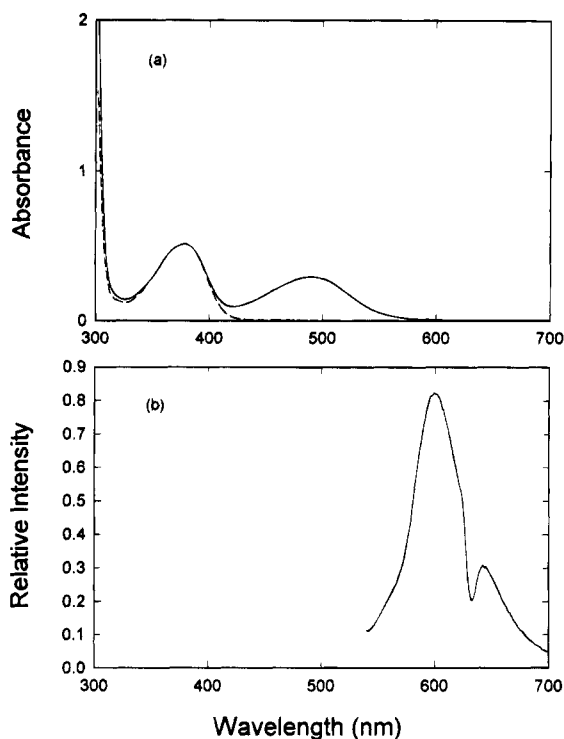


Figure 2. Absorption and fluorescence spectrum of dye I doped epoxy film for one-photon lasing.

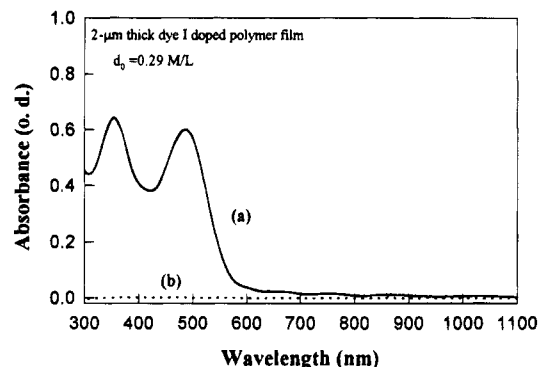


Figure 3. (a) Absorption spectrum of dye I doped poly-HEMA film. (b) Absorption spectrum of pure poly-HEMA film.

was 7 mm long. A 2 μm thick dye I doped poly-HEMA film was prepared for the absorption measurement. Figure 3 shows the absorption spectrum of the dye I doped poly-HEMA film. It is worth mentioning that we chose HEMA as the monomer for the polymer rod because of its good optical transparency and fairly high solubility for dye I. But HEMA is more difficult to impregnate into glass compared with methyl methacrylate (MMA) because of high viscosity.

In our experimental setup, the input pump IR laser beam was provided by a Q-switched Nd:YAG pulsed laser source with a wavelength of 1.06 μm, pulse width of 10 ns, spectral width of ~1 cm⁻¹, angular divergence ~1.3 mrad, and repetition rate of 2 Hz.

To achieve cavity lasing, two parallel plane dielectric-coating mirrors were employed to form a cavity. The pump beam, focused via a *f* = 10 cm lens was coupled into the cavity by normal incidence. The lasing spectra could be measured by using a 0.5 m grating spectrograph in conjunction with an optical multichannel analyzer (OMA-III) system. The temporal behavior of the TPA cavity lasing was recorded by using a fast photodiode detector in conjunction with a 350 MHz oscilloscope (Tektronix 2467 with the C1001 video camera).

(b) *Sol-gel glass composite for two-photon pumped lasing:* The sol-gel process is a technique to prepare glass and ceramics, employing various precursor and additives at room temperature. A sol-gel glass as a matrix has an advantage

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Table 2. Optical and Two-Photon Pumped Lasing Properties of Dye I Doped Different Matrixes

matrix	Vycor glass (0.0015 M)	sol-gel glass (0.0015 M)	poly-HEMA (0.008 M)	cyclopentanone solution
linear absorption peak (nm)			485	480
absorption bandwidth (nm)			80	100
one-photon fluorescence peak (nm)	575	568	577	590 (0.001 M)
one-photon fluorescence bandwidth (nm)	60	55	55	58
lasing peak (nm)	600	590	597	623 (0.03 M)
lasing bandwidth (nm)	8	8	8	14
1.06 μm pump pulsewidth (ns)	10	10	10	10
lasing pulsewidth (ns)	2-5	1.5-4	2-5	1.5-4

over an organic polymer matrix because it has excellent optical transparency and is a more rigid system. The glass-PMMA composite was prepared in three stages: first a low-density bulk glass was prepared (using this method, we made bulk glass density about 0.7 g/cm³, refractive index about 1.472)²² and then the dye I in cyclopentanone solution was impregnated into the bulk glass. After removal of cyclopentanone, the dye-doped glass was immersed into MMA and 1% mol ratio AIBN solution. The MMA monomer was impregnated into the glass and polymerized in a sealed container at 40 °C for a week. The final sample was cleaned and polished. The polishing method consisted of the following stages: manual grinding on 65 μm grade diamond grinding wheels; automatic grading on SiC paper (500, 800, and 1200 grit in gradual steps) using tap water as lubricant; automatic polishing on cloths using 6, 1, and 0.25 μm grade diamond pastes as an abrasive, in gradual steps. A commercial alcoholic-based fluid was used as the lubricant for the last stage. The automatic procedure was performed with a Metaserv 2000 grinding and polishing machine. The final composite has a dye concentration of about 1.5×10^{-3} M with 32 vol % silica and 68 vol % PMMA.

With the same method, we also prepared dyes II-IV sol-gel glass-PMMA composites. We also obtained two-photon pumped lasing in all these composites.

(c) *Vycor glass-PMMA composite for two-photon pumped lasing:* Vycor glass was purchased from Corning. Its average pore size is about 40 Å. Following the same method of preparation of the sol-gel glass-PMMA composite, we prepared the dye I doped Vycor glass-PMMA composite, with a dye I concentration of about 1.5×10^{-3} . The peaks of the lasing wavelength obtained in this matrix are listed in Table 2.

III. Results and Discussion

The decomposition temperatures shown in Table 1 indicate that all these dyes are relatively thermally stable. The decomposition temperature of dye I is about 264 °C.

For the one-photon-pumped cavity lasing, the spectral maximum of the lasing emission was located at about 590 nm. The overall lasing range was about 10–20 nm wide. After 100 min of continuous running at 5 Hz (i.e., 3×10^4 lasing pulses), the output laser pulse energy dropped to one-third of the initial value. It is believed that by optimizing the system and improving the optical quality of the matrix, the lasing lifetime and efficiency can be considerably increased.

Figure 4 shows the fluorescence spectrum of the dye I doped poly-HEMA rod excited with the 1.06 μm radiation as well as the cavity lasing spectrum of the same sample rod pumped with the 1.06 μm laser beam. The lasing output/pump input characteristic curve is shown in Figure 5. Each data point was an average result over 10 laser pulses by using a gated integrator and boxcar average system, and the solid line is the best-fitted curve based on the square law that should

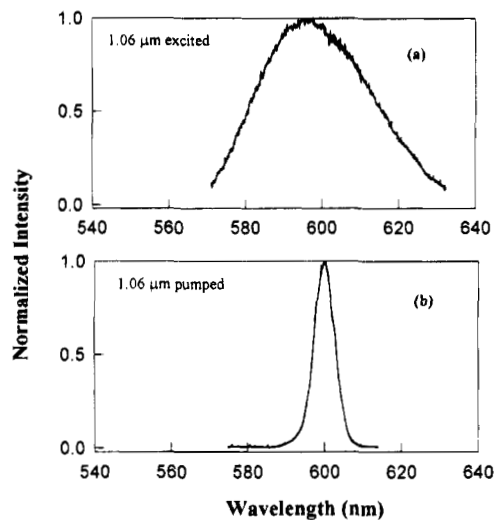


Figure 4. (a) Fluorescence spectrum of dye I doped poly-HEMA rod excited with 1.06 μm radiation. (b) Cavity lasing spectra of the same sample rod pumped with 1.06 μm laser beam.

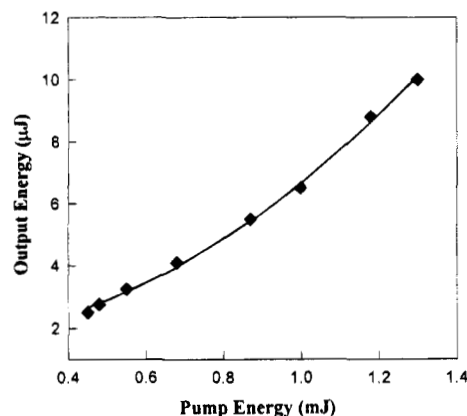


Figure 5. Two-photon pumped laser output of dye I doped poly-HEMA rod.

be followed for a two-photon excitation process. The energy conversion efficiency from pump input to lasing output can be estimated as $\eta \sim 0.8\%$ at an input energy level of 1.3 mJ. However, at this pump level, the measured one-pass two-photon absorption in the 7-mm-long rod was only about 23%. Therefore, the real conversion efficiency from the absorbed pump energy to the lasing output should be corrected to $\eta \sim 3.5\%$. At the same energy level, the lasing lifetime was 4×10^4 pulses. The damage threshold was 430 MW/cm² (at 1 Hz). The dye I molecular TPA cross section could be estimated as $\sim 1.2 \times 10^{-46}$ cm⁴ sec, based on the measured nonlinear absorption data for a given input intensity level. This is more than 2 orders of magnitude larger than the value reported for rhodamine and other common dyes. It is believed that the lasing efficiency

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and lifetime can be considerably increased by further improving the optical quality of the rod and optimization of the system.

It has been demonstrated that for one photon pumped lasing, under the same conditions, a dye molecule in a host sol-gel glass-PMMA matrix has higher photostability and conversion efficiency than that of a polymer host.²² Under comparable conditions, however, our experimental results shows that the two-photon pumped lasing properties of glass composites do not show much superior results compared with that of a polymer composite.

However, in sol-gel and Vycor glass composites, a lower dye concentration was needed to observe two-photon pumped cavity lasing. We believe it is because of the excellent optical quality of sol-gel and Vycor glass; scattering loss is much smaller in glass than that for the polymer matrix. On the basis of our results, we believe that two approaches will improve two-photon pumped lasing properties of glass composite: (1) designing a monomer with high dye solubility, low viscosity, good optical transparency; (2) further modifying the chemical structure of dye molecule to enhance its thermal stability and solubility.

Conclusion

We have synthesized a series of dyes that have very strong one- and two-photon-pumped cavity lasing prop-

erties. The lasing lifetime of dye I doped polymer film for the leaky waveguide laser, in terms of number of pulses, was 3×10^4 pulses, and lasing efficiency was 12%. By doping these dyes into different solid polymer and glass matrixes, we observed two-photon-pumped solid cavity lasing behavior. For a dye I doped poly-HEMA rod, the two-photon pumped cavity lasing efficiency was $\eta \sim 3.5\%$, and lasing lifetime was 4×10^4 pulses at 2 Hz repetition rate. Compared with common dye materials, such as rhodamine, our dyes possess a more than 2 orders magnitude larger molecular two-photon absorption cross section and a much stronger frequency upconversion fluorescence using near-IR excitation. Under the same conditions, for sol-gel and Vycor glass matrixes, a lower dye concentration was needed to observe two-photon pumped cavity lasing compared with that of polymer matrixes.

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