

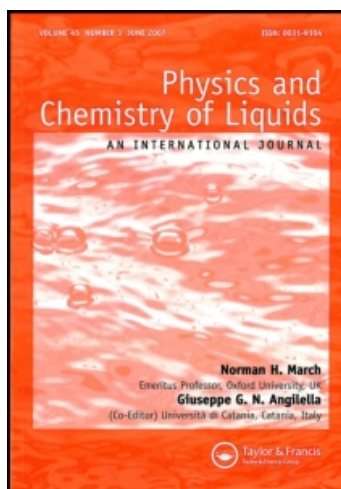
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### Synthesis and Properties of a New Two-photon-absorbed Material Heaps

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# SYNTHESIS AND PROPERTIES OF A NEW TWO-PHOTON-ABSORBED MATERIAL HEASPS

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A new dye Trans-4-[*p*-(*N*-hydroxyethyl-*N*-ethylamino)styryl]-*N*-methylpyridinium *p*-toluene sulfonate (HEASPS) was synthesized, and the two-photon absorption (TPA), TPA-induced frequency up-conversion emission, and two-photon pumped (TPP) frequency up-converted lasing properties of this new dye were experimentally studied. This new dye has a moderate TPA cross-section of  $\sigma_2 = 4.7 \times 10^{-48} \text{ cm}^4 \cdot \text{s}/\text{photon}$  at 1064 nm, but exhibits a high lasing efficiency. The net conversion efficiency from the absorbed 1064 nm pump pulse energy to the 626 nm up-converted lasing energy is 18.2% at the pump energy level of 1.9 mJ.

**Keywords:** Lasing properties; Two-photon absorption

## 1. INTRODUCTION

Two-photon absorption (TPA), put forward first in 1930s and developed rapidly in 1990s, is the process in which two-photons are simultaneously absorbed to an excited state *via* virtual state. Materials with large TPA cross section are gaining increasing attention due to their demonstrated potential applications in many areas such as optical data storage [1–3], three dimensional fluorescence imaging [4],

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lithographic micro-fabrication [5,6], up-converted lasing [7–13], optical power limiting [14,15]. Recently, a number of organic dyes that exhibit large two-photon absorption (TPA) cross-section and strong frequency up-conversion emission have been synthesized, and a considerable amount of effort has been devoted to the frequency up-conversion laser materials and devices which produce a shorter wavelength lasing output when pumped with longer wavelength input, from which one can get a broad range of the visible lasing by pumping with infrared laser source.

In this paper we report a new chromophore HEASPS recently synthesized by our research group. It manifests highly TPP lasing efficiency when pumped by a pulsed 1064 nm infrared laser beam. The synthesis process, the systematic measurements of linear and nonlinear optical properties, as well as TPP cavity lasing behavior for solution sample of this new dye, are also reported in this paper.

## 2. SYNTHESIS

The new dye reported here is Trans-4-[*p*-(*N*-hydroxyethyl-*N*-ethylamino)styryl]-*N*-methylpyridinium *p*-toluene sulfonate (abbreviated as HEASPS thereafter). The packing diagram and the molecule structure of HEASPS are shown in Figure 1. The Synthesis procedure is presented as below. Nuclear magnetic resonance spectroscopy were determined on FX-90Q NMR spectrometer. Decomposition temperatures of the dye was measured on Perkin Elmer TGS-2 thermogravimetric analyzer under nitrogen atmosphere.

4-(*N*-methyl-*N*-hydroxyethylamino)benzaldehyde (compound 1) and 4-(*N*-ethyl-*N*-hydroxyethylamino)benzaldehyde (compound 2) were synthesized according to Ref. [16]. At room temperature, compound 1 is a pale yellow solid, and compound 2 is brown oil. White powder of 4-methyl-*N*-methyl pyridinium iodide (compound 3) was synthesized according to Ref. [7].

Silver *p*-toluene sulfonate (compound 4) 34 g (0.2 mol) silver nitrate was dissolved in 100 mL distilled water, then it was mixed with a 10.6 g (0.1 mol) Na<sub>2</sub>CO<sub>3</sub>/100 mL water solution. The as-formed Ag<sub>2</sub>CO<sub>3</sub> precipitate was washed with water repeatedly and removed into a beaker containing a stirrer and 200 mL distilled water. Then 38 g

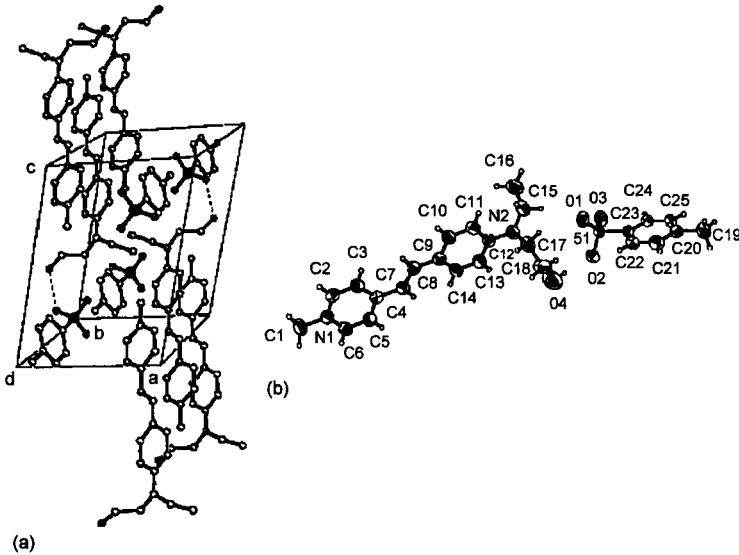


FIGURE 1 (a) Packing diagram and (b) molecule structure of HEASPS.

(0.2 mol) of *p*-toluene sulfonic acid monohydrate was added into the beaker in parts with heating and stirring simultaneously in the course of 1 hr. After removing some unsolvable impurities by filtration, we kept the hot transparent solution stand until colorless parallelepiped crystals were formed in the course of natural cooling and evaporating. 52.2 g product was obtained in all, yield 93%.

Trans-4-[*p*-(*N*-hydroxyethyl-*N*-ethylamino)styryl]-*N*-methylpyridinium *p*-toluene sulfonate (HEASPS) HEASPS was synthesized by using 5.0 g (0.026 mol) of compound (2), 6.2 g (0.026 mol) of compound (3) and 7.25 g (0.026 mol) of silver *p*-toluene sulfonate (compound 4)/100 mL acetonitrile. The silver iodide precipitate was filtered off from the solution. During the slow evaporation of the clear red filtrate, purple-red parallelepiped crystals were isolated. Calcd. For  $C_{25}H_{30}N_2O_4S$ : C, 66.05; H, 6.60; N, 6.16. Found: C, 64.95; H, 6.64; N, 6.03. IR spectrum (KBr)  $\nu/cm^{-1}$ : 1642.3 m, 1581.5 s, 1521.7 s, 1398.7 m, 1224.5 m, 1170.1 s, 1122.5 m, 1057.8 m, 1029.7 m, 1008.4 m, 826.7 s, 680.0 s, 569.6 s.  $^1H$ NMR(DMSO- $d_6$ ) (300 MHz;TMS)  $\delta_H$ : 1.114(3H, *t*, *J* 6.78 Hz), 2.286(3H, *s*), 3.360(1H, *s*), 3.557(2H, *q*, *J* 5.49), 4.159(3H, *s*), 6.773(2H, *d*, *J* 9.16), 7.109(2H, *d*, *J* 7.69),

7.135(1H, *d*, *J* 7.69), 7.469(2H, *d*, *J* 8.05), 7.556(2H, *d*, *J* 9.16), 7.884(1H, *d*, *J* 16.48), 8.021(2H, *d*, *J* 6.59), 8.662(2H, *d*, *J* 6.59). HEASPS melts at 198°C and decomposes at 338°C. In TGA and DTA experiments, no obvious weight loss was found for HEASPS before its melting point. The results of the above thermal analysis indicate that the compound is thermal and chemical stable.

### 3. OPTICAL PROPERTIES

#### 3.1. Linear Optical Properties

The linear absorption spectra of the HEASPS sample was measured on a Hitachi U-3500 UV-vis-IR recording spectrophotometer by using quartz cuvette with 1 cm path length. Figure 2 shows the linear absorption spectra of a 1 cm path HEASPS solution sample in DMF with solute concentration of  $d_0 = 0.00001$  mol/l, in which the solvent influence is not included. From the spectra, we can see that there is a strong absorption band with the peak absorption located at 484 nm and a bandwidth of 90 nm, and there is no linear absorption in the entire spectral range from 600 to 1400 nm.

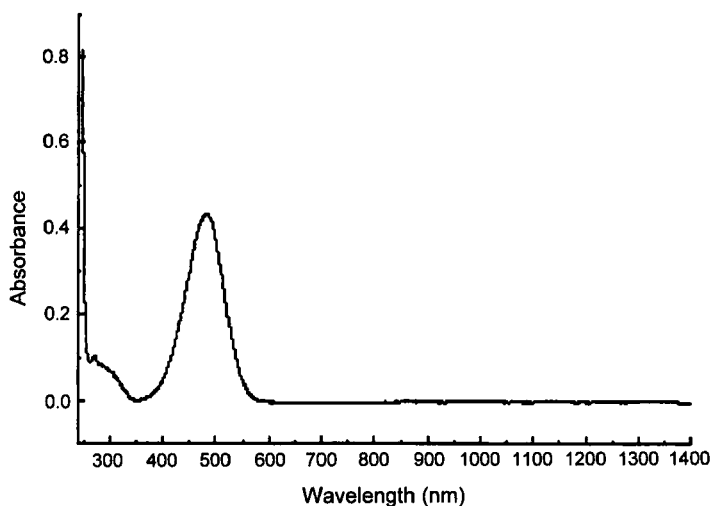


FIGURE 2 Linear absorption spectra of HEASPS in DMF with 1 cm path and 0.00001 mol/l concentration.

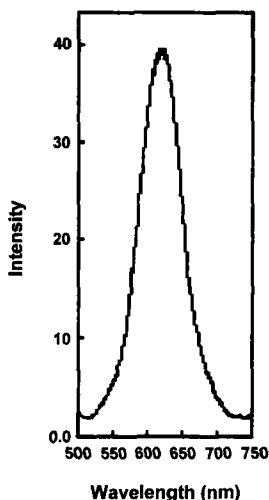


FIGURE 3 One-photon induced emission spectra of HEASPS in DMF with 1 cm path and 0.00001 mol/l concentration.

Figure 3 shows the measured fluorescence spectra for a 1 cm path HEASPS solution with the concentration of 0.00001 mol/l. The single-photon induced fluorescence spectra was measured by a spectra fluophotometer (Rf5000U from Schmadza) with the spectra resolution of 1 nm. The peak wavelength of the single-photon induced fluorescence was 620 nm with a bandwidth of 70 nm.

## 3.2. Nonlinear Optical Properties

### 3.2.1. TPA Cross-section Measurement

From Figures 2 and 3, we can see that though there is no linear absorption in the entire spectral range from 600–1400 nm, the two-photon energy of the near IR radiation between 900–1100 nm falls within the strong absorption band of HEASPS solutions. Experimental studies have shown that a quite strong frequency up-converted fluorescence can be easily observed from the sample even with an unfocused mode-locked IR laser beam at the wavelength range mentioned above. This suggests that a very strong TPA process may occur inside the sample.

Z-scan system with an open aperture ( $S = 1$ ) is depicted in Figure 4, it is insensitive to the nonlinear refraction, and can be used to measure

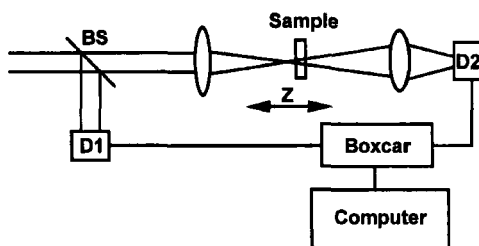


FIGURE 4 The open-aperture Z-scan apparatus in which the ratio  $D2/D1$  is recorded as a function of the sample position.

the nonlinear absorption cross-section. Such Z-scan traces with no aperture are expected to be symmetric with respect to the focus ( $Z = 0$ ), where they have a minimum transmittance (*e.g.*, multi-photon absorption) or a maximum transmittance (*e.g.*, saturation of absorption). In fact the nonlinear coefficients  $\beta$  can be easily calculated from the transmittance curves.

For a temporally Gaussian pulse, the normalized energy transmittance can be given as [17],

$$T(z, S = 1) = \frac{1}{\sqrt{\pi}q_0(z, 0)} \int_{-\infty}^{+\infty} \ln(1 + q_0(z, 0)e^{-\tau^2}) d\tau$$

where  $q_0(z, t) = \beta I_0(t)L_{\text{eff}}/(1 + z^2/z_0^2)$ ,  $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ ,  $L$  is the sample length and  $\alpha$  is the linear absorption coefficient. When there is no linear absorption (*e.g.*,  $\alpha \rightarrow 0$ ),  $L_{\text{eff}}$  equals  $L$ .

For  $|q_0| < 1$ , the transmittance can be expressed in terms of the peak irradiance in a summation form more suitable for numerical evaluation,

$$T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{3/2}}$$

Thus, once an open-aperture Z-Scan ( $S = 1$ ) is performed, the nonlinear absorption coefficient  $\beta$  can be unambiguously deduced and if the concentration  $d_0$  (in units of mol/l) of the solution is known, the molecular TPA cross section  $\sigma_2$  (in units of  $\text{cm}^4 \cdot \text{s}/\text{photon}$ ) can be determined by using the following relationship,

$$\beta = \sigma_2 N_0 = h\gamma\sigma_2 N_A d_0 \times 10^{-3}$$

We have accomplished TPA cross section measurement for the HEASPS sample with the thickness of 2 mm and a relatively high concentration of  $d_0 = 0.05$  mol/l, by using a focused 35 ps, 1064 nm mode-locked Nd:YAG laser. Figure 5 depicts the open-aperture trace at a peak irradiance  $I_0 = 3.64$  GW/cm<sup>2</sup>. Using the above equations, we can get the nonlinear coefficient  $\beta = 0.76$  cm/GW, thus  $\sigma_2 = 4.7 \times 10^{-48}$  cm<sup>4</sup>·s/photon. The final result of  $\sigma_2$  of HEASPS is given as above with an experimental uncertainty of  $\pm 15\%$ .

### 3.2.2. Two-photon Excited Fluorescence Emission

The TPA induced emission spectra of 1 cm path HEASPS in DMF of 0.00001 mol/l concentration excited with 1064 nm laser beam is basically the same as that of one-photon induced in the relative fluorescence yield ratios and the corresponding spectral distribution. Figure 6 illustrates the TPA induced emission spectra of 1 cm path HEASPS in DMF of 0.05 mol/l concentration. It can be seen that the peak wavelength and the bandwidth are 640 nm, 70 nm respectively. Compared Figure 6 to Figure 3, we can see that the TPA induced emission spectra of the sample HEASPS in much higher concentration has a red-shift as comparing to that in lower concentration. This can be explained by the reabsorption of the dye material.

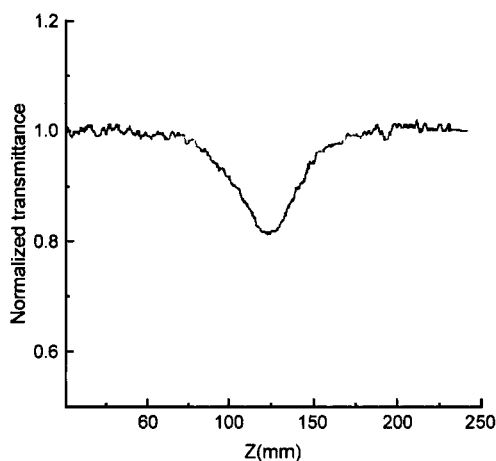


FIGURE 5 Normalized open-aperture Z-scan transmittance of HEASPS in DMF with concentration of 0.05 mol/l using 35 ps pulses at  $\lambda = 1064$  nm with  $I_0 = 3.64$  GW/cm<sup>2</sup>.



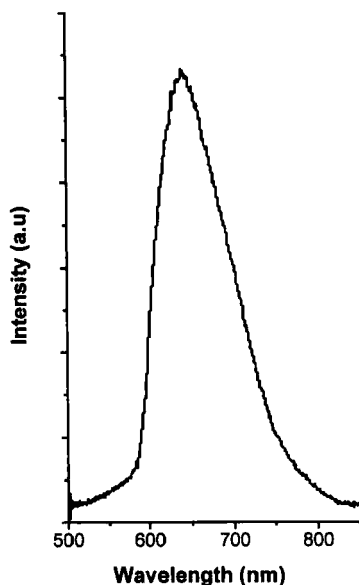


FIGURE 6 Two-photon induced emission spectra of HEASPS in DMF with 1 cm path and 0.05 mol/l concentration.

#### 4. TWO-PHOTON-PUMPED SUPERRADIANT LASING PROPERTIES

The experiment setup for measurement of the TPP frequency up-converted superradiant laser is shown in Figure 7. Osc is a mode-locked Nd:YAG laser with an output wavelength of 1064 nm, pulse duration of 150 ps, spectral width of  $1 \text{ cm}^{-1}$ , angular divergence of 1.5 mrad, and a repetition rate of 10 Hz. The pumping laser pulses come into the media through an attenuator (composed of a  $\lambda/2$  plate and a polarizer), a beam splitter, and a focus lens with focal length of 25 cm. The laser media of HEASPS in DMF with concentration of 0.05 mol/l filled in a 1 cm-long quartz cuvette is put on the focus point of the focus lens. At this concentration level, the single path TPP gain could be so high that a highly directional single-path superradiant lasing (or cavityless lasing) could be observed in both the forward and backward directions if the pump intensity was higher than a certain threshold. The split beam from the beam splitter is used as a reference

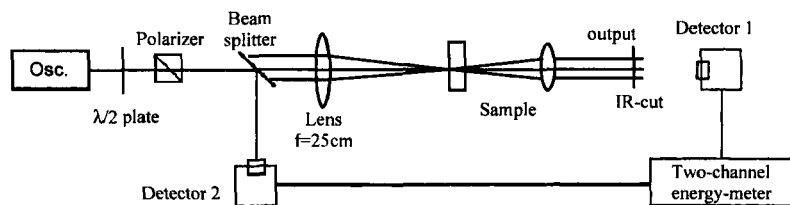


FIGURE 7 Experiment setup of TPP HEASPS frequency up-conversion superradiant laser.

to calculated the input energy. The reference beam energy and the frequency up-converted laser output are measured by a two-channel energy-meter simultaneously.

The output spectra of frequency up-converted superradiant laser is shown in Figure 8. The bandwidth of the up-converted laser spectra is 13.6 nm at the central wavelength of 626 nm, and the relative shape and bandwidth of the spectra basically remains the same when the pump energy level changes from the threshold 0.24 mJ to 1.9 mJ. There is a red-shift of the lasing peak wavelength relative to the corresponding one-photon induced fluorescence (the concentration of HEASPS in DMF is 0.00001 mol/l) peak position, and a blue-shift relative to the corresponding two-photon induced fluorescence (the concentration of HEASPS in DMF is 0.05 mol/l) peak position. This can be explained by the reabsorption effect of the emitted radiation propagating within the sample. Comparing Figure 2 to Figure 3, it can

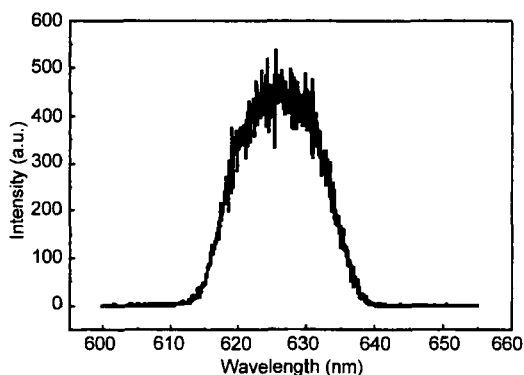


FIGURE 8 TPP HEASPS frequency up-conversion cavity lasing spectral distribution.

be seen that there is a considerable overlap between the linear absorption spectrum and the one-photon induced fluorescence spectrum. Within the overlapping spectral range, laser would be much more difficult to oscillate owing to linear attenuation in the medium, therefore laser is much easier to oscillate in the red-side of the overlapping range. Experiment shows that a higher concentration of the solution will lead to a greater red-shift of the lasing spectrum due to reabsorption effect. A blue-shift of the lasing peak wavelength

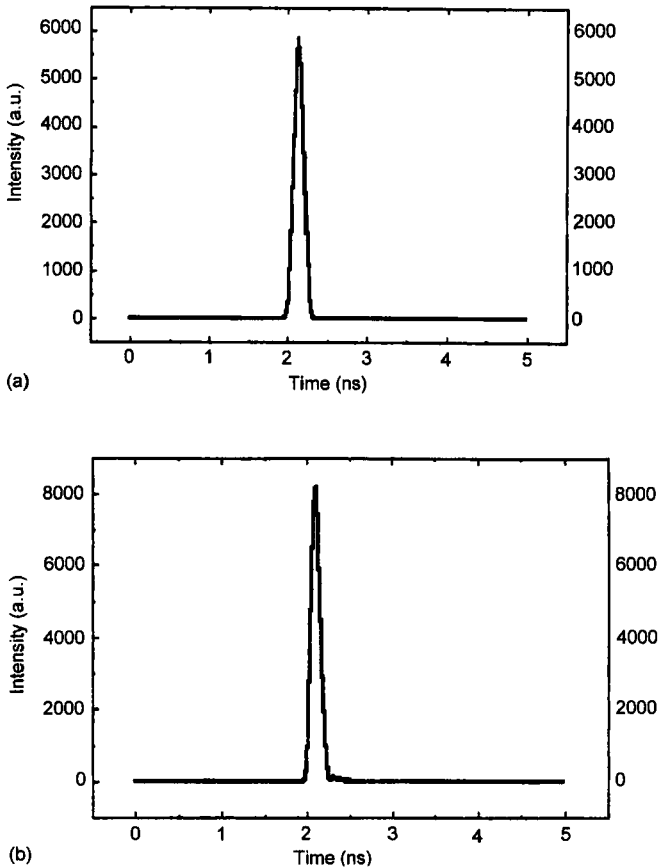


FIGURE 9 Temporal profiles of the pump pulse and TPP lasing pulse of HEASPS recorded by the streak Camera HAMAMATSU C5680. (a) Temporal profile of the pump pulse with pulse duration 142 ps; (b) Temporal profile TPP lasing pulse with pulse duration of 120 ps.

relative to the corresponding two-photon induced fluorescence peak position (the concentration of HEASPS in DMF is 0.05 mol/l) can be explained as that the red-shift of the lasing peak wavelength is less than that two-photon induced fluorescence (the same concentration 0.05 mol/l). This is determined by the cavity loss and gain of the laser.

The temporal waveforms of the pump pulse and the output lasing pulse were recorded by the Streak Camera HAMAMATSU C5760. Figure 9 illustrates the temporal waveforms of the pump pulse and TPP lasing pulse at the pump level of 1.9 mJ, respectively. It can be seen that the lasing pulse duration (120 ps) is shorter than the pump pulse width (142 ps) due to the lasing threshold requirement and the quadratic relationship between the emission intensity and the pump intensity during TPA processes.

Figure 10 shows the output/input curve of the frequency up-converted HEASPS laser. From it we can see that the output energy of the two samples increases as the pump level increase. At the pump energy level of 1.90 mJ, the output lasing energy is 173  $\mu$ J. The slope efficiency is 9.1% for HEASPS (Only forward output was included). If the backward output was taken into account, the slope efficiency should be 18.2% at this pump energy level.

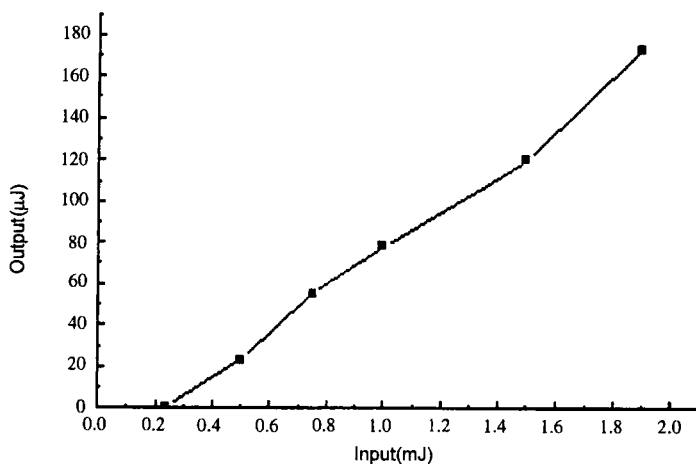


FIGURE 10 The characteristic lasing output/input curve of the frequency up-converted HEASPS laser.

## 5. CONCLUSION

A new dye Trans-4-[*p*-(*N*-hydroxyethyl-*N*-ethylamino)styryl]-*N*-methylpyridinium *p*-toluene sulfonate (HEASPS) was synthesized, and the two-photon absorption (TPA), TPA-induced frequency up-conversion emission, and two-photon pumped (TPP) frequency up-converted superradiantlasing properties of HEASPS, were experimentally studied. This new dye has a moderate TPA cross-section of  $\sigma_2 = 4.7 \times 10^{-48} \text{ cm}^4 \cdot \text{s/photon}$  at 1064 nm, but exhibits a high lasing efficiency. The slope efficiency is 18.2% at the pump energy level 1.9 mJ.

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### References

- [1] Strickler, J. H. and Webb, W. W. (1991). *Opt. Lett.*, **16**, 1780.
- [2] Parthenopoulos, D. A. and Rentzepis, P. M. (1989). *Science*, **245**, 843.
- [3] Cumpston, B. H., Ananthavel, S. P., Barlow, S., Dyer, D. L., Ehrlich, J. E., Erskine, L. L., Heikal, A. A., Kuebler, S. M., Sandy Lee, I.-Y., McCord-Maughon, D., Qin, J., Röckel, H., Rumi, M., Wu, X. L., Marder, S. R. and Perry, J. W. (1999). *Nature*, **51**, 398.
- [4] Denk, W., Strickler, J. H. and Webb, W. W. (1990). *Science*, **73**, 248.
- [5] Maruo, S., Nakamura, O. and Kawata, S. (1997). *Opt. Lett.*, **22**, 132.
- [6] Wu, E. S., Strickler, J. H., Harrell, W. R. and Webb, W. W. (1992). *SPIE Proc.*, **1674**, 776.
- [7] Zhao, C. F., He, G. S., Bhawalkar, J. D., Park, C. K. and Prasad, P. N. (1995). *Chem. Mater.*, **7**, 1979.
- [8] He, G. S., Yuan, L. X., Cui, Y. P., Li, M. and Prasad, P. N. (1997). *J. Appl. Phys.*, **81**, 2529.
- [9] He, G. S., Yuan, L. X., Prasad, P. N., Abbotto, A., Facchetti, A. and Pagani, G. A. (1997). *Opt. Commun.*, **140**, 49.
- [10] He, G. S., Kim, K. S., Yuan, L. X., Cheng, N. and Prasad, P. N. (1997). *Appl. Phys. Lett.*, **71**, 1619.
- [11] He, G. S., Signorini, R. and Prasad, P. N. (1998). *IEEE J. Quantum Electron.*, **34**, 7.
- [12] Bhawalkar, J. D., He, G. S., Park, C. K., Zhao, C. F., Ruland, G. and Prasad, P. N. (1996). *Opt. Commun.*, **124**, 33.

- [13] He, G. S., Signorini, R. and Prasad, P. N. (1998). *Appl. Opt.*, **37**, 5720.
- [14] Tutt, L. W. and Boggess, T. F. (1993). *Prog. Quantum Electron.*, **17**, 299.
- [15] Jbunning, T., Natarajan, L. V., Schmitt, M. G., Epling, B. L. and Crane, R. L. (1991). *Appl. Opt.*, **30**, 4341.
- [16] Reinhart, B. A., Brott, L. L., Clason, S. J., Dillard, A. G., Bhatt, J. C., Kannan, R., Yuan, L. X., He, G. S. and Prasad, P. N. (1998). *Chem. Mater.*, **10**, 1863.
- [17] Mansoor Sheik-Bahse, Ali A. Said, Tai-Huei Wei, David J. Hagan and Van Stryland, E. W. (1990). *IEEE J. Q. E.*, **26**, 760.