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Two-photon absorption and frequency-upconversion properties of a new organic dye HMASPS

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Abstract **Two-photon absorption (TPA) and frequency-upconversion properties of a new upconversion laser dye *trans*-4-[*p*-(N-hydroxyethyl-N-methyl-amino)styryl]-N-methylpyridinium toluene-*p*-sulfonate (abbreviated to HMASPS) were reported in this note. The linear absorption, TPA, single-photon induced fluorescence, TPA induced fluorescence and TPA induced upconverted lasing spectra of HMASPS solution in dimethyl formamide (abbreviated to DMF) were measured at room temperature. The red shift for the central wavelength of TPA induced fluorescence peak, which was compared with that of the single-photon induced fluorescence peak, and the blue shift for that of TPA induced upconverted lasing compared with that of TPA induced fluorescence, were explained by using re-absorption effect. TPA peak was at 930 nm. There is an 11 nm blue shift for two-photon energy of TPA peak compared with the linear absorption peak. The molecular TPA cross-section σ_2' at 1064 nm was measured to be 6.0×10^{-48} cm^4 • s/photon by using the open aperture Z-scanning system. The highest upconversion efficiency was measured to be 8.4% at 1064 nm.**

Keywords: organic dye, HMASPS, two-photon absorption, frequency-upconverted lasing.

Two-photon absorption (TPA) and its application are one of the interesting topics in photoelectronic materials. TPA materials are expected to be used in frequency-upconverted lasing[1], optical power limiting and stability[2–4], three-dimensional (3D) optical data storage[5], 3D microfabrication[6] and photodynamic therapy[7]. In 1931, Göppert-Mayer first realized that an atom or molecule could absorb two photons simultaneously[8]. But TPA process was quadratically dependent on the illumination intensity, little progress on TPA had been made before the invention of laser. High-power pulse laser can provide the necessary optical power intensity to the study of TPA process. However, due to the relatively low TPA cross-section of most materials, the two-photon process is limited in its applications. Recently, people found that some organic dyes had high TPA cross-section, which makes the widespread applications of TPA effect possible.

TPA pumped frequency-upconverted laser is an important application of TPA dye. TPA upconversion laser has several advantages over other techniques of coherent frequency upconversion such harmonic generation based on nonlinear optical crystals as (i) elimination of plasematching requirement, (ii) feasibility of using semiconductor lasers as pump sources and (iii) capability of adopting waveguide and fiber configurations. In addition, using long-wavelength as pump source can prolong the lifetime of the dye.

1 Materials and methods

(i) Materials synthesis. Up till now, the correlation between the structure of organic dye and TPA properties has not been well understood. As a rule of thumb, however, most TPA molecules are large polar π-conjugated systems with excellent planar molecular configuration and donor-accepter substituents. Based on this consideration, we have synthesized a new dye *trans*-4-[*p*-(N-hydroxyethyl-N-methylamino)styryl]-N-methylpyridinium toluene-*p*-sulfonate (abbreviated to HMASPS) that processes excellent planarity and large π-electron conjugation system (fig.1). We believe that this structural characteristic contributes to enhancing TPA and upconversion lasing.

(ii) Experimental. (1) Measurement of linear optical properties. The linear absorption spectrum and single-photon induced fluorescence spectrum of HMASPS solution in dimethyl formamide (DMF) with 1×10^{-5} mol/L concentration was measured by using Hitachi U-3500 recording spectrophotometer and Hitachi 850 fluospectrophotometer, respectively. The solution was filled into 1-cm-path quartz cell.

(2) Measurement of nonlinear transmittance. Fig. 2 shows the experimental setup for nonlinear transmittance of this dye at different wavelengths. The pump laser beam came from a picosecond OPA(optical parameter amplifier) operating at the wavelengths from 400 to 2000 nm. The output energy, pulse duration and repetition rate were 0.8 mJ, 40 ps, 5 mrad and 10 Hz, respectively. The laser beam was focused through an f=15 cm lens onto the center of a HMASPS solution sample in DMF at 0.05 mol/L concentration filled in a 1-cm-path quartz cell. Two-channel energymeter (EPM 2000 molectron) was used to detect the incident and transmitted energy. A filter was used to cut the upconverted lasing.

(iii) Measurement of TPA fluorescence spectrum and upconversion lasing spectrum. Fig. 3 shows the experimental setup for TPA fluorescence spectrum and upconversion lasing spectrum. The laser beam was from a mode-locked picosecond Nd:YAG laser (Continuum PY61C-10, pulse duration 40 ps, pulse energy 3 mJ, repetition 10 Hz). The laser beam was focused by lens-1 (f =15 cm) onto a 1-cm-path quartz cell filled with =15 cm) HMASPS solution in DMF with 0.0753 mol/L. The up-

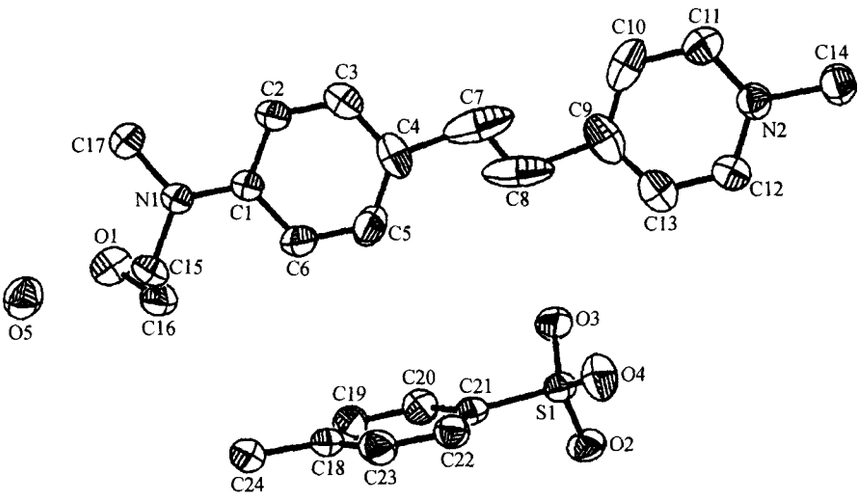

Fig. 1. Molecular structure of HMASPS.

converted fluorescence or lasing was focused by lens-2 (*f* onto the spectrophotometer. The transmitted pump laser was cut off by a filter. An attenuator was used to adjust the energy to the spectrophotometer. The TPA fluorescence spectrum and upconverted lasing spectrum were measured by using Hamamatsu C5094 spectrophotometer and Hamamatsu C5680-01 streak camera. 5% of the pump laser were split to the detector of delayer.

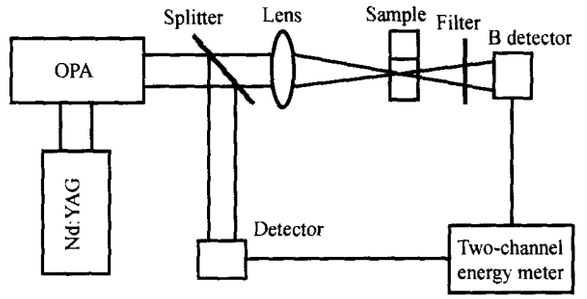

Fig. 2. Experimental setup for the measurement of nonlinear transmittance of HMASPS solution in DMF with a concentration of 0.05 mol/L.

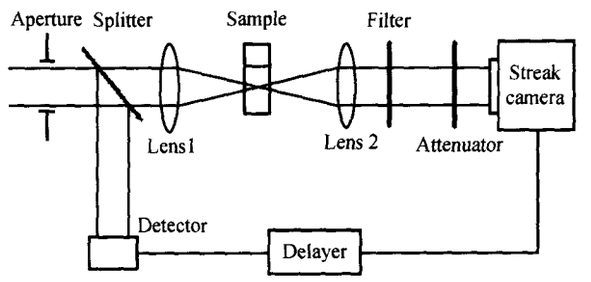

Fig. 3. Experimental setup for the measurement of TPA induced fluorescence and upconverted lasing spectra.

2 Results and discussion

Fig. 4-1 shows the linear absorption of this dye. There is linear absorption from 350 to 600 nm, with the absorption peak and bandwidth of 476 and 60 nm, respectively. There is no linear absorption in the entire range from 600 to 1200 nm. So the dye solution is red. But two-photon energy of the wavelengths from 700 to 1160 nm just falls into the strong linear absorption band. The TPA process is expected to take place in this wave band.

Fig. 5 shows the TPA induced nonlinear transmittance from 720 to 1100 nm. The influence of linear absorption has been removed. From fig. 5 one can see that there is TPA in the entire wave band from 720 to 1100 nm with the strongest absorption at 930 nm. Comparing fig. 5 with fig. 4-1, one can see that there is an 11 nm blue shift for the two-photon energy of TPA peak compared with the linear absorption peak. At 1064 nm, there is relatively strong TPA, so the dye can be pumped by using N: YAG laser operating at 1064 nm.

Fig. 4-2 shows the single-photon fluorescence spectrum of HMASPS solution in DMF at 1×10^{-5} mol/L. The central wavelength and bandwidth is 620 and 80 nm respectively. Comparing fig. 4-1 with 4-2, one can see that there is a part overlap between the red side of absorption spectrum and blue side of fluorescence spectrum. This overlap will enlarge when the concentration of the solution increases.

Intense red upconverted fluorescence emission can be observed in all directions when the dye sample was pumped by the focused infrared laser beam. If the pumped energy is above a certain threshold, a highly directional single path upconverted lasing could be observed in both the forward and backward directions. This light is the stimulated radiation when pumped with intense infrared pulse laser beam. Fig. 4-3 and 4-4 are the TPA lasing spectrum and fluorescence spectrum. Comparing fig. 4-2 with 4-3, one can see that there is a 15 nm red shift for the central wavelength of TPA fluorescence peak compared with that of single-photon induced fluorescence spectrum.

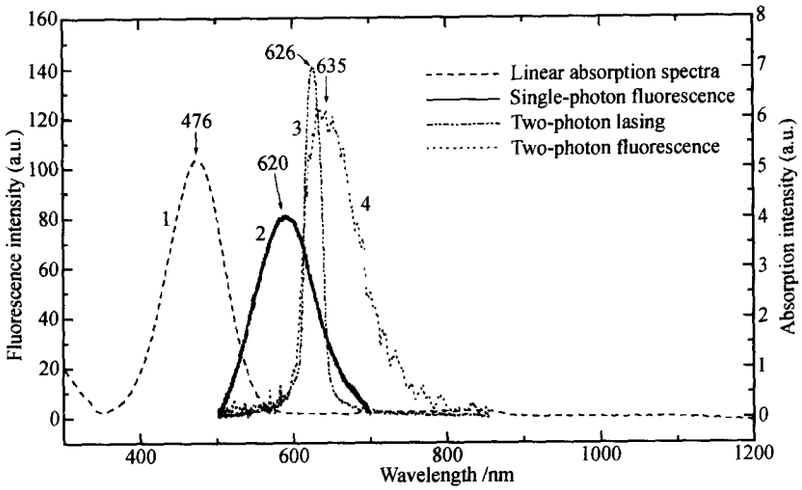

Fig. 4. Linear absorption spectrum (1), single-photon induced fluorescence spectrum (2), TPA induced upconverted lasing spectrum (3) and TPA induced fluorescence spectrum (4) of HMASPS solution in DMF. For (1) and (2) the concentration is 1×10^{-5} mol/L, for (3) and (4) the concentration is 0.0753 mol/L.

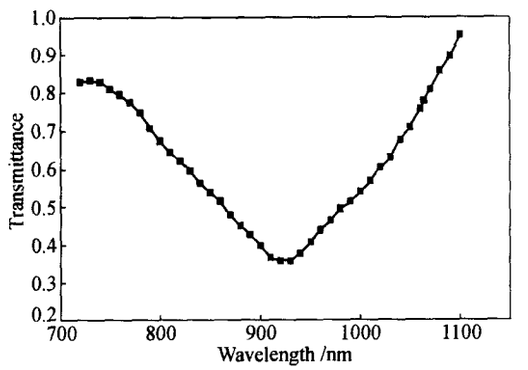

Fig. 5. Nonlinear transmittance of HMASPS solution in DMF with a concentration of 0.05 mol/L.

This phenomenon can be explained by using the re-absorption effect. As mentioned above, there is a part overlap at 500—600 nm between the linear absorption and single-photon fluorescence spectra and this overlap will enlarge when the concentration increases. The solution will absorb the fluorescence. Single-photon fluorescence spectrum was measured at low concentration, the re-absorption effect can be neglected. TPA induced fluorescence is measured at high concentration, the re-absorption effect cannot be neglected. The blue side of the fluorescence spectrum decreases due to the re-absorption. So the blue side of the TPA induced fluorescence spectrum is asymmetry and there is a red shift.

From fig. 4 one can also see that there is a 9 nm blue shift for the central wavelength of TPA induced upconverted lasing spectrum compared with that of TPA fluorescence spectrum. This blue shift can also be explained by using re-absorption effect. Single-photon induced fluorescence spectrum at low concentration represents the emission properties of the dye molecule. Linear absorption is smaller at short wavelength, but the fluorescence efficiency is smaller. Due to the interaction of the two aspects, a certain wavelength can be easily emitted from the solution sample. This wavelength corresponds to the central wavelength of TPA lasing.

The TPA cross section σ_2' at 1064 nm was measured to be 6.0×10^{-48} cm^4 • s/photon by using an open-aperture Z-scanning system. The concentration of the dye was 0.05 mol/L and the incident intensity was 3.64 GW/cm^2. The experimental uncertainty was within $\pm$ 15%.

The upconversion efficiencies of HMASPS solution in DMF at different concentrations were measured. The experimental results are shown in table 1. Every data are average values of 10 pulses. From table 1 one can see that the highest upconversion efficiency is 8.4% when the concentration is 0.05 mol/L. The upconversion efficiency is lower when the concentration is higher or lower. The upconversion efficiency of ASPI is 3.5% reported by He et al.[1]. Considering the absorption of the quartz cell and the forward emitted upconverted laser, the upconversion efficiency is much higher. So this new dye is expected to be used in upconversion laser.

Table 1 Experimental data for upconversion efficiency of HMASPS solution in DMF at different concentrations

Concentration /mol • L^{-1}	Input energy /mJ	Output energy /mJ	Upconversion efficiency (%)
0.075	2.33	0.174	6.3
0.060	1.95	0.162	8.3
0.050	2.02	0.169	8.4
0.030	2.45	0.146	6.0

3 Conclusion

A new organic dye HMASPS with large TPA cross-section and excellent lasing properties has been synthesized in our research group. The highest upconversion efficiency is 8.4% when the dye solution is pumped by focused 1064 nm laser beam. Linear and nonlinear optical properties of the dye solution were systematically studied. The red shift for the central wavelength of TPA induced fluorescence spectrum, which was compared with single-photon induced fluorescence spectrum, and the blue shift for TPA induced lasing spectrum, which was compared with TPA induced fluorescence spectrum, were explained by using the re-absorption effect. TPA cross-section was 6.0×10^{-48} cm^4 • s/photon at 1064 nm. The strongest TPA was at 930 nm. There is an 11 nm blue shift for two-photon energy of TPA peak compared with the linear absorption peak. Due to the high upconversion efficiency, this dye is expected to be used in upconversion laser. If the dye is doped into some solid matrix, it can be used to make solid-state dye upconversion laser.

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The ultraviolet and blue luminescence properties of ZnO:Zn thin film

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Abstract **The ultraviolet (UV) and blue luminescence of Zn-rich zinc oxide thin film deposited by electron-beam evaporation have been investigated at room temperature (RT). We observed that the UV and blue electroluminescence (EL) emission band centered around 480 nm which is blue shifted in comparison with that of the ZnO thin film prepared by low pressure metal organic chemical vapor deposition (LP MOCVD). The UV emission is much stronger than blue emission in the photoluminescence (PL) spectra. The field-induced ionization of excited luminescent centers of ZnO:Zn thin film at high electric field and the difference between PL and EL are discussed. The experiments show that the ZnO:Zn thin film provides a hopeful new mechanism to obtain UV and blue emission.**

Keywords: ZnO: Zn thin film, blue EL, UV PL.

The cathodoluminescence properties of ZnO phosphor powder have been studied for several decades. Recently, to meet the challenges of field emitting device (FED) and the need of blue emission in EL flat panel display, there has been great interest in the study of ZnO. ZnO is the crystal lographic structure of hexagonal, it is a direct band material with a band gap of 3.2 eV at RT. One particularly interesting feature is the high exciton binding energy of 60 meV. This ensures that UV and blue emission can be obtained at RT. The notable properties are higher electronic conductivity, better chemical stability, lush materials source and lower cost. It is a kind of excellent candidate for preparation optoelectronic devices and will be useful for exploitation and application of ZnO. But it is difficult to grow high quality ZnO thin film by the old thin film deposition technology and the application of ZnO as luminescent materials are seriously limited. Recently, this problem had been overcome step by step due to the improvement on the thin film deposition technology.

In 1997, the optically pumped excitonic UV laser emission from ZnO thin films was first reported by scientists of Hongkong and Japan[1, 2]. Since the wavelength of UV emission from ZnO is shorter than the blue emission