

## Synthesis and Characterization of a New Organic Up-conversion Laser Dye HMASPS

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**Abstract:** A new organic dye, *trans*-4-[4'-(N-hydroxyethyl-N-methylamino)styryl]-N-methylpyridinium *p*-toluene sulfonate (HMASPS) has been synthesized and its structure has been determined. Pumped with a 1064 nm, 50 ps laser pulses, 0.05 mol/L HMASPS/DMF solution showed the two-photon pumped (TPP) output/input efficiency of 8.4% which is higher than that of *trans*-4-[*p*-(N-hydroxyethyl-N-methylamino) styryl]-N-methylpyridinium iodide (ASPI)<sup>1</sup> at the same pump level.

**Keywords:** C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>S.H<sub>2</sub>O, TPP, up-conversion, laser dye.

### Introduction

Two-photon pumped up-conversion materials used as the laser media have the advantage of being pumped at longer wavelengths (*e.g.* at 1064 nm), where the organic dyes are relatively photostable, and emission at shorter wavelengths (*e.g.* at 625 nm). With the TPP up-conversion, the range of the lasing materials is expanded in lasing device fabrication. Materials with high lasing efficiency are in great demand.

In the course of exploring strong two-photon absorption (TPA) compounds, symmetric and asymmetric intramolecular charge transfer organic molecules have been reported<sup>2,3</sup>. To date, the structure-TPA property correlation has not been well understood. It seems certain that most of TPP lasing molecules are large polar  $\pi$ -conjugated system with excellent planar molecular configuration and donor-acceptor substituents. The high polarity, we believe, is the necessary structural condition for the TPP up-conversion lasing.

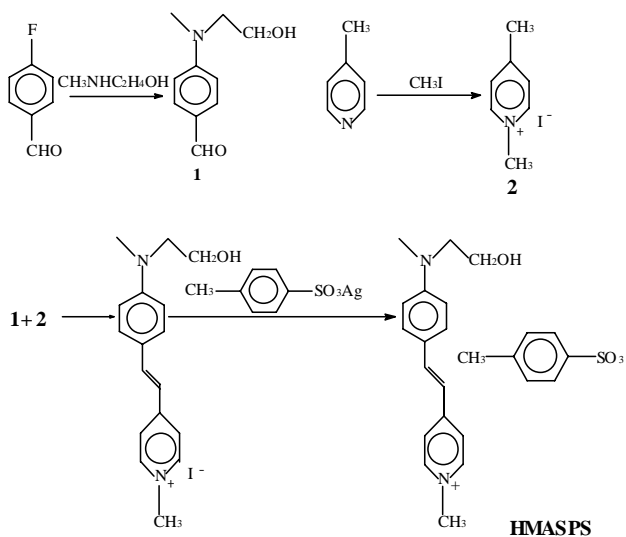
Based on above structural-TPP-lasing correlation consideration, we synthesized a new organic salt HMASPS. The structure determination has been carried out. Two-photon induced fluorescence and TPP lasing behavior for HMASPS in solution is presented.

### Synthesis

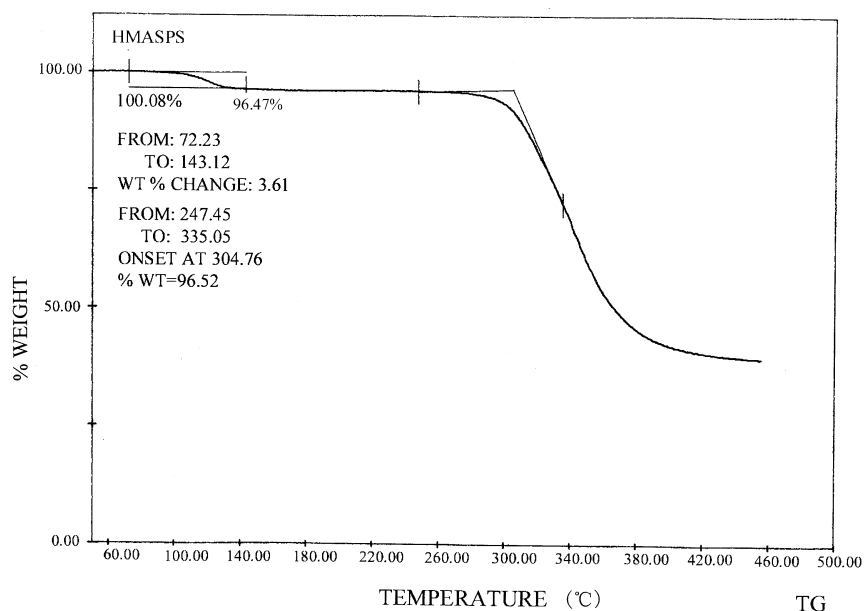
In a 250 mL one-neck flask with a stirrer and a condenser, 4.66 g (0.026 mol) of 4-(N-hydroxyethyl-N-methyl amino) benzaldehyde<sup>4</sup> (compound **1**), 6.20 g (0.026 mol) of 4-methyl-N-methyl pyridinium iodide<sup>5</sup> (compound **2**), 100 mL of acetonitrile and four drops of piperidine were added. The solution was heated and refluxed at 80°C for four

hours. Then it was added into a 7.25 g (0.026 mol) of silver *p*-toluene sulfonate/100 mL

**Scheme I**



**Figure. 1** The TGA curve of HMASPS.



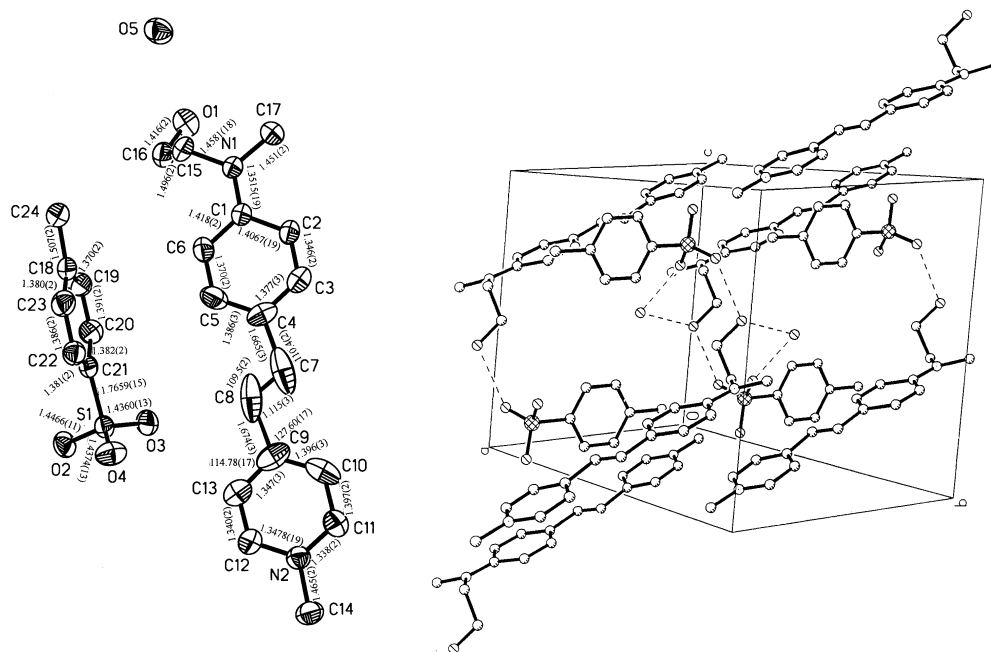
acetonitrile solution with stirring and heating in a one-neck flask and refluxing for about two hours. After stirring at room temperature overnight, the silver iodide precipitated was filtered off. During the evaporation of the clear red solution, shining microcrystals were crystallized out and recrystallized from acetonitrile obtaining purple-red parallelepiped crystals. Structure analysis reveals that a water molecule

co-crystallizes with the HMASPS salt. TGA curve shows that 3.61% of weight loses in the heating process from 72°C to 143°C. HMASPS decomposes above 304°C (see **Figure 1**). The melting point is 186°C revealed by DTA thermal analysis. Calcd For  $C_{24}H_{28}N_2O_4S \cdot H_2O$ : C, 62.86; H, 6.54; N, 6.11. Found: C, 62.87; H, 6.64; N, 5.96.

### Structure

A crystal of  $0.5 \times 0.6 \times 0.7$  mm<sup>3</sup> was mounted on a Rigaku R-AXIS IIC IP diffractometer and the diffraction data were collected by IP method. By using SHELXL-97 programs, the structure was solved by direct method and refined by Full-matrix least-squares on  $F^2$ . HMASPS belongs to monoclinic system,  $P2_1/n$  space group,  $a=9.929$  (2) Å,  $b=19.549$  (4) Å,  $c=12.100$  (2) Å,  $\alpha=90^\circ$ ,  $\beta=96.11^\circ$  (3),  $\gamma=90^\circ$ ,  $V=2335.3$ (8) Å<sup>3</sup>,  $Z=4$ ,  $D_c=1.304$  g cm<sup>-3</sup>,  $R=0.0776$ ,  $wR=0.2303$ . X-ray diffraction analysis showed that HMASPS crystal co-crystallized with water molecules forming the monohydrate with the formula of  $C_{24}H_{28}N_2O_4S \cdot H_2O$ . Due to abundant hydrogen bonds existed in the crystal, HMASPS is endowed with many excellent crystalline habits such as easy crystallization from solution and easy growing 3-dimensional large size (see **Figure 2**). The maximum atomic derivations to their corresponding molecular least square planes are no more than 0.1Å. The bond lengths of benzene ring and pyridinium ring in HMASPS are aromatic characterized.

**Figure 2** The molecule structure and packing diagram of HMASPS.

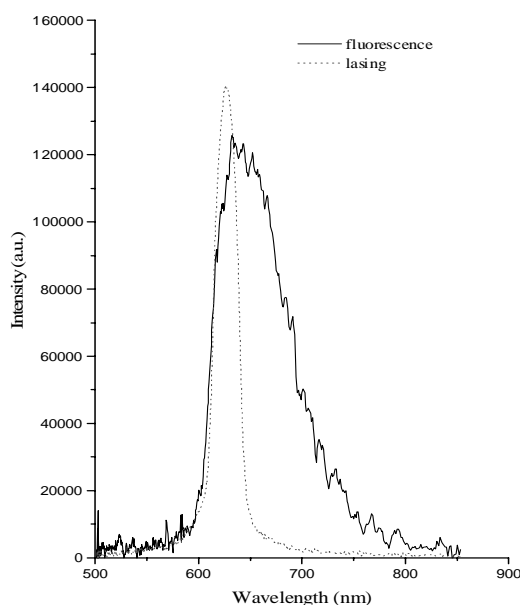


### Two-photon fluorescence and lasing test

The up-conversion fluorescence and lasing spectra were recorded by a passively mode-locked Nd:YAG laser as a pump source, and a single-scan streak camera

(Hamamatsu Model C1587) together with a polychromator as a recorder. The two-photon-excited fluorescence peak for HMASPS is located at 642 nm (see **Figure 3**). The narrow lasing peak is at 626 nm (for a solution of  $7.53 \times 10^{-2}$  mol/L HMASPS/DMF) with a width at half maximum of 25 nm which is blue-shifted by  $\sim 18$  nm compared to its corresponding two-photon-excited fluorescence peak. The overall energy conversion efficiency is 8.4% for HMASPS (output/input energy is 0.169 mJ/2.02 mJ). The pumping energy at lasing threshold was measured to be 0.24 mJ for HMASPS. At the exact same experimental conditions, the conversion efficiency of ASPI is 7.1% (output/input energy is 0.149 mJ/2.10 mJ). We believe the polar aromatic p-toluene sulfonate anion has also some contribution to the up-conversion emission process.

**Figure 3** Two-photon (by 1064 nm laser pulses) excited fluorescence and TPP lasing spectra of  $7.53 \times 10^{-2}$  mol/L HMASPS/DMF solution.



### Acknowledgment

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