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A New Organic Up-conversion Laser Dye HEASPS

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Abstract: A new organic dye, *trans*-4-[*p*-(N-hydroxyethyl-N-ethylamino)styryl]-N-methyl-pyridinium *p*-toluene sulfonate (HEASPS) has been synthesized and its structure has been determined. Pumped with a 1064 nm, 50 ps laser pulses, 0.05 mol/L HEASPS/DMF solution showed the two-photon pumped (TPP) output/input efficiency of 9.1% which is higher than that of known TPP laser dyes *trans*-4-[*p*-(N-hydroxyethyl-N-methylamino) styryl]-N-methylpyridinium iodide (ASPI) and *trans*-4-[*p*-(N-hydroxyethyl-N-methylamino) styryl]-N-methylpyridinium *p*-toluene sulfonate (HMASPS) at the same experimental conditions.

Keywords: $C_{25}H_{30}N_2O_4S$, TPP, up-conversion, laser dye.

Two-photon absorption (TPA) is such a process in which a molecule simultaneously absorbs two photons to access an excited state. The charm of the materials with large TPA cross section is due to the virtue of using near-IR two-photon as pump source for UV-visible excitation, which leads to a deeper penetration in the media. In addition, the quadratic intensity dependence of the two-photon process allows for excitation of chromophores with a high degree of spatial selectivity. In laser device fabrication, materials with high two-photon pumped up-conversion lasing efficiency have received close attention partly due to their prospective applications[1-3]. Compared with the second harmonic generation, TPP up-conversion lasing doesn't need phase-matching, so a variety of material forms and a wide tuning range can be selected.

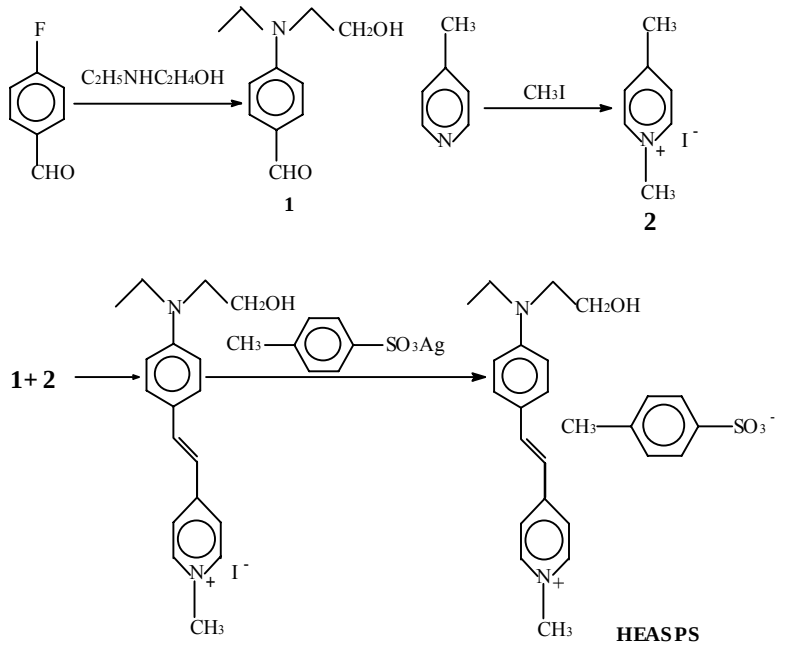
In this article, we report another new organic up-conversion laser dye *trans*-4-[*p*-(N-hydroxyethyl-N-ethylamino)styryl]-N-methylpyridinium *p*-toluene sulfonate (HEASPS).

Synthesis

In a 250 mL one-neck flask with a stirrer and a condenser, 5.00 g (0.026 mol) of 4-(N-hydroxyethyl-N-ethylamino) benzaldehyde[4] (compound **1)**, 6.20 g (0.026 mol) of 4-methyl-N-methyl pyridinium iodide[3] (compound **2)**, 100 mL of acetonitrile and four drops of piperidine were added. The solution was heated and refluxed at 90℃ for four hours. Then it was added into a 7.25 g (0.026 mol) of silver *p*-toluene sulfonate/100

mL 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 precipitate was filtered off. During the evaporation of the clear red solution, shinning microcrystals were crystallized out and recrystallized from acetonitrile obtaining purple-red parallelepiped crystals. The melting point, measured by DTA thermal analysis, is 198℃. Calcd For $C_{25}H_{30}N_2O_4S$: C, 66.05; H, 6.60; N, 6.16. Found: C, 65.65; H, 6.63; N, 5.86.

Reaction Scheme



Structure

A crystal of $0.25 \times 0.30 \times 0.30$ mm^3 was mounted on a Bruker P4 four-circle diffractometer. By using SHELXL-97 programs, the structure was solved by direct method and refined by Full-matrix least-squares on F^2. HEASPS belongs to triclinic system, $p\bar{1}$ space group, a=9.4237(8) Å, b=9.6976(8) Å, c=13.2841(9) Å, α =86. 655° (6), β =74. 064° (3), γ =85. 891° (7), V=1163.40(16)Å^3, Z=2, D_c=1.298 g cm^{-3}, R=0.0573, wR=0.1832. HEASPS cation is almost perfectly planar (see **Figure. 1**). In fact, the maximum atomic derivation to their corresponding molecular least-square plane is no more than 0.1 Å. The bond lengths of benzene ring and pyridinium ring in HEASPS is all aromatic characterized. The bridge bond lengths of C4-C7-C8-C9 of HEASPS are also highly conjugated. The planar and the conjugated geometric configuration reveal that the HEASPS cation has a highly delocalized π electronic

system.

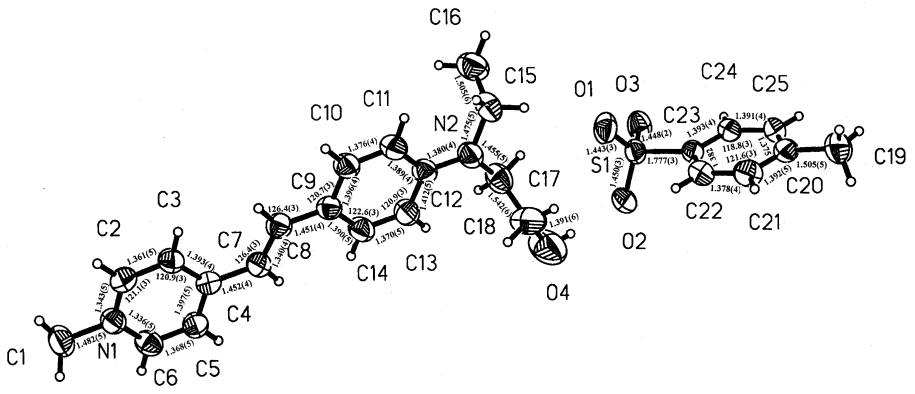


Figure. 1 The molecule structure diagram of HEASPS.

Two-photon pumped fluorescence and lasing test

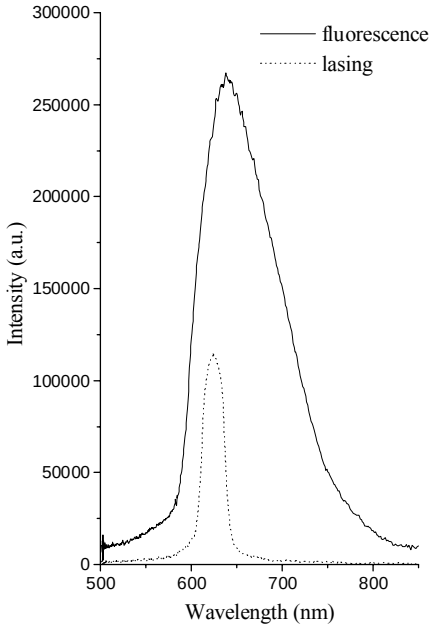
The up-conversion fluorescence and lasing spectra were recorded by a passively mode-locked Nd:YAG laser as a pump source, and a single-scan streak camera (Hamamatsu Model C1587) together with a polychromator as a recorder. **Figure. 2** is the two-photon excited fluorescence and TPP up-conversion lasing spectra for 3.72×10^{-2} mol/L HEASPS/DMF solution. The two-photon-excited fluorescence peak is located at 642 nm. The narrow TPP lasing spectra is at 624 nm with a width at half maximum of ~25 nm. The lasing peak is blue-shifted by ~18 nm compared to fluorescence peak. The TPP energy up-conversion efficiency for HEASPS/DMF solution at different concentration is shown in **Table 1**. An optimal concentration is 0.025 mol/L, with the up-conversion efficiency of 15.5%. It means that a close relationship exists between the concentration of the dye solution and the efficiency. **Table 1** also shows the efficiency for 5.00×10^{-2} mol/L HMASPS/DMF and ASPI/DMF solution for comparison. At the same concentration and at the same pump level, HEASPS/DMF shows the efficiency of 9.1% and HMASPS/DMF shows the efficiency of 8.4%, both of which are higher than that of ASPI/DMF solution. The polar aromatic *p*-toluene sulfonate anion has also some contribution to the up-conversion emission process.

Table 1. The TPP up-conversion lasing efficiency for varied HEASPS/DMF solution concentrations and that of HMASPS/DMF and ASPI/DMF solution at 5.00×10^{-2} mol/L.

	Concentration (mol/L)	Input (mJ)	Output (mJ)	Efficiency (%)
HEASPS/DMF	0.050	1.90	0.173	9.1
	0.025	2.13	0.332	15.5

	0.020	2.07	0.282	13.6
HMASPS/DMF	0.050	2.02	0.169	8.4
ASPI/DMF	0.050	2.10	0.146	7.1

Figure. 2 The two-photon excited fluorescence and TPP up-conversion lasing spectra of 3.72×10^{-2} mol/L HEASPS/DMF solution.



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