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Synthesis, Characterization and Non-linear Optical Properties of a New Organic Dye: DEAHAS

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Abstract: *Trans*-4- (N-2-hydroxyethyl-N-ethyl amino)-4´-(diethyl amino)stilbene (DEAHAS) has been synthesized and characterized by ^{1}H NMR, IR and elemental analysis. Linear absorption, single-photon induced fluorescence and two-photon induced fluorescence are experimentally studied. DEAHAS has an effective two-photon absorption cross-sections of $\sigma_2 = 1.19 \times 10^{-46}$ cm^4 • s/photon at 532 nm by using an open aperture Z-scan technique and exhibits a strong two-photon induced blue fluorescence of 430 nm when pumped with 800 nm laser irradiation.

Keywords: Synthesis, two-photon-induced fluorescence, DEAHAS.

Two-photon absorption (TPA) is a process in which two photons are simultaneously absorbed to an excited state *via* a virtual state. The synthesis of organic optical materials with large TPA cross section has become a subject of great interest in recent years due to various application such as three-dimensional fluorescence imaging[1], optical data storage[2,3] and lithographic microfabrication[4-6]. Recently we have synthesized a new organic dye DEAHAS that is a symmetrically substituted stilbene-type chromophore and exhibits strong two-photon induced fluorescence. The synthesis method and nonlinear optical properties of this new dye are reported in this paper.

Experimental

Synthesis of DEAHAS

IR spectra were measured on a Nicolet FT-IR 20 SX spectrometer. Nuclear magnetic resonance spectra were measured on a FX-90Q NMR spectrometer. Element analyses were performed on Perkin 2400 (II).

4-(N-2-hydroxyethyl-N-ethyl amino)benzaldehyde and [4-(diethyl amino)benzyl]-triphenylphosphinium iodine were synthesized by our laboratory.

1.93 g (0.01 mol) 4-(N-2-hydroxyethyl-N-ethyl amino)benzaldehyde was dissolved in 100 mL tetrahydrofuran. Then the orange solution was poured into a reaction flask with 8.26 g (0.015 mol) of [4-(diethyl amino)benzyl]triphenylphosphinium iodine under

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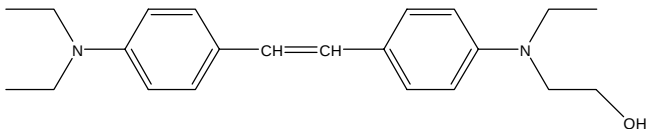
the dry N_2. The final solution was dropped into the mixture solution of *tert*-butanol and potassium *tert*-butoxide at 0° C. After a further 20 h stirring, the yellow mixture was obtained. The solvent was removed by distillation after neutralized by diluted HCl. The residue was poured into ice water, and extracted by dichloromethane. The organic layer was removed by evaporation and purified by column chromatography on silica gel using acetidin-petroleum ether (volume ratio = 1:3) as eluent. The bright green slice crystals were obtained with yield of 30% and mp 134.6° C. ^{1}H NMR, δ ($CDCl_3$, 90 MHz): 7.35 (d, 4H, J= 8.29Hz); 6.72-7.22 (m, 6H); 3.77 (t, 2H, J= 6.34 Hz); 3.40-3.57 (m, 8H); 1.98 (s, 1H); 1.15 (t, 9H, J= 6.82 Hz). IR (KBr) ν : 3281.7-3286.9(-OH); 3012.6(aromatic C=C-H,w); 2968.2(C=C-H,ms); 1609.2(C=C,s) 1521 (aromatic C=C,s) cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_2O$: C 78.11; H 8.87; N 8.28%. Found: C 77.97; H 8.94; N 8.21%.

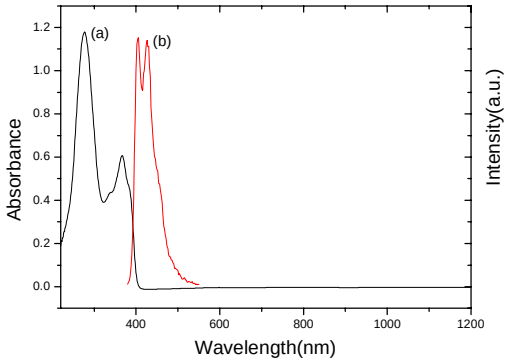
Figure 1 Chemical structure of DEAHAS



Linear optical properties

The linear absorption spectrum was measured on a Hitachi U-3500 UV-VIS-IR recording spectrophotometer by using a 1 cm quartz cuvette. **Figure 2** shows the linear absorption spectrum and one-photon induced emission spectrum of DEAHAS in ether with a solute concentration of $d_0 = 1\times10^{-5}$mol/L, in which the solvent influence is not included. The spectral curve has shown that there is a strong absorption band with the peak absorption located at 277 nm and a weak absorption at 367 nm, respectively. There is no linear absorption in the entire spectral range from 400 to 1200 nm. It also has shown the measured fluorescence spectrum for a 1cm path DEAHAS solution with a concentration of d_0 = 0.00001 mol/L when excited at the central wavelength of 370 nm. The single-photon induced fluorescence spectrum was measured by an Edinburgh FLS 920

Figure 2 Linear absorption spectra and one-photon induced emission spectra of DEAHAS



(a) linear absorption spectrum and (b) one-photon induced emission spectrum

fluorescence spectrometer. There are two strong fluorescence peaks located at 404 nm and 426 nm, respectively.

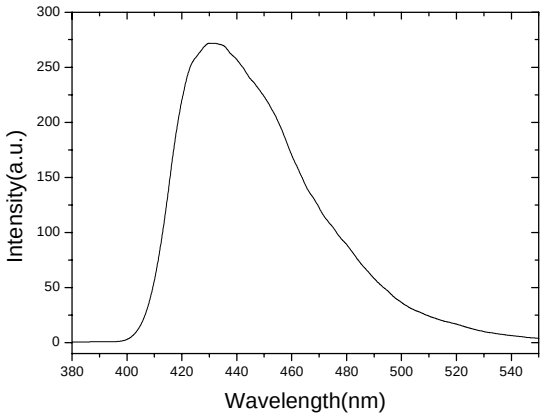
Nonlinear optical properties

Normalized open-aperture Z-scan transmittance of DEAHAS in $CHCl_3$ with concentration of 2×10^{-3} mol/L uses 20 ns pulses at λ =532 nm with I_0 = 2.26 GW/cm^2. The nonlinear coefficient β of DEAHAS is 0.098 cm/GW and the two-photon cross section σ_2 is 1.19×10^{-46} cm^4 • s/photon by using the following relationship: $\beta = \sigma_2 N_0$.

The two-photon induced emission spectrum can be observed when the solution of sample pumped with 800 nm, 76 MHz, 200 fs pulse Ti: sapphire femosecond laser and a detector with photo multiplier tube. **Figure 3** illustrates the TPA induced emission spectrum of 1 cm path DEAHAS in ether of 0.01 mol/L concentration. It can be seen that the peak wavelength and the bandwidth are 430 nm and 52 nm, respectively. Comparing **Figure 3** and **Figure 2**, we can see that the TPA induced emission spectrum of the sample HEAHAS with much higher concentration has a redshift as compared to that in the lower concentration sample. This can be explained by the reabsorption of the dye material.

In conclusion, a new organic dye DEAHAS was synthesized. The single-photon induced fluorescence and two-photon induced fluorescence are experimentally studied when the solution of sample pumped with 800 nm laser irradiation, it shows a strong two-photon induced blue fluorescence at 430 nm. So we believe that it is a quite promising application value as a useful nonlinear optical material.

Figure 3 Two-photon induced emission spectrum of DEAHAS



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