Synthesis and Nonlinear Optical Characterization of a New Two-photon Absorbing Organic Dye: DMAHAS

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***Trans*-4-(*N*,*N'*-dimethyl amino)-4'-(*N*-2-hydroxyethyl-*N'*-ethyl amino) stilbene (DMAHAS) has been synthesized and characterized by ^{1}H NMR spectra, IR spectra and elemental analysis. Linear absorption, single-photon induced fluorescence and two-photon induced fluorescence were experimentally studied. This new dye has a moderate two-photon absorption cross-section of $\sigma_2 = 0.91 \times 10^{-46}$ cm^4·s/photon at 532 nm by using an open aperture *Z*-scan technique. The result indicates that DMAHAS shows a strong two-photon induced blue fluorescence of 432 nm when pumped with 800 nm laser irradiation.**

Keywords synthesis, two-photon-induced fluorescence, TPA cross-section, DMAHAS

Introduction

The potential for use of two-photon absorbing molecules in applications ranging from optical limiting[1-3] to three dimensional (3D) fluorescence microscopy[4] and 3D microfabrication and optical data storage[5,6] has stimulated research on the design, synthesis, and characterization of new molecules with large two-photon absorptivities.[7,8] The two-photon absorption (2PA) process considered here involves the simultaneous absorption of two photons, either degenerating or nondegenerating, at wavelengths well beyond the linear absorption spectrum of a particular molecule. The major feature[9] distinguishing one-photon absorption (1PA) from two-photon absorption is the fact that the rate of energy absorption is as a function of incident intensity. In one-photon absorption, the rate of light absorption is directly proportional to the incident intensity. By contrast, in simultaneous two-photon absorption, the rate of energy absorption is proportional to the square of the incident intensity. This quadratic or nonlinear dependence has substantial implications. For example, in a medium containing one-photon absorbing chromophores, significant absorption occurs all along the path of a focused light beam of suitable wavelength. This can lead to, *e.g.*, photon-degradation or photonbleaching. In 2PA, negligible absorption occurs except in the immediate vicinity of the focal point of a light beam of approapriate energy. This simultaneous absorption of two or more photons requires high peak power, which is now available from commercial ultrafast pulsed lasers. Thus, certain materials can undergo two-photon absorption at wavelengths far beyond their linear absorption spectrum.

Recent reports of molecular structures with considerably enhanced two-photon absorption cross-section have aroused considerable interest in this phenomenon from both fundamental and applications perspectives.[10-14] In this paper, we report a new organic dye DMAHAS which exhibits a strong two-photon induced blue fluorescence and large 2PA cross-section. Both the nonlinear transmission method utilizing nanosecond pulses and the open aperture *Z*-scan technique have been used to obtain effective 2PA cross-section. The synthetic procedure, linear absorption, and two-photon induced fluorescence are reported in this paper.

Experimental

Reagents

All chemicals were of analytical grade and used with further purification. Xylene, CH_3OH, $(CH_3)_3COH$ and petroleum ether were dried over anhydrous $CaCl_2$ for 24 h and then distilled. THF is refluxed with natrium and then distilled.

Synthesis and characterizations

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 a Perkin 2400 (II) analyzer.

4-(*N*-2-hydroxyethyl-*N'*-ethyl amino) benzaldehyde was synthesized according to the reported methods.[15]

4-(N,N'-dimethyl amino)benzalcohol 5.68 g (0.15 moL) of $NaBH_4$ was added in batches into a reaction flask with 14.9 g (0.1 mol) of 4-(*N*, *N'*-dimethyl

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amino)benzaldehyde which was dissolved in 200 mL of anhydrous methanol forming solution. After stirring for 1 h at room temperature, the mixture solution was heated to reflux for about 2 h. Then it was cooled to room temperature and poured into ice water. The organic layer was extracted by dichloromethane and dried with $MgSO_4$. The pale – yellow oil can be obtained in yield of 90% after the solvent was removed. The product was purified by column chromatography on silica gel using acetidin-petroleum ether (volume ratio = 1 : 1) as eluent. ^1H NMR ($CDCl_3$, 90 MHz) δ: 7.20 (d, J = 8.8 Hz, 2H, 2-H and 6-H of C_6H_4), 6.71 (d, J = 8.8 Hz, 2H, 3-H and 5-H of C_6H_4), 4.51 (s, 2H, OCH_2), 2.91 (s, 6H, $2\times CH_3$), 2.49 (s, 1H, OH).

4-(N, N'-dimethylamino) benzyl triphenylphosphinium iodide 22.5 g (0.086 mol) of PPh_3, 15.5 g (0.258 mol) of HAc and 14.3 g (0.086 mol) of KI were added into a flask with 13.0 g (0.086 mol) of 4-(*N*, *N'*-dimethylamino)benzalcohol which was dissolved in 200 mL of $CHCl_3$ and 7 mL of H_2O forming solution. The mixture was refluxed for about 10 h and then the solvent was removed. The residue was cooled at room temperature and to which 300 mL of xylene was added. The precipitate can be obtained when the mixture was stirred. The solid was recrystallized using xylene-CH_2Cl_2 (1 : 1) and white crystal can be obtained in yield of 85%. ^1H NMR ($CDCl_3$, 90 MHz) δ: 7.73—7.58 (m, 15H, $3\times PC_6H_5$), 6.84 (d, J = 8.8 Hz, 2H, 2-H and 6-H of NC_6H_4), 6.43 (d, J = 8.8 Hz, 2H, 3-H and 5-H of C_6H_4), 4.94 (d, J = 13.16 Hz, 2H, CH_2), 2.87 (s, 6H, $2\times CH_3$).

Synthesis of DMAHAS (Fig. 1) 1.93 g (0.01 mol) of 4-(*N*-2-hydroxyethyl-*N'*-ethyl amino) benzaldehyde was dissolved in 100 mL of THF forming solution. Then the orange solution was poured into a reaction flask with 7.85 g (0.015 mol) of 4-(*N*, *N'*-dimethyl amino) benzyl triphenylphosphinium iodine under dry N_2. The final solution was dropped into the mixed solution of *tert*-butanol and potassium *tert*-butoxide at 0 ℃. After a further stirring for 20 h, the yellow mixture was obtained. The solvent was removed by distilling after neutralized by diluted HCl. The residue was poured into ice water, and extracted by dichloromethane. The organic layer was evaporated and purified by column chromatography on silica gel using acetidin-petroleum ether (volume ratio = 1 : 1) as eluent. The bright green slice crystals were obtained in yield of 60%. ^1H NMR ($CDCl_3$, 90 MHz) δ: 7.30 (d, J = 7.31 Hz, 4H, NC_6H_4), 6.60—7.02 (m, 6H, C_6H_4 and CH = CH); 3.78 (t, J = 6.34 Hz, 2H, OCH_2), 3.40—3.55 (m, 4H, NCH_2); 2.86 (s, 6H, $2\times CH_3$), 2.08 (s, 1H, OH), 1.15 (t, J = 6.82 Hz, 3H, CH_3); IR (KBr) ν: 3278, 3010, 1608, 1520 cm^{-1}. Anal. calcd for $C_{20}H_{26}N_2O$: C 77.22, H 8.36, N 9.01; found C 77.43, H 8.22, N 8.87.

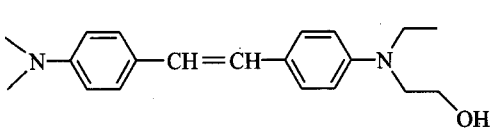

Fig. 1 Chemical structure of DMAHAS.

Results and discussion

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. Fig. 2 shows the linear absorption spectrum of DMAHAS in toluene with a solute concentration of d_0 = 0.00001 mol/L, in which the solvent influence is not included. The spectral curve shows that there is a wide absorption band with two peaks located at 289 nm and 367 nm respectively. There is no linear absorption in the entire spectral range from 400 to 1200 nm.

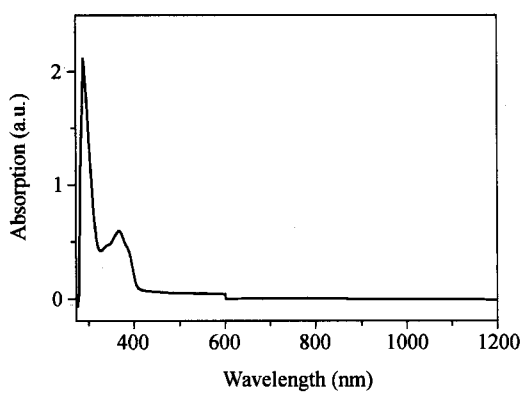

Fig. 2 Linear absorption spectrum of DMAHAS in toluene with a 1-cm path and d_0 = 0.00001 mol/L.

Fig. 3 shows the measured fluorescence spectrum for DMAHAS in toluene with a 1-cm path and a concentration of d_0 = 0.00001mol/L. The one-photon induced fluorescence spectrum was measured by an Edinburgh FLS 920 fluorescence spectrometer. There is a wide emission band with two peaks located at 408 nm and 430 nm, respectively.

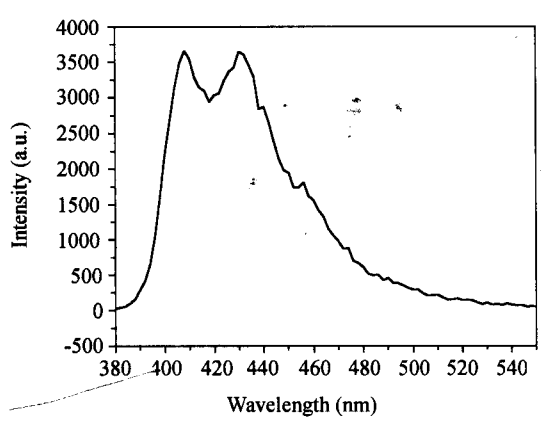

Fig. 3 One-photon induced emission spectrum of DMAHAS in toluene with a 1-cm path and d_0 = 0.00001 mol/L.

Nonlinear optical properties

TPA cross-section from Fig. 2 and Fig. 3, it can be seen that though there is no linear absorption in the entire spectral range from 500 to 1200 nm, the two-photon energy of the near IR radiation between 800 and 1100 nm falls within the strong absorption band of DMAHAS solution. Experimental results show that a quite strong frequency upconverted fluorescence can be easily observed when the solution of the sample was pumped with 800 nm laser irradiation. This suggests that a very strong TPA process may occur inside the sample.

The TPA cross-section was determined by using an open aperture Z-scan technque. The pulsed radiation of 532 nm wavelength was provided by frequency-doubled Q-switched Nd; YAG laser. The pulse duration was determined to be (20 ± 1) ns (full width at half maximum) using photodetector. The laser was capable of generating the pulses with repetition rates of up to 30 Hz. In the Z-scan experiments, however, a repetition rate of 1 Hz was used. The spatial profile of the pulses was of nearly Gaussian form after employing a spatial filter. A beam spliter was used to divide the beam into two arms. The beam reflected by the beam splitter was taken as the reference arm representing the incident light; the other beam was focused through the sample. Double-detector energy-meter (EPM 2000, Molectron) was used in the measurement of input (I_0) /output (I) energy. The sample was contained in a 1-mm thick quartz cell mounted on a translation stage controlled by the computer, which moved the sample position along the Z-axis.

For a temporally Gaussian pulse, for $|q_0| < 1$, the transmittance can be expressed in terms of the peak irradiance in a summation form more suitable for numerical evaluation,[16]

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

Thus, once an open-aperture Z-scan ($S = 1$) is performed, the nonlinear absorption coefficient β 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 σ_2 can be determined by using the following relationship,

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

Fig. 4 depicts the open-aperture trace at a peak irradiance $I_0 = 2.26$ GW/cm^2. Using the above equations, we can get the nonlinear coefficient $\beta = 0.075$ cm/GW, thus $\sigma_2 = 0.91 \times 10^{-46}$ cm^4·s/photon. The final result of σ_2 of DMAHAS is given as above with an experimental uncertainty of $\pm 15\%$.

Two-photon excited fluorescence emission: The two-photon induced emission spectrum can be observed when pumped with 800 nm, 76 MHz, 200 fs pulse Ti: sapphire femosecond laser and a detector with photo-multiplier tube. Fig. 5 illustrates the TPA induced emission spectrum of DMAHAS in toluene with a 1-cm path and $d_0 =$ 0.01mol/L. It can be seen that the peak wavelength and the band width are 432 nm and 57 nm, respectively. Comparing Fig. 3 and Fig. 5, we can see that the TPA induced emission spectrum of the sample DMAHAS with much higher concentration has a red shift as compared to that with much lower concentration sample. This can be explained by the reabsorption of the dye material.

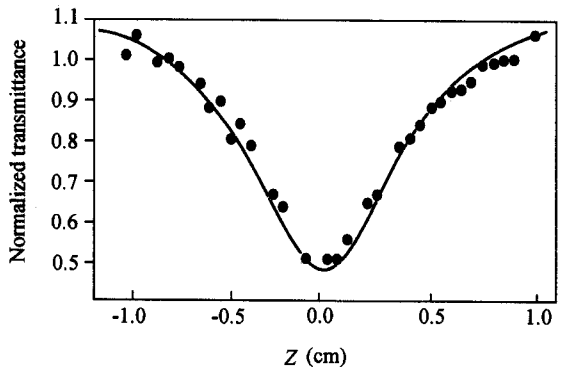

Fig. 4 Normalized open-aperture Z-scan transmittance of DMAHAS in $CHCl_3$ with concentration of 0.002 mol/L using 20 ns pulses at $\lambda = 532$ nm with $I_0 = 2.26$ GW/cm^2.

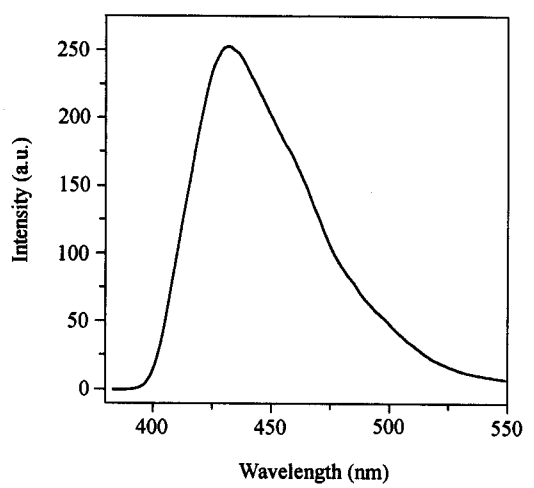

Fig. 5 Two-photon induced emission spectrum of DMAHAS in toluene with a 1-cm path and $d_0 = 0.01$ mol/L.

Conclusions

In conclusion, a new organic dye DMAHAS was synthesized. Linear absorption, single-photon induced fluorescence and two-photon induced fluorescence were studied. This new dye has a moderate TPA cross-section of $\sigma_2 = 0.91 \times 10^{-46}$ cm^4·s/photon at 532 nm. When pumped with 800 nm laser irradiation, it shows a strong two-photon induced blue fluorescence of 432 nm. So we believe that it is quite promising as a useful nonlinear optical material.

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