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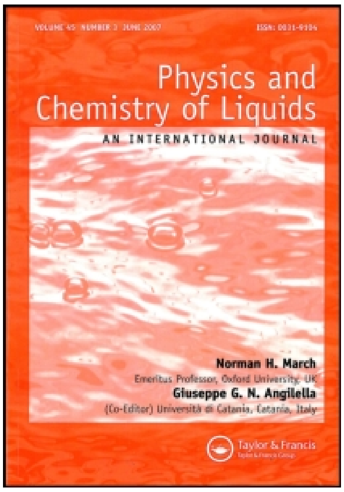

Physics and Chemistry of Liquids

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Synthesis and Nonlinear Optical Characterization of a New Organic Dye DMAHAS

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SYNTHESIS AND NONLINEAR OPTICAL CHARACTERIZATION OF A NEW ORGANIC DYE DMAHAS

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The title compound DMAHAS has been synthesized and characterized by ^{1}H-NMR spectra, IR spectra, and elemental analyses. Linear absorption, single-photon induced fluorescence and two-photon induced fluorescence are experimentally studied. This new dye has a moderate two-photon absorption cross-section of $\sigma_2 = 0.91 \times 10^{-46}\,\mathrm{cm}^4 \cdot$ s/photon at 532 nm by using an open aperture *Z*-scan technique. When pumped with 800 nm laser irradiation, DMAHAS shows a strong two-photon induced blue fluorescence of 432 nm.

Keywords: Two-photon absorption; *Z*-scan; Optical properties; DMAHAS

1. 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 (TPA) process considering 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 from two-photon absorption is the fact that the rate of energy absorption is as a function of incident intensity. In one-photon, 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

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lead to, e.g. photondegradation or photonbleaching. In TPA, negligible absorption occurs except in the immediate vicinity of the focal point of a light beam of appropriate 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 TPA cross-section have generated considerable interest in this phenomenon from both fundamental and applications perspectives [10–14]. In this article, we report a new organic dye DMAHAS which exhibits a strong two-photon induced blue fluorescence and large TPA cross-section. Both the nonlinear transmission method utilizing nanosecond pulses and the open aperture *Z*-scan technique have been used to obtain effective TPA cross-section. The synthesis of procedure, linear absorption, and two-photon induced fluorescence are reported in this article.

2. EXPERIMENTAL

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*-ethylamino)benzaldehyde was synthesized according to the methods reported [15].

4-(N, N-dimethylamino)benzalcohol 0.15 mol $NaBH_4$ was added in batches into a reaction flask with 0.1 mol 4-(*N*, *N*-dimethylamino)benzaldehyde which was dissolved in 200 mL anhydrous methanol. After stirring 1 h at room temperature, the mixture solution was heated to reflux 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 after the solvent was removed. The product was purified by column chromatography on silica gel using acetidin-petroleum ether (volume ratio = 1 : 1) as solvent. ^{1}H-NMR ($CDCl_3$, 90 MHz) δ: 7.20 (2H, d, $J = 8.78$ Hz); 6.71 (2H, d, $J = 8.78$ Hz); 5.25 (1H, s), 4.51 (2H, s), 2.91 (6H, s).

[4-(N, N-dimethylamino)benzyl]triphenylphosphinium salt 22.5 g PPh_3, 15 gHAc and 14.2 g KI were added into a flask with 15 g 4-(*N*, *N*-dimethylamino)benzylalcohol which was dissolved in 200 mL $CHCl_3$ and 7 mL H_2O. The mixture was refluxed about 10 h and then the solvent was removed. The residue was cooled at room temperature and added into 300 mL xylene. The precipitate can be obtained when the mixture was stirred. The solid was recrystallized using xylene–CH_2Cl_2 and white crystal can be obtained. ^{1}H-NMR ($CDCl_3$, 90 MHz): δ: 7.66–7.30 (15H, m); 6.86 (2H, d, $J = 8.3$ Hz); 6.45 (2H, d, $J = 8.77$ Hz); 4.94 (2H, d, $J = 13.16$ Hz); 2.87 (s, 6H).

The synthesis of DMAHAS 0.01 mol 4-(*N*-2-hydroxyethyl-*N*-ethylamino) benzaldehyde was dissolved in 100 mL THF. Then the orange solution was poured into a reaction flask with 0.015 mol [4-(*N*, *N*-dimethylamino)benzyl]triphenylphosphinium salt under the dry N_2. The final solution was dropped into the mixed solution of *tert*-butanol and potassium *tert*-butoxide at 0°C. After a further 20 h's stirring, the

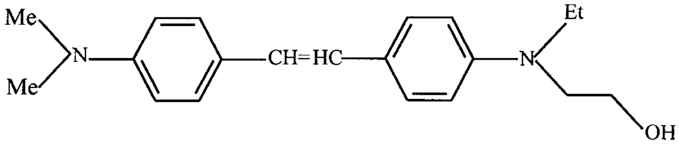

FIGURE 1 Chemical Structure of DMAHAS.

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 removed by evaporation and purified by column chromatography on silica gel using an appropriate solvent as eluent. The bright green slice crystals were obtained with yield of 60% (Fig. 1). ^{1}H-NMR ($CDCl_3$, 90 MHz); δ: 7.30 (4H, d, $J = 7.31$ Hz); 6.60–6.73 (6H, m); 3.78 (2H, t, $J = 6.34$ Hz); 3.40–3.55 (4H, m); 2.86 (s, 6H); 2.08 (s, 1H); 1.08 (3H, t, $J = 6.82$ Hz). Calcd for $C_{20}H_{26}N_2O$: C, H, N: C, 77.22; H, 8.36; N, 9.01. Found: C, 78.43; H, 8.17; N, 8.89. IR ν (KBr) cm^{-1}: 3277–3282 (–OH); 3010.3 (aromatic C = C, s); 2966.1 (C = C–H, ms); 1608.0 (C = C, s); 1520.0 (aromatic C = C, s).

3 RESULTS AND DISCUSSION

3.1 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 curette. Figure 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 has shown that there is a wide absorption band with two peaks located at 289 and 367 nm respectively. There is no linear absorption in the entire spectral range from 400 to 1200 nm.

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

3.2 Nonlinear Optical Properties

3.2.1 TPA Cross-section Measurement

The TPA cross-section was determined by using an open aperture *Z*-scan technique. The pulsed radiation of 532 nm wavelength was provided by frequency-doubled *Q*-switched 1064 nm 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

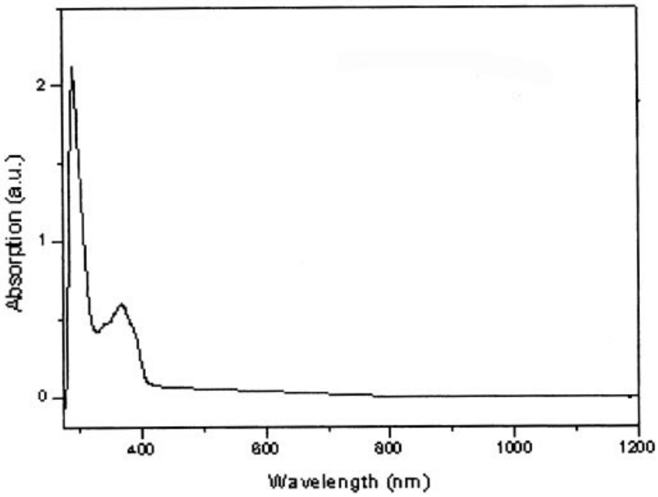

FIGURE 2 Linear absorption spectra of DMAHAS in toluene with a 1 cm path and $d_0 = 0.00001$ mol/L.

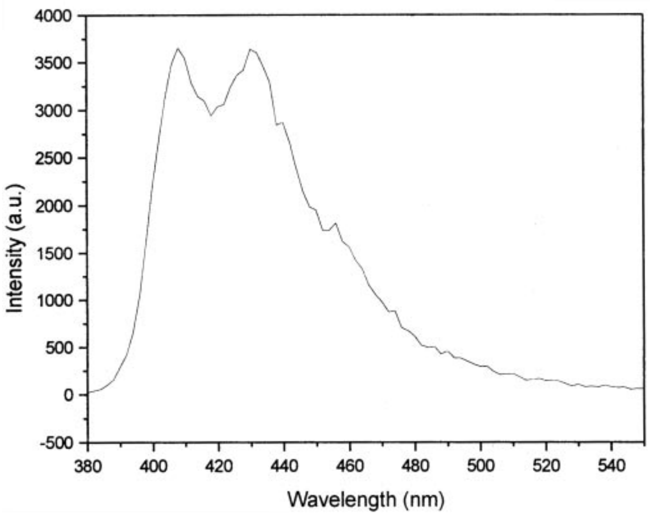

FIGURE 3 One-photon induced emission spectra of DMAHAS in toluene with a 1 cm path and $d_0 = 0.00001$ mol/L.

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],

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

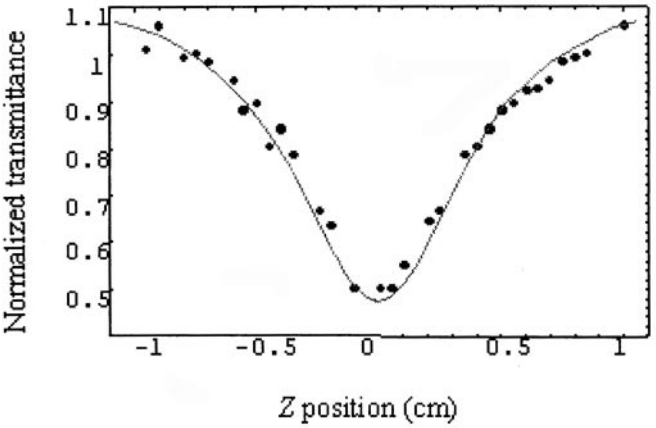

FIGURE 4 Normalized open-aperture *Z*-scan transmittance of DMAHAS in $CHCl_3$ with concentration of 0.002 mol/L.

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,

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

Figure 4 depicts the open-aperture trace at a peak irradiance $I_0 = 2.26\,\mathrm{GW/cm^2}$. Using the above equations, we can get the nonlinear coefficient $\beta = 0.075\,\mathrm{cm/GW}$, thus $\sigma_2 = 0.91 \times 10^{-46}\,\mathrm{cm^4\,s/photon}$. The final result of σ_2 of DMAHAS is given as above with an experimental uncertainty of ±20%.

3.2.2 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. Figure 5 illustrates the TPA induced emission spectrum of 1 cm path DMAHAS in toluene of 0.01 mol/L concentration. It can be seen that the peak wavelength and the bandwidth are 432 and 57 nm, respectively. Comparing Figs. 3 and 5, we can see that the TPA induced emission spectrum of the sample DMAHAS with much higher concentration has redshift as compared to that in the much lower concentration sample. This can be explained by the reabsorption of the dye material.

4 CONCLUSIONS

In conclusion, a new organic dye DMAHAS was synthesized. Linear absorption, single-photon induced fluorescence and two-photon induced fluorescence are experimentally studied. This new dye has a moderate TPA cross-section of $\sigma_2 = 0.91 \times 10^{-46}\,\mathrm{cm^4\,s/photon}$ at 532 nm. When pumped with 800 nm laser irradiation,

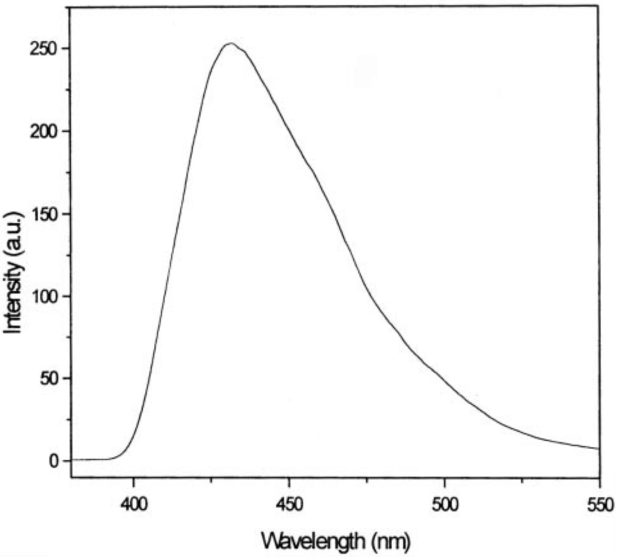

FIGURE 5 Two-photon induced emission spectrum of DMAHAS in toluene with a 1 cm path and $d_0 = 0.01$ mol/L.

it shows a strong two-photon induced blue fluorescence of 432 nm. So we believe that it is a quite promising application value as a useful nonlinear optical material.

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