

# Synthesis and Properties of a New Two-photon-absorbed Material DMAEAS

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*Trans*-4-(*N,N'*-dimethyl amino)-4'-(*N,N'*-diethyl amino) stilbene (DMAEAS) has been synthesized and characterized by  $^1\text{H}$  NMR spectra, IR spectra, and elemental analyses. Its linear absorption, single-photon induced fluorescence and two-photon induced fluorescence are experimentally studied. This new dye has a great two-photon absorption (TPA) cross-section of  $\sigma_2 = 1.16 \times 10^{-46} \text{ cm}^4 \cdot \text{s}/\text{photon}$  at 532 nm by using an open aperture Z-scan system. When pumped with 800 nm laser irradiation, DMAEAS shows a strong two-photon induced blue fluorescence of 440 nm.

**Keywords** synthesis, two-photon-induced fluorescence, TPA cross-section, DMAEAS

## Introduction

Substituted stilbenes have significant potential applications such as fluorescence microscopy, two-photon photodynamic therapy, optical power limiting, three-dimensional storage, and three-dimensional microfabrication.<sup>1-4</sup> These dyes have strong tendency of intra-molecular charge transfer under the excited state. As a result, they usually exhibit large two-photon absorption (TPA), in the meanwhile emit strong up-converted fluorescence. On the other hand, their solutions generally display linear transmission of  $> 90\%$  at wavelength of  $\geq 500 \text{ nm}$ . So it is especially suitable for the optical power limiting applied in protecting the eyes of people, sensors and sensitive optical components. Moreover, they have the ability of two-photon initiated polymerizations, which can be further applied in three-dimensional microfabrication.<sup>5</sup> Here we report a new asymmetrically substituted stilbene *trans*-4-(*N,N'*-dimethyl amino)-4'-(*N,N'*-diethyl amino) stilbene (DMAEAS) (Fig. 1) that exhibits great TPA cross-section and strong two-photon induced blue fluorescence.

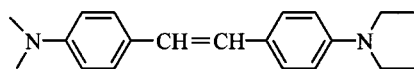


Fig. 1 Chemical structure of DMAEAS.

## Experimental

### Reagents

All chemicals were of analytical grade and used with further purification. Xylene,  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3)_3\text{COH}$  and petroleum ether were dried over anhydrous  $\text{CaCl}_2$  for 24 h and then distilled.  $\text{Et}_3\text{N}$  was dried with  $\text{KOH}$ , and THF is refluxed with sodium 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 an FX-90Q NMR spectrometer. Element analyses were performed on a Perkin 2400 (II) apparatus.

4-(Diethyl amino)benzaldehyde was synthesized according to the methods reported.<sup>6</sup>

4-(Diethyl amino) benzalcohol 5.68 g (0.15 mol) of  $\text{NaBH}_4$  was added in batches into a reaction flask with 17.7 g (0.1 mol) of 4-(diethyl amino)benzaldehyde dissolved in 200 mL of anhydrous methanol. After being stirred for 1 h at room temperature, the mixture solution was heated to reflux for 2 h. Then it was cooled to room temperature and poured into ice water. The organic layer was extracted with dichloromethane and dried with  $\text{MgSO}_4$ . The pale-yellow oil could be obtained with yield of 95% after the solvent was removed. The product was purified by column chromatography on silica gel using acetidin-petroleum ether ( $V:V, 1:1$ ) as eluent.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 7.20 (d,  $J = 8.8 \text{ Hz}$ , 2H, 2-H and 6-H of  $\text{C}_6\text{H}_4$ ), 6.66 (d,  $J = 8.8 \text{ Hz}$ , 2H, 3-H and 5-H of  $\text{C}_6\text{H}_4$ ), 4.51 (s, 2H,  $\text{OCH}_2$ ), 3.34 (q,  $J = 6.8 \text{ Hz}$ , 4H,  $2 \times \text{CH}_2\text{N}$ ), 2.02 (s, 1H, OH), 1.14 (t,  $J = 6.8 \text{ Hz}$ , 6H,  $2 \times \text{CH}_3$ ).

4-(Diethyl amino) benzyl triphenylphosphonium iodide 22.5 g (0.086 mol) of  $\text{PPh}_3$ , 15.5 g (0.258 mol) of  $\text{HAc}$  and 14.3 g (0.086 mol) of  $\text{KI}$  were added into a flask with 15.4 g (0.086 mol) of 4-(diethyl amino)benzalcohol dis-

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Received July 11, 2002; revised September 10, 2002; accepted October 25, 2002.

Project supported by the Major State Basic Research Development Program (No. G1998061402) and the National Natural Science Foundation of China (No. 50173015).

solved in 200 mL of  $\text{CHCl}_3$  and 7 mL of  $\text{H}_2\text{O}$ . The mixture was refluxed for 10 h and then the solvent was removed. The residue was cooled at room temperature and added into 300 mL of xylene. The precipitate could be obtained with yield of 85% when the mixture was stirred. The solid was recrystallized using xylene- $\text{CH}_2\text{Cl}_2$  and white crystal can be obtained.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 7.82–7.56 (m, 15H,  $3 \times \text{PC}_6\text{H}_5$ ), 6.83 (d,  $J = 8.3$  Hz, 2H, 2-H and 6-H of  $\text{NC}_6\text{H}_4$ ), 6.41 (d,  $J = 8.3$  Hz, 2H, 3-H and 5-H of  $\text{C}_6\text{H}_4$ ), 4.90 (d,  $J = 12.7$  Hz, 2H,  $\text{CH}_2$ ), 3.27 (q,  $J = 7.3$  Hz, 4H,  $2 \times \text{NCH}_2$ ), 1.09 (t,  $J = 7.3$  Hz, 6H,  $2 \times \text{CH}_3$ ).

**Synthesis of DMAEAS** 1.49 g (0.01 mol) of 4-(dimethyl amino)benzaldehyde was dissolved in 100 mL of THF. Then the orange solution was poured into a reaction flask with 8.27 g (0.015 mol) of 4-(diethyl amino)benzyl triphenylphosphonium iodine under the dry  $\text{N}_2$ . The final solution was dropped into the mixed solution of *tert*-butanol and potassium *tert*-butoxide at 0 °C. After stirring for further 20 h, the yellow mixture was obtained. The solvent was removed by distilling after neutralization with diluted HCl. The residue was poured into ice water, and extracted with dichloromethane. The organic layer was removed by evaporation and purified by column chromatography on silica gel using acetidin-petroleum ether ( $V:V$ , 1:1) as eluent. The bright green slice crystals were obtained with yield of 60% and m. p. of 161 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.35 (d,  $J = 8.3$  Hz, 4H,  $\text{C}_6\text{H}_4$ ), 6.65–6.84 (m, 6H,  $\text{C}_6\text{H}_4$  and  $\text{CH}=\text{CH}$ ), 3.36 (q,  $J = 7.3$  Hz, 4H,  $2 \times \text{NCH}_2$ ), 2.95 (s, 6H,  $2 \times \text{CH}_3$ ), 1.17 (t,  $J = 7.3$  Hz, 6H,  $2 \times \text{CH}_3$ ); IR (KBr)  $\nu$ : 2978.6 (w, aromatic C=C-H), 2924.5 (ms, C=C-H), 1609.7 (s, C=C), 1519.9 (s, aromatic C=C)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{20}\text{H}_{26}\text{N}_2$ : C 81.63, H 8.84, N 9.52; found C 81.78, H 9.16, N 9.14.

## 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 and one-photon induced emission spectrum of DMAEAS in DMF 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 336 nm and 371 nm respectively. There is no linear absorption in the entire spectral range from 420 to 1200 nm.

Fig. 3 shows the measured fluorescence spectrum for a 1-cm path DMAEAS solution with a concentration of  $d_0 = 0.00001$  mol/L. The single-photon induced fluorescence spectrum was measured by an Edinburgh FLS 920 fluorescence spectrometer. There is a wide absorption band with two peaks located at 420 nm and 438 nm, respectively.

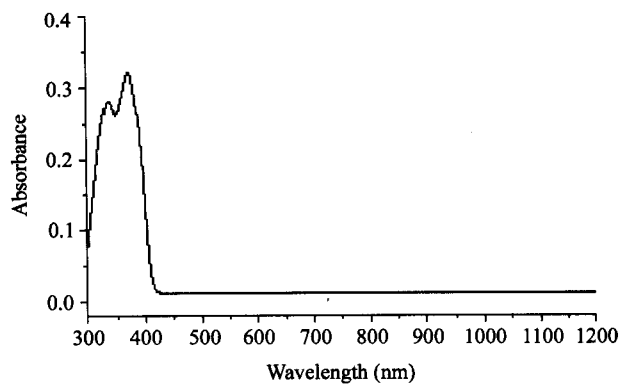


Fig. 2 Linear absorption spectra of DMAEAS in DMF with a 1-cm path and  $d_0 = 0.00001$  mol/L.

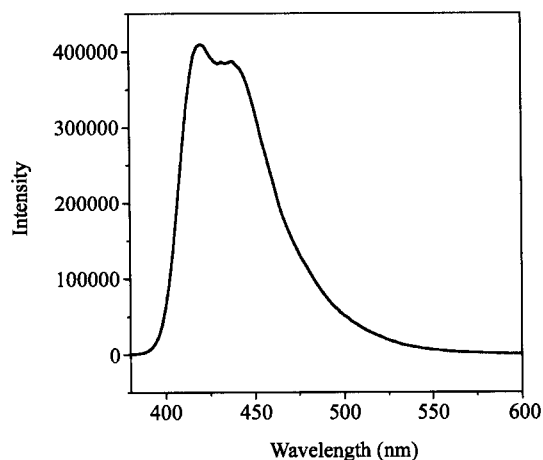


Fig. 3 One-photon induced emission spectrum of DMAEAS in DMF with a 1-cm path and  $d_0 = 0.00001$  mol/L.

### Nonlinear optical properties

#### TPA cross-section

From Fig. 2 and Fig. 3, it can be seen that although 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 DMAEAS solution. Experimental studies have shown that a quite strong frequency up-converted 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.

Z-Scan system with an open aperture ( $S = 1$ ) is insensitive to the nonlinear refraction, and can be used to measure the nonlinear absorption cross-section. Such Z-scan traces with no aperture are expected to be symmetric with respect to the focus ( $Z = 0$ ), where they have a minimum transmittance (*e.g.*, multi-photon absorption) or a maximum transmittance (*e.g.*, saturation of absorption). In fact the nonlinear coefficient  $\beta$  can be easily calculated from the transmittance curves.

For a temporally Gaussian pulse, the normalized energy transmittance can be given as<sup>7</sup>

$$T(z, S = 1) = \frac{1}{\sqrt{\pi}q_0(z,0)} \int_{-\infty}^{\infty} \ln(1 + q_0(z,0))e^{-r^2} dr \quad (1)$$

where  $q_0(z, t) = \beta I_0(t) L_{\text{eff}} / (1 + z^2/z_0^2)$ ,  $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ ,  $L$  is the sample length and  $\alpha$  is the linear absorption coefficient. When there is no linear absorption (*e.g.*,  $\alpha \rightarrow 0$ ),  $L_{\text{eff}}$  equals  $L$ .

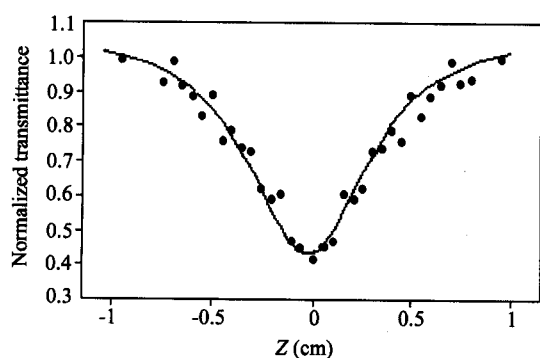
For  $|q_0| < 1$ , the transmittance can be expressed in terms of the peak irradiance in a summation form more suitable for numerical evaluation,

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

Thus, once an open-aperture  $Z$ -scan ( $S = 1$ ) is performed, the nonlinear absorption coefficient  $\beta$  can be unambiguously deduced and if the concentration  $d_0$  (in unit of mol/L) of the solution is known, the molecular TPA cross section  $\sigma_2$  (in unit of  $\text{cm}^4 \cdot \text{s}/\text{photon}$ ) can be determined by using the following relationship:

$$\beta = \sigma_2 N_0 = h\nu\sigma_2 N_A d_0 \times 10^{-3} \quad (3)$$

We have accomplished TPA cross section measurement for the DMAEAS sample with the thickness of 2 mm and a relatively high concentration of  $d_0 = 0.002$  mol/L, by using a focused 20 ns, 1064 nm mode-locked Nd:YAG laser. Fig. 4 depicts the open-aperture trace, at a peak irradiance  $I_0 = 2.26$  GW/ $\text{cm}^2$ . Using the above equations, we can get the nonlinear coefficient  $\beta = 0.095$  cm/GW, thus  $\sigma_2 = 1.16 \times 10^{-46}$   $\text{cm}^4 \cdot \text{s}/\text{photon}$ . The final result of  $\sigma_2$  of DMAEAS is given as above with an experimental uncertainty of  $\pm 15\%$ .

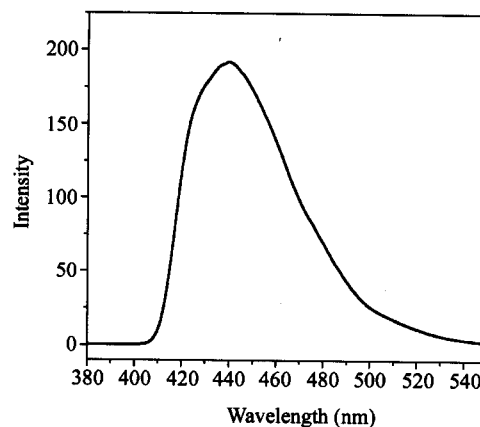


**Fig. 4** Normalized open-aperture  $Z$ -scan transmittance of DMAEAS in  $\text{CHCl}_3$  with concentration of 0.002 mol/L using 20 ns pulses at  $\lambda = 532$  nm with  $I_0 = 2.26$  GW/ $\text{cm}^2$ .

#### 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 femtosecond laser and a detector with photo multiplier tube. Fig. 5 illustrates the TPA induced emission spectrum of 1-cm path DMAEAS in DMF of 0.01 mol/L concentration.

It can be seen that the peak wavelength and the bandwidth are 440 nm and 54 nm, respectively. Comparing Fig. 3 and Fig. 5, we can see that the TPA induced emission spectrum of the sample DMAEAS with much higher concentration has a red-shift as compared to that in the much lower concentration sample. This can be explained by the reabsorption of the dye material.



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

In conclusion, a new organic dye DMAEAS was synthesized. Its linear absorption, single-photon induced fluorescence and two-photon induced fluorescence are experimentally studied. This new dye has a great TPA cross-section of  $\sigma_2 = 1.16 \times 10^{-46}$   $\text{cm}^4 \cdot \text{s}/\text{photon}$  at 532 nm. When pumped with 800 nm laser irradiation, it shows a strong two-photon induced blue fluorescence of 440 nm. So we believe that it is quite promising for application as a useful nonlinear optical material.

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