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Synthesis and nonlinear optical properties of new symmetrically substituted stilbenes

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Abstract

Three new chromophores and *trans*-4-(*N*-(ethyl 4″-nitrobenzoate)-*N*-ethyl amino)-4′-(dimethyl amino) stilbene (DMANHAS) have been synthesized and whose chemical structures have been characterized by ^{1}H NMR, IR, and elemental analyses. Linear absorption, single-photon-induced fluorescence and two-photon-induced fluorescence are experimentally studied. *Trans*-4-(*N*-2-hydroxyethyl-*N*-ethyl amino)-4′-(dimethyl amino)stilbene (DMAHAS) and *trans*-4-(*N*-2-hydroxyethyl-*N*-ethyl amino)-4′-(diethyl amino)stilbene (DEAHAS) have effective two-photon absorption cross-sections of $\sigma_2 = 0.91 \times 10^{-46}\,\mathrm{cm}^4\,\mathrm{s/photon}$ and $\sigma_2 = 1.19 \times 10^{-46}\,\mathrm{cm}^4\,\mathrm{s/photon}$ at 532 nm by using an open aperture Z-scan technique, respectively. When pumped with 800 nm laser irradiation, DMAHAS and DEAHAS indicate strong two-photon-induced blue fluorescence of 436 and 440 nm, respectively, while *trans*-4-(*N*-(ethyl 4″-nitrobenzoate)-*N*-ethyl amino)-4′-(diethyl amino) stilbene (DEANHAS) and DMANHAS exhibit no fluorescence.

Keywords: Synthesis; Two-photon absorption; *Z*-scan; Nonlinear optical properties; DEAHAS; DMAHAS; DEANHAS; DMANHAS

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 process of two-photon absorption (2PA) distinguishing one-photon absorption (1PA) considered here involves the simultaneous absorption of two photons, either degenerate or non-degenerate, at wavelengths well beyond the linear absorption spectrum of a particular molecule [9]. Though a subject of contemporary investigation, the simultaneous absorption of two quanta of energy was first predicted in 1931 by Goeppert-Mayer [10]. In present research, a number of chromophores with large two-photon absorption cross-sections have been provided by theoretical and experimental studies [11–15]. Among them, symmetrically substituted stilbene-type chromophores are most widely noticed: first, because of their larger two-photon absorption cross-section values as compared to the respective asymmetric counterparts, [15] and second because they offer the advantage of high transmission at the range of visible spectrum (400–800 nm). Although symmetric molecules show very small dipole moments in the ground state, quantum chemical calculations have confirmed that the substantial change in both transition dipole moment and quadrupole moment [12] upon excitation for this type of molecules contributes to inter-molecular charge transfer and results in their larger two-photon absorptivities. Therefore, to synthesize this type of symmetric chromophores is of great importance to their applications.

In this paper, we use an efficient methodology to synthesize *p*-substituted benzyltriphenylphosphinium salts that were used to synthesize these three new chromophores and DMANHAS. Although the molecular structure of DMANHAS had been mentioned [16], but its nonlinear optical properties have not been detailed. Here we synthesized this compound and three new chromophores. The systematic measurements of one-photon/two-photon absorption cross-section and

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one-photon/two-photon fluorescence of these dyes are all reported in this paper.

2. Experimental

2.1. 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. Et_3N was dried with KOH, and THF was refluxed with natrium and then distilled.

2.2. 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 and 4-(*N*-2-hydroxyethyl-*N*-ethyl amino)benzaldehyde were synthesized according to the methods reported [17].

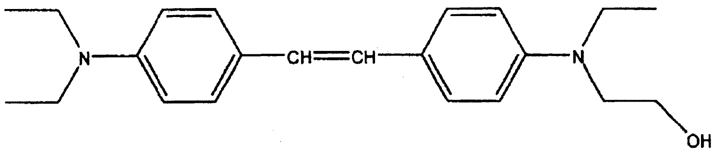
4-(Diethyl amino)benzalcohol: 5.68 g (0.15 mol) of $NaBH_4$ was added in batches into a reaction flask with 17.7 g (0.1 mol) of 4-(diethyl amino)benzaldehyde which was dissolved in 200 mL anhydrous methanol. After stirring for 1 h at room temperature, the mixture solution was heated to reflux about 2 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 with a yield of 95%. ^1H NMR, $\delta(CDCl_3$, 90 MHz): 7.20 ($d, J = 8.8$ Hz, 2H); 6.66 ($d, J = 8.8$ Hz, 2H); 4.51(*s*, 2H), 3.34 ($q, J = 6.8$ Hz, 4H), 2.02 (*s*, 1H), 1.14 ($t, J = 6.8$ Hz, 6H). Anal. Calcd for $C_{11}H_{17}NO$: C 73.74%, H 9.50%, and N 7.82%. Found: C 73.82%, H 9.47%, and N 7.85%.

[4-(Diethyl amino)benzyl]triphenylphosphinium iodide: 22.5 g (0.086 mol) of PPh_3, 15.5 g (0.258 mol) of AcOH and 14.3 g (0.086 mol) of KI were added into a flask with 15.4 g (0.086 mol) of 4-(diethyl amino)benzalcohol which was dissolved in 200 mL of $CHCl_3$ and 7 mL of H_2O. The mixture was refluxed for about 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 when the mixture was stirred. The solid was recrystallized using xylene–CH_2Cl_2 and white crystal can be obtained. The yield is of 75%. ^1H NMR, $\delta(CDCl_3$, 90 MHz): 7.82–7.56 (*m*, 15H); 6.83 ($d, J = 8.3$ Hz, 2H); 6.41($d, J = 8.3$ Hz, 2H), 4.90($d, J = 12.7$ Hz, 2H), 3.27 ($q, J = 7.3$ Hz, 4H), 1.09 ($t, J = 7.3$ Hz, 6H). Anal. Calcd for $C_{29}H_{31}NPI$: C 63.16%, H 5.63%, and N 2.54%. Found: C 63.29%, H 5.58%, and N 2.57%.

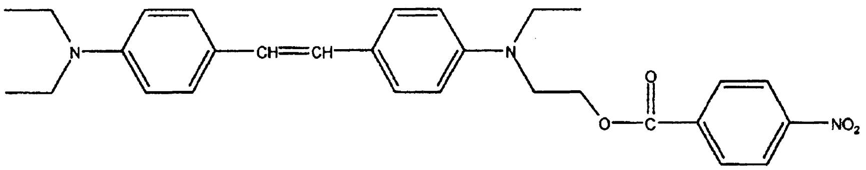
Synthesis of *trans*-4-(*N*-2-hydroxyethyl-*N*-ethyl amino)-4′-(diethyl amino)stilbene (DEAHAS): 1.93 g (0.01 mol) of 4-(*N*-2-hydroxyethyl-*N*-ethyl amino)benzaldehyde was dissolved in 100 mL tetrahydrofuran. Then the orange solution was poured into a reaction flask with 8.26 g (0.015 mol) of [4-(diethyl amino)benzyl]triphenylphosphinium iodine under 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 stirring, the yellow mixture was obtained. The solvent was removed by distilling after being 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 a yield of 30% and m.p. of 134.6°C. ^1H NMR, $\delta(CDCl_3$, 90 MHz): 7.35 ($d, J = 8.29$ Hz, 4H); 6.72–7.22 (*m*, 6H); 3.77 ($t, J = 6.34$ Hz, 2H); 3.40–3.56 (*m*, 8H); 1.98 (1H, *s*); 1.15 ($t, J = 6.82$ Hz, 9H). IR (KBr)*v*: 3281.7–3286.9 (–OH), 3012.6 (aromatic C = C–H, *w*), 2968.2 (C = C–H, *ms*), 1609.2 (C = C, *s*), and 1521 (aromatic C = C, *s*) cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_2O$: C 78.11%, H 8.87%, and N 8.28%. Found: C 77.97%, H 8.94%, and N 8.21%.

Synthesis of *trans*-4-(*N*-(ethyl 4″-nitrobenzoate)-*N*-ethyl amino)-4′-(diethyl amino) stilbene (DEANHAS). 1.02 g (0.0055 mol) of 4-nitrobenzoyl chloride was dissolved in 30 mL CH_2Cl_2. Then the pale-yellow solution was dropped into a flask with 1.86 g (0.0055 mol) of DEAHAS which was dissolved in 30 mL CH_2Cl_2 and 1 mL Et_3N. The mixture was refluxed about 24 h and cooled to room temperature. Then the red solution 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 = 1:1) as eluent. The amber powder can be obtained after the eluent was removed with a yield of 75% and m.p. of 128.5°C. ^1H NMR, $\delta(CDCl_3$, 90 MHz): 8.30 ($d, J = 8.30$, 2H); 8.23 ($d, J = 8.23$, 2H); 7.36 ($d, J = 8.29$ Hz, 4H); 6.73–7.23 (*m*, 6H); 4.54 ($t, J = 6.34$ Hz, 2H); 3.42–3.79 (*m*, 8H); 1.18 ($t, J = 4.41$ Hz, 9H). IR(KBr)*v*: 2930.0 (aromatic, C = C–H, *ms*), 2871.0 (C = C–H, *ms*), 1715.5 (C = O, *s*), 1608.3 (C = C, *s*), and 1518.3 (aromatic, C = C, *s*) cm^{-1}. Aanl. Calcd for $C_{29}H_{33}N_3O_4$: C 71.46%; H 6.78%; and N 8.62%. Found: C 71.78%; H 6.52%; and N 8.49%.

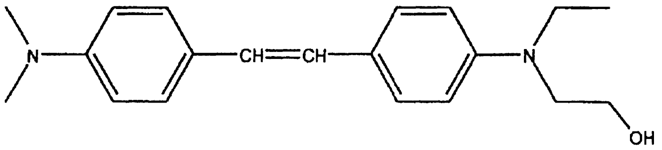
Using a similar method, we synthesized new compound of *trans*-4-(*N*-2-hydroxyethyl-*N*-ethyl amino)-4′-(dimethyl amino)stilbene (DMAHAS) with green grain crystals. The yield is of 35% and m.p. is of 146.6°C.



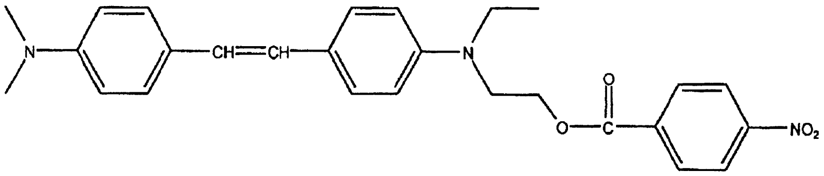
DEAHAS



DEANHAS



DMAHAS



DMANHAS

Fig. 1. Chemical structure of four chromophores.

^{1}H NMR ($CDCl_3$, 90 MHz): δ: 7.30 (4H, $d, J=7.31$ Hz); 6.60–7.02 (m, 6H); 3.78 ($t, J=6.34$ Hz, 2H); 3.40–3.55 (m, 4H); 2.86 (s, 6H); 2.08(s, 1H); 1.15 ($t, J=6.82$ Hz, 3H). IR (KBr)v: 3278–3285 (–OH), 3010.3 (aromatic C = C, s), 1608.0 (C = C, s), and 1520.0 (aromatic C = C, s) cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_2O$: C 77.22%, H 8.36%, and N 9.01%. Found: C 77.43%, H 8.22%, and N 8.87%.

The amber powder, *trans*-4-(N-(ethyl 4″-nitrobenzoate)-N-ethyl amino)-4′-(dimethyl amino) stilbene (DMANHAS), were obtained by the similar synthetically method. The yield is of 77% and m.p. is of 143°C ^{1}H NMR, δ($CDCl_3$, 90 MHz): 8.30 ($d, t=8.28$, 2H), 8.25 ($d, t=8.24$ Hz, 2H); 7.34 ($d, J=7.31$ Hz, 4H); 6.60–7.02 (m, 6H); 4.51 ($t, J=6.34$, 2H); 3.42 ~ 3.78 (m, 4H), 2.97(s, 6H); 1.17 ($t, d=5.85$ Hz, 3H). IR(KBr)v: 3013.1 (aromatic C = C–H, w), 2971.7 (C = C–H, ms), 1724.3 (C = O, s), 1607.8 (C = C, s), and 1523.7 (aromatic C = C, s) cm^{-1}. Anal. Calcd for $C_{27}H_{29}N_3O_4$: C, H, N: C 70.59%, H 6.32%, and N 9.15%. Found: C 70.86%, H 6.13%, and N 9.09%. (Fig. 1)

3. Results and discussion

3.1. Linear optical properties

The linear absorption spectrum was measured on an Hitachi U-3500 UV–VIS–IR recording spectrophotometer by using a 1 cm quartz curette. Fig. 2 shows the linear absorption spectrum of four dyes in CH_2Cl_2 with a solute concentration of $d_0 = 0.00001$ mol/L, in which the solvent influence is not included. From Fig. 2 one can see that the linear absorption spectra of DMAHAS and DMANHAS show the maximum peaks located at 368 and 366 nm, respectively. While DEAHAS and DEANHAS all possess their maximum peaks located at 370 nm. There is no linear absorption in the entire spectral range from 420 to 1200 nm for four chromophores.

Fig. 3 shows the measured one-photon fluorescence spectra of four dyes for a 1 cm path in CH_2Cl_2 with a concentration of $d_0 = 0.00001$ mol/L. It was measured by an Edinburgh FLS 920 fluorescence spectrometer.

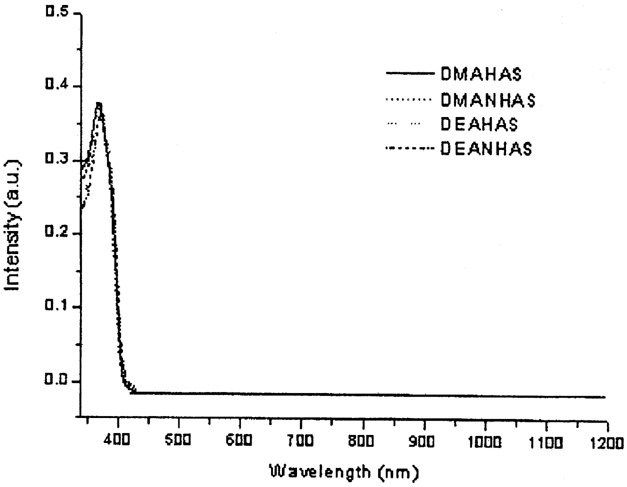


Fig. 2. Linear absorption spectra of four chromophores in CH_2Cl_2 with a 1 cm path and $d_0 = 0.00001$ mol/L.

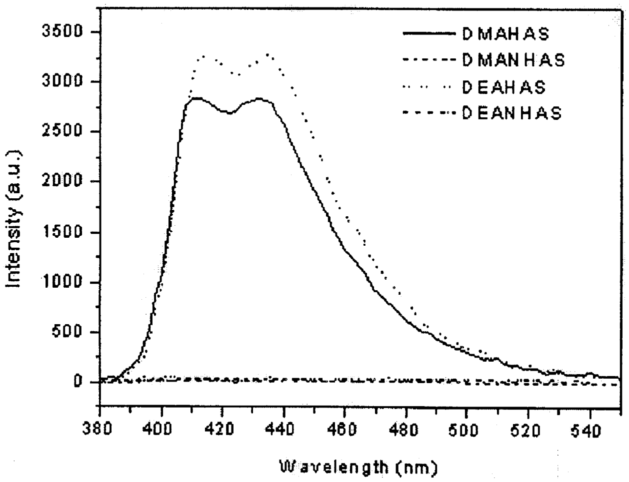


Fig. 3. One-photon induced emission spectra of four chromophores in CH_2Cl_2 with a 1 cm path and $d_0 = 0.00001$ mol/L.

From Fig. 3 one can see that DEAHAS and DMAHAS show strong fluorescence intensity while DEANHAS and DMANHAS exhibit no fluorescence. DEAHAS and DMAHAS all have two wide absorption bands with peak wavelengths at 414, 434, 412 and 432 nm respectively. Fig. 3 shows that the fluorescence intensity of DEAHAS is stronger than that of DMAHAS and the maximum peak wavelength is red shifted. This can be explained by increasing the donor strength.

3.2. Nonlinear optical properties

3.2.1. 2PA cross-section measurement

From Fig. 2 one can see that there is no linear absorption in the entire spectral range from 420 to 1200 nm, nevertheless green radiation in 532 nm is strongly absorbed by the dyes solution. Therefore, an effective two-photon absorption process can occur inside the samples. The 2PA cross-section of DEAHAS and DMAHAS were measured due to their strong fluorescence intensity. It was determined by using an open aperture Z-scan technique. The pulsed radiation of 532 nm wavelengths 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 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 [18]:

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

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 2PA cross-section σ_2 can be determined by using the following relationship:

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

Figs. 4 and 5 depict the open-aperture trace of DEAHAS and DMAHAS at a peak irradiance $I_0 = 2.26\ \mathrm{GW/cm^2}$, respectively. Using the above equations, the nonlinear coefficient β of DEAHAS and DMAHAS is 0.098 and 0.075 cm/GW, respectively. And the 2PA cross-section σ_2 of them is 1.19×10^{-46} and $0.91 \times 10^{-46}\ \mathrm{cm^4\,s/photon}$, respectively. The final result of σ_2 is given as above with an experimental uncertainty of $\pm 20\%$.

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. Fig. 6 illustrates the 2PA-induced emission spectrum of four dyes in CH_2Cl_2 at 0.01 mol/L concentration. It can be seen that the maximum peak wavelength and the bandwidth of DEAHAS are 440 and 61 nm, respectively. For DMAHAS, the maximum peak wavelength and the bandwidth are 436 and 55 nm, respectively. No fluorescence was observed for DEANHAS and DMANHAS. The fluorescence intensity of DEAHAS is stronger than that of DMAHAS and the maximum peak wavelength is red shifted compared to DMAHAS. This can also be explained by increasing the donor strength. The single-photon and two-photon fluorescence of DEANHAS and DMANHAS disappeared compared to DEAHAS and DMAHAS. The reason may be explained by fast intramolecular electron transfer [16]. Comparing Figs. 3 and 6, one can see that the 2PA induced emission spectrum of DMAMAS and DEAHAS with much higher concentration have a red shift as compared to that in the much lower concentration sample. This can be explained by the reabsorption of the dye material (Table 1).

4. Conclusions

In conclusion, three new organic dyes and DMANMAS have been synthesized and their chemical structures have been characterized by IR, ^{1}H NMR and elemental analyses, respectively. DEAHAS and DMAHAS exhibit effective 2PA cross-section and strong two-photon-induced blue fluorescence. While DEANHAS and DMANHAS show no fluorescence due to fast intramolecular electron transfer. The results indicate that varying the electron-donating or electron-accepting strength of the end groups can vary the charge

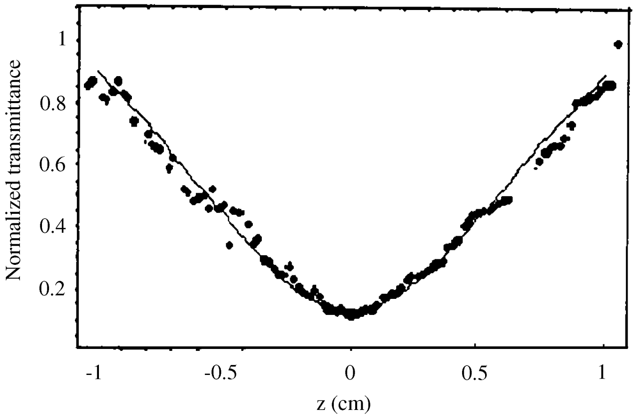


Fig. 4. Normalized open-aperture Z-scan transmittance of DEAHAS in $CHCl_3$ with concentration of 0.002 mol/L using 20 ns pulses at $\lambda = 532$ nm with $I_0 = 2.26$ GW/cm^2.

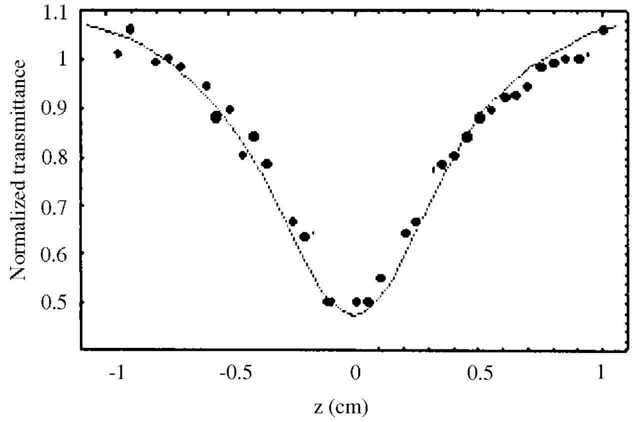


Fig. 5. Normalized open-aperture Z-scan transmittance of DMAHAS in $CHCl_3$ with concentration of 0.002 mol/L using 20 ns pulses at $\lambda = 532$ nm with $I_0 = 2.26$ GW/cm^2.

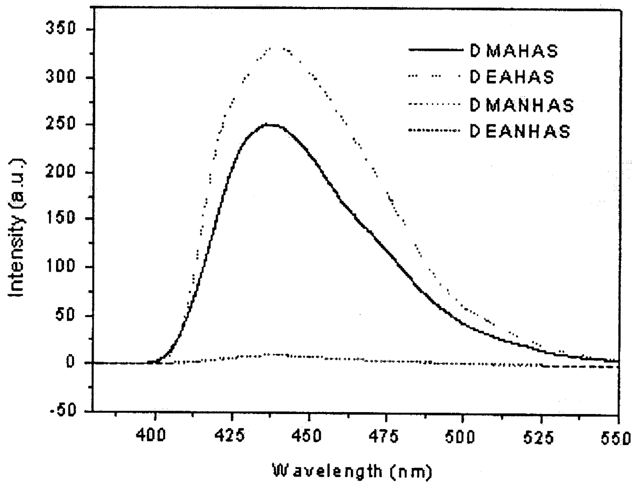


Fig. 6. Two-photon-induced emission spectrum of four choromophores in CH_2Cl_2 with a 1 cm path and $d_0 = 0.01$ mol/L.

Table 1
Linear and nolinear optical properties of four chromophores

Compd.	$\square^{1PA}_{max}$/nm	$\square^{2PA}_{max}$/nm (σ_2, cm^4 s/photon)	$\square^{1PF}_{max}$/($\square$ex) nm	$\square^{2PF}_{max}$/($\square$ex) nm
DEAHAS	370	532 1.19×10^{-46}	414, 434 (370)	440 800
DEANHAS	370		No (370)	No 800
DMAHAS	368	532 0.91×10^{-46}	412, 414 (370)	436 800
DMANHAS	366		No (370)	No 800

redistribution that can lead to the fluorescence quenched.

Acknowledgments

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References

[1] J.D. Bhawalkar, G.S. He, P.N. Prasad, Rep. Prog. Phys. 59 (1996) 1041.

[2] J.W. Perry, K. Mansour, I.-Y.S. Lee, X.-L. Wu, P.V. Bedworth, C.-T. Cheng, D. Ng, S.R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe, Science 273 (1996) 1553.

[3] J.E. Ehrlich, X.-L. Wu, L.-Y.S. Lee, Z.-Y. Hu, H. Röckel, S.R. Marder, J.W. Perry, Opt. Lett. 22 (1997) 1843.

[4] W. Denk, J.H. Strickler, W.W. Webb, Science 248 (1990) 73.

[5] J.H. Strickler, W.W. Webb, SPIE Proc. 1398 (1990) 107.

[6] S. Maruo, O. Nakamura, S. Kawata, Opt. Lett. 22 (1997) 132.

[7] M. Albota, D. Beljonne, J.-L. Brédas, J.E. Ehrlich, J.-Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S.R. Marder, D. McCord-Maughon, J. Perry, W.H. Röckel, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, C. Xu, Science 281 (1998) 1653.

[8] B.A. Reinhardt, L.L. Brott, S.J. Clarson, A.G. Dillard, J.C. Bhatt, R. Kannan, L. Yuan, G.S. He, P.N. Prasad, Chem. Mater. 10 (1998) 1863.

[9] R.R. Birge, in: D.S. Kliger (Ed.), Ultrasensitive Laser Spectroscopy, Academic Press, New York, 1983 (Chapter 2).

[10] M. Goeppert-Mayer, Ann. Phys. 9 (1931) 273.

[11] O.-K. Kim, K.-S. Lee, H.Y. Woo, K.-S. Kim, G.S. He, J. Swiatkiewicz, P.N. Prasad, Chem. Mater. 12 (2000) 284.

[12] M.A. Albota, D. Beljonne, J.L. Bredas, J.E. Ehrtich, J.Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S.R. Mader, D.M. Maughon, J.W. Perry, H. Rocket, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, C. Xu, Science 281 (1998) 1653.

[13] M. Rumi, J.E. Ehrlich, A.A. Heikal, J.W. Perry, S. Barlow, Z. Hu, D.M. Maughon, T.C. Parker, H. Rockel, S. Thayumanavan, S.R. Marder, D. Beljonne, J.-L. Bredas, J. Am. Chem. Soc. 122 (2000) 9500.

[14] B.A. Reinhard, L.L. Brott, S.J. Clarson, A.G. Dillard, J.C. Bhatt, R.L.Yuan Kannan, G.S. He, P.N. Prasad, Chem. Mater. 10 (1998) 1863.

[15] X.-M. Wang, C. Wang, W.-T. Yu, Y.-F. Zhou, X. Zhao, Q. Fang, M.-H. Jiang, J. Canr. Chem. 79 (2001) 174.

[16] B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Keikal, S.M. Kuebler, I.-Y.S. Lee, D.M. Maughon, J. Qin, H. Röckel, M. Rumi, X.L. Wu, S.R. Marder, J.W. Perry, Nature 398 (1999) 51.

[17] C.F. Zhao, C.K. Park, P.N. Prasad, et al., Chem. Mater. 7 (6) (1995) 1237.

[18] S. Bahse, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, IEEE J. Quantum Electron. 26 (1990) 760.