

# Multi-photon absorption and optical limiting from six stilbazolium derivatives: donor influences

Chuanlang Zhan <sup>a,\*</sup>, Yunjing Li <sup>b</sup>, Dehua Li <sup>b</sup>, Duoyuan Wang <sup>a</sup>, Yuxin Nie <sup>b</sup>

<sup>a</sup> *Laboratory of Colloids and Interface Science and Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, CAS, Beijing 100080, PR China*

<sup>b</sup> *Laboratory of Optical Physics, Institute of Physics, CAS, Beijing 100080, PR China*

Received 1 May 2004; accepted 3 January 2005

Available online 16 February 2005

## Abstract

The linear absorption, multi-photon absorption and subsequently induced optical limiting from Six Stilbazolium derivatives with different donor units were studied with a mode-locked/Q-switched Nd:YAG pulses with a duration of 35 ps and a repetition of 10 Hz at 1064 nm. The measured molecular 3PA and 2PA cross-sections ( $\sigma_3/\sigma_2$ ) were in the order of  $10^{-76}$  cm<sup>6</sup> s<sup>2</sup> and  $10^{-47}$ – $10^{-46}$  cm<sup>4</sup> s/photon, respectively. It was observed that the  $\sigma_3$  values increase linearly with increasing the electron-donating ability of the donor units, from *N*-methylpyrrole, to pyrrole, to furan, and to thiophene. Similar influences were observed for the  $\sigma_2$  values. © 2005 Elsevier B.V. All rights reserved.

PACS: 42.70.–a; 42.65.–k; 33.80.Rv; 42.79.–e

Keywords: Stilbazolium derivative; Nonlinear optics; Three-photon absorption; Two-photon absorption; Optical limiting

## 1. Introduction

Multi-photon absorption (MPA) includes two- and three-photon absorption (2PA and 3PA). One of potential applications of MPA is optical limiting to protect eyes and sensors from intense laser. Up to now, many kinds of organic compounds were reported to display strong MPA, including stilbazolium derivatives [1–7], oligophenylenevinylene derivatives [8–10], and  $\pi$ -conjugated dendrimers [11–13]. In general, these molecules are constructed by several donors (D), acceptors (A), and conjugated bridges ( $\pi$ ) with following chemical structures: D- $\pi$ -A, D- $\pi$ -A- $\pi$ -D/A- $\pi$ -D- $\pi$ -A. As an interesting candidate displaying strong MPA, stilbazolium derivatives constructed by a strong A and D through a

carbon–carbon  $\pi$  bond have been paid much attention for 10 years [1–7].

Stilbazolium derivatives were published as early as 1976 [14]. Since then, they were widely investigated because they showed interested photophysical and photochemical properties, for example, the fluorescent intensity was reported to be strongly dependent on the temperature, solvent polarity and viscosity [15–17]. On basis of the above properties, stilbazolium derivatives were reported to show potential applications in photoconductors [18], fluorescent sensors [15,16] and indicators [19].

One of the key features of stilbazolium derivatives is the strong intramolecular charge-transfer (ICT) transition. This makes stilbazolium derivatives as a competitive candidate of organic nonlinear optical (NLO) materials and yields high optical nonlinearities including 2nd, 3rd, and 5th orders. For the 2nd optical nonlinearity, stilbazolium derivatives were observed to have high

\* Corresponding author. Tel.: +86 10 82615803; fax: +86 10 62559373.

E-mail address: [clzhan@iccas.ac.cn](mailto:clzhan@iccas.ac.cn) (C. Zhan).

molecular first hyperpolarizabilities ( $10^{-27}$ – $10^{-26}$  esu) [20–23] and large second-harmonic generation (SHG), as an example, the SHG of trans-2-(*p*-*N,N*-dimethylaminobenzyl)-1-(4-*N*-methylpyridinium)-ethene *p*-toluene sulfonic salt was reported to be 1000-times larger than that of urea [24]. Moreover, stilbazolium derivatives also show large 3rd- and 5th-order optical nonlinearities. When excited by near IR pulses, they not only display strong 2PA with 2PA cross-sections ( $\sigma_2$ ) as high as  $10^{-47}$ – $10^{-46}$  cm<sup>4</sup> s/photon [1–5], but also 3PA with 3PA cross-sections ( $\sigma_3$ ) in the order of  $10^{-76}$  cm<sup>6</sup> s<sup>2</sup> [6,7]. Otherwise, they also exhibit strong reversed-saturable absorption (RSA) or saturable absorption (SA) effects [25,26] and yield high 3rd-order nonlinear refractive index [27] when excited by visible pulses with a wavelength at 532 nm. The measured molecular 3rd-order optical nonlinearity with Z-scan and degenerate four-wave mixing is in the order of  $10^{-32}$ – $10^{-31}$  esu [25–27].

It was observed that molecular structure showed a large influence on the 2PA and 3PA effect. For D- $\pi$ -A conjugated molecules, decrease of the strength of D (or A) leads to a decrease of 2PA intensity [28], while for 3PA effect, we observed that increasing the acceptor strength can enhance the 3PA intensity of stilbazolium derivatives [6]. How about the influences of donors on the 3PA of stilbazolium derivatives? In this article, we investigate the linear and 3PA/2PA properties from six stilbazolium derivatives with different D units (Fig. 1) and observe that 3PA cross-sections increase with increasing the electron-donating ability of D units.

## 2. Results and discussion

### 2.1. Linear absorption properties

The six stilbazolium derivatives were all synthesized by using the inorganic-base catalyzed condensation procedure and characterized by using H-NMR, mass spectra, and elemental analysis [29]. The linear and nonlinear properties of the six stilbazolium derivatives were measured similar to the reported procedures [30]. Fig. 2 shows the linear absorption (1PA) spectra of the six molecules in dimethyl sulfoxide (DMSO) measured in the range of 300–1200 nm. Noting that there is no linear absorption in the near IR range, and solvent and spectroscopic cell influences on 1PA have been subtracted.

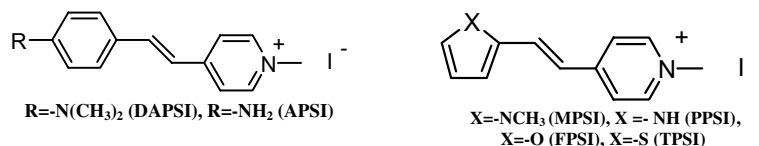


Fig. 1. Chemical structures and abbreviations of the six stilbazolium derivatives.

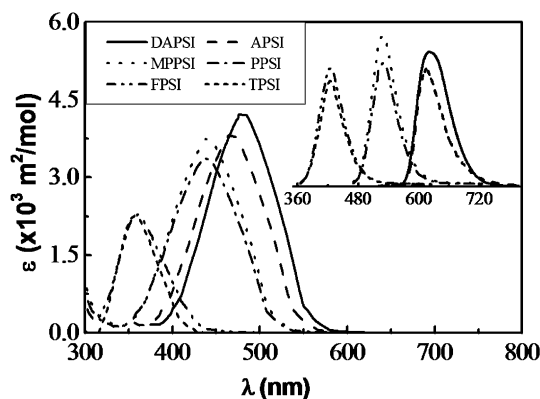


Fig. 2. Linear absorption and 1PA induced fluorescent spectra (insert) of the DMSO solutions of the six stilbazolium derivatives.

As shown in Fig. 2, the 1PA bands of both DAPSI and APSI are all in the range of 350–600 nm with  $\lambda_a$  at 468 and 455 nm, respectively. The blue-shift tendency is in consistent with the strength of D units. MPPSI, PPSI, FPSI, and TPSI also show the same tendency. Both the 1PA bands and  $\lambda_a$  all show blue-shift with donating strength from *N*-methyl pyrrole, to pyrrole, to furan, to thiophene units. For examples, the 1PA of both MPPSI and PPSI occur in the range of 300–550 nm with at 426 and 428 nm, and that of both FPSI and TPSI range from 300 to 460 nm with  $\lambda_a$  at 378 and 375 nm, respectively. The following results are obtained from the UV–Vis spectra:

- (a) there is no 1PA in the range of 600–1200 nm for DAPSI and APSI. Thus, it is rational that these two molecules show 2PA effect under excitation of near-IR pulses, as reported that molecule DAPSI showed strong 2PA effect under excitation of ns pulses at 1064 nm [4];
- (b) for MPPSI and PPSI, because there are linear absorptions simultaneously at 532 and 355 nm, so 2PA and 3PA could be generated under excitation of near-IR pulses. However, the 1PA intensity at 532 nm is much weaker than that at 355 nm, for examples, the molar absorption coefficients are  $0.11 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$  for MPPSI and  $0.01 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$  for PPSI. This suggests that MPPSI and PPSI would show a direct 3PA process, while possibly mixed by 2PA and induced excited-state absorption;

(c) there is no 1PA in the range of 470–1200 nm for FPSI and TPSI. In another word, there is no linear absorption at 532 nm or 1064 nm, respectively corresponding to 2PA or 1PA at the working wavelength of the 1064 nm. Therefore, a direct 2PA or 1PA process could be ruled out for these two molecules, and a direct 3PA process was expected.

## 2.2. 1PA, 2PA, and 3PA induced fluorescence

Insert of Fig. 2 shows the fluorescent spectra of the DMSO solutions of the six molecules. The fluorescent peaks ( $\lambda_f$ ), respectively localize at 620, 615, 520, 520, 425, and 425 nm for DAPSI, APSI, MPPSI, PPSI, FPSI, and TPSI. As Fig. 3 shown, the up-converted fluorescent intensity measured at  $\lambda_f$  of ethanol solution of APSI exhibits a quasi-square dependence on incident intensity at 1064 nm. The fitted exponent, e.g.  $n$ -value is 1.85 for APSI through  $y = a + bx^n$ . This confirms that a direct 2PA process in fact occurs for APSI, just as DAPSI does [4]. While for MPPSI and FPSI, the measured up-conversion fluorescent intensity shows a characteristic quasi-cubic dependence on the incident intensity with fitted  $n$ -values of 2.89 and 2.83, respectively. These  $n$ -values including that for APSI are some-what less than cubic or square dependence. This could be due to the occurrence of the non-radiation process other than the fluorescent emission process [6].

Such quasi-cubic dependence characterizes a direct 3PA or other resonant  $\chi^{(5)}$  processes [6,7,31–33], for examples, a 1PA process followed by a direct 2PA or a direct 2PA process followed by a 1PA. For MPPSI and PPSI, it is rationally assume that there is some-what contributions to 3PA from the  $\chi^{(5)}$  process, e.g. a 2PA process followed by direct 1PA. However, 3PA supposedly dominates the nonlinear absorption effect of MPPSI and PPSI because of the weak 1PA at 532 nm,

the 2PA working wavelength of 1064 nm laser. It is clear that this effect could be ruled out for FPSI and TPSI because of the absence of both 1PA (1064 nm) and 2PA (532 nm) at the working wavelength of the 1064 nm pulses, as shown by 1PA spectra. Thus, one could conclude that a direct 3PA process occurs for FPSI and TPSI.

## 2.3. Multi-photon absorption and donor influences

The values of 2PA and 3PA coefficients ( $\alpha_2$  and  $\alpha_3$ ) were obtained by fitting the measured relation of the transmitted intensity ( $I(L)$ ) vs. incident intensity ( $I_0$ ) with Eq. (1) [1–3] and (2) [6,7,31–33], respectively.

$$I(L) = \ln(1 + I_0 L \alpha_2) / L \alpha_2 \quad (1)$$

$$I(L) = I_0 / \sqrt{1 + 2\alpha_3 L I_0^2} \quad (2)$$

where  $L$  is the light path-length (1 cm). Fig. 4 shows the transmitted intensity as a function of the incident intensity. In which each data point is an average result over several tens pulses. The dashed line corresponding to the data for the pure DMSO shows a linear behavior, indicating that there is no nonlinear response in the measured intensity levels for the solvent itself. The solid lines are the best fitted curves predicted by Eq. (1) or (2). The best fitting values of  $\alpha_2$  and  $\alpha_3$  for these six molecules are listed in Table 1. Based on the known value of  $\alpha_2$  and  $\alpha_3$ , the  $\sigma_2$  and  $\sigma_3$  values listed in Table 1 were respectively estimated with Eqs. (3) and (4).

$$\alpha_2 = \sigma_2 N_A d_0 \times 10^{-3} / h\nu \quad (3)$$

$$\alpha_3 = \sigma_3 N_A d_0 \times 10^{-3} / (h\nu)^2 \quad (4)$$

where  $d_0$  is the solute concentration,  $N_A$  the Avogadro number, and  $h\nu$  the energy of an incident photon. The measured  $\sigma_2$  values are in the order of  $10^{-47}$ –

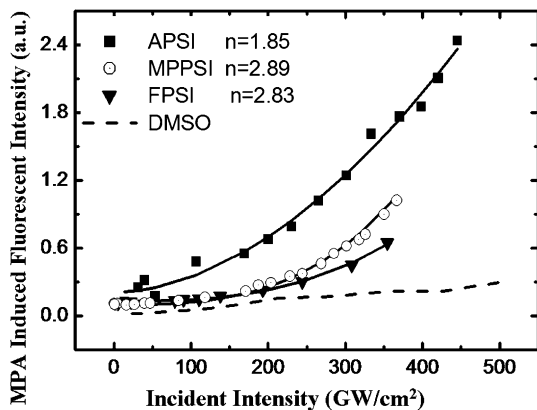


Fig. 3. Quasi-square and cubic dependence of 2PA and 3PA induced fluorescence intensity vs. incident intensity at 1064 nm for APSI, MPPSI and FPSI measured at  $\lambda_f$ .

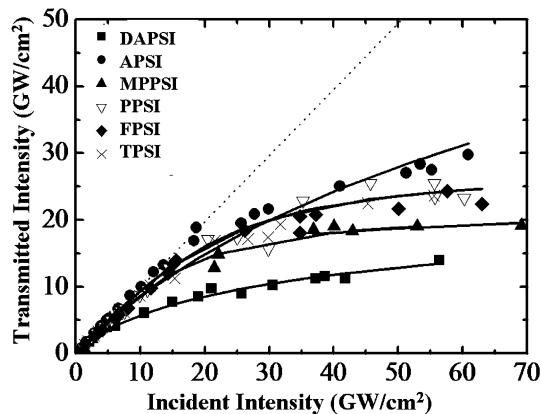


Fig. 4. The obvious nonlinear responses of the transmitted intensity vs. incident intensity at 1064 nm for the DMSO solutions of the six molecules. The dashed line is corresponding to the pure DMSO.

Table 1

The 2PA/3PA coefficients, cross-sections, concentrations of the six molecules, along with the estimated experimental errors of measured  $\sigma_2/\sigma_3$  values

Molecules number	$d_0 \times (10^{-3} \text{ mol/l})$	$\alpha_2/\alpha_3 \times (\text{cm/GW})/(10^{-21} \text{ cm}^3/\text{W}^2)$	$\sigma_2/\sigma_3 \times (10^{-46} \text{ cm}^4 \text{ s/photon})/(10^{-76} \text{ cm}^6 \text{ s}^2)$
DAPSI <sup>a</sup>	0.30	0.18	1.9(±0.2)
APSI <sup>a</sup>	0.33	0.04	0.40(±0.04)
MPPSI	0.31	1.2	2.3(±0.2)
PPSI	0.22	0.70	1.9(±0.2)
FPSI	0.31	0.82	1.6(±0.2)
TPSI	0.33	0.82	1.5(±0.2)

<sup>a</sup> These two molecules show two-photon absorption.

$10^{-46} \text{ cm}^4 \text{ s/photon}$ , which is similar to the reported stilbazolium derivatives [3,4]. The measured  $\sigma_3$  values are as high as  $10^{-76} \text{ cm}^6 \text{ s}^2$  and comparable to that of 6-propionyl-2-dimethylamino-naphthalene (PRODAN) [32] and 2,5-bibenzthiozole-3,4-didecyloxy thiophene (BBT-DOT) [33], and the reported stilbazolium derivatives [6,7]. Additionally, these  $\sigma_3$  values are about 3–6 orders of magnitude larger than the corresponding values of chloronaphthalene [30] and benzene [34].

Electron excessivity ( $\rho(C)_D$ ) has been suggested to be used to characterize the electron-donating ability of five-member rings with  $\rho(C)_D$  values of  $-0.350$ ,  $-0.331$ ,  $-0.179$ ,  $-0.135$ , respectively for *N*-methylpyrrole, pyrrole, furan, and thiophene [22,35]. Correlation of the measured  $\sigma_3$  with  $\rho(C)_D$  values shows a quasi-linear dependence on the electron-donating ability, indicating that the donor influences on the 3PA intensity. The  $\sigma_2$  values of molecule DAPSI is larger than that of APSI confirms the similar influence of donor on 2PA intensity.

#### 2.4. Optical limiting

As Fig. 4 shown, the six molecules in DMSO solution all show strong optical limiting. The optical limiting ability decreases as the order of DAPSI  $\gg$  MMPSI  $>$  PPSI  $\approx$  FPSI  $\approx$  TPSI  $>$  APSI. Among which DAPSI shows the strongest optical limiting. The optical limiting threshold ( $F_{th}$ ) [36] of DAPSI is as low as  $4 \text{ GW/cm}^2$ , and the transmitted intensity is limited under  $13 \text{ GW/cm}^2$  at the incident intensity  $< 58 \text{ GW/cm}^2$ . The values of  $F_{th}$  are about  $7 \text{ GW/cm}^2$  for MPPSI, and  $11 \text{ GW/cm}^2$  for PPSI, FPSI, and TPSI, and  $13 \text{ GW/cm}^2$  for APSI.

### 3. Conclusions

The linear and multi-photon absorptive properties from six stilbazolium derivatives with different donor units were investigated by using a 1064 nm and ps pulses. The measured  $\sigma_3$  values are as high as  $10^{-76} \text{ cm}^6 \text{ s}^2$  for the stilbazolium derivatives with *N*-methyl pyrrole, pyrrole, furan, and thiophene as donor units. The  $\sigma_3$  values were observed to increase with donating strength of the five-member rings. In addition-

ally, other two molecules with *N,N*-dimethylaminobenzyl and aminobenzyl as donor units show 2PA effects with  $\sigma_2$  values in the order of  $10^{-47}$ – $10^{-46} \text{ cm}^4 \text{ s/photon}$  and an obvious donor influence was also observed.

### Acknowledgments

The project is supported by NSFC (No. 50172049, 20303024), and by the Foundation of Laboratory of Optical Physics, Institute of Physics, The Chinese Academy of Sciences. The authors also thank Bao-Hua Feng and Xiu-Lan Zhang for their help in the experiment setup.

### References

- [1] G.S. He, J.D. Bhawalkar, C.F. Zhao, P.N. Prasad, Appl. Phys. Lett. 67 (1995) 2433.
- [2] G.S. He, G.C. Xu, P.N. Prasad, B.A. Reinhardt, J.C. Bhartt, A.G. Dillard, Opt. Lett. 20 (1995) 435.
- [3] G.S. He, L.X. Yuan, P.N. Prasad, Opt. Commun. 140 (1997) 49.
- [4] G.S. He, R. Signorini, P.N. Prasad, IEEE J. Quantum. Electron. 34 (1998) 7.
- [5] C.L. Zhan, Y.J. Li, D.Q. Zhang, D.H. Li, W. Xu, D.Y. Wang, Z.Z. Lu, L.Z. Zhao, Y.X. Nie, D.B. Zhu, Chem. Phys. Lett. 347 (2001) 410.
- [6] C.L. Zhan, D.H. Li, D.Q. Zhang, Y.J. Li, D.X. Wang, D.Y. Wang, Z.Z. Lu, L.Z. Zhao, Y.X. Nie, D.B. Zhu, Chem. Phys. Lett. 353 (2002) 138.
- [7] D.Y. Wang, C.L. Zhan, Y. Cheng, Y.J. Li, Z.Z. Lu, L.Z. Zhao, Y.X. Nie, Chem. Phys. Lett. 369 (2003) 621.
- [8] 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.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, C. Xu, Science 281 (1998) 1653.
- [9] S.J.K. Pond, O. Tsutsumi, M. Rumi, O. Kwon, E. Zojer, J.-L. Brédas, S.R. Marder, J.W. Perry, J. Am. Chem. Soc. 126 (2004) 9291.
- [10] G.P. Bartholomew, M. Rumi, S.J.K. Pond, J.W. Perry, S. Tretiak, G.C. Bazan, J. Am. Chem. Soc. 126 (2004) 11529.
- [11] M. Drobizhev, A. Karotki, Y. Dzenis, A. Rebane, Z. Suo, C.W. Spangler, J. Phys. Chem. B 107 (2003) 7540.
- [12] J. Yoo, S.K. Yang, M.-Y. Jeong, H.C. Ahn, S.-J. Jeon, B.R. Cho, Org. Lett. 5 (2003) 645.
- [13] L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, M. Blanchard-Desce, Org. Lett. 6 (2004) 47.
- [14] N. Richard, W. Peter, Arch. Phenom. 509 (1976) 649.
- [15] H. Ephardt, P. Fromherz, J. Phys. Chem. 93 (1989) 7717.

- [16] B. Strehmel, H. Seifert, W. Rettig, *J. Phys. Chem.* 101 (1997) 2232.
- [17] C.L. Zhan, D.Y. Wang, *J. Photochem. Photobio. A* 147 (2002) 93.
- [18] M.M. Habashy, F.E.L. Zawawi, M.S. Antonious, A.K. Sheriff, M.S.A. Abdel-Mottaleb, *Indian J. Chem. A* 24 (1985) 908.
- [19] L.M. Loew, S. Scully, L. Simpson, A.S. Waggoner, *Nature* 281 (1979) 497.
- [20] D.W. Bruce, R.G. Venning, M. Grayson, *Adv. Mater. Opt. Electron.* 4 (1994) 293.
- [21] X.M. Duan, H. Konami, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, *J. Phys. Chem.* 100 (1996) 17780.
- [22] C.L. Zhan, D.Y. Wang, *Acta Phys.-Chim. Sin.* 15 (1999) 338, 15 (1999) 805.
- [23] C.L. Zhan, D.Y. Wang, *Acta Chim. Sin.* 58 (2000) 24, 59 (2001) 213.
- [24] S.R. Marder, J.W. Perry, W.P. Schaefer, *Science* 245 (1989) 626.
- [25] W.F. Sun, M. McKerns, C.M. Lawson, G.M. Gray, C.L. Zhan, D.Y. Wang, *Proc. SPIE* 4106 (2000) 280.
- [26] W.F. Sun, C.M. Lawson, G.M. Gray, C.L. Zhan, D.Y. Wang, *Proc. SPIE* 4462 (2001) 17.
- [27] W.F. Sun, C.M. Lawson, G.M. Gray, C.L. Zhan, D.Y. Wang, *Appl. Phys. Lett.* 78 (2001) 1817.
- [28] L. Antonov, K. Kamada, K. Ohta, F.S. Kamounah, *Phys. Chem. Chem. Phys.* 5 (2003) 1193.
- [29] C.L. Zhan, D.Y. Wang, *Photograph. Sci. Photochem.* 18 (2000) 121.
- [30] C.L. Zhan, D.H. Li, D.Q. Zhang, Y.J. Li, W. Xu, D.Y. Wang, Z.Z. Lu, L.Z. Zhao, Y.X. Nie, D.B. Zhu, *J. Opt. Soc. Am. B* 19 (2002) 369.
- [31] A.C. Selden, *Nature (Phys. Sci.)* 229 (1971) 210.
- [32] G.S. He, J.D. Bhawalhar, P.N. Prasad, *Opt. Lett.* 20 (1995) 1524.
- [33] J.D. Bhawalhar, G.S. He, P.N. Prasad, *Opt. Commun.* 119 (1995) 587.
- [34] J.R. Cable, A.C. Albercht, *J. Chem. Phys.* 85 (1986) 3155.
- [35] I.D.L. Albert, T.J. Marks, M.A. Ratner, *J. Am. Chem. Soc.* 119 (1997) 6575.
- [36] A. Hochbaum, Y.Y. Hsu, J.J. Hagan, *Proc. SPIE* 2229 (1994) 48.