Ultrafast Energy Transfer and Enhanced Two-Photon Absorption in a Novel Porphyrin Side-Chain Polymer *

WANG Hui(王惠)[1**], HUANG Ya-Ping(黄亚萍)[1], DENG Li(邓莉)[1], ZHAO Fu-Li(赵福利)[1], LIN Wei-Zhu(林位株)[1], WANG Jian(王坚)[2], LIANG Zhao-Xi(梁兆熙)[2]

[1]*State Key Laboratory of Photoelectronic Materials and Technologies, Zhongshan University, Guangzhou 510275*
[2]*Institute of Polymer Science, Zhongshan University, Guangzhou 510275*

(Received 11 August 2004)

Ultrafast relaxation processes and transient two-photon absorption are studied in a novel porphyrin side-chain polymer, 5-hydroxy-10,15,20-triphenyl-porphyrin-poly(glycidyl methacrylate) (HTPP-PGMA), by using picosecond luminescence spectroscopy and femtosecond pump–probe techniques. HTPP-PGMA exhibits the ultrafast initial luminescence decay (∼300 ps), which is absent in the conventional porphyrin monomer such as TPP. Enhanced two-photon absorption was observed in HTPP-PGMA; the corresponding Im $\chi^{(3)}$ is about 2.8×10^{-11} esu, which is almost one order of magnitude larger than that of the conventional porphyrin monomer (TPP) ($\sim1.3\times10^{-12}$ esu). The ultrafast energy transfer plays an important role in the excited-state relaxation dynamics observed in HTPP-PGMA. The potential application of HTPP-PGMA in optical switching is discussed.

PACS: 78. 47. +p, 42. 65. -k, 78. 55. Kz

Porphyrin-based molecules and their derivatives have been extensively studied because of their importance in natural photosynthesis, which has potential application in the design of optoelectronic and all-optical devices.[1−3] Earlier investigations have shown that conventional porphyrin compounds and their derivatives possess large resonant third-order nonlinearities.[4,5] However, their excited-state lifetime is usually on the nanosecond timescale, which is much longer than that of the conjugated polymers.[6−8]

A practical all-optical switching requires that the materials combine large optical nonlinearities and ultrafast response times, as well as adequate transparency. In searching for improved materials, the study of structure-property relationships is necessary. Time-resolved optical studies such as transient absorption have been often used to investigate the excited-state dynamics of organics and polymers. However, the signals obtained in transient absorption spectroscopy are a superposition of several nonlinear optical processes. A direct method to identify the ultrafast excited-state relaxation processes is the measurement of the temporal evolution of luminescence after photoexcitation. In this Letter, we report the study of the excited-state relaxation and transient two-photon absorption in a novel porphyrin side-chain polymer, 5-hydroxy-10,15,20-triphenyl-porphyrin-poly(glycidyl methacryate) (HTPP-PGMA) by using picosecond luminescence spectroscopy and femtosecond pump–probe techniques. For comparison, the excited-state dynamics of a conventional monomer porphyrin, 5,10,15,20-tetraphenylporphyrin (TPP), has also been measured. The results show an ultrafast initial excited-state decay in HTPP-PGMA, however, which is absent in TPP. HTPP-PGMA also exhibits an enhanced two-photon absorption process; the corresponding Im$\chi^{(3)}$ is almost one order of magnitude larger than that of TPP. The energy transfers among the porphyrin chromophores may play an important role in the ultrafast excited-state relaxation in HTPP-PGMA. The potential application in optical switching is discussed.

The molecular structures of both the samples investigated are shown as the insets in Figs. 1(a) and 1(b). The HTPP-PGMA is a copolymer of 5-hydroxy-10, 15,20-triphenyl-porphyrin (HTPP) and poly(glycidyl methacrylate) (PGMA), whose solution in $CHCl_3$/DMF was cast on clean glass slide for a certain period of time at 90° C forming thin homogeneous films. The chromophore contents determined by HNMR were about 12 wt.%. The TPP solution cast film was fabricated from a polymer blend consisting of 10 % TPP in poly(methyl methacrylte) (PMMA). The film thicknesses of HTPP-PGMA and TPP were approximately 2.5 and 2.0 μm.

The measurement of the time-resolved luminescence decay dynamics was performed by using an active mode-locked and frequency-doubled Nd:YAG laser, which generated 135 ps pulses with a wavelength of 532 nm, the average power of 240 mW and a repetition rate of 82 MHz. The luminescences were collected by a set of lens and recorded in a synchroscan streak camera. The transient two-photon absorption mea-

* Supported by the National Natural Science Foundation of China under Grant Nos 60478013, 10274170 and 60178020, and the Natural Science Foundation of Guangdong Province under Grant No 021705.

** Email: stswh@zsu.edu.cn

©2004 Chinese Physical Society and IOP Publishing Ltd

surements of HTPP-PGMA and TPP films were performed with a typical pump–probe set-up. The light source is a mode-locked Ti:sapphire laser producing 50 fs pulses with a wavelength of 780 nm, the average power of 260 mW and a repetition rate of 110 MHz. The output of this system was split into pump and probe beams, whose energy ratio is adjusted to be 4:1. The linear polarization of probe beam was set parallel with respect to that of the pump beam. The final two-photon absorption signal is obtained by removing the coherent artifact.[7]

The linear absorption spectra of both sample films are shown in Figs. 1(a) and 1(b). Besides a small red-shift (~20 nm), the absorption spectrum of HTPP-PGMA is almost identical to that of TPP, which consists of a very narrow absorption band around 413 nm (B bands) and a set of weaker long wavelength absorption bands (Q bands) around 510, 550, 590, 648 nm, which are typical for porphyrin-based systems.[9,10]

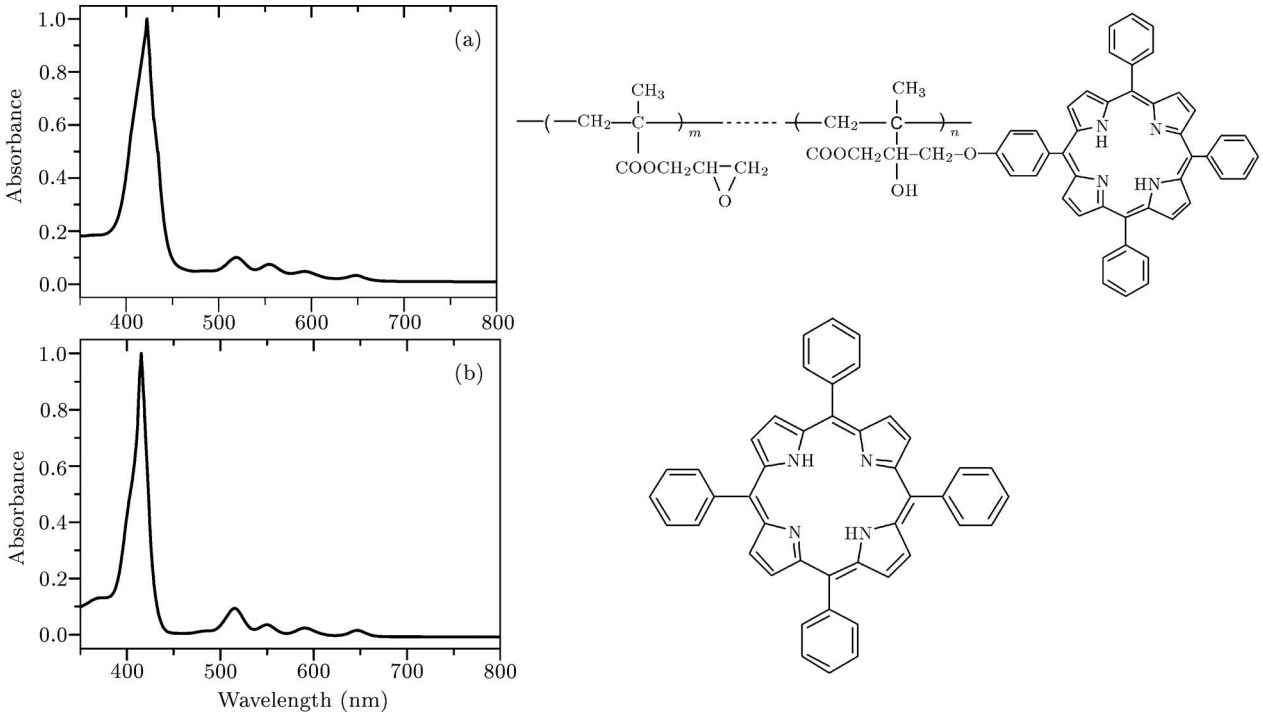


Fig. 1. Linear absorption spectra of HTPP-PGMA (a) and TPP (b) films, as well as the molecular structures of HTPP-PGMA and TPP.

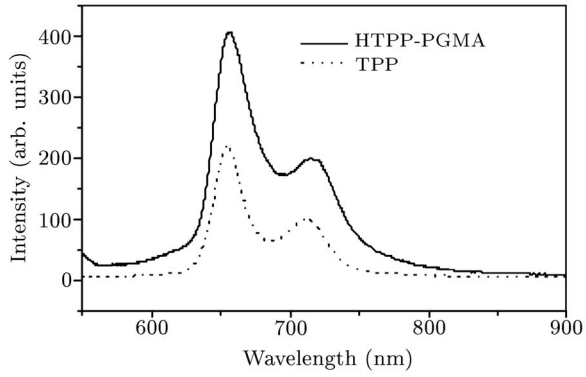


Fig. 2. Steady-state luminescence spectra of HTPP-PGMA and TPP.

The steady-state luminescence spectra of HTPP-PGMA and TPP with 532 nm excitation near a peak of the Q-band absorption are shown in Fig. 2. Also, besides a slight red-shift, the luminescence spectrum of HTPP-PGMA is almost identical with that of TPP. The luminescence spectrum of HTPP-PGMA consists of a main emission band around 650 nm and a lower vibronic replica around 720 nm, which show the general steady-state emission features of porphyrin-based systems.[9,11]

The temporal evolution of luminescence at 650 and 720 nm for HTPP-PGMA and TPP are shown in Figs. 3(a) and 3(b), respectively. HTPP-PGMA exhibits the two-component decay: an initial fast component and a following slow component, which are fitted about 300 ps, 1.3 ns and 300 ps, 1.8 ns at 650 nm and 720 nm, respectively, by using a biexponential function convoluted with the apparatus function. The initial luminescence relaxation dynamics in HTPP-PGMA is evidently independent to the spectral position. For TPP, no initial fast relaxation was observed. The lifetime of TPP is long compared to the experimental time window.

Figure 4 shows the time-resolved luminescence spectra of HTPP-PGMA. Within about 400 ps, the

spectrum evolves into a shape very similar to the steady-state spectrum shown in Fig. 2. No significant transient red-shift of the time-resolved luminescence spectrum has been observed.

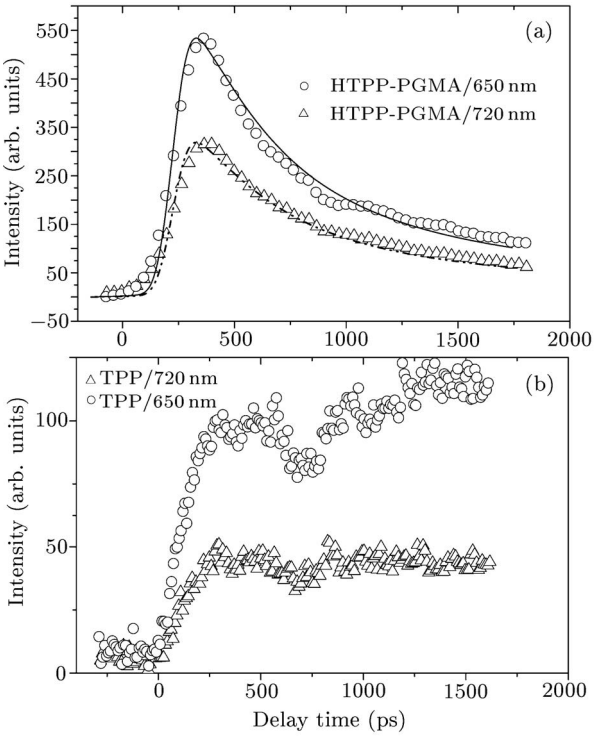


Fig. 3. Picosecond transient luminescences of HTPP-PGMA (a) and TPP (b) at 650 and 720 nm.

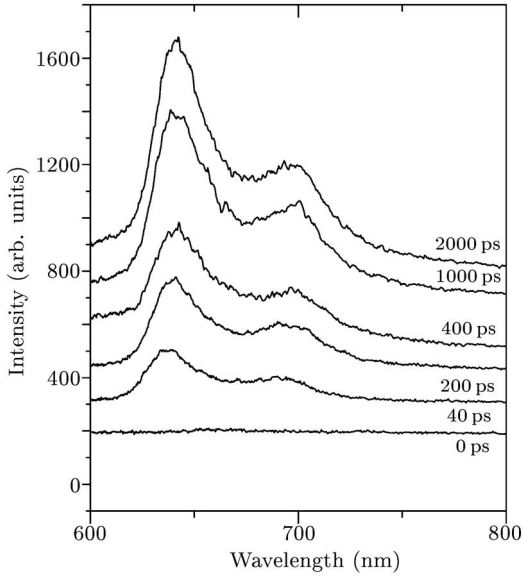


Fig. 4. Time-resolved luminescence spectra of HTPP-PGMA after photoexcitation at 532 nm.

The transient two-photon absorption processes for HTPP-PGMA and TPP are depicted in Fig. 5. HTPP-PGMA exhibits a two-photon absorption signal stronger than TPP. As a third-order nonlinear optical effect, the imaginary part of the third-order nonlinearity Im $\chi^{(3)}$ is estimated as 2.8×10^{-11}esu, which is almost one order of magnitude larger than that of TPP (about 1.3×10^{-12}esu).[12]

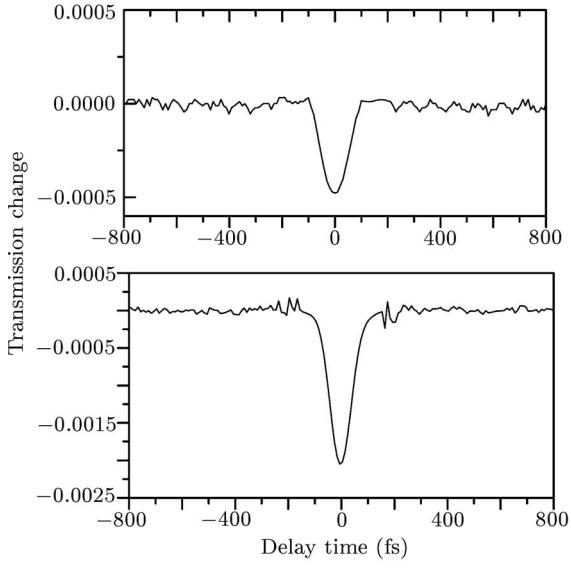


Fig. 5. Transient two-photon absorption curves of HTPP-PGMA and TPP at 780 nm.

The ultrafast relaxation dynamics and enhanced two-photon absorption observed in HTPP-PGMA may attributed to its molecular structure as shown in Fig. 1, in which the local ordered arrangement of porphyrin side-chain chromophores may result in strong coupling among the porphyrin moieties.[9,13] The strong interactions usually lead to rapid electron transition in organic and polymer systems.[9] In the case of HTPP-PGMA, there is no donor–acceptor system so that the charge transfer (CT) process is impossible. The dominant process responsible for the initial ultrafast relaxation in HTPP-PGMA as shown in Fig. 3 should be the nonradiative energy transfer among the neighbouring porphyrin chromophores. A similar result has been observed in other porphyrin derivatives.[10] Compared with conjugated polymer films,[14–16] the absence of the red-shift of the transient luminescence spectrum and the independence of the decay time of luminescence on spectral position as shown in Figs. 3 and 4 indicate that both the intermolecular and intramolecular energy transfers may make contributions to the ultrafast excited-state relaxation. In comparison with the hexameric benzoporphyrin (PB6) ($\sim$ 3.8 ns) and the earlier reported conjugated polymers ($\sim$ 5 ns),[10,15] HTPP-PGMA exhibits a much faster energy transfer process. In the case of TPP, dispersing porphyrin chromophores with large separations may suppress the energy transfer, which is related to the slower relaxation dynamics compared with HTPP-PGMA. Furthermore, the spa-

tial arrangement of the pophyrin chromophores in HTPP-PGMA may result in the π-orbital overlaps on either side of the place of each porphyrin chromophore, forming an extended π-electron delocalization along the main chain, which is confirmed by the red shift of linear absorption spectrum and enhanced third-order optical nonlinearity observed in HTPP-PGMA films. The value of the nonresonant $\mathrm{Im}\chi^{(3)}$ is about two orders of magnitudes larger than the earlier reported porphyrin compounds.[4]

The third-order nonlinear optical properties of organics and polymers provide the means to control light with light i.e. all-optical switching. In addition, to be practical useful for ultrafast all-optical switching, the materials should have ultrafast response and relaxation times (picosecond or less), minimal loss (nonresonant nonlinearity), good processability and environment stability.[17,18] However, the conventional porphyrin compounds and most conjugated polymers do not form good thin films as pure materials although large $\chi^{(3)}$ and fast response time are reported.[9,19,] For HTPP-PGMA, the particular molecular structure confers good solubility in solvents, and ultrafast excited-state decay and enhanced nonresonant third-order nonlinearity have been observed in our experiment compared with the porphyrin compounds. It is believed that further study will improve its nonlinear optical properties.

In summary, time-resolved excited-state relaxation and two-photon absorption have been investigated in a novel porphyrin side-chain polymer HTPP-PGMA by using picosecond luminescence spectroscopy and femtosecond pump–probe techniques. Compared with the conventional porphyrin monomer TPP and other porphyrin derivatives, HTPP-PGMA exhibits much faster excited-state decay and larger third-order nonlinearity. In conjunction with its excellent processability and good transparency, the HTPP-PGMA may be attractive for developing fast all-optical switches. Further studies on related systems are in progress.

References

[1] Martin S J, Anderson H L and Bradley D D C 1994 *Chem. Phys.* **4** 227

[2] Qureshi F M, Martin S J, Long X, Bradley D D C, Henari F Z, Blau W J, Smith E C, Wang C H, Kar A R and Anderson H I 1998 *Chem. Phys.* **231** 87

[3] Wasielewski M R 1992 *Chem. Rev.* **92** 435

[4] Rao D V G L N, Aranda F J, Remy D E and Roach J F 1994 *Int. J. Nonlinear Opt. Phys.* **3** 511

[5] Terazima M, Shimizu H and Osuka A 1997 *J. Appl. Phys.* **81** 2946

[6] Blau W, Byrne H and Dennis W M 1985 *Opt. Commun.* **56** 25

[7] D'Souza F, Deviprasad G R, EI-Khouly M E 2001 *J. Am. Chem. Soc.* **123** 5277

[8] Devadoss C, Bharathi P and Moore J S 1996 *J. Am. Chem. Soc.* **118** 9633

[9] Schweitzer G, de Belder G, Latterini L, Karni Y, Rowan A E, Nolte R J M and de Schryver F C 1999 *Chem. Phys. Lett.* **303** 261

[10] Cerullo G, Stagira S, Zavelani-Rossi M, de Silvestri S, Virgili T, Lidzey D G and Bradley D D C 2001 *Chem. Phys. Lett.* **335** 27

[11] O'Keefe G E, Denton G J, Harvey E J, Phillips R T, Friend R H and Anderson H L 1996 *J. Chem. Phys.* **104** 805

[12] Wang H, Lai T S, Lin W Z, Mo D, Meng O Y and Gong K C 1993 *Chin. Phys. Lett.* **11** 491

[13] Hegmann F A 2003 *La Physique au Canada* **59** 127

[14] Kersting R, Lemmer U, Mahrt R F, Leo K, Kurz H, Bassler H and Gobel E O 1993 *Phys. Rev. Lett.* **70** 3820

[15] Samuel I D W, Rumbles G and Collison C J 1995 *Phys. Rev.* B **52** R11573

[16] Lemmer U, Mahrt R F, Wada Y, Greiner A, Bassler H and Gobe E O 1993 *Chem. Phys. Lett.* **209** 243

[17] Kuang L, Chen Q Y, Sargent E H and Wang Z Y 2003 *J. Am. Chem. Soc.* **125** 13648

[18] Zhou J, Cao Z Q, Chen Y L, Chen Y X, Sun M, Sun D C and Li F M 1997 *Opt. Lett.* **22** 1482

[19] Norwood R A and Sounik J R 1992 *Appl. Phys. Lett.* **60** 295