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## Two-photon absorption spectrum of the photoinitiator Lucirin TPO-L

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**ABSTRACT** Two-photon absorption induced polymerization provides a powerful method for the fabrication of intricate three-dimensional microstructures. Recently, Lucirin TPO-L was shown to be a photoinitiator with several advantageous properties for two-photon induced polymerization. Here we measure the two-photon absorption cross-section spectrum of Lucirin TPO-L, which presents a maximum of 1.2 GM at 610 nm. Despite its small two-photon absorption cross-section, it is possible to fabricate excellent microstructures by two-photon polymerization due to the high polymerization quantum yield of Lucirin TPO-L. These results indicate that optimization of the two-photon absorption cross-section is not the only material parameter to be considered when searching for new photoinitiators for microfabrication via two-photon absorption.

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### 1 Introduction

Two-photon absorption processes have attracted much interest due to their potential applications in optical sciences, biology and microfabrication technologies. The quadratic dependence of the two-photon absorption rate on laser intensity allows spatial confinement of the excitation, a feature exploited in three-dimensional optical storage [1–4], two-photon fluorescence imaging [5, 6], two-photon photodynamic therapy [7, 8], and microfabrication via two-photon induced polymerization [9–11]. Two-photon initiated polymerization in particular is a very interesting tool to fabricate sophisticated microstructures for optical circuitry [12], optical data storage [13], three-dimensional micromechanical actuators [14–16] and photonic crystals [13, 17].

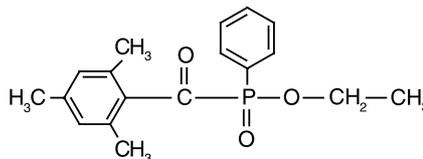
In general, photopolymerization of mixtures of monomers and oligomers requires a photoinitiator, many of which are commercially available. Although new photoinitiators with higher two-photon absorption cross-sections, a key parameter for two-photon polymerization, have been de-

signed in the last five years [13, 18], these molecules are still not readily available. To determine the optimal conditions for two-photon polymerization, the two-photon absorption cross-sections of some conventional commercial photoinitiators have been measured [19]. Lucirin TPO-L (ethyl-2,4,6-trimethylbenzoylphenylphosphine oxide), an acylphosphine oxide radical photoinitiator whose molecular structure is shown in Fig. 1, was demonstrated to be an efficient initiator of polymerization under two-photon excitation [20]. Furthermore, unlike most radical photoinitiators, Lucirin TPO-L is a liquid with broad solubility that can be mixed easily with most resin formulations.

In this paper we present the degenerate two-photon absorption cross-section spectrum of Lucirin TPO-L and interpret this spectrum with the aid of quantum chemistry calculations. Although the two-photon absorption cross-section of Lucirin TPO-L is small ( $< 1.2$  GM), we can microfabricate structures with high integrity and definition using moderate laser powers (10 mW), due to the high polymerization efficiency of Lucirin TPO-L (radical quantum yield of 0.99). The high polymerization efficiency makes Lucirin TPO-L an excellent photoinitiator for microfabrication via two-photon absorption polymerization over a large spectral range in the visible/infrared.

### 2 Experimental

We prepared Lucirin TPO-L/ethanol solution with concentrations of  $7 \times 10^{-3}$  and  $9 \times 10^{-1}$  mol L<sup>-1</sup>, for linear and nonlinear optical measurements, respectively. The samples were placed in 2 mm thick quartz cuvettes for spectroscopic measurements. The linear absorption spectrum was recorded using a spectrophotometer equipped with an inte-



**FIGURE 1** Molecular structure of lucirin TPO-L

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grating sphere detector. The two-photon absorption spectrum was obtained using the Z-scan technique [21].

In the Z-scan technique, the two-photon absorption cross section is determined by moving the sample through the focal plane of a focused Gaussian beam and monitoring the changes in the far field intensity. For a two-photon absorption process, the light field creates an intensity dependent absorption,  $\alpha = \alpha_0 + \beta I$ , where  $I$  is the laser beam intensity,  $\alpha_0$  is the linear absorption coefficient and  $\beta$  the two-photon absorption coefficient. For non-resonant conditions, such as two-photon absorption, the change in the transmitted power is integrated over time (assuming a pulse with a Gaussian temporal profile) to give the normalized energy transmittance [21],

$$T = \frac{1}{\sqrt{\pi}q_0(z, 0)} \int_{-\infty}^{\infty} \ln \left[ 1 + q_0(z, 0)e^{-\tau^2} \right] d\tau, \quad (1)$$

where  $q_0(z, t) = \beta I_0(t)L(1 + z^2/z_0^2)^{-1}$ ,  $L$  is the sample thickness,  $z_0$  the Rayleigh length,  $z$  the sample position and  $I_0$  the laser intensity.

The nonlinear coefficient  $\beta$  is obtained by fitting (1) to the Z-scan data [21] with  $\beta$  as a free parameter. The two-photon absorption cross-section,  $\delta$ , is determined from  $\delta = h\nu\beta/N$ , where  $h\nu$  is the excitation photon energy and  $N$  is the number of molecules per  $\text{cm}^3$ . Usually the two-photon absorption cross-section  $\delta$  is expressed in units of Göppert-Mayer (GM), where  $1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4\text{s mol}^{-1}\text{photon}^{-1}$ .

For the Z-scan experiment we used a 150 fs, 775 nm and 1 kHz Ti:sapphire laser as the pump for an optical parametric amplifier, which delivers 120 fs pulses with wavelengths ranging from 600 to 810 nm. The output beam of the optical parametric amplifier is spatially filtered to produce a Gaussian beam profile. The transmitted signal through the sample is measured using a silicon photo-detector coupled to a lock-in amplifier. To further improve the sensitivity of the Z-scan technique we used the fastscan Z-scan method, [22] which averages Z-scan traces while the sample is oscillated through the focal plane, allowing the measurement of transmittance changes of only a few percent. In order to avoid photodegradation during the Z-scan, besides using relatively small irradiances, we performed the measurements in a flow cell geometry.

The resin used in this work consists of a mixture of two tri-acrylate monomers and Lucirin TPO-L as photoinitiator. Tris(2-hydroxyethyl)isocyanurate triacrylate (monomer A) increases the microstructure hardness, while ethoxylated(6) trimethylolpropane triacrylate (monomer B) reduces shrinkage upon polymerization [20].

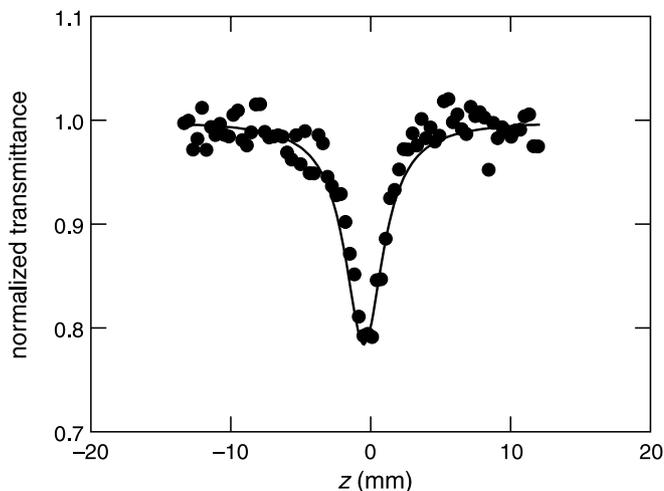
To fabricate microstructures we used a 130 fs, 800 nm Ti:sapphire laser oscillator beam focused into the sample with a 0.65 NA microscope objective. We used an average laser power of 10 mW measured after the objective. The sample consists of a drop of resin placed inside a spacer located on top of a microscope slide whose surface is treated with (3 acryloxypropyl)trimethoxysilane to increase adhesion of the final structure to the glass substrate. The resin is contained inside the spacer by a cover slip. The sample is positioned in the axial  $z$ -direction using a motorized stage, and the laser is scanned across the resin in the  $xy$  direction using a pair of galvano mir-

rors. After the desired microstructure is fabricated, the sample is immersed in ethanol to wash away the unsolidified resin.

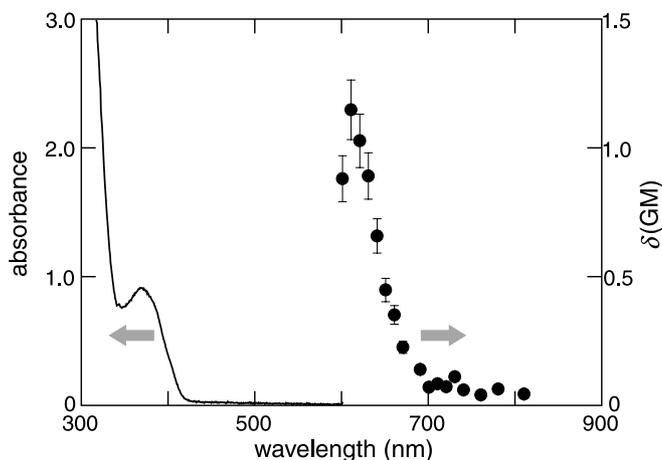
### 3 Results

Figure 2 shows a Z-scan curve [21] for Lucirin TPO-L, for an off-resonance pump wavelength of 610 nm. The decrease in the normalized transmittance at the focal point  $z = 0$  is due to two-photon absorption. By fitting (1) to the experimental data (solid line) we obtain a value for the two-photon absorption cross-section  $\delta$ . The value we obtain for  $\delta$  is independent of the incident laser intensity, as one would expect for a pure two-photon absorption process.

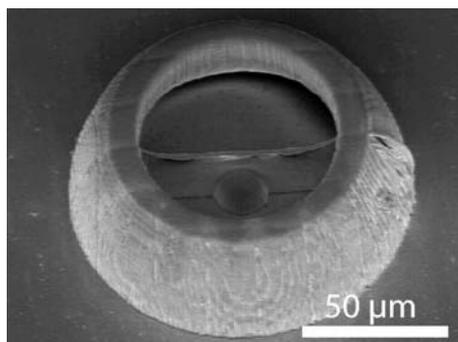
Figure 3 shows the linear absorption spectrum of Lucirin TPO-L as a solid line and the values of  $\delta$  (circles) obtained from Z-scan measurements at different excitation wavelengths. The linear absorption increases towards shorter wavelengths and displays a peak around 365 nm. The spectrum shows that Lucirin TPO-L does not exhibit any linear absorption beyond 440 nm; it is completely transparent at the near-infrared wavelength used in the Z-scans experiments and



**FIGURE 2** Z-scan curve at 610 nm for lucirin TPO-L (circles), using an intensity of approximately  $2 \text{ GW/mm}^2$ . The curve represents a fit of Eq. (1) to the data



**FIGURE 3** Linear absorption spectrum (curve; left axis) and two-photon absorption cross-section spectrum (circles; right axis) of lucirin TPO-L



**FIGURE 4** Scanning electron micrograph of microstructures fabricated by two-photon absorption polymerization; 30° tilted view of a hemispherical structure

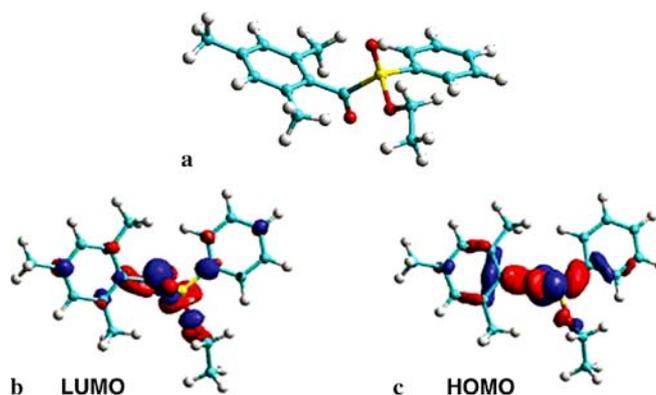
the two-photon polymerization microfabrication. The two-photon absorption spectrum, on the other hand, has a large peak at 610 nm and a second, much smaller peak at 730 nm.

Figure 4 shows a scanning electron micrograph of a three-dimensional microstructure fabricated in the acrylate-based resin using Lucirin TPO-L as a photoinitiator for the two-photon polymerization at 800 nm. It should be pointed out that the two-photon absorption cross-section at this wavelength is very small, as seen in Fig. 3. The fabricated microstructure is an open hemisphere containing a smaller hemisphere that is divided by a plane. Microstructures fabricated in this way have high definition and excellent integrity, indicating that Lucirin TPO-L efficiently induces photopolymerization via two-photon absorption.

#### 4 Discussion

The peak in the two-photon absorption spectrum at 610 nm (Fig. 3, circles) corresponds to a two-photon transition to the band located around 300 nm in the linear absorption spectrum (Fig. 3, curve). The value of the two-photon absorption peak (1.2 GM) is comparable with results obtained for other photoinitiators [19]. The small two-photon absorption peak at 730 nm corresponds to twice the wavelength of the one-photon absorption peak at 365 nm. For symmetric molecules, one-photon allowed transitions are two-photon forbidden [23–26]. However, Lucirin TPO-L has an asymmetric molecular geometry (Fig. 1), and so we can expect these selection rules to be relaxed. Indeed, as evidenced by the correspondence between the peaks in the two-photon and linear absorption spectra in Fig. 3, two-photon transitions can reach the same final state as one-photon transitions.

To explain the small two-photon absorption cross-section values observed in Fig. 3 we determined the molecular geometry of Lucirin TPO-L and the frontier molecular orbitals. Figure 5a shows the molecular geometry of Lucirin TPO-L obtained via *ab initio* (6–31 G\*) calculations. Due to the presence of the phosphorus atom the molecule has a nonplanar structure. The lowest unoccupied and highest occupied molecular orbitals, shown in Fig. 5b and c, respectively, were obtained using the semi-empirical ZINDO/1 method [27, 28]. The orbitals indicate that Lucirin TPO-L does not have a high conjugation length with most of the charge localized in the central portion of the molecule. A high two-photon



**FIGURE 5** (a) Molecular geometry of the lucirin TPO-L molecule obtained from *ab initio* calculations. (b) Lowest unoccupied molecular orbital and (c) highest occupied molecular orbital obtained using the semi-empirical ZINDO/1 method

cross section requires high conjugation and molecular planarity [29, 30], both of which are absent in Lucirin TPO-L, which explains the small two-photon absorption cross-section of this photoinitiator.

In spite of the small two-photon absorption cross-section, Lucirin TPO-L has been recently shown to be an effective photoinitiator [20]. The polymerization action spectrum, which is proportional to the product of the two-photon absorption cross section  $\delta(\omega)$  and the radical quantum yield  $\phi_2(\omega)$ , contains a peak around 725 nm [20]. The authors attribute this peak to a corresponding peak in the two-photon absorption spectrum and estimate the radical quantum yield to be 0.99 at 800 nm. Our measurements of the two-photon absorption spectrum  $\delta(\omega)$  in Fig. 3 confirm this conclusion: we directly observed a peak in  $\delta(\omega)$  at 730 nm and the two-photon cross-section is small, indicating that the radical quantum yield must be high. It is this high radical quantum yield that makes Lucirin TPO-L an effective photoinitiator.

Lucirin TPO-L generates radicals when it is excited to the triplet state [31]. Due to the two-photon excitation puts the molecule in a singlet state, the high radical quantum yield must therefore be due to an efficient singlet–triplet conversion. Indeed, the low fluorescence quantum yield of Lucirin TPO-L [31] suggests a high singlet–triplet conversion efficiency. This high efficiency can be attributed to the presence of the phosphorous atom in the molecule, which enhances the spin–orbit coupling, increasing the intersystem crossing rate [32].

Although photoinitiators with much higher two-photon absorption cross-sections [13, 18] are available, our results point out that initiators with small two-photon absorption cross-sections are also suitable for the fabrication of microstructures as long as they have a high radical quantum yield, in agreement with other results already reported for other initiators [18, 33–35].

#### 5 Conclusion

We measured the two-photon absorption cross-section spectrum of Lucirin T-POL in the wavelength range from 600 to 810 nm using the Z-scan technique. The maximum value of two-photon absorption cross-section is

1.2 GM, which is low compared to some organic molecules [30, 36, 37], but comparable to other photoinitiators reported in the literature [19]. Using quantum-chemical calculations we established that the low nonlinear optical properties of this molecule arise from its nonplanarity and low conjugation length. Despite the small two-photon absorption cross-section exhibited by Lucirin TPO-L, its high polymerization quantum yield permits the fabrication of microstructures with excellent structural integrity and definition, demonstrating the potential of Lucirin TPO-L for microfabrication by two-photon polymerization.

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## REFERENCES

- S. Kawata, Y. Kawata, *Chem. Rev.* **100**, 1777 (2000)
- A.S. Dvornikov, P.M. Rentzepis, *Opt. Commun.* **119**, 341 (1995)
- D.A. Parthenopoulos, P.M. Rentzepis, *J. Appl. Phys.* **68**, 5814 (1990)
- D.A. Parthenopoulos, P.M. Rentzepis, *Science* **245**, 843 (1989)
- C. Xu, W. Zipfel, J.B. Shear, R.M. Williams, W.W. Webb, *Proc. Nat. Acad. Sci. USA* **93**, 10763 (1996)
- P.T.C. So, C.Y. Dong, B.R. Masters, K.M. Berland, *Ann. Rev. Biomed. Eng.* **2**, 399 (2000)
- J.D. Bhawalkar, G.S. He, P.N. Prasad, *Rep. Prog. Phys.* **59**, 1041 (1996)
- T.J. Dougherty, B.W. Henderson, S. Schwartz, J.W. Winkelman, R.L. Lipson, In: *Photodynamic Therapy*, ed. by B.W. Henderson, T.J. Dougherty (Marcel Dekker, New York, 1992), p. 1
- S. Kawata, H.B. Sun, T. Tanaka, K. Takada, *Nature* **412**, 697 (2001)
- H.B. Sun, S. Kawata, *Nmr – 3d Analysis – Photopolymerization* (Springer, Berlin, 2004), p. 169
- M. Miwa, S. Juodkazis, T. Kawakami, S. Matsuo, H. Misawa, *Appl. Phys. A* **73**, 561 (2001)
- M.P. Joshi, H.E. Pudavar, J. Swiatkiewicz, P.N. Prasad, B.A. Reianhardt, *Appl. Phys. Lett.* **74**, 170 (1999)
- B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.Y.S. Lee, D. McCord-Maughon, J.Q. Qin, H. Rockel, M. Rumi, X.L. Wu, S.R. Marder, J.W. Perry, *Nature* **398**, 51 (1999)
- P. Galajda, P. Ormos, *Appl. Phys. Lett.* **78**, 249 (2001)
- T. Watanabe, M. Akiyama, K. Totani, S.M. Kuebler, F. Stellacci, W. Wenseleers, K. Braun, S.R. Marder, J.W. Perry, *Adv. Funct. Mater.* **12**, 611 (2002)
- Z. Bayindir, Y. Sun, M.J. Naughton, C.N. LaFratta, T. Baldacchini, J.T. Fourkas, J. Stewart, B.E.A. Saleh, M.C. Teich, *Appl. Phys. Lett.* **86**, 064105 (2005)
- J. Serbin, A. Ovsianikov, B. Chichkov, *Opt. Express* **12**, 5221 (2004)
- S.M. Kuebler, K.L. Braun, W.H. Zhou, J.K. Cammack, T.Y. Yu, C.K. Ober, S.R. Marder, J.W. Perry, *J. Photochem. Photobiol. A* **158**, 163 (2003)
- K.J. Schafer, J.M. Hales, M. Balu, K.D. Belfield, E.W. Van Stryland, D.J. Hagan, *J. Photochem. Photobiol. A* **162**, 497 (2004)
- T. Baldacchini, C.N. LaFratta, R.A. Farrer, M.C. Teich, B.E.A. Saleh, M.J. Naughton, J.T. Fourkas, *J. Appl. Phys.* **95**, 6072 (2004)
- M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, *IEEE J. Quantum Electron.* **QE-26**, 760 (1990)
- I.J. Blewett, J. Stokes, A. Tookey, A.K. Kar, B.S. Wherrett, *Opt. Laser Technol.* **29**, 355 (1997)
- R.R. Birge, B. Parsons, Q.W. Song, J.R. Tallent, In: *Molecular Electronics*, ed. by J. Jortner, M. Ratner (Blackwell Science, London, 1997)
- W.L. Peticola, *Ann. Rev. Phys. Chem.* **18**, 233 (1967)
- L. Antonov, K. Kamada, K. Ohta, F.S. Kamounah, *Phys. Chem. Chem. Phys.* **5**, 1193 (2003)
- D.P. Craig, T. Thirunamachandran, *Molecular Quantum Electrodynamics – An Introduction to Radiation Molecule Interaction* (Dover Publications, New York, 1998)
- M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985)
- J. Ridley, M. Zerner, *Theoret. Chim. Acta* **32**, 111 (1973)
- J.W. Perry, M. Albota, S. Ananthavel, D. Beljonne, J.L. Bredas, B. Cumpston, D.L. Dyer, J.E. Ehrlich, A.A. Heikal, S.E. Hess, T. Kogej, S.M. Kuebler, I.Y.S. Lee, M.D. Levin, S.R. Marder, D. McCord-Maughon, H. Rockel, M. Rumi, G. Subramanian, W.W. Webb, X.L. Wu, C. Xu, *Abstr. Pap. Am. Chem. Soc.* **217**, U378 (1999)
- M. Albota, D. Beljonne, J.L. Bredas, J.E. Ehrlich, J.Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S. Marder, D. McCord-Maughon, J.W. Perry, H. Rockel, M. Rumi, G. Subramanian, W.W. Webb, X.L. Wu, C. Xu, *Science* **281**, 1653 (1998)
- C.S. Colley, D.C. Grills, N.A. Besley, S. Jockusch, P. Matousek, A.W. Parker, M. Towrie, N.J. Turro, P.M.W. Gill, M.W. George, *J. Am. Chem. Soc.* **124**, 14952 (2002)
- N.J. Turro, *Modern Molecular Photochemistry* (University Science Books, Sausalito, 1991)
- K.D. Belfield, K.J. Schafer, Y.U. Liu, J. Liu, X.B. Ren, E.W. Van Stryland, *J. Phys. Organ. Chem.* **13**, 837 (2000)
- W.H. Zhou, S.M. Kuebler, K.L. Braun, T.Y. Yu, J.K. Cammack, C.K. Ober, J.W. Perry, S.R. Marder, *Science* **296**, 1106 (2002)
- C. Martineau, R. Anemian, C. Andraud, I. Wang, M. Bouriau, P.L. Baldeck, *Chem. Phys. Lett.* **362**, 291 (2002)
- A. Bhaskar, G. Ramakrishna, Z.K. Lu, R. Twieg, J.M. Hales, D.J. Hagan, E. Van Stryland, T. Goodson, *J. Am. Chem. Soc.* **128**, 11840 (2006)
- S.L. Oliveira, D.S. Correa, L. Misoguti, C.J.L. Constantino, R.F. Aroca, S.C. Zilio, C.R. Mendonca, *Adv. Mater.* **17**, 1890 (2005)