

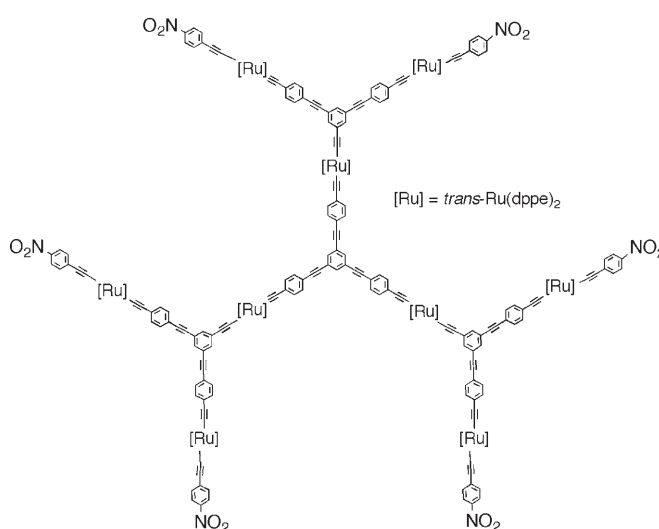
Two-Photon and Three-Photon Absorption in an Organometallic Dendrimer**

Marek Samoc, Joseph P. Morrall, Gulliver T. Dalton, Marie P. Cifuentes, and Mark G. Humphrey*

Dedicated to Professor Gerhard Erker on the occasion of his 60th birthday

Multiphoton absorption is of intense interest for a variety of potential applications, such as optical power limiting, data storage, multiphoton microscopy, microfabrication, and frequency up-conversion lasing.^[1] Multiphoton processes possess significant advantages, such as superior resolution, which enables precise spatial control for the various applications, together with the possibility of using infrared lasers at wavelengths that are technologically important in biology, medicine, and telecommunications. Thus far, most studies have considered two-photon absorption (2PA).^[2] Enormous strides have been made in our understanding of how molecular structure controls 2PA efficiency by examining a range of compounds with dipolar, quadrupolar, and octupolar geometries. Three-photon absorption (3PA) may be superior to 2PA, because its cubic dependence on incident-light intensity leads to superior spatial confinement of the excitation volume and it also affords the possibility of using a much longer excitation wavelength. Whereas there have been several reports of three-photon processes resulting from 2PA followed by excited-state absorption (ESA),^[3] there have been fewer studies of instantaneous 3PA^[4] and very few examining the wavelength dependence of 3PA.^[5] We report herein the first such study for an organometallic dendrimer and a record 3PA coefficient that highlights the potential of organometallic dendrimers.

The synthesis of the dendrimer employed in the present study (**1**; dppe = 1,2-bis(diphenylphosphanyl)ethane) is described elsewhere.^[6] The nonlinear absorption properties of **1** were evaluated by Z-scan experiments in the spectral range



625–1500 nm by employing fs pulses, the latter minimizing contributions from ESA and therefore giving a better prospect of affording the intrinsic nonlinearity; the short wavelength limit was chosen to ensure that all data were collected in the region of optical transparency of the dendrimer. Both closed-aperture and open-aperture Z-scan measurements were undertaken, thus permitting simultaneous evaluation of spectral dependences of both components of the complex hyperpolarizability (γ_{real} and γ_{imag}); this is only the second such study for an inorganic compound.^[7] The results for the range 625–950 nm are shown in Figure 1.

Figure 1 reveals that γ_{real} is negative over this spectral range, whereas γ_{imag} is positive with a maximum at around

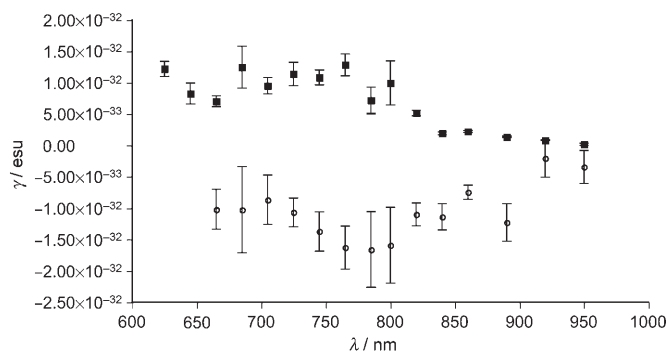


Figure 1. Experimental values of γ_{real} (open circles) and γ_{imag} (filled squares) for **1**.

[*] J. P. Morrall, G. T. Dalton, Dr. M. P. Cifuentes, Prof. M. G. Humphrey
Department of Chemistry
Australian National University
Canberra, ACT 0200 (Australia)
Fax: (+61) 2-6125-0760
E-mail: mark.humphrey@anu.edu.au
M. Samoc, J. P. Morrall, G. T. Dalton
Laser Physics Centre
Research School of Physical Sciences and Engineering
Australian National University
Canberra, ACT 0200 (Australia)

[**] Organometallic Complexes for Nonlinear Optics, Part 38. This work was supported by the Australian Research Council. We thank the Johnson-Matthey Technology Centre for the generous loan of ruthenium salts. M.G.H. thanks the ARC for an Australian Professorial Fellowship, and M.P.C. thanks the ARC for an Australian Research Fellowship. Part 37: C. E. Powell, M. P. Cifuentes, M. G. Humphrey, A. C. Willis, J. P. Morrall, M. Samoc, *Polyhedron*, DOI: 10.1016/j.poly.2006.05.007.

750 nm. We verified that the data centered at 750 nm correspond to a 2PA process, but, on extending the study to longer wavelengths, we found that the open-aperture scans in the range 1000–1300 nm also show substantial nonlinear absorption. The data in this spectral range are consistent with the dominance of a 3PA process (Figures 2 and 3).

Figure 4 shows the one-photon absorption spectrum of **1** together with two-photon (a) and three-photon (b) absorption profiles; the latter are plotted against two and three times the fundamental photon wavenumber, respectively, for ease

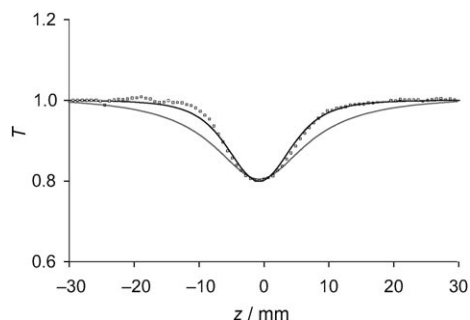


Figure 2. Open-aperture Z-scan data at 1200 nm for a solution of **1** in CH_2Cl_2 (open squares) and theoretical curves calculated for $w_0 = 52 \mu\text{m}$ (determined from closed-aperture scans for pure solvent) assuming 2PA (gray line) or 3PA (black line). T = transmission.

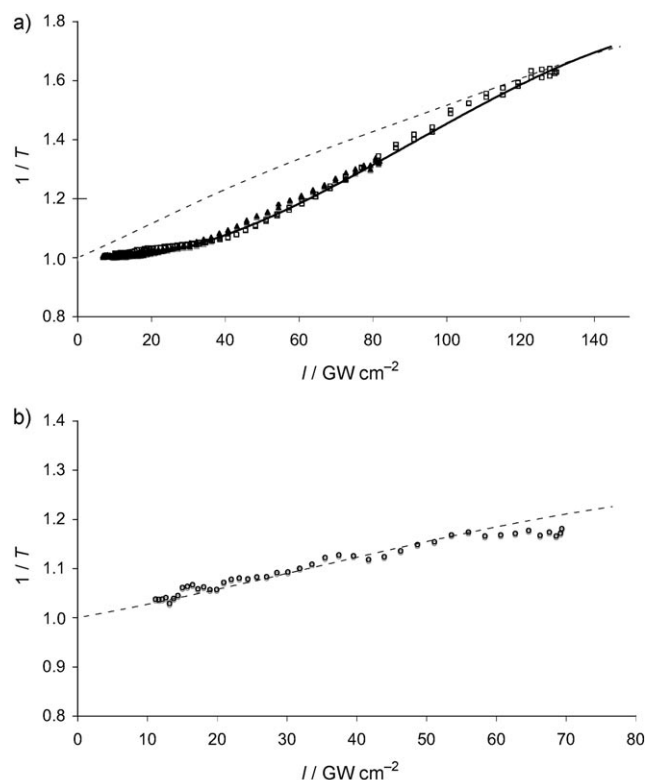


Figure 3. a) Nonlinear absorption (plotted as the inverse of transmission vs intensity) at 1100 nm measured with 0.95- and 1.7- μs pulses (triangles and squares, respectively) compared with theoretical 2PA (dashed line) and 3PA (solid line) dependences. b) Nonlinear absorption at 850 nm plotted in the same way, measured with 0.55- μs pulses.

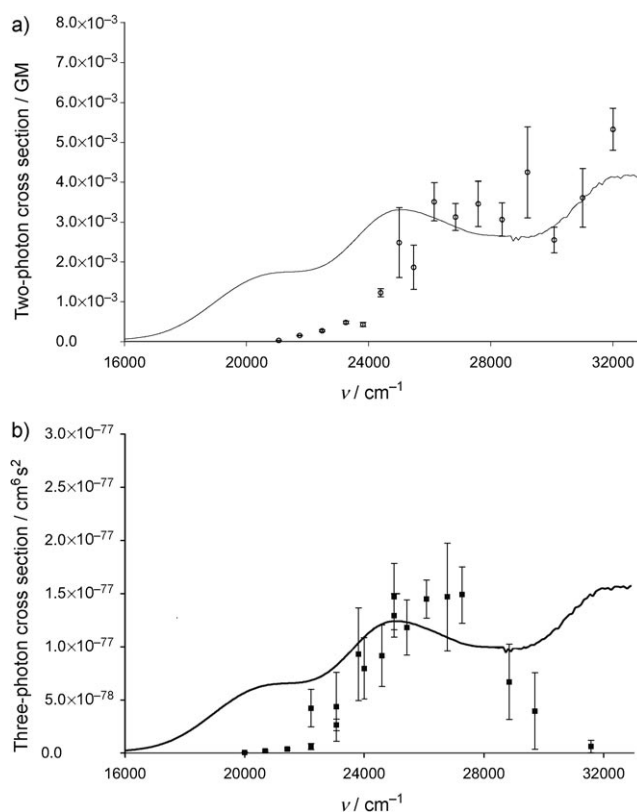


Figure 4. Comparison of the two-photon (a) and three-photon (b) absorption profiles for **1** with the one-photon spectrum (solid line) of a solution in CH_2Cl_2 (ca. 10^{-5} M). Experimental multiphoton absorption cross sections are reported as open circles (2PA) and filled squares (3PA) and are plotted against twice and three-times the fundamental photon wavenumber, respectively.

of comparison with the linear absorption profile. It is immediately evident that both two-photon and three-photon absorption profiles are significantly different from the one-photon profile. Whereas the one-photon profile shows an overlap of at least two separate bands [centered at $25\,300 \text{ cm}^{-1}$ (395 nm) and $21\,400 \text{ cm}^{-1}$ (467 nm)], the multiphoton absorptions do not show evidence of a transition corresponding to the long-wavelength shoulder. This observation is consistent with the two transitions having a vastly different degree of delocalization: the long wavelength transition corresponds to a MLCT transition localized in the nitrophenylalkynylruthenium units, and the shorter wavelength transition involves large changes in the multipolar distribution of the electron density in the molecule. This behavior is different from that observed by us for a similar dendrimer that contains peripheral metal atoms only.^[7]

The maxima of twice the two-photon and three-times the three-photon absorption profiles are blue-shifted relative to the maxima of the one-photon absorption spectrum; this shift appears to be larger in the case of the two-photon absorption spectrum. This difference in blue shift may arise from the differing transition symmetry requirements for two-photon and three-photon absorption and thus different contributions to the multiphoton absorption profile of the component vibronic transitions, but a theoretical calculation or simula-

tion for further understanding of this effect is not possible at present. The maximum value of σ_2 at approximately $13\,500\text{ cm}^{-1}$ (3000–4000 GM) reveals that, even with its large molecular weight ($M = 10\,448$), this compound is a very strong two-photon absorber in this wavelength range, similar in magnitude of σ_2 to organic 2PA materials. The maximum value for σ_3 at approximately 8700 cm^{-1} ($1.5 \times 10^{-77}\text{ cm}^6\text{s}^2$) is exceptionally large for a molecule examined under fs-pulse conditions,^[4,5] thus highlighting the potential of organometallic dendrimers as 3PA materials.

Experimental Section

Measurements were carried out in the wavelength range 625 to 1500 nm. The short wavelength limit was determined by the onset of one-photon absorption of solutions of **1**, which has an absorption tail extending into the red wavelength range of the visible spectrum. The measurements were carried out on solutions of **1** in dichloromethane (0.8–1 % w/w) placed in a 1-mm-thick glass cell. The laser system used in this study was a Clark-MXR CPA-2001 Ti-sapphire regenerative amplifier that pumped a Light Conversion TOPAS optical parametric amplifier. For the measurements in this study it was necessary to use the doubled signal, the doubled idler, and the signal from the OPA in three different wavelength ranges. The Z-scan setup was adjusted to provide a beam waist of typically $w_0 = 40\text{--}60\text{ }\mu\text{m}$ so that the Rayleigh range (z_R) was always longer than the total thickness of the cell (about 3 mm). Under such conditions the Z-scan signal can be considered to arise from the cumulative contributions of the solvent and solute as well as from the glass walls of the cell.

The experimental open-aperture and closed-aperture Z-scans were analyzed with a custom fitting program that allows one to derive information on the real and imaginary parts of the nonlinear phase shift. The results obtained for the solution of **1** were compared with those obtained for pure solvent placed in an identical glass cell and with data obtained for a 3-mm-thick silica plate. The light intensity was adjusted (by using appropriate neutral density filters) to obtain the nonlinear phase shifts of the order of, but generally not exceeding, about 1 rad. This value corresponds to light intensities of the order of 100 GW cm^{-2} . The light intensities and nonlinearities were calibrated by using the closed-aperture scans on fused silica, assuming for simplicity that the dispersion of the nonlinear refractive index of silica can be neglected in the wavelength range covered. Thus, it has been assumed that $n_{2,\text{silica}} = 3 \times 10^{-16}\text{ cm}^2\text{W}^{-1}$ (see reference [9]) independent of the wavelength.

The real and imaginary parts of the cubic hyperpolarizability γ (see reference [10] for definitions and examples of other data for organometallic complexes) were determined for **1** from the difference between the nonlinear phase shift for a cell with the solution of **1** and that for a cell with the solvent alone. This typically results in relatively large errors for the real part of the hyperpolarizability of the solute as it is determined against contributions from the solvent, whereas the imaginary part of γ has lower errors because the solvent does not show any nonlinear absorption in the wavelength and light intensity range used.

The two- and three-photon cross sections were determined from fits of the open-aperture scans in the wavelength ranges in which the shapes of the scans indicated linear or higher-order light-intensity dependence of the absorption, respectively. Light-intensity dependences of the nonlinear absorption were studied by changing either the beam focusing or the pulse energy as shown in the example in Figure 3a. Numerical integration of Equation 30 in reference [8] (suitably modified for the case of three-photon absorption) was used to compute the theoretical two-photon- and three-photon-dominated

open-aperture scans. The cross sections were defined by Equation (1),

$$\frac{d\Phi}{dz} = -N\sigma_1\Phi - N\sigma_2\Phi^2 - N\sigma_3\Phi^3 - \dots \quad (1)$$

in which Φ is the photon flux, N is the density of absorbing molecules, and σ_i are the linear and nonlinear absorption cross sections. (Note that some authors prefer to define multiphoton absorption cross sections with a numerical factor of two and three, respectively, in front of the relevant terms in the above equation.)

Received: June 12, 2006

Revised: October 20, 2006

Published online: December 5, 2006

Keywords: absorption · alkynyl ligands · dendrimers · nonlinear optics · ruthenium

- [1] T. C. Lin, S. J. Chung, K. S. Kim, X. P. Wang, G. S. He, J. Swiatkiewicz, H. E. Pudavar, P. N. Prasad, *Polymers for Photonics Applications II*, Vol. 161, Springer, Berlin, **2003**, p. 157.
- [2] Selected examples: a) S. J. Chung, K. S. Kim, T. H. Lin, G. S. He, J. Swiatkiewicz, P. N. Prasad, *J. Phys. Chem. B* **1999**, *103*, 10741; b) A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* **1999**, *18*, 5195; c) 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* **2002**, *296*, 1106; d) M. Drobizhev, A. Karotki, A. Rebane, C. W. Spangler, *Opt. Lett.* **2001**, *26*, 1081; e) O. Mongin, L. Porres, L. Moreaux, J. Mert, M. Blanchard-Desce, *Org. Lett.* **2002**, *4*, 719; f) S. J. K. Pond, O. Tsutsumi, M. Rumi, O. Kwon, E. Zojer, J. L. Bredas, S. R. Marder, J. W. Perry, *J. Am. Chem. Soc.* **2004**, *126*, 9291.
- [3] See, for example: a) R. Anémian, Y. Morel, P. L. Baldeck, B. Paci, K. Kretsch, J.-M. Nunzi, C. Andraud, *J. Mater. Chem.* **2003**, *13*, 2157; b) R. L. Sutherland, M. C. Brant, J. Heinrichs, J. E. Rogers, J. E. Slagle, D. G. McLean, P. A. Fleitz, *J. Opt. Soc. Am. B* **2005**, *22*, 1939; c) B. Paci, J.-M. Nunzi, R. Anémian, C. Andraud, A. Collet, Y. Morel, P. L. Baldeck, *J. Opt. A* **2000**, *2*, 268.
- [4] a) S. Maiti, J. B. Shear, R. M. Williams, W. R. Zipfel, W. W. Webb, *Science* **1997**, *275*, 530; b) G. S. He, P. P. Markowicz, T.-C. Lin, P. N. Prasad, *Nature* **2002**, *415*, 767; c) M. Drobizhev, A. Karotki, Yu. Dzenis, M. Kruk, A. Rebane, Z. Suo, C. W. Spangler, *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5211*, 38; d) M. Drobizhev, A. Karotki, M. Kruk, Yu. Dzenis, A. Rebane, Z. Suo, C. W. Spangler, *J. Phys. Chem. B* **2004**, *108*, 4221; e) M. Drobizhev, A. Rebane, Z. Suo, C. W. Spangler, *J. Lumin.* **2005**, *111*, 291; f) Q. Zheng, G. S. He, C. Lu, P. S. Prasad, *J. Mater. Chem.* **2005**, *15*, 3488.
- [5] a) Z. Suo, M. Drobizhev, C. W. Spangler, N. Christensson, A. Rebane, *Org. Lett.* **2005**, *7*, 4807; b) A. Rebane, N. Christensson, M. Drobizhev, Yu. Stepanenko, C. W. Spangler, *Opt. Express* **2005**, *13*, 6033.
- [6] A. M. McDonagh, C. E. Powell, J. P. Morrall, M. P. Cifuentes, M. G. Humphrey, *Organometallics* **2003**, *22*, 1402.
- [7] C. E. Powell, J. P. Morrall, S. A. Ward, M. P. Cifuentes, E. G. A. Notaras, M. Samoc, M. G. Humphrey, *J. Am. Chem. Soc.* **2004**, *126*, 12234.
- [8] M. Sheikh-Bahae, A. A. Said, T. Wei, D. J. Hagan, E. W. van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760.
- [9] D. Milam, *Appl. Opt.* **1998**, *37*, 546.
- [10] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1999**, *43*, 349.