

# Third-order optical nonlinearities of metallotetrabenzoporphyrins and a platinum poly-yne

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The third-order optical nonlinearities of two metallotetrabenzoporphyrins and a platinum poly-yne dissolved in tetrahydrofuran were measured by using picosecond and nanosecond laser pulses. The pulse-width-dependent measurements indicated that excited-state absorption was present in both classes of material along with non-resonant two-photon absorption.

Different classes of organic compounds and polymers are currently being studied intensively in an effort to identify materials with large third-order nonlinearity ( $\chi^3$ ) for various switching applications.<sup>1</sup> Direct measurement of intensity-dependent total transmission of ultrashort laser pulses is one of the many ways of measuring the imaginary part of  $\chi^3$ . However, intensity-dependent transmission of laser beams can arise not only from (single-photon non-resonant) two-photon absorption, which is characterized by the two-photon absorption coefficient  $\beta$ , but also from excited-state absorption, which is characterized by the absorption cross section  $\sigma$ . We were able to differentiate between the two processes, and to determine the values of  $\beta$  and  $\sigma$  for our materials, by measuring intensity-dependent transmission with the use of laser beams of different pulse widths. We also measured the real part of  $\chi^3$  of our materials by using the optical Kerr gate technique.

The materials examined in this study were metallotetrabenzoporphyrins and a platinum poly-yne. Rao *et al.*<sup>2</sup> have reported the optical nonlinearity of metallotetrabenzoporphyrins and metal-free tetrabenzoporphyrins measured by the degenerate four-wave-mixing technique. Complementary measurements of the  $\chi^3$  of the benzoporphyrins are presented here and compared directly with those of the platinum poly-yne, which we have found to be a promising nonlinear-optical material.<sup>3,4</sup>

The benzoporphyrins chosen for this study are the compounds numbered 4 and 7 in Ref. 2; here we refer to them as benzoporphyrin 1 and benzoporphyrin 2, respectively. The platinum poly-yne that we have chosen is the polymer number 4 in Ref. 4. The intensity-dependent absorption measurements were performed by using picosecond- and nanosecond-duration laser beams. The picosecond

laser consisted of a mode-locked Quantel Nd:YAG laser that was frequency doubled to 532 nm. The duration of the laser pulse was 21 ps (FWHM), and the beam was focused to a spot size of 50  $\mu\text{m}$  (FWHM) through a 50-cm focal-length lens. The nanosecond-duration beam (FWHM 6 ns) was obtained from a Quantel Q-switched frequency-doubled (to 532 nm) laser and was focused to a spot size of 143  $\mu\text{m}$  (FWHM) by a 50-cm focal-length lens. The nonlinear sample was placed at the focus of the laser beam in a glass cell with a 2-mm path length. A standard half-wave plate/polarizer combination was used to vary the amount of energy incident on the sample, and the total amount of transmitted energy was measured by a silicon detector as a function of the incident energy.

Figure 1 shows the dependence of the energy transmission through the samples as a function of the incident intensity. If nonresonant two-photon absorption were the only mechanism giving rise to the transmission drop, we would expect the nanosecond and the picosecond curves for each material to be superimposed because the process would be dependent only on the incident intensity. The separation between the curves indicates that some other mechanism is also contributing to the drop in the energy transmission.

Figure 2 shows the same results but with the transmission plotted as a function of the incident fluence rather than the intensity. For the benzoporphyrins, the transmission is almost completely fluence dependent, indicating that some fluence-dependent process, such as excited-state absorption, is the primary cause of the nonlinearity. For the poly-yne sample, the energy transmissions of the nanosecond and picosecond pulses at the same fluence differ to a much greater extent, indicating that a combination of excited-state absorption and non-

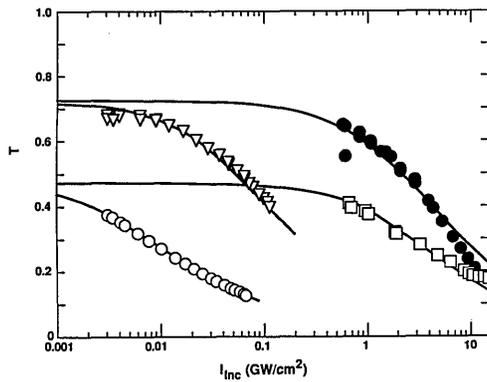


Fig. 1. Energy transmission of the samples measured as a function of the incident intensity. The filled circles and triangles represent the data for the poly-yne sample for the picosecond and the nanosecond lasers, respectively. The squares and the open circles represent the data for the benzoporphyrin 2 sample for the picosecond and nanosecond laser measurements, respectively. The solid curves are the best fits to the data to the theoretically calculated absolute value of the transmission.

resonant two-photon absorption is most likely governing the nonlinearity.

The equation for the intensity ( $I$ ) of a laser beam propagating (in the  $z$  direction) through a nonlinear medium in which linear absorption, two-photon absorption, and excited-state absorption are present can be written as

$$\frac{dI}{dz} = -\alpha I - \beta I^2 - \sigma NI, \quad (1)$$

where  $\alpha$  is the linear absorption coefficient,  $\beta$  is the two-photon absorption coefficient,  $\sigma$  is the excited-state absorption cross section, and  $N$  is the population density of the excited states created by the absorption process. The population density  $N$  is governed by the equation

$$\frac{dN}{dt} = \frac{\alpha I}{h\nu} - \frac{N}{\tau}, \quad (2)$$

where  $\tau$  is the decay time for the excited state and  $h\nu$  is the energy of a laser photon.

In Eq. (2) we have ignored the contribution of two-photon absorption to the excited-state population density  $N$  because of the observed dependence of the nonlinear transmission on the incident intensity. The nonlinear transmission  $T_{nl}$  is defined as the total energy transmission  $T$  divided by the linear transmission. Theoretically, the plot of  $T_{nl}^{-1} - 1$  as a function of the peak intensity  $I_0$  would be a straight line for small values of  $I_0$  if there were no two-photon contribution to  $N$  (Ref. 5); if only two-photon absorption contributed to  $N$ , the plot of  $T_{nl}^{-1} - 1$  versus  $I_0$  on a log-log graph would be a straight line with slope 2 when  $I_0$  is small. If both one- and two-photon-absorption processes contributed to  $N$ , the slope of the plot would be expected to lie between 1 and 2. We found that for all the samples, at low values of the incident intensities, the  $T_{nl}^{-1} - 1$  versus  $I_0$  plots obtained experimentally are close to straight lines with slope 1.

Equations (1) and (2) were solved numerically by using the finite-difference method. The incident laser beam was assumed to have Gaussian temporal

and spatial profiles, and the value of  $T$  (defined on p. 232 of Ref. 5) was calculated. The values of the parameters  $\beta$ ,  $\sigma$ , and  $\tau$ , given in Table 1, were obtained by fitting  $T$  to the experimental data (Figs. 1 and 2). For the benzoporphyryns the deviation of the experimental data from theory at high values of the incident fluence in Fig. 1 may be due to fluorescence. Because the transmission is higher than the theoretical value, no higher-order nonlinear-optical processes are present. Further, saturable absorption is unlikely to be the cause of this deviation because the deviation is fluence dependent rather than intensity dependent.

To obtain an independent measurement of  $\tau$ , a time-resolved experiment was performed with a weak probe beam (at 532 nm) variably delayed with respect to the pump beam. The change in the probe transmission dropped to  $1/e$  of its peak value in 3 ns for the poly-yne sample and in  $>10$  ns for the porphyrin samples, thus showing that the values presented in Table 1 are approximately correct.

For benzoporphyrin compound 2, only an upper limit for  $\beta$  could be determined because excited-state absorption dominated both the nanosecond and the picosecond behavior. The  $\beta$  of ZnSe is given in Table 1 for comparison.

The real part of the nonlinearity of the materials was measured by using an optical Kerr gate setup.<sup>4</sup> The wavelength of the pump and the probe beams was 1.064  $\mu\text{m}$ , so the effects of linear absorption could be ignored. The results of the measured values of the nonlinear refractive index  $n_2$  of the solutions are shown in Table 2, along with the value of the real part of  $\chi^3$  and the value of the hyperpolarizability  $\gamma'$ . To our knowledge, this is the first measurement of the real part of  $\chi^3$  of the porphyrin compounds. The  $n_2$  and  $\chi^3$  of  $\text{CS}_2$  (Ref. 8) are provided in Table 2 for comparison. We also measured the values of the real part of the nonlinearity at 532 nm and found them to be of the same order of magnitude as the 1.064- $\mu\text{m}$  values. A comparison of Tables 1 and 2 shows that the imaginary parts of the susceptibility and the hyperpolarizability (measured at 532 nm) are larger than the real parts (measured at 1.064  $\mu\text{m}$ ) by factors of 5–10; these materials therefore are not suitable for optical

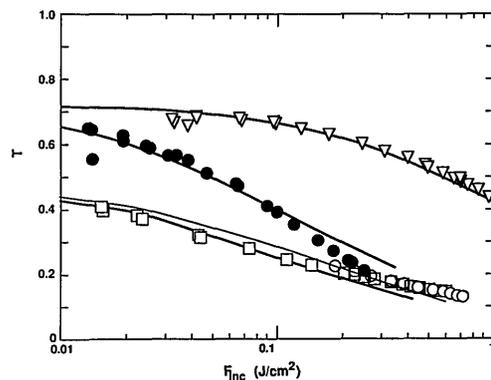


Fig. 2. Energy transmission of the samples measured as a function of the incident fluence. The symbols and solid curves represent the same samples and calculations as in Fig. 1.

**Table 1. Values of  $\beta$ ,  $\sigma$ , and  $\tau$  Obtained from the Best Fits to  $T$  (Figs. 1 and 2)<sup>a</sup>**

	Concentration (g/L)	$\alpha$ (cm <sup>-1</sup> )	$\beta$ (cm/GW)	$\sigma$ (10 <sup>-17</sup> cm <sup>2</sup> )	$\tau$ (ns)	Im( $\chi^3$ ) (10 <sup>-13</sup> esu)	$\gamma''$ (10 <sup>-30</sup> esu)
Benzoporphyrin 1	0.46	2.4	2.5 ± 0.2	3.0 ± 0.25	15.0 ± 2.5	9 ± 1	0.8 ± 0.08
Benzoporphyrin 2	0.46	3.8	≤ 0.5	3.0 ± 0.25	15 ± 2.5	≤ 1.8	≤ 0.16
Poly-yne	90.4	1.6	3.5 ± 0.35	1 ± 0.2	4.6 ± 0.5	13 ± 1.3	0.0054 ± 0.0005

$${}^a\beta(\text{ZnSe}) = 5.5 \text{ cm/GW}, {}^b\text{Im}(\chi^3)(\text{esu}) = (n^2\epsilon_0 c \lambda / 2\pi)\beta, {}^c\text{and } \gamma = (\chi^3 / L^4 N_1). {}^d$$

**Table 2. Values of the Real Part of  $\chi^3$ <sup>a</sup>**

	Concentration (g/L)	$n_2$ (10 <sup>-10</sup> cm <sup>2</sup> /MW)	Re( $\chi^3$ ) (10 <sup>-14</sup> esu)	$\gamma'$ (10 <sup>-33</sup> esu)
Benzoporphyrin 1	0.46	7.8 ± 3.5	7.8 ± 3.5	1.0 ± 0.5
Benzoporphyrin 2	0.46	9.1 ± 4.5	9.1 ± 4.5	1.8 ± 0.9
Poly-yne	90.4	26 ± 5	26 ± 5	0.12 ± 0.03

$${}^a n_2(\text{CS}_2) = 3.3 \times 10^{-8} \text{ cm}^2/\text{MW}, {}^b \chi^3(\text{CS}_2) = 3 \times 10^{-12} \text{ esu}, \text{ and } \text{Re}(\chi^3) = 2n^2 c \epsilon_0 n_2. {}^c$$

**Table 3. Measured Values of the Nonlinearities of Some Recently Studied Organic Materials**

Material (Method)	Re( $\chi^3$ ) (10 <sup>-13</sup> esu)	Im( $\chi^3$ ) (10 <sup>-13</sup> esu)	$ \chi^3 $ (10 <sup>-13</sup> esu)	$\sigma$ (10 <sup>-17</sup> cm <sup>2</sup> )	Limiting Fluence (mJ/cm <sup>2</sup> )
Pt Phthalocyanine <sup>10</sup> (degenerate four-wave mixing)			2		
Metal cluster compounds <sup>11</sup> (optical limiting)					500
Polysilane <sup>12</sup> (Z scan)	4	4			
Metallophthalocyanines <sup>13</sup> (Z scan)				2.3	
Platinum poly-yne <sup>a</sup>	2.6	13		1	100
Benzoporphyrin 1 <sup>a</sup>	0.8	9		3	100

<sup>a</sup>See text.

switching applications (in the visible spectrum) that rely only on the nonlinear change of phase.<sup>9</sup>

In Table 3, a comparison of the measured (not extrapolated) nonlinearities of some recently studied organic materials is presented. The competitive values of the absorptive nonlinearities of the platinum poly-yne and the zinc benzoporphyrin, along with their chemical stability and broadband transparency in the visible spectrum, make them strong candidates for some optical applications.

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- All the quantities in these equations are in mks units;  $n$  (=1.45) is the refractive index of the solvent,  $c$  is the speed of light,  $\epsilon_0$  is the vacuum permittivity, and  $\lambda$  is the wavelength of light. The relationships among  $n_2$ ,  $\beta$ , and  $\chi^3$  were derived starting from Maxwell's wave propagation equation, with the nonlinear polarization defined as  $P_{nl} = \epsilon_0 \chi^3 (EE)E$ . The relationship between  $\gamma$  and  $\chi^3$  is obtained from Ref. 2, where  $L$  is a local field factor, given by  $L = (n^2 + 2)/3$ , and  $N_1$  is the number density of the solute in the solution, given by  $N_1 = AC/M$  ( $A$  is Avogadro's number,  $C$  is the concentration of the solution, and  $M$  is the molecular weight of the solute). To obtain  $\chi^3$  in cgs esu units, we use the conversion formula  $\chi^3(\text{esu}) = (9 \times 10^8) / 4\pi \chi^3(\text{mks})$ .
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