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Dispersion of the Third-Order Nonlinear Optical Properties of an Organometallic Dendrimer¹Clem E. Powell,[†] Joseph P. Morrall,^{†,‡} Simone A. Ward,[†] Marie P. Cifuentes,[†] Eleni G. A. Notaras,^{†,‡} Marek Samoc,^{*,‡} and Mark G. Humphrey^{*,†}

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Although the third-order nonlinear optical (NLO) properties of organic molecules have been the subject of many investigations,² most reports only provide the third-order polarizability γ at a fixed wavelength. Spectral dependences of two-photon absorption cross sections (related to the imaginary part of the third-order polarizability) have been studied,^{3–5} but there is very little data on the dispersion of both the real and imaginary parts of the third-order polarizability γ ,^{6,7} without which structure–property relationships are difficult to develop. Organometallic complexes have attracted significant recent interest, because the presence of the metal often results in intense charge-transfer transitions in the linear optical spectrum that may result in compounds with enhanced nonlinearity^{8–11} and because the accessibility of multiple oxidation states may afford compounds with which one can reversibly modulate (“switch”) nonlinearity.^{1,11–15} Despite these advantages, there are no extant studies of the dispersion of γ_{real} and γ_{imag} of organometallic (or indeed inorganic) complexes. We present herein the wavelength dependence of both the real part and the imaginary part of the nonlinearity γ of an organometallic dendrimer. We interpret the dispersion of γ_{imag} in terms of competition between two-photon absorption and saturable absorption processes. Our modeling of the dispersion of both γ_{imag} and γ_{real} has broad implications for our understanding of the NLO properties of complex molecules.

The new dendrimer (Figure 1) was prepared using “steric control”¹⁶ and was characterized by various spectroscopic data and elemental analyses.¹⁷ Because of the acceptor nitro groups on its periphery, the dendrimer has a charge-transfer character, and its absorption spectrum (Figure 2) is red-shifted compared to the analogous dendrimer without acceptor groups.¹⁶ We expected that the red-shift of the absorption maximum would result in enhanced nonlinear properties of the molecule, including increased two-photon absorption (cf. ref 3). However, our initial measurements at 800 nm revealed no two-photon absorption effect; instead, a negative value of the nonlinear absorption coefficient β was obtained (β is usually defined by the relation $\alpha = \alpha_0 + \beta I$, and so a positive value of β indicates an absorption coefficient, α , that increases with intensity I , as in the case of two-photon absorption, and a negative value of β indicates saturable absorption). This prompted a detailed investigation in which we evaluated the nonlinear absorption characteristics of the dendrimer over a range of wavelengths, in the form of the imaginary part of the hyperpolarizability γ_{imag} . The Z-scan experiment allowed us to simultaneously evaluate the real part of the hyperpolarizability γ_{real} . (Note that the accuracy is lower for γ_{real} than for γ_{imag} . This is because the nonlinear absorption of the solvent is negligible in the wavelength and intensity ranges used

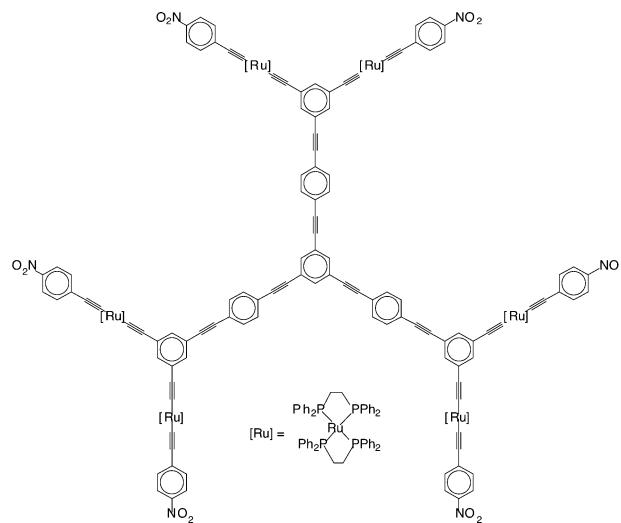


Figure 1. Structure of the organometallic dendrimer.

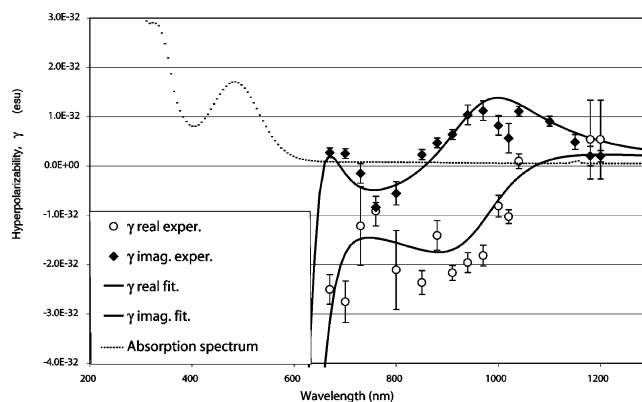


Figure 2. Experimental and calculated values of γ_{real} and γ_{imag} for the organometallic dendrimer. The absorption spectrum (against air, in arb units) of a dilute solution of the dendrimer in dichloromethane is also shown (the small peak at ca. 1150 nm is due to overtone absorption of the solvent).

by us, and thus the nonlinear absorption of the dendrimer can be determined relatively precisely; in contrast, the refractive nonlinearity of the dendrimer is measured as an increment to the refractive nonlinearity of the solvent and glass walls of the cuvette.)

Figure 2 shows experimental results obtained in this study, as well as an interpretation of the dispersion of the real and imaginary parts of γ using simplified dispersion formulas. The nonlinear absorption results reveal a range (ca. 700–850 nm) in which the sign of β (and therefore γ_{imag}) is negative, corresponding to absorption saturation. Outside this range, the sign of β is positive, indicating the dominance of two-photon absorption. γ_{real} is negative

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across most of the measurement range, positive values being obtained around 1200 nm (two unreliable data points for γ_{real} at ca. 1100 nm were not plotted).

Interpretation of the dispersion cannot be accomplished in a comprehensive way until the structure of the energy levels of the dendrimer is known in detail. At present we have based our interpretation on the results of the linear optical spectroscopy, assuming that resonances with two transitions seen in the absorption spectrum at ca. 330 and 480 nm are relevant for the nonlinear properties. Because a change of sign of β is seen, our interpretation assumed a superposition of two competing processes: two-photon absorption and absorption bleaching.

The general sum-over-states expressions for the dispersion of the third-order polarizability are known (see, for example, ref 18) and can be used for the interpretation of the complex polarizability, providing that one accounts for damping factors. The full expressions contain a large number of terms, but since our interest is in the hyperpolarizability $\gamma(-\omega; \omega, -\omega, \omega)$ at relatively low frequencies ω , the most important terms in the expansion are those close to resonance. For two-photon resonances with two excited states at ω_a and ω_b , these are the terms containing denominators with frequency differences $\omega_a - 2\omega$ and $\omega_b - 2\omega$. In contrast, the spectral dependence of absorption bleaching can be modeled with terms containing single-photon resonances, containing $\omega_a - \omega$ in the denominator. (It should be noted that a Z-scan measurement does not allow one to differentiate between instantaneous and non-instantaneous processes modifying the absorption coefficient because of the action of the electromagnetic field of the laser pulse and because of the depletion of the ground state.)

With the above ideas in mind, the line-fitting in Figure 2 was derived from a simplified, three-term expression for γ :

$$\gamma = \left[\frac{A}{\nu_a - 2\nu - i\Gamma_1} + \frac{B}{\nu_b - 2\nu - i\Gamma_2} - \frac{C}{\nu_a - \nu - i\Gamma_1} \right] \times \frac{1}{(\nu_a - \nu - i\Gamma_1)^2}$$

where A , B , and C were adjustable constants and wavenumbers ν were used instead of frequencies. This expression was optimized to fit simultaneously the experimental data for both the real and imaginary parts of γ , resulting in the following parameters: (i) the values of the damping constants Γ_1 and Γ_2 were 2660 and 2211 cm^{-1} , respectively, (ii) the resonance frequencies taken for the calculations were $\nu_a = 20\,462\text{ cm}^{-1}$ and $\nu_b = 31\,250\text{ cm}^{-1}$, corresponding to wavelengths of 489 and 320 nm (slightly shifted from the absorption spectra maximum values), and (iii) the values of the constants A , B , and C were 5.17×10^{-21} , 4.05×10^{-21} , and 6.78×10^{-21} in $\text{cm}^2 \text{statVolt}^{-2}$, respectively.

Despite the obvious shortcomings of employing a simplified expression, agreement of the observed dispersion of the nonlinear absorption and refraction (as represented by γ_{imag} and γ_{real}) with that predicted on the basis of the above equation is quite satisfactory. The coincidence of the two-photon absorption peak with twice the wavelength of the lowest one-photon transition is intuitively

expected. The second peak due to resonance at $\nu = \nu_b/2$ is apparently distorted by the presence of a nearby one-photon resonance at $\nu = \nu_a$, leading to a negative nonlinear absorption contribution.

In conclusion, this study demonstrates that the dispersion of cubic nonlinearity in complex molecules such as organometallic dendrimers can be understood in terms of an interplay of two-photon absorption and absorption saturation and that simple dispersion relations can reproduce the behavior of both the real and imaginary components of the hyperpolarizability. Further studies testing these observations are currently underway.

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Supporting Information Available: Details of the preparation and procedures and spectroscopic and analytical data for the dendrimer, its precursor complexes, and the nonlinear optical measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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