

## Nonlinear absorption of soluble octasubstituted metallophthalocyanines at 1.064 $\mu\text{m}$

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### Abstract

The nonlinear absorption and refraction of octasubstituted metallophthalocyanines ( $R_8\text{PcM}$ ;  $M = 2\text{H}, \text{Cu}$ ) in solution is measured in the picosecond regime by the Z-scan technique at a wavelength of 1.064  $\mu\text{m}$ . The results at different pulsewidths show that the nonlinear absorption process is dominated by two-photon absorption in the metal-free compound, and by excited state absorption in the Cu-substituted molecule.

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Metallophthalocyanines (MPc), planar conjugated  $\pi$ -electron systems, are interesting materials due to their potential applications to a variety of fields such as chemical sensors, molecular metals, electrochromic and photovoltaic cells, etc. [1]. Moreover, they present promising nonlinear refraction and absorption properties that may be useful for optical switching and optical limiting devices [2–9].

The electronic third order nonlinear optical properties of Pc's have been extensively investigated by third harmonic generation (THG), [2–5] most of the experiments being performed on thin films. In this case, the nonlinearity is exclusively associated with the bound electrons and is free from other contributions that may be present in other experiments, such as degenerate four-wave-mixing (DFWM) [6] or Z-

scan. [7] Recently, THG spectroscopy on evaporated [4] and MBE [5] films has been used to identify two photon states, which have been shown to play an important role in the nonlinear response.

From the perspective of optical limiting, phthalocyanines offer many possibilities as reverse saturable absorbers [10]. They exhibit large excited singlet and triplet state absorption [11] at wavelengths in the visible spectral region between the two main absorption bands of MPc (at around 532 nm), where the linear absorption is quite weak.

The objective of this work was to measure the nonlinear absorption of solutions of octasubstituted metallophthalocyanines ( $R_8\text{PcM}$ ;  $M = 2\text{H}$  or  $\text{Cu}$ , see Fig. 1) via Z-scan experiments at 1.064  $\mu\text{m}$ . The NLA at this wavelength is relatively weak, so our goal is not to explore the limiting applications of these materials, but to study the mechanisms for nonlinear absorption and the effect of the metal. The electronic nonlinear optical properties of these com-

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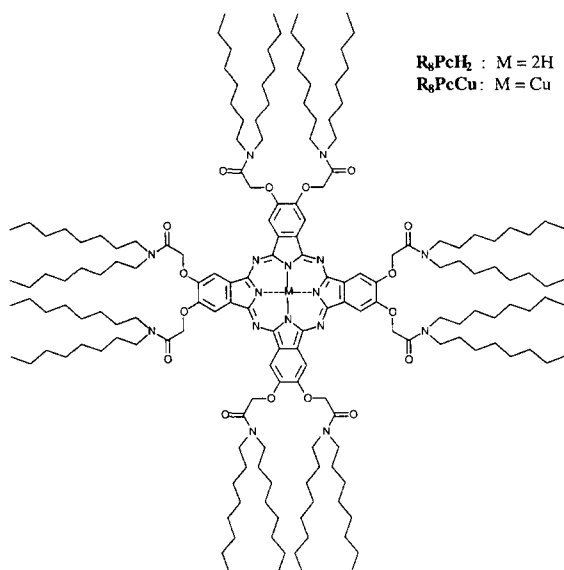


Fig. 1. Chemical structure of octasubstituted metallophthalocyanines ( $R_8PcM$ :  $M = 2H, Cu$ ).

pounds have been already investigated at a molecular level by THG (at  $1.34 \mu\text{m}$ ) and electric field induced second harmonic generation (EFISH) in solution (at  $1.06 \mu\text{m}$ ) [12]. They have also been studied at a macroscopic level on samples deposited as LB films (at  $1.06$  and  $1.94 \mu\text{m}$ ) [13]. In both cases the third order nonlinearity was shown to be one order of magnitude larger for the metallo-compounds as compared to the metal-free molecule. This behavior was attributed to the presence of two-photon states in the  $1\text{--}1.3 \mu\text{m}$  region, probably associated with d–d transitions due to the metal. Another important result of those experiments was the identification of an additional two-photon state near  $500 \text{ nm}$ , present in both  $R_8PcH_2$  and  $R_8PcCu$ , in good correlation with experiments performed in other MPc samples [4].

In this study we measure the nonlinear absorption and refraction using the Z-scan experimental technique [7]. A focused Gaussian beam is incident on a  $1 \text{ mm}$  thick cell containing chloroform solutions of  $R_8PcM$  ( $3 \times 10^{-3} \text{ mol/liter}$ ). In the Z-scan the normalized transmittance through an aperture in the far field is monitored as a function of the sample position with respect to the focal position. Open-aperture Z-scans (where all transmitted light is collected) provide the nonlinear absorption of the sample, while the closed-aperture Z-scans (where an

aperture that transmits 40% of the light in the linear regime is placed after the sample) allow determination of the nonlinear refraction [7]. The source light for the experiments is a Q-switched, mode-locked Nd:YAG laser operating at  $1.064 \mu\text{m}$ , producing single switched-out pulses of tens of picosecond duration. Experiments were performed at different pumping energies, ranging between  $5$  and  $31 \mu\text{J}$ . Additionally, by selection of output coupler etalons in the laser cavity, picosecond pulses of two different pulsewidths are obtained ( $23$  and  $32 \text{ ps}$   $\text{HW1/eM}$ ). The Gaussian beam radius at the focus ( $\omega_0$ ) is measured to be  $26 \mu\text{m}$  ( $\text{HW1/e}^2\text{M}$ ), giving a Rayleigh range of  $z_0 = 2 \text{ mm}$ .

We measured the linear optical absorption spectra for these solutions, as well as for solutions with considerably lower concentrations. We find no difference between the spectra for low and high concentrations, confirming that only monomeric species are involved, as has been previously reported [14]. These spectra have already been reported in Ref. [12]. The spectrum for  $R_8PcH_2$  has a B band centered at around  $346 \text{ nm}$  and a split Q band in the lower energy region between  $698$  and  $661 \text{ nm}$ . A split Q band is typical for metal free phthalocyanines because of the degeneracy introduced by the symmetry due to the two hydrogen atoms. The Cu-substituted compound  $R_8PcCu$  exhibits a single Q band at  $670 \text{ nm}$  and also a very weak absorption at  $1.085 \mu\text{m}$ , probably associated with d to d transitions of the metal. The linear transmittance ( $T_L$ ), the absorption coefficient ( $\alpha$ ) and the ground state absorption cross-section ( $\sigma_0$ ) at  $1.064 \mu\text{m}$  for the studied compounds are listed in Table 1.

Fig. 2 shows the Z-scan results for  $R_8PcH_2$  at  $16.6$  and  $22.5 \mu\text{J}$  input energy with  $23$  and  $32 \text{ ps}$  ( $\text{HW1/eM}$ ) pulsewidths, which give almost the same input irradiance of  $37 \text{ GW/cm}^2$ . The nonlinear ab-

Table 1

Linear parameters for chloroform solutions of octasubstituted metallophthalocyanines ( $R_8PcM$ ) at an excitation wavelength of  $1.064 \mu\text{m}$ .  $T_L$ : Linear transmission;  $\alpha$ : absorption coefficient;  $N_0$ : Molecular density;  $\sigma_0$ : ground state absorption cross-section

Compound	$T_L$ (%)	$\alpha$ ( $\text{cm}^{-1}$ )	$N_0$ ( $\text{cm}^{-3}$ )	$\sigma_0$ ( $\text{cm}^2$ )
$R_8PcH_2$	96.7	0.3356	$1.90 \times 10^{18}$	$1.77 \times 10^{-19}$
$R_8PcCu$	93.7	0.6507	$2.34 \times 10^{18}$	$2.78 \times 10^{-19}$

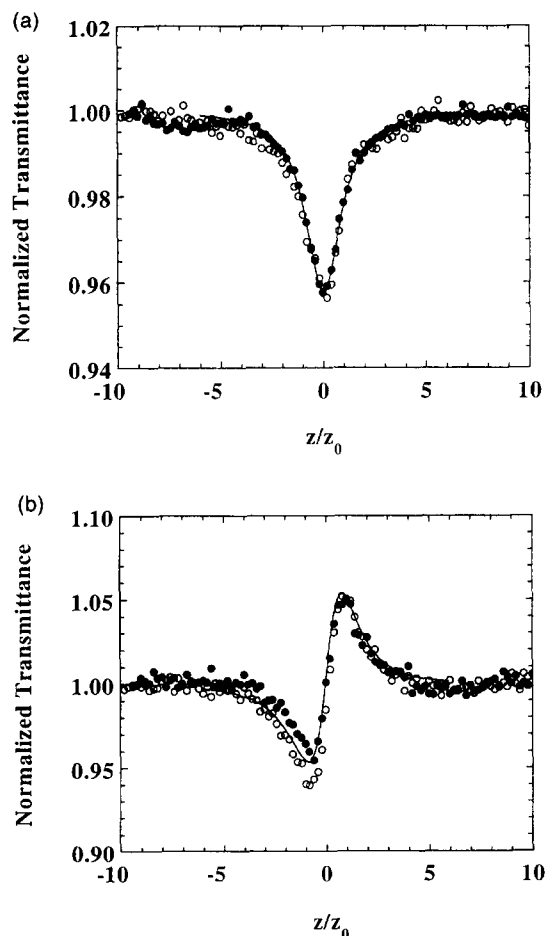


Fig. 2. Open (a) and closed (b) aperture Z-scan experimental results of chloroform solution of  $R_8PcH_2$  in 1 mm cell at  $22.5 \mu J$  input energy, 32 ps pulse width, giving  $37.1 \text{ GW/cm}^2$  irradiance (filled circles) and at  $16.6 \mu J$  input energy, 23 ps pulse width, giving  $37.7 \text{ GW/cm}^2$  irradiance (open circles). Solid lines are the best fits using the 2PA model.

sorption was determined from the open-aperture Z-scans (Fig. 2a). Clearly, the nonlinear absorption is irradiance-dependent rather than fluence-dependent [15]. The same behavior is observed for the nonlinear refraction, through the closed-aperture Z-scans from Fig. 2b (here the data has been divided by the open aperture data to eliminate the absorption effect) [7]. The solid lines in Fig. 2 show best fits using a model based on pure 2PA for the nonlinear absorption and pure nonlinear refractive index  $n_2$  for the nonlinear refraction, assuming Gaussian spatial and temporal

laser intensity profiles [7]. The fitting parameter in the curves of Fig. 2a is the 2PA coefficient  $\beta$ , where  $\beta$  is defined by  $dI/dz = -\beta I^2$ ;  $I$  is the incident irradiance and  $z$  is the coordinate along the propagation direction. The mean value  $\beta = (4.0 \pm 0.5) \times 10^{-2} \text{ cm/GW}$  was obtained over different energies and pulsewidths. By fitting the data of Fig. 2b, we find the nonlinear refraction coefficient  $n_2$  of the solution to be  $n_2 = (2.0 \pm 0.3) \times 10^{-6} \text{ cm}^2/\text{GW}$ , where  $n_2$  is defined from the index change ( $\Delta n = n_2 I$ ). This positive nonlinear refraction, however, is mainly due to the solvent (chloroform). Because of the small 2PA signal, the change in the refractive index caused by 2PA-excited states is much smaller than the change induced by the  $n_2$  of the solvent. This explains the fact that the closed-aperture Z-scan curves for  $R_8PcH_2$  (Fig. 2b) are similar in magnitude and sign (positive) to those obtained for pure chloroform. This indicates that the nonlinear process in  $R_8PcH_2$  is dominated by two-photon absorption (2PA).

The addition of a metal (Cu, in this case) changes the predominant mechanism for both nonlinear absorption and refraction. For  $R_8PcCu$  we plot in Fig. 3a the open aperture Z-scan results obtained at two different energies (5 and  $17 \mu J$ ) for the two available pulsewidths (23 and 32 ps HW1/eM). In this case the nonlinear process is independent of pulsewidth and hence is fluence (energy per unit area) dependent. Hence, the nonlinear process that leads to a change in transmittance in  $R_8PcCu$  is excited-state absorption (ESA) [8]. As before, by performing closed aperture Z-scans, we obtain information about the refractive nonlinearity. Fig. 3b shows the contribution of  $R_8PcCu$  only (after extracting the solvent contribution) to the change in the refractive index. Performing the experiment at different energies (10 and  $17 \mu J$ ), we find the same nonlinear refractive response for 23 and 32 ps (HW1/eM) pulses. This implies that the nonlinear refraction is also associated with the production of excited states.

A three level model accurately explains the ESA nonlinear behavior for picosecond pulses [8]. The molecules excited by linear absorption can make a further transition to a higher excited state, giving rise to nonlinear absorption. Making a few approximations that work very well with picosecond pulses, the equations that give the change in irradiance and

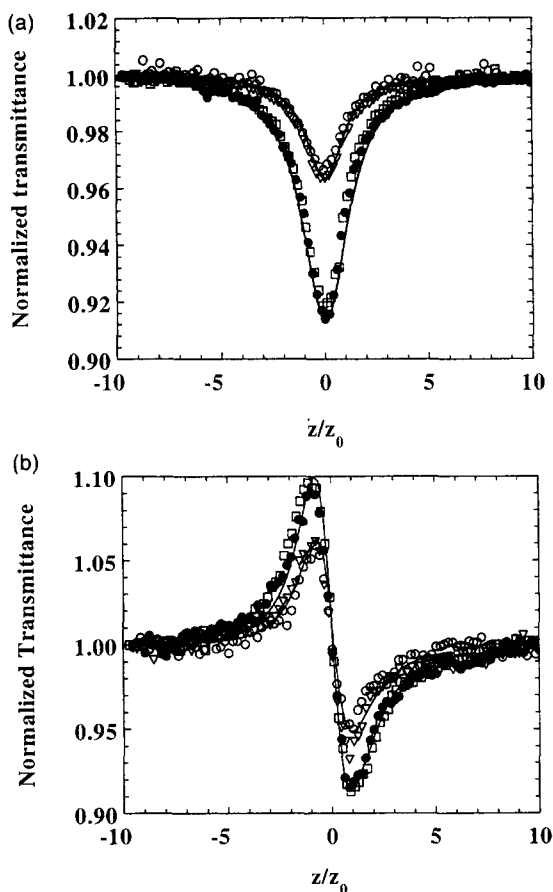


Fig. 3. Open (a) and closed (b) aperture Z-scan experimental results of chloroform solutions of  $R_8PcCu$  in 1 mm cells at different pulsewidths and pumping energies: 23 ps (open circles) and 32 ps (triangles) at 5  $\mu J$  (a) and 10  $\mu J$  (b), and 23 ps (squares) and 32 ps (filled circles) at 17  $\mu J$  (a and b). The chloroform contribution was extracted from the closed aperture Z-scans (b). Solid lines are the best fits using the ESA model.

phase shift (giving rise to nonlinear absorption and, respectively, refraction) are:

$$\frac{dI}{dz} = -\alpha I - \sigma_a N_e I \quad \text{and} \quad \frac{d(\Delta\Phi)}{dz} = \sigma_r N_e,$$

where  $N_e$  is the population of the excited state and is given by the rate equation:

$$\frac{dN_e}{dt} = \frac{\alpha I}{\hbar\omega}.$$

Given the linear material parameters (see Table 1) and the pulse characteristics (energy, duration, shape in time and space), the rate equations are solved and

fit to the experimental data (Fig. 3a). As a consequence, the excited state absorption cross-section obtained is  $\sigma_a = (1.40 \pm 0.15) \times 10^{-18} \text{ cm}^2$ . The excited state refractive cross-section used to generate the fits in Fig. 3b is  $\sigma_r = (-2.2 \pm 0.3) \times 10^{-18} \text{ cm}^2$ . This is a defocussing nonlinearity (i.e.  $\Delta n < 0$ ) and comparing with the results for  $R_8PcH_2$  we can see that the addition of the Cu in the molecule gives a negative contribution to the nonlinear refraction.

In conclusion, from Z-scan experiments it has been shown that the nonlinear absorption and refraction of metallophthalocyanines at 1.064 microns appears to be strongly dependent on the presence of the central metal ion. While the nonlinear behavior is due to two photon absorption for  $R_8PcH_2$ , excited state absorption is the dominant process for  $R_8PcCu$ . The two photon absorption in  $R_8PcH_2$  is consistent with THG studies [4] of phthalocyanines in solution that show the existence of two-photon states in the 500 nm region.

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