Picosecond and nanosecond third order nonlinear optical characterization of Cu & Ni phthalocyanines using Z-scan technique

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ABSTRACT

Herein we present our results from the picosecond and nanosecond nonlinear optical studies of two novel phthalocyanines {[$(SO_3Na)_4CuPc$] and [$(SO_3Na)_4NiPc$]} using the Z-scan technique. Open aperture Z-scan data revealed that the picosecond nonlinear absorption was dominated by three-photon absorption while in the nanosecond domain reverse saturable absorption prevailed. Closed aperture data with nanosecond pulses indicated strong thermal, negative nonlinearity while picosecond excitation demonstrated positive nonlinearity. The nonlinearity in CuPc was higher than in NiPc in both the time domains. The nonlinear coefficients extracted from the fits to experimental data were large compared to some of the recently reported works on similar molecules.

Key words: Nonlinear optical properties, Z-scan, Three-photon absorption, Phthalocyanines

1. INTRODUCTION

We have recently been investigating new classes of porphyrins and phthalocyanines measuring their third-order nonlinear optical (NLO) properties, including their figures of merit, employing the techniques of Z-scan and DFWM, in the cw, nanosecond (ns), picosecond (ps), and femtosecond (fs) time domains for their prospective applications in the fields of optical limiting and all-optical switching.[1-15] Several groups have argued about nuances of these materials in extensive range of photonic applications.[16-35] Our comprehensive experiments and detailed modeling, along with the obtained nonlinear coefficients, strongly suggest that these molecules are potential molecules with large nonlinear coefficients in ns, ps, and fs time domains with ultrafast response times. More so, phthalocyanines and their derivatives possess attractive third-order nonlinearities and figures of merit with outstanding applications in optical limiting and ultrafast all-optical switching.[6-15] For optical limiting applications the potential molecule should possess imperative qualities such as (1) small linear absorption (2) strong nonlinear (excited-state/reverse saturable) absorption (3) broad spectral response (d) ability to be doped in glasses/polymers for devices (e) cost-effectiveness (f) strong laser tolerance and (g) robust design/synthesis strategies. A large nonlinear refractive index and fast non-resonant electronic response of the molecules are essential for optical switching. Both resonant and non-resonant optical nonlinearities of various phthalocyanines have been investigated in the last decade. The processes leading to non-resonant nonlinearity are usually fast (picosecond/femtosecond domain), which are good candidates for optical switching. On the other hand, the processes causing resonant nonlinearity are usually slow (nanosecond), which results in huge optical nonlinearity. Resonant nonlinear optical materials are widely utilized for Q-switching. Many of the phthalocyanines investigated recently possess only a miscellany of the above desired characteristics. However, the advantage with these classes of molecules is the versatility with which one can tailor their optical properties through central metal ion, peripheral and axial substitutions. The efforts from material scientists, chemists, and physicists are ensuing to establish competent molecules with better figures of merit. It is vital that any new molecule synthesized or modified should be examined under rigorous conditions with laser pulses of various energies and durations to arrive at the exact figures of merit in each domain. Our efforts have been directed towards achieving this objective though studies of novel water soluble

phthalocyanines. Herein we present our results on the picosecond and nanosecond nonlinear optical studies of [(SO$_3$Na)$_4$CuPc] and [(SO$_3$Na)$_4$NiPc] using the Z-scan technique.

2. EXPERIMENTS
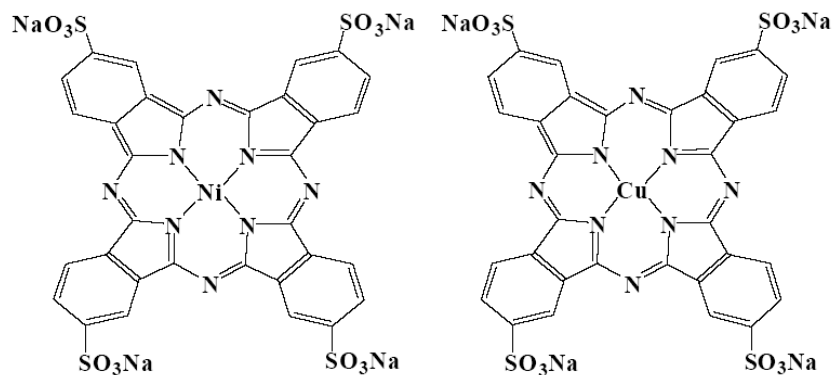
Molecular weight: 979.40   **Molecular weight: 984.25**

Figure 1 Structures of NiPc and CuPc used in the present study

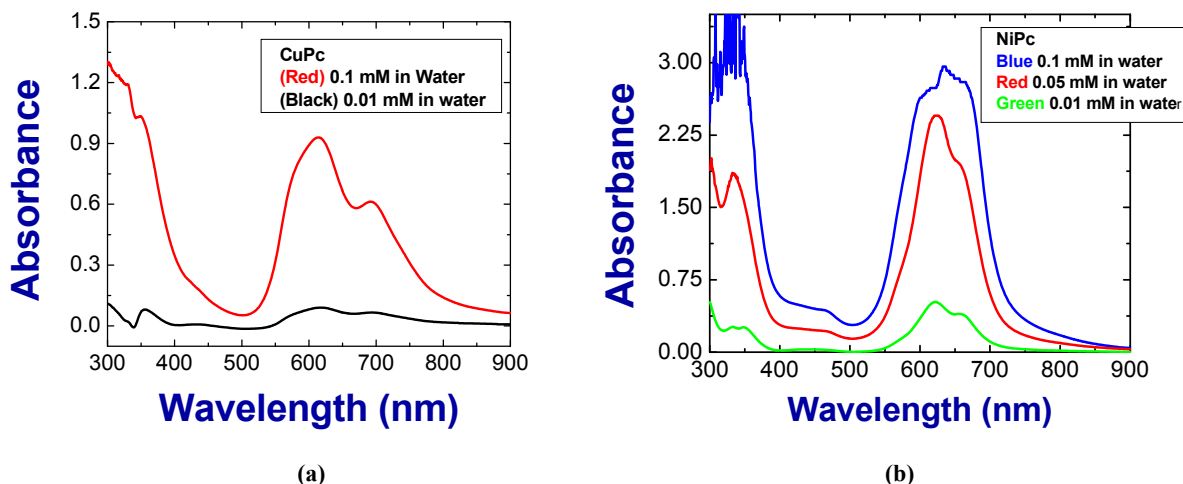(a)   (b)

Figure 2 Absorption spectrum of (a) CuPc and (b) NiPc dissolved in distilled water.

CuPc and NiPc were purchased from Aldrich and used as is. The IUPAC name of samples are as follows: CuPc (Copper tetrasulfonic phthalocyanine) is 2(3), 9(10), 16(17), 23(24)-sodium salt of tetrasulfonicacid copper phthalocyanine and Nipc (Nickel tetrasulphonic phthalocyanine) is 2(3), 9(10), 16(17), 23(24)-sodium salt of tetrasulfonicacid nickel-phthalocyanine. Neat solutions of CuPc and NiPc were dissolved in de-ionized water as solvent with typical concentrations of (0.5-1) × 10^{-4} M. The solutions were taken in 1-mm quartz cuvettes. Figure 1 shows the molecular structures and their respective molecular weights. Initially the samples were excited by picosecond (ps) laser pulses (Legend, Coherent; Ti:Sapphire laser) at a wavelength of 800 nm, 2 ps pulse duration and a repetition rate of 1 kHz. Maximum output energy from the amplifier was ~2.5 mJ. Typically pulses with energy of few μJ were used for the experiments. The pulses were spatially and temporally Gaussian and the input beam diameter was ~4 mm. For nanosecond (ns) Z-scan experiments[36,37] the sample was excited by a frequency doubled Nd:YAG laser with 6 ns pulse

duration and 10 Hz repetition rate. The beam was focused using a convex lens of focal length (f = 120 mm) in both the cases. The peak intensities used in picosecond experiments were in the 10-200 GW/cm^2 range with 87-90% linear transmission at 800 nm. The peak intensities used for nanosecond excitation was ~(1-30)×10^8 W/cm^2 and the linear transmittance at 532 nm was >85%. Similar peak intensities were maintained in the scans to ensure identical experimental conditions for both the samples. Closed aperture scans were performed at lower intensities to avoid contribution from the higher order nonlinearities. The nonlinear absorption coefficients were extracted from the Z-scans recorded as a function of intensity and the values at lower peak intensities are considered in this study to avoid higher order effects. The experiments were repeated more than once and the best data were used for obtaining the nonlinear optical coefficients from the best fits.

Figures 2(a) and 2(b) shows the absorption spectra of the CuPc and NiPc, respectively, investigated in this study and recorded at different concentrations. Absorption spectrum of all the Pc's consists of two intense bands; one known as Q-band around 600-800 nm in the visible region and the other one, known as B band (Soret band), in the 300-400 nm region. The Q-band, arising from the π- π* transition, is usually composed of smaller bands. The Q-band of the absorption spectrum is the characteristic of a particular phthalocyanine. Introduction of metal into phthalocyanine molecules has a variable effect on the intensity and spacing of its absorption spectrum. However, the general features of the phthalocyanine spectrum remains intact. On the introduction of the metal ions at the centre , the weakest absorption bands disappear and the spectrum gets shifted to the lower wavelengths. The extent of the spectral shift is proportional to the atomic number of the central atom. It may also be noted that with respect to increase in π electron conjugation, Q- band gets red shifted .

3. RESULTS & DISCUSSION
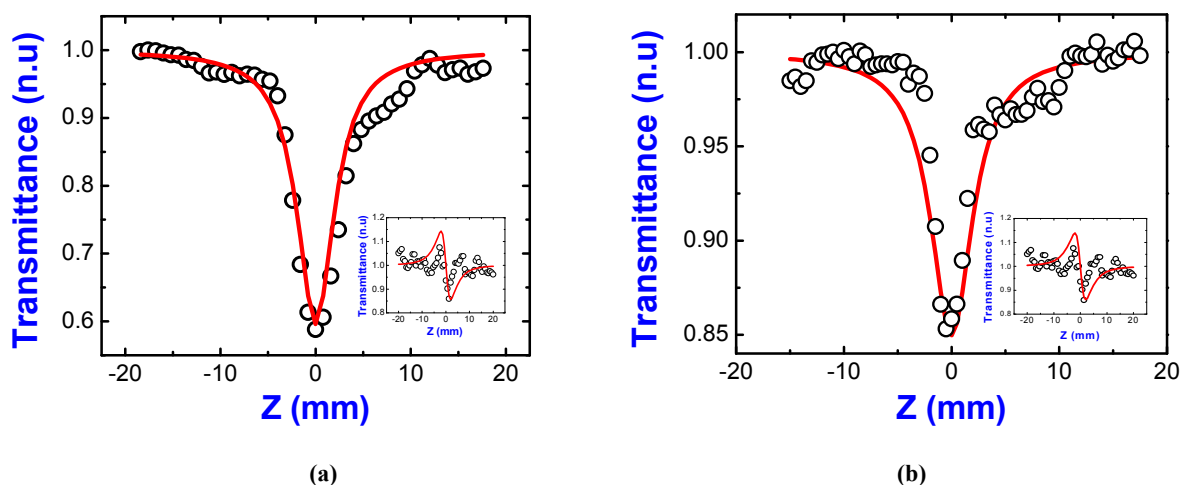
Figure 3 Nanosecond open aperture Z-scan data (open circles) along with the fits (solid lines) for (a) CuPc with a peak intensity of 2 × 10^8 W/cm^2 and (b) NiPc with a peak intensity of 30 × 10^8 W/cm^2. Inset shows the closed aperture data.

Figures 3(a) and 3(b) shows representative, normalized open aperture scans of Cupc & Nipc recorded with 532 nm, 6 ns pulses. We observed reverse saturation absorption (RSA) in these molecules for input intensities in the ~150-600 MW/cm^2 range. For intensities >10^8 W/cm^2 the normalized transmittance in CuPc, especially, dropped to <0.6 indicating strong nonlinear absorption behavior. It is well established that nonlinear absorption in such materials due to ns pulses has contribution from both excited singlet and /or triplet states from two-photon absorption depending on the excitation wavelength.[38-39] However, for 532 nm excitation we can approximate the nonlinear absorption to an effective process and evaluate the nonlinear absorption coefficient, β. The role of instantaneous two-photon absorption in the present case is negligible due to the excitation wavelength of 532 nm, which is far from two-photon resonance. The values of nonlinear absorption coefficient β estimated from the fits, using equation (1), were ~25 cm/GW for CuPc and ~1.1 cm/GW for NiPc.

$$\mathbf{T(z) = 1 - \frac{\beta I_0 L_{eff}}{2^{3/2}(1+\frac{z^2}{z_0^2})}}$$

(1)

where β represents third order nonlinear absorption coefficient, $\mathbf{I_0}$ is peak intensity at the focal point, $L_{eff} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$ and z_0 is the Rayleigh range , α_0 is the linear absorption coefficient and L is the sample thickness .

Insets of figure 2 demonstrate the closed aperture behavior with both the molecules exhibiting negative nonlinearities. These curves represent normalized data obtained after division of closed aperture data with the open aperture data to eliminate the contribution of nonlinear absorption. The values of n_2 estimated from the fits were $\sim 120 \times 10^{-15}$ cm^2/W for CuPc and $\sim 47 \times 10^{-15}$ cm^2/W for NiPc. These data undoubtedly suggests that CuPc has superior nonlinearity compared to NiPc.

Assuming a spatial and temporal Gaussian profile for laser pulses and utilizing the open aperture Z-scan theory for multi-photon absorption (MPA) given by Sutherland et al.[37] we have the general equation for open aperture (OA) normalized energy transmittance given by:

$$T_{OA(nPA)} = \frac{1}{\left[1+(n-1)\alpha_n L \left(I_{00}/\left(1+\left(z/z_0\right)^2\right)\right)^{n-1}\right]^{1/n-1}}$$

(2)

where α_n is the effective MPA coefficient (n = 2 for 2PA; n = 3 for 3PA, and so on); and I_{00} is the input irradiance. If we retain only the 2PA term and ignore all other terms, we have an analytical expression for OA Z-scan for merely two-photon absorbers. Similarly retaining the 3PA term and ignoring the other terms provides us an analytical expression for OA scans for only three-photon absorbers.

$$T_{OA(2PA)} = \frac{1}{1+\alpha_2 L_{eff}\left(I_{00}/\left(1+\left(z/z_0\right)^2\right)\right)}$$

(3)

$$T_{OA(3PA)} = \frac{1}{\left[1+2\alpha_3 L'_{eff}\left(I_{00}/\left(1+\left(z/z_0\right)^2\right)\right)^2\right]^{1/2}}$$

(4)

with **n** being the order or absorption process, $\mathbf{I_{00}}$ is the peak intensity, **Z** is the sample position, $\mathbf{z_0} = \pi\omega_0^2/\lambda$ is the Rayleigh range; $\mathbf{\omega_0}$ is the beam waist at the focal point (Z = 0), λ is the laser wavelength; effective path lengths in the sample of length L for 2PA, 3PA is given as $L_{eff} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$. , $L'_{eff} = \frac{1-e^{-2\alpha_0 L}}{2\alpha_0}$.

Figure 4 shows representative open aperture scans for (a) Nipc and (b) Cupc recorded at 800 nm using ~2 ps pulses with peak intensities of ~160 GW/cm^2. We observed strong reverse saturation (RSA) kind of behavior in this intensity range. Obtained experimental data was fitted using equation (4) and we found the best fit was obtained with the transmission equation for three-photon absorption (3PA). It was evident from the fits (2PA fits not shown in the figure) that 3PA was the dominant mechanism for the observed RSA kind behavior since the 2PA fits were not matching with the experimental data, especially near the focal region (close to z = 0). The values of $\mathbf{\alpha_3}$ estimated were $\sim 15 \times 10^{-5}$ cm^3/GW^2 for CuPc and $\sim 14 \times 10^{-5}$ cm^3/GW^2 for NiPc. Molecules possessing strong two-photon and three-photon absorption coefficients find useful applications in the field of biological imaging, where the resolution can be improved drastically compared to one-photon absorption based studies. [40-43]

Insets of figures 4(a) and 4(b) illustrate the typical closed aperture curves obtained for Nipc & Cupc with peak intensity of ~160 GW/cm^2. It is apparent that both CuPc and NiPc show positive nonlinearity as indicated by the valley-peak structure. The closed aperture data was fitted to the standard equation for closed aperture transmittance. The values of n_2 estimated from the fits were ~1.5×10^{-15} cm^2/W for CuPc and ~1.4×10^{-15} cm^2/W for NiPc. In the picosecond case the solvent contribution is important in both closed aperture and open aperture scans. However, we ensured that the solvent contribution is minimal at these peak intensities. Separate studies on pure solvent alone indicated the value of n_2 to be ~10^{-16} cm^2/W at these peak intensities clearly suggesting the negligible contribution. It is apparent that the n_2 values in the ps domain are at least one order of magnitude lower than those obtained with ns pulses. We expect the response with ns pulses to be predominantly of thermal in origin while with the ps pulses the response is largely electronic in nature. All the nonlinear optical coefficients estimated from the experimental fits are summarized in table 1. The values presented here embrace an error bar of ±30% arising from the errors in estimation of peak intensities, fittings, and incorrect concentration calculations.

The values presented here compare very well with some of the novel molecules investigated by our group and others in the recent past.[9-14, 31-35,46-47] For example, García-Frutos[46] et al. reported nonlinear coefficient value of ~7.76×10^{-8} cmW^{-1} for one of their molecule studied using nanosecond pulses. Shi et al[47] reported nonlinear refractive index value of 6×10^{-16} cm^2/W for ZnPcBr$_4$ dissolved in DMSO studied using 21 ps pulses. Our studies revealed nonlinearity values 2.5 times that of ZnPcBr$_4$. Enhanced nonlinear coefficients obtained in CuPc compared to NiPc are intriguing. The heavy metal atom effect contribution to this augmentation seems farfetched since the atomic weights of both these are not very different. The structure and absorption spectra of these molecules are similar suggesting a completely different mechanism for the differences in nonlinearities. Further detailed studies are essential and in progress to isolate the causes.

Our future studies will concentrate on (a) Studying the optical limiting properties of these molecules at different wavelengths (b) Evaluate the electronic time response of these molecules using femtosecond pulses and pump-probe technique (c) Attempts to dope these materials in polymers for potential device applications (d) Establish routes to synthesize nanoparticles of these phthalocyanines, possibly enhancing their nonlinearities.[44-45]

(a)

(b)
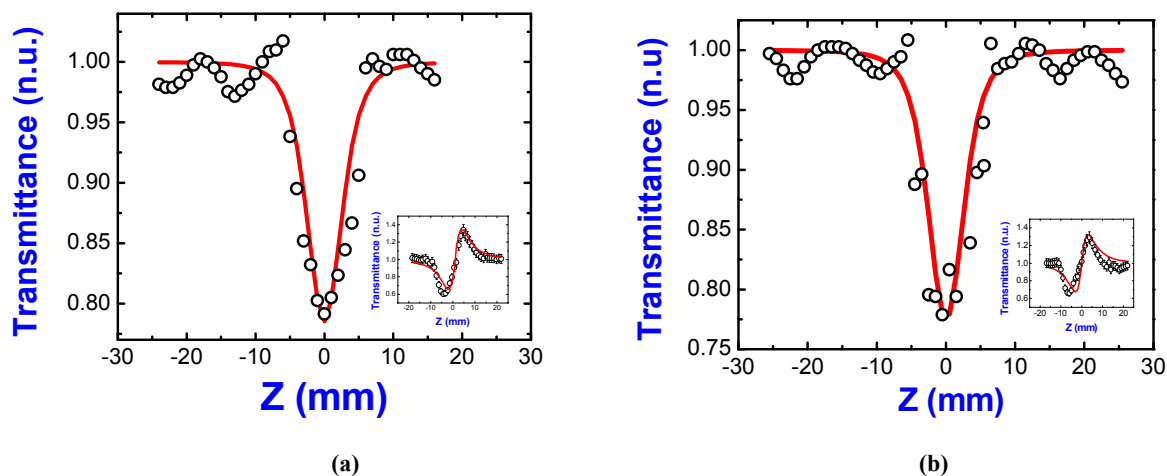
Figure 4 Picosecond open aperture Z-scan data (open circles) along with the fits (solid lines) for (a) CuPc and (b) NiPc. Inset shows the closed aperture data.

SAMPLE	Nanosecond n_2 $(\times 10^{-15} \text{ cm}^2/\text{W})$	Nanosecond NLA (β) $\times 10^{-9} \text{ cm/W}$	Picosecond n_2 $(\times 10^{-15} \text{ cm}^2/\text{W})$	Picosecond NLA (α_3) $[\times 10^{-23} (\text{cm}^3/\text{W}^2)]$
CuPc	120.0	25.0	1.5	15.0
NiPc	47.0	1.1	1.4	14.0

Table 1 Summary of the nonlinear coefficients obtained from the fits to Z-scan data for CuPc and NiPc.

4. CONCLUSIONS

In conclusion we have studied the ns and ps NLO properties of two water soluble phthalocyanines (CuPc and NiPc) which pointed out strong nonlinearities in both the time scales. Picosecond data indicated strong positive nonlinearity and presence of three-photon absorption while the ns data depicted strong negative nonlinearity and reverse saturable absorption. The nonlinear coefficients were estimated from the fits and the values suggest potential applications of these materials in the fields of optical limiting and bio-imaging.

5. ACKNOWLEDGEMENTS

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