# Ultrafast nonlinear optical studies of 3,8,13,18-Tetrachloro-2,7,12,17tetramethoxyporphyrin and its derivatives

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# ABSTRACT

Recently we synthesized 3,8,13,18-tetrachloro-2,7,12,17-tetramethoxyporphyrin and its metallo-derivatives [1]. The free-base molecule is unique owing to the presence of an electron donating methoxy group and electron withdrawing chloro group on the adjacent  $\beta$ - positions of each pyrrole moiety. We could synthesize these molecules through two different routes; the first route provided pure isomer, albeit in low yield, whereas the second route provided mixture of isomers with higher yield [1]. Herein we report the third-order nonlinear optical properties of these porphyrins obtained from Z-scan measurements using ~40 fs, 800 nm pulses. Open aperture data confirmed the presence of saturable absorption whereas the closed aperture data indicated a positive nonlinearity. We have compared the data of the pure isomer with that of the mixture of isomers.

Keywords Z-scan, Porphyrins, femtosecond, saturable absorption.

# 1. INTRODUCTION

Porphyrins are a class of important biological pigments, endowed with rich photophysical properties owing to their conjugated  $18\pi$ -electron aromatic system. Further, the properties of this macrocyclic tetrapyrrolic system can be easily modulated via substitution at one or more of the peripheral meso- and/or  $\beta$ -positions [1]. Thus, porphyrins are not only of interest to synthetic chemists, but also to researchers from various disciplines like biology, physics, material engineering and theoretical studies [1]. Porphyrins, Phthalocyanines, and Porphycenes have been investigated by our research group over the last two decades for their nonlinear optical properties [2-21]. Porphyrin based oligomers, in association with other chromophores and polymers derived from porphyrins demonstrate interesting nonlinear optical behavior and hence hold great promise as second and third order NLO materials, as broadband optical limiters, in all optical switching, and in two-photon photodynamic therapy (PDT) [22-28]. The basis of design in most of these systems for better NLO response is to have suitable donor and acceptor functionalities at the periphery of the aromatic porphyrin ring or the extended multi-porphyrinic systems. In this regard, monomeric porphyrin units were also studied as either reference for designing more accomplished systems or as standalone systems to gain understanding about their nonlinear optical response. Presence of multiple donor and acceptor functional groups at the porphyrin periphery is achieved either through direct link or through phenyl bridge or a combination of both. Also, it is known that direct linkage of functional groups at the porphyrin periphery impart a greater influence on the electronic properties of the macrocyclic ring. In this regard,  $\beta$ -octasubstituted porphyrins which could be synthesized quite conveniently could emerge as attractive target systems. However, there are very few reports containing substituents other than alkyl groups at all the  $\beta$ -positions of porphyrins [28-34]. In particular, pyrroles containing simultaneously one electron donating and one electron withdrawing substituents at their adjacent  $\beta$ -pyrrole positions are rare [35-39]. These types of molecules may possess interesting nonlinear optical properties owing to this special arrangement of multiple donor and acceptor substituents. Towards this proposal, our recently reported symmetrical type I 3,8,13,18-tetrachloro-2,7,12,17-tetramethoxyporphyrin 1 appears very promising [40]. This molecule is unique, in the sense it contains an electron donating methoxy and electron withdrawing chloro group on the adjacent  $\beta$ - positions of each pyrrole moiety. Therefore, we studied its nonlinear optical behavior along with its Zn(II) and Ni(II) derivatives (designated as Zn1 and Ni1, respectively).

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# 2. EXPERIMENTAL DETAILS

Porphyrin 1 was synthesized according to the reported procedure [40]. Separately, we realized that synthesis of compound 1 and related asymmetric systems need a great deal of modulation to obtain the pure products in very low yields, for example in the present case yield of pure 1 is 5.8% vs 48% as mixture of isomers (Scheme 1) [39]. Therefore, we are interested to investigate the spectroscopic properties of the mixture of isomers of 1, designated as 1-M along with their metallo-derivatives designated as Zn1-M and Ni1-M including their nonlinear optical behaviors. The objective is to find out if the properties of the mixture of isomers are at least similar, if not better, than that of the pure isomer, because separation of the individual isomers from the high yielding mixture is very tedious and sometimes impossible. In general, we observed an increase in solubility of the isomeric mixture compared to their pure counterpart, confirmed from the optical density of the saturated solutions in UV-Vis spectroscopy. The absorption and emission spectral studies of the pure porphyrins and their isomeric mixture display very minimal shift except in case of the Soret band of the Zn1-M (blue shifted by about 5 nm) compared to the pure Zn1 as can be observed from figure 2 and table1. The absorption spectra show a relatively more red shift of the Soret band upon insertion of zinc, whereas nickel insertion could lead to only minor red shift of absorption bands than freebase 1.



Figure 1 Structure of porphyrin 1.



Figure 2 Absorption spectra of 1 and its, Zn(II) and Ni(II) derivatives in chloroform (both pure and mixture of isomers).

Porphyrins	UV-Vis (nm, logɛ)	Fluorescence in nm ( ${m \Phi}$ )
1	383(4.85), 502(3.80), 539(3.81), 571(3.60), 626(3.64)	629, 659, 696(0.045)
1-M	385, 502, 539, 572, 627	629, 659, 696
Zn1	409(5.02), 540(3.99), 579(4.03)	584, 638 (0.032)
Zn1-M	404, 538, 579	583, 636
Ni1	391(5.06), 519(3.88), 558(4.34)	
Ni1-M	390, 521, 561	

Table 1 UV-Vis and emission studies of the porphyrins in chloroform at 25 °C.

The NLO studies were carried out, for the first time to our knowledge, on the above said porphyrin derivatives using ~40 fs (FWHM) pulses using Z-scan technique [41]. All the measurements were performed using 800 nm pulses with a repetition rate of 1 kHz obtained from an amplified Ti:sapphire laser system (Legend, Coherent). The amplifier was seeded with pulses of duration ~15 fs (FWHM) with a spectral bandwidth of 55-60 nm (FWHM) from the oscillator (Micra, Coherent). The pulses were nearly transform limited and this was confirmed from MIIPS measurements [42] using Silhouette (Coherent). The pulse duration measured was 38.4 fs and was 1.02 times the transform limit. A quartz cuvette (1-mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length. The beam waist ( $2\omega_0$ ) at focal plane was estimated to be 52±2 µm with a corresponding Rayleigh ranges ( $Z_r$ ) of 2.65±0.2 mm. Typically, <1 µJ energy pulses resulting in 0.1-1 TW/cm<sup>2</sup> peak intensities were used for the experiments.



Figure 3 Typical MIIPS data obtained for femtosecond amplified pulses using the MIIPS technique and Silhouette (Coherent)



Figure 4 Experimental set up for Z-scan experiments.

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Figure 2 shows the schematic of experimental set up used. The sample was translated using a high resolution stage (Newport, ILS250PP) and the transmitted light was collected using a lens and a photodiode (Thorlabs, SM1PD2A) combination. An aperture was placed in front of the lens for closed aperture scans and total light was collected during open aperture scans. The photodiode output was fed to a lock-in amplifier (7265, Signal Recovery). Neutral density filters were used to cut down the input intensity before the sample and also the intensity reaching photodiode. The translation stage and the photodiode/lock-in were controlled by a personal computer using a Labview program. Since the ultrashort pulses passed through several optical components before entering the sample the pulse duration was estimated (theoretically) to be ~50 fs and this value was used for peak intensity calculations. Fresnel losses from the optics were considered during these calculations.

#### **3. THEORY**

The equation for nonlinear absorption is given by [4]

$$\frac{dI}{dZ} = -\alpha_0 I + \beta I^2$$

The open aperture Z-scan data have been fitted by time integration of sample transmittance assuming a Gaussian temporal profile. The fitting to experimental data was done using the equation

$$T_{OA}(z) = \frac{1}{\pi^{1/2} q_o} \int_{-\infty}^{\infty} \ln \left[ 1 + q_o e^{-x^2} \right] dx$$

where  $T_{OA}(z)$  is the normalized transmittance as a function of z,  $q_0 = \beta I_0 L_{eff}$ ,  $\beta$  = nonlinear absorption coefficient and

I<sub>0</sub> is the intensity,  $L_{eff} = \frac{1 - e^{\alpha_0 L}}{\alpha_0}$ , are effective path lengths in a sample of length L and  $\alpha_0$  is the linear absorption

coefficient. The closed aperture data were fitted using the equation,

$$T_{CA} = 1 + 4\Delta\phi \frac{x}{(1+x^2)(9+x^2)}$$

where T is the normalized transmittance,  $\Delta \phi$  is the nonlinear phase shift,  $x = Z/Z_r$  is the normalized position with respect to the Rayleigh range.

$$\Delta\phi = \Delta\phi_0 e(\frac{-2r^2}{w^2})$$

and

$$\Delta \phi_0 = \frac{k n_2 I_0 L_{eff}}{1 + \frac{z^2}{z_0^2}}$$
$$I_0 = \frac{I_{00}}{(1 + \frac{z^2}{z_0^2})}$$

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where  $I_{00}$  is the peak intensity at focus calculated using the relation

$$I_{00} = \frac{2E}{\pi^{3/2} w_0^2 (HW \frac{1}{e^2} M) \tau_p (HW \frac{1}{e} M)}$$

E is the input pulse energy,  $\tau$  is the pulse duration,  $2\omega_0$  is the beam diameter at focus.

# 4. RESULTS AND DISCUSSION

Typical concentrations of porphyrins **1**, **Ni1**, and **Zn1** used in NLO experiments were 0.118 mM, 0.04 mM, and 0.07 mM, respectively, and figure 5 illustrates the data. Closed aperture data revealed positive nonlinearity for all the samples. The order of magnitude estimated from the fits to experimental data was  $\sim 10^{-17}$  cm<sup>2</sup>/W. Open aperture scans revealed saturable absorption type of behaviour and the magnitude of nonlinear coefficients extracted were  $\sim 10^{-13}$  cm/W. Saturable absorption has potential applications in mode-locking of ultrafast laser systems. Due to large peak powers associated with these short pulses, input energies play a significant role in their propagation through the sample. For pulse energies >1.5 µJ we could clearly observe the Supercontinuum being generated from the solvent (chloroform) affecting the transmission in open aperture data. Therefore, we restricted the input energies to a few hundred nJ for all the experiments and ensured that the transmittance changes were from the solute only.

For similar input energies, pure solvent in a similar cuvette was scanned and both closed aperture and open aperture data were obtained. The results are presented in figure 6. The sign of solvent nonlinearity was positive with magnitude of  $\leq 0.5 \times 10^{-17}$  cm<sup>2</sup>/W and nonlinear absorption coefficient of  $\leq 0.5 \times 10^{-13}$  cm/W. The NLO coefficients of the porphyrins along with solvent are recorded in table 2. It is evident that the solute contribution was higher than that of the solvent.



Figure 5 Closed aperture (top) and open aperture (bottom) data of pure 1, Ni1, and Zn1 in chloroform. Open circles are experimental data and solid lines are theoretical fits. Peak intensities used for both the scans are mentioned in the closed aperture data.



Figure 6 Closed aperture (left) and open aperture (right) data of solvent chloroform. Open circles are experimental data and solid lines are theoretical fits.

Another set of experiments were performed upon the mixture of isomers 1-M, Ni1-M, and Zn1-M with concentrations 0.39 mM, 0.34 mM, and 0.195 mM, respectively, and figure 7 depicts the data obtained. Closed aperture data revealed negative nonlinearity for 1-M and Ni1-M where as Zn1-M displayed positive nonlinearity. The order of magnitude of  $n_2$  was again ~10<sup>-17</sup> cm<sup>2</sup>/W.

Sample	β (cm/W)×10 <sup>-13</sup>	$n_2 (cm^2/W) \times 10^{-17}$
CHCl <sub>3</sub>	0.50	0.50
1	0.80	1.00
Ni1	2.00	2.00
Zn1	2.25	2.00
1-M	1.90	1.20
Ni1-M	3.00	2.00
Zn1-M	0.80	0.80

Table 2 Nonlinear coefficients of all the porphyrins studied along with the solvent chloroform.



Figure 7 Closed aperture (top) and open aperture (bottom) data of 1-M, Zn1-M, and Ni1-M. Open circles are experimental data and solid lines are theoretical fits. Peak intensities used for both the scans are mentioned in the closed aperture data.

Open aperture scans revealed saturable absorption type of behaviour and the magnitude of nonlinear coefficients extracted were  $\sim 10^{-13}$  cm/W. The linear absorption of these molecules near 800 nm is negligible and since these pulses possess extremely large bandwidth ( $\sim 26$  nm FWHM and a total width  $\sim 50$  nm near 800 nm at the sample) and large peak intensities we strongly believe that the saturation may possibly be from the higher singlet states. The presence of two-photon states near 400 nm for all these molecules further suggests that this could be 2PA saturation.



Figure 8 Open aperture data for large peak intensities (2  $TW/cm^2$ ) indicating a complicated behavior of nonlinear absorption in ZnTCTMP and TCTMP. Solid lines are only a guide to the eye.

Figure 8 shows the open aperture scans of ZnTCTMP and TCTMP recorded at a peak intensity of 2 TW/cm<sup>2</sup>. It is obvious that the nonlinear absorption switches from saturable type to reverse saturable type indicating complicated behavior. Further increase in peak intensity resulted in Supercontinuum generation and the dip magnitude increased drastically. These measurements clearly suggest that at lower peak intensities saturable absorption is indeed the nonlinear absorption mechanism.

Further pump-probe studies using fs and sub-ps pulses are essential to identify the exact state(s) involved in saturation. Though the magnitudes of nonlinearity ( $n_2$ ) remained the same in both the cases the reason for change in the sign of nonlinearity in case of **1-M** and **Ni1-M** also requires further investigation. An estimated error of ±30%, in the nonlinear coefficients calculated, was deduced from the errors in (i) the estimation of beam waist and thereby the Rayleigh range and peak intensities (ii) pulse-to-pulse energy fluctuations (iii) calibration of neutral density filters (iv) fitting procedures (v) concentration measurements etc.

#### **5. CONCLUSIONS**

In conclusion, we have studied the NLO properties of tetrachloromethoxyporphyrins. Our studies of porphyrins synthesized (pure and mixture of isomers) display similar magnitude of NLO coefficients. The measurements were performed with ~40 fs pulses, for the first time to our knowledge, and truly represent electronic contribution to the nonlinearity. Closed aperture data demonstrated positive nonlinearity for 1, Ni1, Zn1, and Zn1-M whereas 1-M and Ni1-M exhibited negative nonlinearity. All the molecules exhibited saturable absorption with similar magnitude of nonlinear absorption coefficients. Further NLO and pump-probe studies using 150 fs pulses are in progress to identify the multi-photon absorption properties of these molecules. Finally, we can conclude that this type porphyrins containing adjacent electron donor and acceptors moieties alternately, may be of great importance and the asymmetric nature of the starting pyrrole which generally led to formation of quite higher yield of the target porphyrin (as a mixture of isomers) as compared to pure form may not reduce the performance a great deal and hence their study can be taken up, *albeit*, with caution as the generality of this strategy is yet to be proved.

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