

# Characterization of the Third-Order Nonlinearity of $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$

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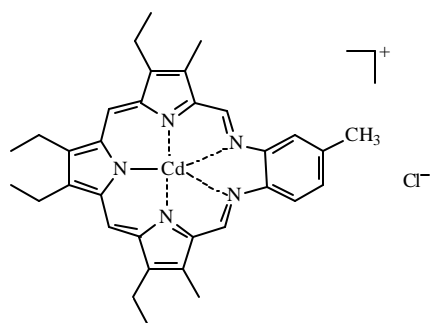
## ABSTRACT

The third-order nonlinear optical properties of a methyl substituted Texaphyrin,  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$ , were studied by degenerate four wave mixing (DFWM) and Z-scan techniques using 40 ps laser pulses at 532 nm. The molecular second-order hyperpolarizability ( $\gamma$ ), the excited-state absorption cross section ( $\sigma_{\text{ex}}$ ), the nonlinear refractive cross section ( $\sigma_r$ ), and the optical limiting performances at both nanosecond and picosecond time scales have been determined. We have also studied the third-order nonlinearity of SiNc, one of the most promising optical limiting materials in literature, for comparison. The  $\gamma$  value for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  is  $6.9 \times 10^{-31}$  esu, which is 4 times as larger as that of SiNc. The nonlinearity of  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  is predominantly electronic in origin with picosecond laser pulses. The excited-state absorption cross section ( $\sigma_{\text{ex}}$ ) and the nonlinear refractive cross section ( $\sigma_r$ ) obtained from the theoretical simulation and calculation of Z-scan results are  $7.0 \times 10^{-17}$  cm<sup>2</sup> and  $1.7 \times 10^{-17}$  cm<sup>2</sup>, respectively. The complex shows strong optical limiting performance via reverse saturable absorption for 5 ns laser pulses. The nonlinear absorption of this molecule for 40 ps laser pulses exhibits a transition from reverse saturable absorption to saturable absorption when the fluence is higher than  $0.3 \text{ J/cm}^2$ . These data suggest that this complex and related complexes are a promising class of nonlinear optical materials.

**Keywords:** Texaphyrins, third-order nonlinearity, molecular second-order hyperpolarizability ( $\gamma$ ), excited-state absorption cross section ( $\sigma_{\text{ex}}$ ), nonlinear refractive cross section ( $\sigma_r$ ), optical limiting, nonlinear absorption, degenerate four wave mixing, Z-scan

## 1. INTRODUCTION

Nonlinear optical materials (NLO) with large intensity-induced refractive index and absorption changes are very useful for numerous optical device applications. One of the most important applications is optical power limiting.<sup>1,2</sup>



**Fig. 1** Chemical structure of the  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  complex

Phthalocyanines,<sup>3,4,5,6,7</sup> porphyrins,<sup>8,9,10</sup> and related macrocyclic metal-organic complexes are very attractive NLO materials for these applications because of their relatively large nonresonant third-order susceptibilities, inherently fast response times, and remarkable chemical and thermal stabilities. Although extensive work has been done on investigation of the third-order susceptibilities and optical limiting performances of phthalocyanines and porphyrins by different techniques, such as third harmonic generation (THG), degenerate four wave mixing (DFWM), and Z-scan, relatively little effort has been devoted to the studies of the nonlinear optical properties of expanded porphyrin system, such as Texaphyrins<sup>11,12</sup> and their analogues.<sup>13,14</sup> Similar to phthalocyanines and porphyrins, Texaphyrins and analogues possess extensively two-dimensional delocalized  $\pi$ -conjugate systems, thus large third-order nonlinearities are expected. In addition, the ease with which the

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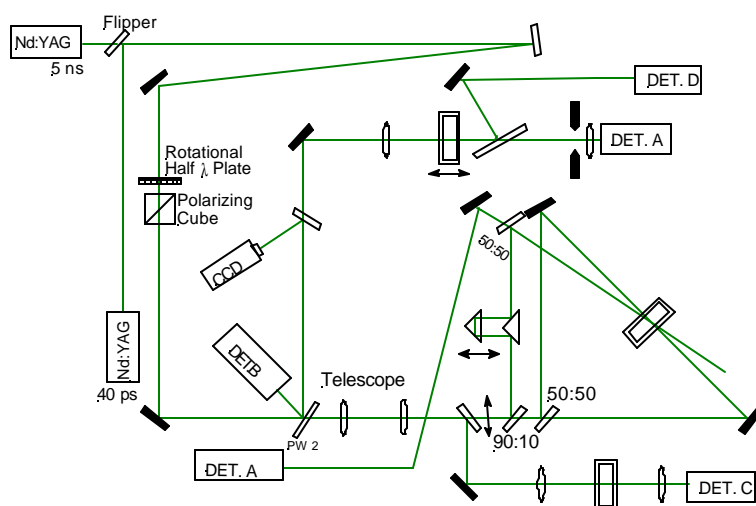
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structures of these complexes may be modified allows the relationship between the molecular structures of the complexes and their third order nonlinearities to be studied.

Recently, our group performed a systematical study of the third-order susceptibilities of a series of asymmetric pentaazadentate porphyrin-like metal complexes ( $[(R-APPC)M]Cl_n$ ), analogues of Texaphyrins, by DFWM experiments using 40 ps laser pulses at 532 nm.<sup>15</sup> The molecular second-order hyperpolarizabilities of these complexes ranged from  $1.1 \times 10^{-31}$  esu to  $1.2 \times 10^{-30}$  esu, which are among the largest values reported to date.<sup>8</sup> We also investigated the optical limiting performances of these materials with 5 ns laser pulses at 532 nm.<sup>16</sup> Our results demonstrated that these complexes exhibited very strong reverse saturable absorption at 532 nm with nanosecond laser pulses and had optical limiting performances closely approaching those of the best materials reported to date,  $PbPc(CP)_4$  and  $SiNc$ .<sup>5,7</sup> These results are extremely promising, however, none of the above experiments can separately determine the contributions of the nonlinear absorption and nonlinear refraction to the third-order susceptibility. In this paper, we investigate the third-order nonlinearity of a methyl substituted Texaphyrin cadmium complex,  $[(CH_3-TXP)Cd]Cl$ , (structure shown in Fig. 1) by DFWM and Z-scan techniques. The molecular second-order hyperpolarizability, the excited-state absorption cross-section and the nonlinear refractive cross-section have been obtained. Additionally, the optical limiting properties of this complex have been evaluated with both nanosecond and picosecond laser pulses.

## 2. EXPERIMENTS

The complex  $[(CH_3-TXP)Cd]Cl$  was synthesized by a procedure described in the literature.<sup>11</sup> Silicon 2,3-naphthalocyanine bis(trihexylsilyloxy) ( $SiNc$ ) was purchased from Aldrich Chem. Co. with a dye concentration of ~95% and was used without further purification. The linear absorption spectrum of a  $3.0 \times 10^{-4}$  mol/L chloroform solution of  $[(CH_3-TXP)Cd]Cl$  in a 2 mm quartz cell was acquired using a Shimadzu UV-3101 PC UV-VIS-NIR scanning spectrophotometer. The lifetime of the first singlet excited state was determined by single photon counting method using a Horiba Naes-1100 time-resolved spectrofluorometer. A  $\sim 10^{-6}$  mol/L solution of the complex in HPLC grade methanol, which was degassed for 10 min, was used for this experiment. The triplet-triplet transient difference spectrum was measured using a laser flash photolysis technique. A Quanta-Ray Co. DCR-2A30A frequency-tripled (355 nm) Q-switched Nd:YAG laser with 5 ns pulse width and output energy of 35 mJ was used as the pump source. A pulsed Xe arc lamp was used as the probe beam. The transient difference spectrum was recorded in 350-600 nm region. A  $1.65 \times 10^{-5}$  mol/L solution of the complex in HPLC grade chloroform, which was degassed with nitrogen for 10 min, was used in this experiment.



**Fig. 2** The configuration of DFWM, Z-scan and optical limiting experiments

The layouts of the DFWM, Z-scan and optical limiting experiments are shown in Fig. 2. A continuum mode-locked frequency-doubled (532 nm) Nd:YAG laser with a temporal pulse width (full width at half maximum, FWHM) of 40 ps is the light source for the DFWM, Z-scan and ps optical limiting experiments. A frequency-doubled, Q-switched Nd:YAG laser with 5 ns pulses and a repetition rate of 10 Hz was used for the ns optical limiting experiment. A mirror mounted on a flipper

was used in the major beam path to switch from ns laser pulses to ps laser pulses. A combination of half-wave plate and polarizing cube was used to attenuate the energy. A prism wedge was used to split the attenuated beam into three parts. One of the reflective beams was used to monitor the incident laser energy. Another reflective beam was directed to the Z-scan experiment. The transmitted beam went to the DFWM setup. Carbon disulfide ( $\text{CS}_2$ ) was used as reference to calibrate the measurements in both DFWM and Z-scan experiments.

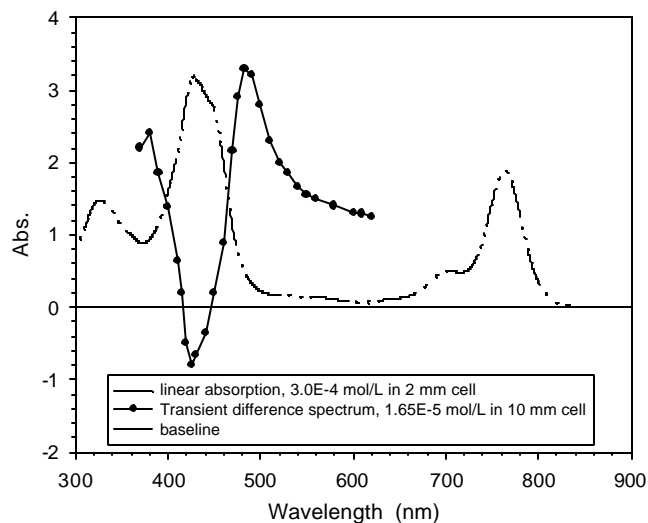
The layout of the DFWM experiment is shown in the center of Fig. 2. The diameter of the laser beam was decreased to 2 – 3 mm by a telescope, and then the beam was split into three beams. The three beams were temporally and spatially overlapped in the sample, which was contained in a 5 mm quartz cuvette, using a standard counterpropagating pump geometry. A variable time delay was introduced into the probe beam. The laser intensities at the sample were 26 – 40  $\text{MW}/\text{cm}^2$  in each of the pump beams and 2.9 – 4.4  $\text{MW}/\text{cm}^2$  in the probe beam. The phase conjugate signal was detected with a silicon photodiode.

The Z-scan experiment, which is at the top of Fig. 2, uses a 50 cm focal length best form lens to focus the laser pulses into a 2 mm quartz cell which contains the sample solution. The Z-scan experiment was performed using 40 ps laser pulses with two different spatial beam profiles. For a Gaussian spatial profile ( $F/83$ ), the beam is focused to a waist of radius  $w_0 = 28.2 \mu\text{m}$  half width at  $1/e^2$  maximum, which corresponds to a Rayleigh range  $z_0 = \pi w_0^2/\lambda$  of 4.7 mm. For a top-hat beam spatial profile, the reflective beam split by the prism wedge (PW2) is expanded to 12mm in diameter and subsequently passed through a 8.6-mm-diameter aperture, and focused by the  $f=50$  cm best form lens. The resulting Airy radius of the focused spot of the top-hat beam is  $37.3 \mu\text{m}$  (using equation  $w_0=1.22\lambda f/d$ , where  $d$  is the diameter of the aperture in front of the focusing lens), and its corresponding Rayleigh range is 8.2 mm. In both cases, the sample thickness of 2 mm is less than the Rayleigh length, allowing it to be treated as a thin sample. A partially closed aperture is placed before the detector, and the detector output is monitored as the position of the sample,  $z$ , is translated along the optical axis relative to the focal plane of the input lens ( $z=0$ ). To measure the open-aperture Z-scan and the closed-aperture Z-scan simultaneously, a small portion of the output beam is split off to record the nonlinear absorption. Z-scan experiments were run on a  $2.4 \times 10^{-4}$  mol/L solution of  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  in methanol and on a  $7.53 \times 10^{-4}$  mol/L solution of SiNc in chloroform.

The optical limiting experimental configuration is shown in the bottom of Fig. 2. Two different time scale laser pulses were used as the light source. For the 5 ns laser pulses, the laser beam was focused at the center of a 2-mm path-length quartz cell by a 25 cm plano-convex lens ( $F/38$ ) giving a spot radius of  $\sim 210 \mu\text{m}$ . For the 40 ps laser pulses, a 30 cm plano-convex lens ( $F/146$ ) was used to focus the beam to a waist radius of  $\sim 100 \mu\text{m}$ . Detector B was used to monitor the incident energy. Optical limiting was obtained by varying the input energy with the half wave plate and polarizer and by monitoring input and output energy with two J4-09 series Moletron joule meters.

### 3. RESULTS AND DISCUSSION

#### 3.1 Photophysical properties of $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$



**Fig. 3** Linear absorption spectrum and transient difference spectrum of  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  in  $\text{CHCl}_3$ .

One consideration in evaluating materials for optical limiting applications is the bandwidth over which the limiting performance is effective. An ideal molecule should exhibit reverse saturable absorption and have a large ratio of excited state absorption cross section  $\sigma_{\text{ex}}$  to ground state cross section  $\sigma_{\text{gr}}$  over a wide spectral range. To determine the spectral range of the  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  complex, the linear absorption spectrum and the transient difference spectrum have been measured. As shown in Fig. 3, the linear absorption spectrum for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  reveals a strong Q(0,0) band centered at 764 nm and a B band centered at 428 nm. Hence, a relatively wide optical window is formed in the 480 – 660 nm region, wherein the transient difference spectrum acquired 100 ns after excitation exhibits a strong absorption band. This suggests that reverse saturable absorption will occur over the 480 – 660 nm spectral range for nanosecond or longer pulses duration, up to the limit imposed by the triplet excited state lifetime.

To gain information about the singlet excited state, a fluorescence measurement of [(CH<sub>3</sub>-TXP)Cd]Cl in chloroform was conducted. Excitation throughout the visible and near UV results in a deep red emission with a maximum around 777 nm. The very small Stokes shift and the mirror image character of this emission relative to the Q-bands indicates that it is a fluorescence from S<sub>1</sub>. The measured fluorescence lifetime in chloroform is 0.87 ns, which is closely related to the very low quantum yield of the fluorescence  $\Phi_f = 0.01$ . This indicates that the intersystem crossing may occur very rapidly. Hence a high quantum yield of triplet excited state, similar to that observed for other Texaphyrin complexes,<sup>17,18</sup> is expected.

### 3.2 Degenerate four wave mixing

The third-order optical susceptibilities of [(CH<sub>3</sub>-TXP)Cd]Cl and SiNc were measured by degenerate four wave mixing (DFWM) at 532 nm using a Continuum model-locked frequency doubled Nd:YAG laser with a temporal pulse width (FWHM) of 40 ps. The  $\chi^{(3)}$  for the solution was obtained by comparison of the magnitude of the phase conjugate signal with that of the CS<sub>2</sub> reference using the equation (1):<sup>19</sup>

$$\mathbf{c}_{\text{sample}}^{(3)} = \mathbf{c}_{\text{ref}}^{(3)} \left( \frac{I_{\text{sample}}}{I_{\text{ref}}} \right)^{1/2} \left( \frac{n_{\text{sample}}}{n_{\text{ref}}} \right)^2 \left( \frac{l_{\text{ref}}}{l_{\text{sample}}} \right) \left( \frac{\mathbf{a}l}{e^{-\mathbf{a}l/2}(1-e^{-\mathbf{a}l})} \right) \quad (1)$$

where  $I$  is the intensity of the conjugate beam,  $n$  is the refractive index,  $l$  is the sample path length, and  $\mathbf{a}$  is the linear absorption coefficient of the solution at 532 nm. The subscript “ref” refers to CS<sub>2</sub>, for which a value of  $\mathbf{c}_{\text{xxxx}}^{(3)} = 6.8 \times 10^{-13}$  esu<sup>20</sup> at 532 nm for the 25 ps laser pulse was used.

When a nonlinear optical material is taken into solution, the third-order macroscopic susceptibility of the solution is assumed to be a pairwise addition of the solvent and solute. The molecular second hyperpolarizability,  $\mathbf{g}_{\text{solute}}$ , can be calculated from<sup>21</sup>

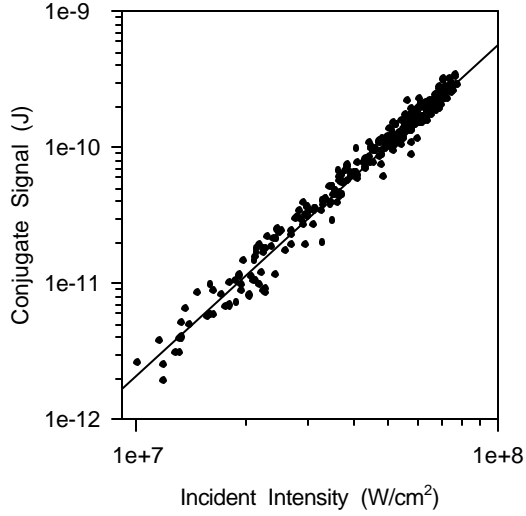
$$\mathbf{c}_{\text{solution}}^{(3)} = L^4 (N_{\text{solvent}} \mathbf{g}_{\text{solvent}} + N_{\text{solute}} \mathbf{g}_{\text{solute}}) \quad (2)$$

where  $N_{\text{solute}}$  and  $N_{\text{solvent}}$  are the number densities of molecules of the solute and solvent per mL, and  $L$  is the local field correction factor given by  $(n^2+2)/3$ .

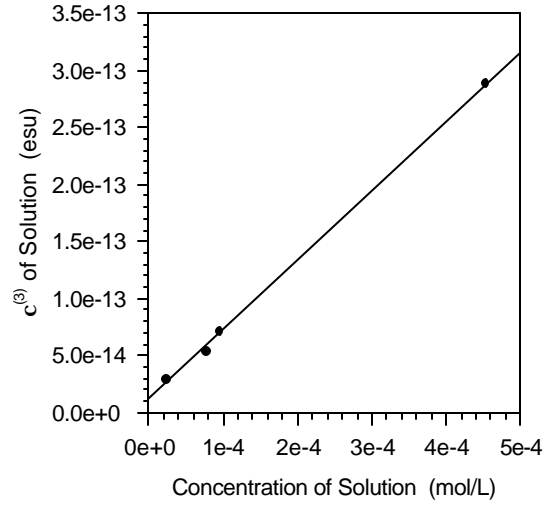
The dependence of the phase conjugate intensity on the incident laser intensity was measured, and a cubic power dependence was observed for CS<sub>2</sub>, a reference third-order nonlinear optical material with a well-characterized  $\mathbf{c}^{(3)}$ , as well as for solutions of [(CH<sub>3</sub>-TXP)Cd]Cl (shown in Fig. 4) and SiNc. The following experiments were performed at the incident intensity where the cubic power dependence is valid.

We measured  $\mathbf{c}^{(3)}$  for methanol solutions of [(CH<sub>3</sub>-TXP)Cd]Cl in the concentration range of  $10^{-5} - 10^{-4}$  mol/L. The dependence of  $\mathbf{c}^{(3)}$  on the concentration of the solution for [(CH<sub>3</sub>-TXP)Cd]Cl is illustrated in Fig. 5. As expected, a linear relationship is observed for the complex, and the molecular second-order hyperpolarizability of the solute is obtained from the slope of the plot. This gives a  $\mathbf{g}$  value of  $6.9 \times 10^{-31}$  esu for [(CH<sub>3</sub>-TXP)Cd]Cl, which is among the largest  $\mathbf{g}$  values reported to date for off-resonant second-order molecular hyperpolarizability.<sup>8</sup> A similar measurement for chloroform solutions of SiNc gave a  $\mathbf{g}$  value of  $1.7 \times 10^{-31}$  esu, which is only one-fourth of that of [(CH<sub>3</sub>-TXP)Cd]Cl.

The third-order nonlinearity of a sample may originate from either electronic, orientational, acoustic, or thermal processes.<sup>22,23</sup> Measurement of the individual components of the  $\mathbf{c}^{(3)}$  tensor may shed light on some of the different mechanisms contributing to the observed DFWM signal. In particular, the value of the ratio  $\mathbf{c}_{\text{xyyx}}^{(3)} / \mathbf{c}_{\text{xxxx}}^{(3)}$  can help to identify the molecular origin of  $\mathbf{c}^{(3)}$ . For an isotropic solution, the ratio  $\mathbf{c}_{\text{xyyx}}^{(3)} / \mathbf{c}_{\text{xxxx}}^{(3)}$  is 1/3 for an instantaneous electronic  $\mathbf{c}^{(3)}$ , but is 3/4 for nuclear reorientation.<sup>24,25,26,27</sup> For CS<sub>2</sub>, whose third-order nonlinearity is known to be dominated by orientational effect, we found  $\mathbf{c}_{\text{xyyx}}^{(3)} / \mathbf{c}_{\text{xxxx}}^{(3)}$  to be 0.74 in good agreement with the reported ratio of 0.70.<sup>24</sup> In contrast, for [(CH<sub>3</sub>-TXP)Cd]Cl, we found  $\mathbf{c}_{\text{xyyx}}^{(3)} / \mathbf{c}_{\text{xxxx}}^{(3)}$  to be 0.38. This result strongly suggests that the nonlinearity of [(CH<sub>3</sub>-TXP)Cd]Cl is predominantly electronic in origin over the ps time scale.



**Fig. 4** Dependence of conjugate signal in xxxx polarization on the laser intensity for the 0.955 mmol/L [(CH<sub>3</sub>-TXP)Cd]Cl in methanol. The slope of the curve is 2.5.



**Fig. 5**  $c^{(3)}$  values vs concentration curve for complex [(CH<sub>3</sub>-TXP)Cd]Cl in methanol. The linear coefficient of confidence  $r=0.999$ .

### 3.3 Z-scan

The Z-scan<sup>28</sup> experiment is a simple technique for measuring the change in phase of a laser beam induced by propagation through a nonlinear material. It gives both the sign and magnitude of this phase change,  $\Delta\Phi$ , which is simply related to the change in index of refraction,  $\Delta n$ . A Z-scan experiment can also separately determine the change in transmission caused by nonlinear absorption that is related to the change in the nonlinear absorption coefficient,  $\Delta\alpha$ . For a third-order nonlinear response, the nonlinear refractive index is related to the on-axis ( $r=0$ ), peak ( $t=0$ ) nonlinear phase shift by<sup>28</sup>

$$n_2(\text{m}^2/\text{W}) = \frac{\Delta\Phi_0 I}{2pL_{\text{eff}} I_0} \quad (3)$$

with,  $L_{\text{eff}} = \frac{(1 - e^{-aL})}{a}$ , where  $a$  is the linear absorption coefficient, and  $I_0$  is the on-axis ( $r=0$ ), peak ( $t=0$ ) irradiance with

the sample at focus ( $Z=0$ ) respectively. For a Gaussian spatial and temporal distribution,  $I_0 = \frac{4\sqrt{\ln 2} E_{\text{total}}}{\sqrt{p^3} w_0^2 t}$ ,

where  $E_{\text{total}}$  is the incident energy on the sample after the reflection from the front surface of the cell is taken into account,  $w_0$  is the beam waist of radius at the focal point,  $t$  is the pulse width (full width at half maximum). The sign of  $\Delta\Phi_0$  and hence  $n_2$  is determined from the relative position of the peak and valley with Z.

To obtain  $\Delta\Phi_0$  from the measured peak-valley transmittance difference  $T_{\text{pv}}$ , the relation between  $\Delta\Phi_0$ ,  $T_{\text{pv}}$  and the aperture linear transmittance  $S$  must be known.  $S$  is the transmittance of the aperture ahead the detector in the absence of a sample. For a top-hat beam Z-scan, a simple empirical fit is<sup>29</sup>

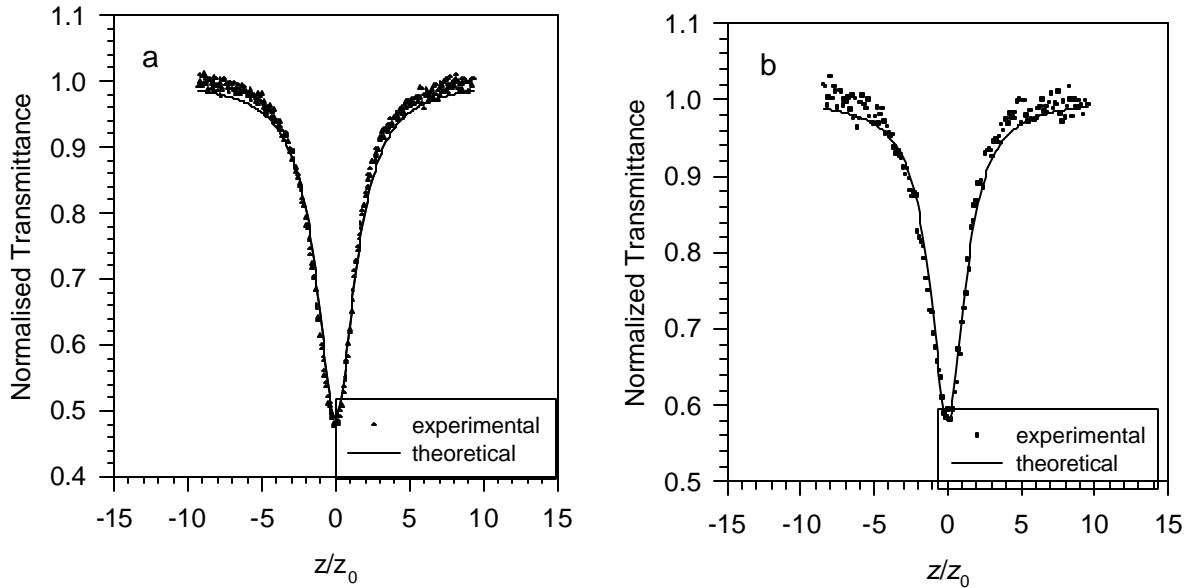
$$\Delta\Phi_0 = 2.7 \tanh^{-1} \left( \frac{T_{\text{pv}}}{2.8(1-S)^{1.14}} \right) \quad (4)$$

Additional information about the nonlinear absorption can be obtained by performing a Z-scan measurement with the aperture completely open. For excited state absorption, the nonlinear transmittance of the sample is given by<sup>30</sup>

$$T(Z) = \frac{\ln\left(1 + \frac{q_0}{1+x^2}\right)}{\left(\frac{q_0}{1+x^2}\right)} \quad (5)$$

with  $x = z/z_0$ , and  $q_0 = \mathbf{a} \mathbf{s}_{ex} F_0(r=0) L_{eff} / 2h\mathbf{n}$ , where  $z$  is the distance of the sample from the focus,  $z_0$  is the Rayleigh length.  $F_0$  is the peak-on-axis fluence, which is related to the incident energy by  $F_0 = 2E_{total} / \rho w_0^2$ .

Open aperture Zscan experiments were performed on  $2.4 \times 10^{-4}$  mol/L solutions of  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  in methanol using 40 ps laser pulses with Gaussian spatial profile. The linear transmittance of the  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  solution (78%) gave a linear absorption coefficient of  $\alpha = 1.2 \text{ cm}^{-1}$ , which corresponds to a ground state absorption cross section of  $8.5 \times 10^{-18} \text{ cm}^2$  by  $\mathbf{a} = 10^{-3} \mathbf{s}_{gr} N_A C$ , where  $C$  is the concentration of moles per liter. A similar measurement on SiNc gives a transmittance of 48% ( $\alpha = 3.6 \text{ cm}^{-1}$ ) at a concentration of  $7.5 \times 10^{-4}$  mol/L in chloroform, corresponding to a ground state absorption cross section of  $8.0 \times 10^{-18} \text{ cm}^2$ .



**Fig. 6** Open aperture Z-scan for 40 ps laser pulses at an incident energy of 1.6 mJ in a 2-mm cell. (a)  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}/\text{CH}_3\text{OH}$ ,  $2.4 \times 10^{-4}$  mol/L; (b)  $\text{SiNc}/\text{CHCl}_3$ ,  $7.53 \times 10^{-4}$  mol/L

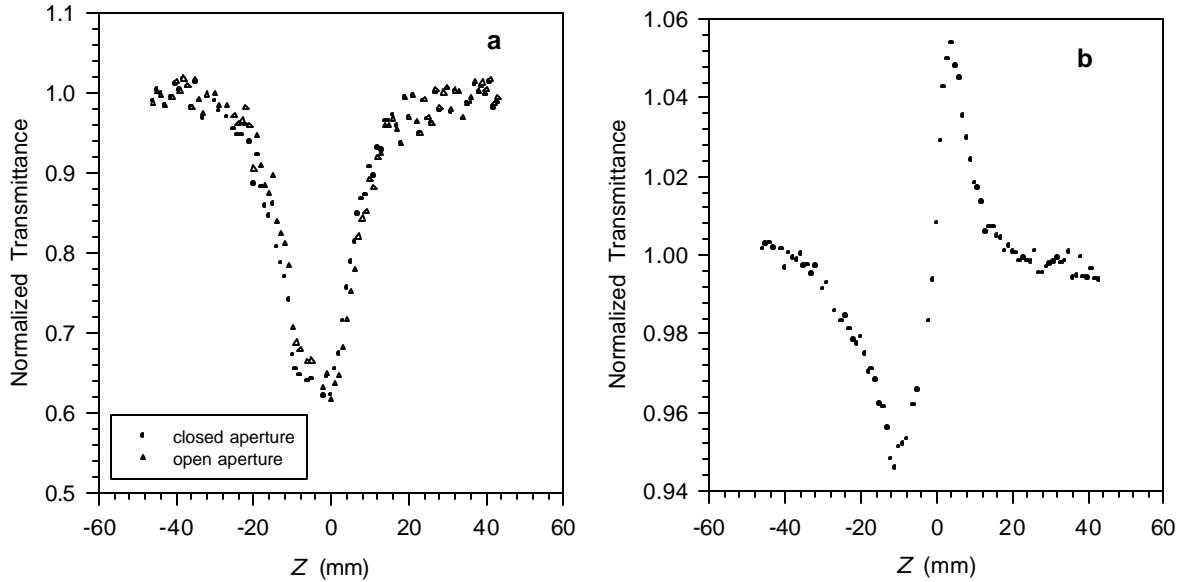
Fig. 6 shows the open aperture Zscan for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  and SiNc solutions at the input energy of 1.6  $\mu\text{J}$  respectively. Both samples clearly exhibit reverse saturable absorption characteristics. The solid lines in Fig. 6 are the results of numerically fitting the data to equation (5). This numerical fit gives a value of  $\mathbf{s}_{ex} \cong 7.0 \times 10^{-17} \text{ cm}^2$  for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  and  $\mathbf{s}_{ex} \cong 1.7 \times 10^{-17} \text{ cm}^2$  for SiNc, respectively. We obtained almost the same values for  $\mathbf{s}_{ex}$  in  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  and SiNc at input energy from 0.5  $\mu\text{J}$  to 4.0  $\mu\text{J}$ . The absolute errors in the  $\mathbf{s}_{ex}$  of  $\pm 9\%$  were possibly from the measurement of concentration, the fluence calculation and curve fitting error.

To determine the nonlinear refractive coefficients of the two samples, we performed closed aperture Z-scan experiments using a top-hat beam (see Section 2). Fig. 7b shows the results of the division of the closed aperture Z-scan data by the open aperture Z-scan data taken simultaneously at the incident energy of 1.70  $\mu\text{J}$  for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  and 1.66  $\mu\text{J}$  for SiNc. The shape of the valley-peak clearly demonstrates that the index change is positive. For the  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  solution, the peak-valley transmittances difference  $\Delta T_{\text{p-v}} = 0.108$  corresponds to an on-axis phase change of 0.384. The nonlinear refractive index  $n_2 = 1.0 \times 10^{-18} \text{ m}^2/\text{W}$  is obtained using Equation 3. This is equivalent to  $3.2 \times 10^{-12}$  esu using the conversion formula,  $n_2(\text{esu}) = \left( \frac{cn_0}{40\pi} \right) n_2(\text{MKS})$ . For the SiNc solution, a similar procedure gives a  $n_2$  of  $9.2 \times 10^{-19} \text{ m}^2/\text{W}$  or  $3.2 \times 10^{-12}$  esu. The contributions of the solvent to  $n_2$  were determined by Z-scan experiments on the pure solvents. These experiments yielded a  $n_2$  of  $2.5 \times 10^{-13}$  esu for methanol and a  $n_2$  of  $9.6 \times 10^{-13}$  esu for chloroform. As expected, no nonlinear absorption was observed in the pure solvents. The effective  $n_2$  for the  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  and SiNc complexes were obtained by subtraction to give  $n_2 = 3.0 \times 10^{-12}$  esu for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  and  $n_2 = 2.2 \times 10^{-12}$  esu for SiNc.

The nonlinear refractive coefficient,  $n_2$ , may not be the best description for cumulative nonlinearities that occur, for example, in reverse saturable absorbing (RSA) dyes. In such dyes, linear absorption is followed by excited-state absorption (ESA) where the excited-state absorption cross section is larger than the ground state absorption cross section. In these systems, the resulting change in refractive index, due to population redistribution, is better described by refractive cross section  $\mathfrak{s}_r$  than by a  $n_2$ . Such an  $\mathfrak{s}_r$  is related to the on-axis phase distortion at focus  $\Delta\Phi_0$  by<sup>31</sup>

$$\Delta\Phi_0 = \frac{\mathbf{a}}{2h\mathbf{n}} \mathfrak{s}_r F_0 L_{\text{eff}} \quad (6)$$

From the phase distortion determined from  $\Delta T_{\text{p-v}}$  in equation (4),  $\mathfrak{s}_r$  values of  $1.7 \times 10^{-17} \text{ cm}^2$  for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  and  $5.3 \times 10^{-18} \text{ cm}^2$  for SiNc are obtained. The  $\mathfrak{s}_r$  value for SiNc obtained here is in very good agreement with the literature value of  $4.7 \times 10^{-18} \text{ cm}^2$ .<sup>4</sup> The excited state refractive cross section for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  is 3 times as larger as that for SiNc.



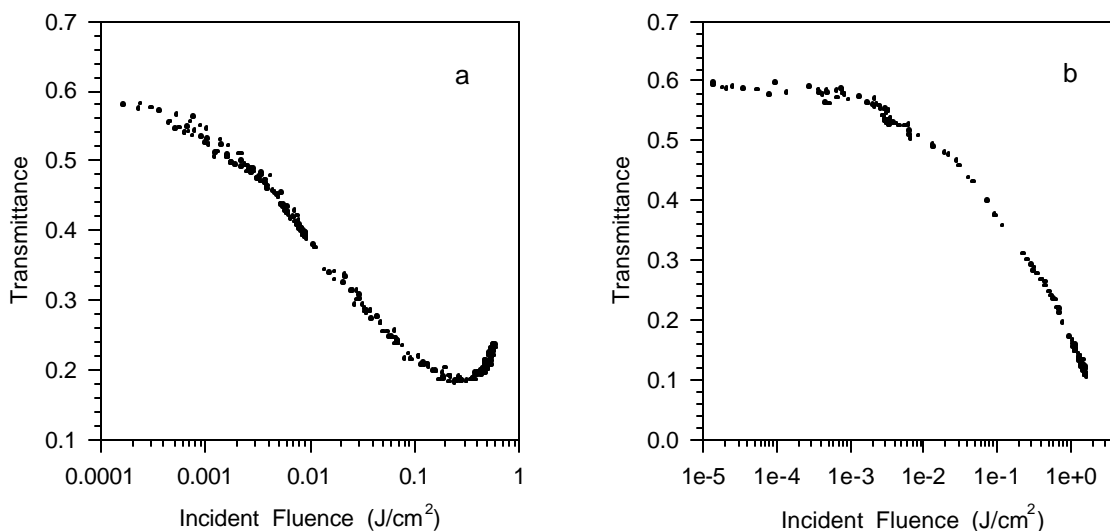
**Fig. 7** Top-hat beams Z-scan experimental curves for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  in methanol using 40 ps laser pulses at 532 nm. The linear transmittance for the sample is 78% at the concentration of  $2.4 \times 10^{-4} \text{ mol/L}$  in a 2 mm cell.

(a) open aperture and closed aperture ( $S=0.68$ ) results

(b) The result of the division of the closed aperture data by the open aperture data

### 3.4 Optical limiting performances

As discussed in 3.1 and 3.3, both the singlet excited state cross section and the triplet excited state cross section for  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  are larger than the ground state absorption cross section. Hence optical limiting based on the reverse saturable absorption is expected for both the nanosecond and picosecond laser pulses. In Figure 8, the transmittance is shown as a function of the incident fluence for both ps and ns pulses. For 5 ns laser pulses, a clear RSA is exhibited by the  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  solution in the range of  $0.001 \text{ J/cm}^2$  to  $1.7 \text{ J/cm}^2$ . The optical limiting threshold<sup>32</sup> ( $F_{th}$ ) of this complex at the concentration of  $4.53 \times 10^{-4} \text{ mol/L}$  is approximate  $1 \text{ mJ/cm}^2$ , and the transmittance for this complex drops to less than 0.1 as the incident fluence is increased to  $1.7 \text{ J/cm}^2$ . These results are comparable to those obtained with SiNc<sup>5</sup> and PbPc.<sup>7</sup> In contrast, for ps pulses, RSA occurs in the range of the incident fluence  $0.0003 \text{ J/cm}^2$  to  $0.3 \text{ J/cm}^2$ . The limiting threshold is near  $0.3 \text{ mJ/cm}^2$ , and the transmittance drops to a minimum of 0.18 when the incident fluence reaches  $0.3 \text{ J/cm}^2$ . Above this point, the transmittance begins to increase while the incident fluence increases, indicating that a saturable absorption (SA) occurs at the fluences greater than  $0.3 \text{ J/cm}^2$ .



**Fig. 8 Transmission versus incident fluence of  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  at the concentration of  $0.453 \text{ mmol/L}$  in  $2 \text{ mm}$  cell in methanol (a)  $40 \text{ ps}$  laser pulses; (b)  $5 \text{ ns}$  laser pulses**

The different optical limiting performances of  $[(\text{CH}_3\text{-TXP})\text{Cd}]\text{Cl}$  with ns and ps pulses are due to the relative contributions of excited singlet-singlet and triplet-triplet absorptions for various pulse durations. For pulse durations much less than the singlet excited state lifetime, the optical limiting response is dominated by singlet-singlet absorption. When pulse durations are much larger than the singlet excited state lifetime and the intersystem crossing rate is very fast, the singlet contribution diminishes, and the contribution of the triplet-triplet absorption becomes dominant. As discussed in sections 3.1, the lifetime of the first singlet excited state is  $0.87 \text{ ns}$ , and the intersystem crossing time is about  $100 \text{ ps}$ . Therefore, for  $5 \text{ ns}$  laser pulses, triplet-triplet absorption is dominant. In contrast, because the  $40 \text{ ps}$  pulse width is shorter than  $\tau_{s_1}$ , the singlet contribution is more significant for  $40 \text{ ps}$  pulses. Due to the larger ratio of  $\frac{\sigma_{s_1}}{\sigma_{gr}} \cong 8$ , RSA occurred. However, in the limit where the intensity is sufficiently high that the pumping rate,  $\sigma_{s_1} I$ , competes with the decay rate  $\frac{1}{\tau_{s_2}}$ , assumed to be in the order of  $(1 \text{ ps})^{-1}$ , population will build up in  $S_2$ . If the absorption cross section of  $S_2$  is less than that of the ground state, SA will occur.

### 3.5 Summary

The values of the molecular second-order hyperpolarizability, the excited state absorption cross section, the excited state refractive cross section obtained in this work, along with the photophysical properties of [(CH<sub>3</sub>-TXP)Cd]Cl and SiNc are summarized in Table I. It is obvious that both the excited state absorption cross sections and the refractive cross section for [(CH<sub>3</sub>-TXP)Cd]Cl are several times larger than those for SiNc. These results demonstrate that [(CH<sub>3</sub>-TXP)Cd]Cl is a very promising optical limiting material.

**Table I Third-order nonlinearity parameters and photophysical parameters for [(CH<sub>3</sub>-TXP)Cd]Cl and SiNc**

Complexes	$S_0$ (10 <sup>-18</sup> cm <sup>2</sup> )	$\gamma$ (10 <sup>-31</sup> esu)	$S_{S_1}$ (10 <sup>-17</sup> cm <sup>2</sup> )	$S_r$ (10 <sup>-18</sup> cm <sup>2</sup> )	$t_{S_1}$ (ns)
[(CH <sub>3</sub> -TXP)Cd]Cl	8.5	6.9	7.0	17	0.87 <sup>a</sup>
SiNc	8.0	1.7	1.7	5.3	3.2 <sup>b</sup>

a. Single photon counting measurement.

b. From reference.<sup>5</sup>

## 4. CONCLUSIONS

The third-order nonlinearity of a new two-dimensional, delocalized  $\pi$ -conjugate system, [(CH<sub>3</sub>-TXP)Cd]Cl, has been investigated by DFWM and Z-scan techniques using 40 ps laser pulses at 532 nm. The optical limiting performances of this complex with both 5 ns and 40 ps laser pulses have also been studied. These results are compared with those of SiNc, one of the most promising optical limiting materials reported to date.

The results demonstrate that most of the third-order nonlinear parameters, such as the molecular second-order hyperpolarizability ( $\gamma$ ), the first singlet excited state cross section ( $S_{S_1}$ ), and the excited state refractive cross section ( $S_r$ ) for the [(CH<sub>3</sub>-TXP)Cd]Cl complex are several times larger than those of the SiNc. The third-order nonlinearity of the [(CH<sub>3</sub>-TXP)Cd]Cl complex is predominantly electronic in origin over the ps time scale and is dominated by excited state absorption. To our knowledge, this is the first measurement of the nonlinear refractive cross section of the expanded porphyrin complexes. This study demonstrates that complexes such as [(CH<sub>3</sub>-TXP)Cd]Cl are very promising nonlinear optical materials for power limiting applications. This ease with which the structures of these complexes may be modified suggests that it should be possible to develop materials with even better optical limiting properties.

## 5. ACKNOWLEDGEMENT

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