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Heavy atom effect on nonlinear absorption and optical limiting characteristics of 5,10,15,20-(tetratolyl) porphyrinato phosphorus (V) dichloride

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Abstract

Optical limiting performance and third-order nonlinearity $\chi^{(3)}$ are investigated in 5,10,15,20-(tetratolyl) porphyrinato phosphorus (V) dichloride ($[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}\mathrm{Cl}_2]^+$). Heavy atom effect exerted by the two axial chlorides is found to result in low fluorescence yield ($\varnothing_{\mathrm{fl}}$), shorter lifetimes of S_1, T_1 and faster intersystem crossing (ISC), leading to larger excited state absorption (ESA) from $T_1 \rightarrow T_n$. This phenomenon is found to lower the limiting threshold by 30 times and increase the second hyperpolarizability by one and three orders in ps and ns time regimes, respectively.

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1. Introduction

Optical limiters are devices that strongly attenuate optical beams to a threshold level at high intensities while exhibiting linear transmittance at low intensities. Such devices are required for the protection of human eye and optical sensors from intense laser fields. There is an intensive search for materials exhibiting such properties, based on nonlinear absorption, photorefraction, nonlinear scattering, thermal beam spreading, excited state absorption (ESA), two-photon absorption (TPA), etc. [1]. Of these processes, ESA plays a very important role for optical limiting in porphyrins. Porphyrins, a class of tetrapyrrolic chromophores, are among the most effective optical limiters in the visible region known to date [2]. The architecture

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of the porphyrin macrocycles is important for developing materials with optimum nonlinearity and response times [3]. Structural modifications to the porphyrin ring can be expected to result in molecules with diverse photophysical and photochemical properties that will in turn affect their optical nonlinearity. This would lead to an increase in a variety of excited state processes including enhanced internal conversion and intersystem crossing (ISC), ion-association, excitation energy transfer, photoinduced electron transfer, etc. [4]. One of the key structural modifications in this regard is the introduction of heavy atoms in the porphyrin ring [5], which in turn, due to faster ISC rate reduces the fluorescence yield, increase triplet formation and hence further enhancing absorption from $T_1 \rightarrow T_n$. Such effects can be conveniently harnessed to enhance the third-order nonlinearity, limiting performance and hence to develop promising materials for optical limiting. ESA is the most important mechanism leading to optical limiting in porphyrins [6,7]. Heavy atom effect in brominated porphyrins [8], and a class of group III and group IV metalloid porphyrins [9], is known to enhance reverse saturable absorption (RSA). Enhancement in optical limiting in phthlocyanines [10] and the third-order nonlinearities [11] of thiophene homologues due to heavy atom effect has also been reported.

Our group has been involved in studies on a class of porphyrins, known as tetratolylporphyrins, for achieving higher optical limiting performance and nonlinear absorption. The tetratolylporphyrins synthesized have higher third-order nonlinearities [12] and efforts are being made to attain large excited state absorption cross-sections through structural modifications. In this paper, we report the nonlinear absorption and optical limiting properties of 5,10,15,20-(tetratolyl) porphyrinato phosphorus (V) dichloride ($[(\mathrm{TTP})\,\mathrm{P^VCl_2}]^+$), with introduction of heavy $\mathrm{Cl^-}$ in place of $(\mathrm{OH})^-$ in 5,10,15,20-(tetratolyl) porphyrinato phosphorous (V) dihydroxide $[(\mathrm{TTP})\mathrm{P^V(OH)_2}]^+$. We observed stronger RSA with the introduction of $\mathrm{Cl^-}$ both in ps and ns regimes. We also report saturation of absorption in RSA at fluences larger than 0.5 J $\mathrm{cm^{-2}}$ with ps pulses. Whereas, no such behavior is observed with ns pulses. Saturation in absorption at high fluences based on higher ESA is reported in cadmium texaphyrin solution [13], 1,1′,3,3,3′,3′-hexamethylindotricarbocyanine iodide (HITCl) [14] and in chloroalumiminum phthalocyanine dye [15]. Although anomalous heavy atom effect on optical limiting performance is reported in lanthanide diphthalocyanines [16], we have not observed any anomaly in our case, as the chloride substitution is in the axial site.

2. Experimental details

Samples of $[(\mathrm{TTP})\mathrm{P^VCl_2}]^+$ and $[(\mathrm{TTP})\mathrm{P^V(OH)_2}]^+$ are synthesized and purified according to the reported procedures in the literature [17]. Each sample is subjected to a column chromatographic purification process prior to the measurements. In all experiments, sample solutions in chloroform are taken in a quartz cell of 1-mm path length. The molecular structure and absorption spectra of these molecules are shown in Fig. 1. This molecule

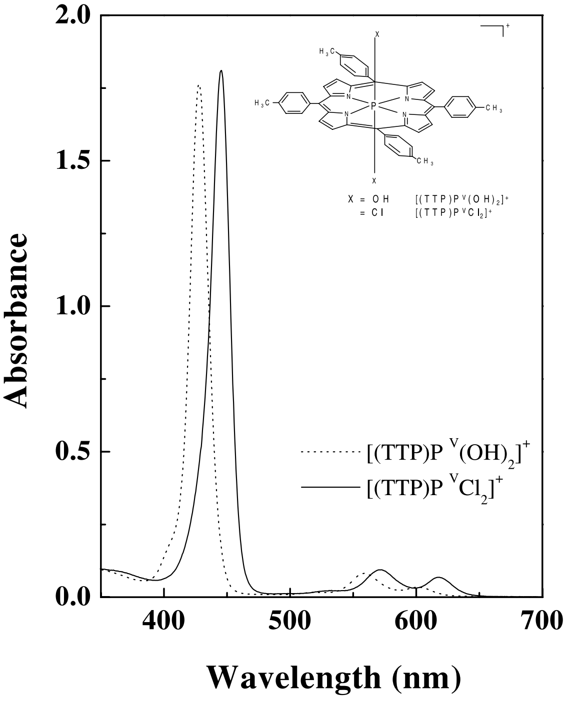

Fig. 1. Absorption spectra of $[(\mathrm{TTP})\mathrm{P^V(OH)_2}]^+$ and $[(\mathrm{TTP})\mathrm{P^VCl_2}]^+$. Inset shows molecular structure.

shows linear absorption features of typical metalloporphyrins, namely the high energy B (Soret) band and the low energy Q band(s). The sample remains stable even after exposure to laser pulses for a long period of time, which is confirmed from indistinguishable absorption spectra recorded before and after the measurements. Frequency doubled Nd:YAG lasers with 25 ps and 6 ns pulse widths, 10 Hz repetition rate are used for the experiments. We have employed standard backward DFWM geometry [12] for the measurement of $\chi^{(3)}$. Optical limiting and open aperture *Z*-scan [18] studies are carried out by focusing the input beam onto the sample with linear transmission of approximately 75% at 532 nm using lenses of 500 mm and of 125 mm focal length to 60 and 30 μm spot size at focus in case of 25 ps and 6 ns pulses, respectively, and the transmitted light is collected with a fast photodiode. The peak fluences used in the *Z*-scan experiments with 25 ps and 6 ns pulses are approximately 0.25–1.3 and 0.5–1.5 J cm^{-2}. The optical limiting and *Z*-scan studies are performed at the same concentration of $\sim 10^{-4}$ M ensuring identical experimental conditions for both ps and ns regimes.

3. Results and discussion

The effective microscopic second hyperpolarizability $\langle\gamma\rangle$ measured with 25 ps pulses and 6 ns pulses for $[(\mathrm{TTP})\ \mathrm{P^V(Cl)_2}]^+$ is $(8.49 \pm 0.46) \times 10^{-30}$ and $(174.48 \pm 7.2) \times 10^{-27}$ esu, respectively. These values are found to be greater than the corresponding values of $[(\mathrm{TTP})\mathrm{P^V(OH)_2}]^+$ by one order in ps regime and by three orders in ns regime, respectively [12]. The ratio of the signals for the conjugate beam in ns DFWM experiment for parallel and perpendicular probe polarizations dropped down by just about 1/3, indicating that the nonlinearity is predominantly electronic in origin. Large enhancement in $\langle\gamma\rangle$ at ns timescale is attributed to the excited triplet state. Greater polarization emanating from electronegative chlorine in the phosphorus porphyrin structure was shown which led to a rise in the measured $\langle\gamma\rangle$ values [19].

Significant reduction in the limiting threshold level for $[(\mathrm{TTP})\mathrm{P^VCl_2}]^+$ compared to $[(\mathrm{TTP})\mathrm{P^V(OH)_2}]^+$, with 6 ns pulses can be seen in Fig. 2. In ns time regime, the limiting threshold ($I_{1/2}$) has reduced by 30 times from 3 J cm^{-2} in case of $[(\mathrm{TTP})\mathrm{P^V(OH)_2}]^+$ to 0.1 J cm^{-2} in case of $[(\mathrm{TTP})\mathrm{P^VCl_2}]^+$. However, we observe a reduction in the limiting threshold by three times from 0.264 to 0.0884 J cm^{-2} in the ps regime. Among the various factors that can be invoked to explain improvement of the optical limiting performance of $[(\mathrm{TTP})\mathrm{P^VCl_2}]^+$ in the ns time regime, faster ISC rate due to the axial chloride substitution leading to heavy atom effect is the most important as it plays a significant role by enhancing the population of the triplet state. The long lifetime of the T_1 state compared to the ns pulse duration, thus leads to larger effective ESA from $T_1 \rightarrow T_n$, leading to reduction in optical limiting threshold and enhancement in second-order hyperpolarizability.

In order to estimate the limits to which these molecules would be showing RSA behavior is seen by recording the *Z*-scan curves at different fluences for the ps and ns regimes. With ps pulses, both the

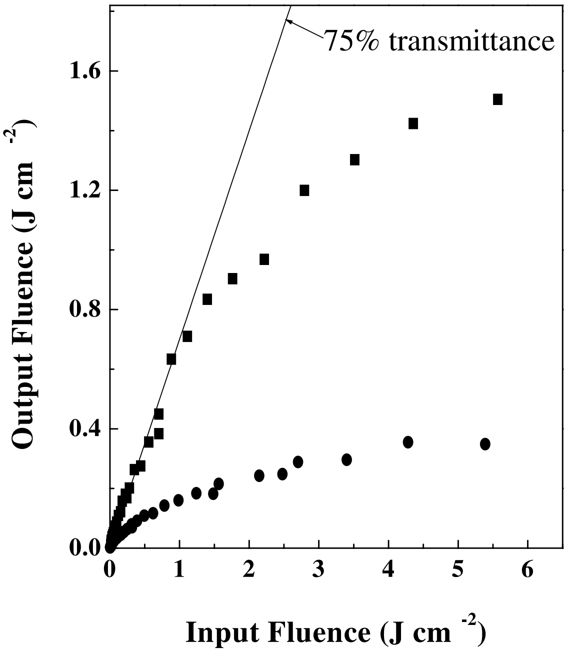

Fig. 2. Optical limiting curves of $[(\mathrm{TTP})\mathrm{P^V(OH)_2}]^+$ (squares) and $[(\mathrm{TTP})\mathrm{P^VCl_2}]^+$ (circles) with 6 ns pulses. Line represents 75% linear transmittance.

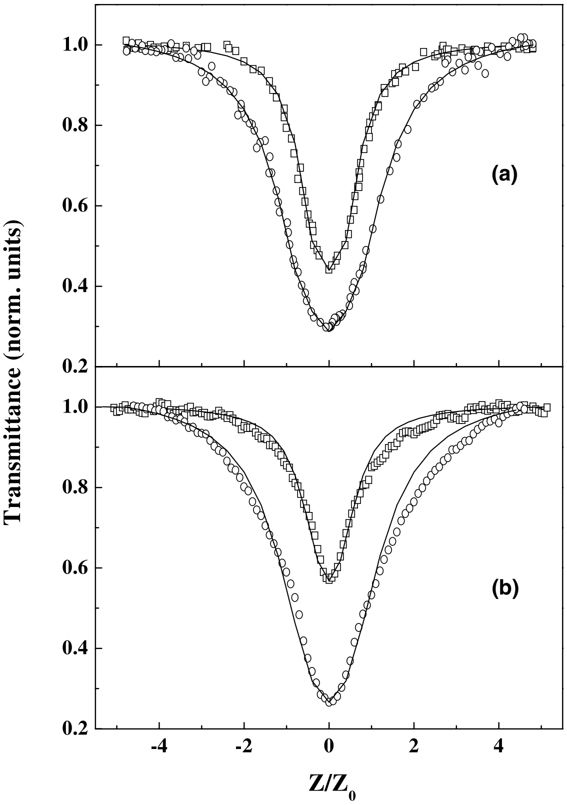

Fig. 3. Open aperture Z-scan curves of $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{OH})_2]^+$ (squares) and $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}\mathrm{Cl}_2]^+$ (circles) showing RSA at low fluences (a) with 25 ps pulses with peak fluences of 0.35 J cm^{-2} at focus and (b) with 6 ns pulse widths. Solid lines show theoretical fit generated using a five level model.

molecules have shown RSA till the fluences of 0.40 J cm^{-2} (Fig. 3(a)). But above this fluence level, both the molecules start showing a gradual increase in the saturation of S_n excited state absorption with increasing input fluence. The Z-scan data with ns pulses (Fig. 3(b)) show only RSA even at high fluences. Fig. 4 shows the open aperture Z-scan curves showing SA followed by RSA at different fluences above 0.40 J cm^{-2} with ps pulses. The symmetrical traces indicate that no other processes such as scattering or damage occur. The fluence at which the saturation of excited states has started (F_{th}) is given in Table 1.

The enhancement in the nonlinear absorption with ns pulses and the saturation effects with ps pulses at higher fluences are investigated by a generalized five level model and the rate equations describing different mechanisms like ground state absorption from $S_0 \rightarrow S_1$, ESA from $S_1 \rightarrow S_n$, $T_1 \rightarrow T_n$ and different relaxation times in the molecule. The rate equations are solved numerically using Runge–Kutta fourth-order method [20]. In the ps regime, the singlet levels S_0, S_1 and S_n play a major role. Hence the five level model effectively becomes a three level model, neglecting the ISC from $S_1 \rightarrow T_1$, as the pulse duration is much shorter than τ_{ISC}. While modeling the ns data, we observe that $S_1 \rightarrow S_n$ absorption shows insignificant contribution, which is due to large population in the T_1 state due to stronger ISC from $S_1 \rightarrow T_1$.

From the theoretical fit to open aperture Z-scan curves with 25 ps pulses, the ESA from $S_1 \rightarrow S_n(\sigma_1)$ and the lifetime of the higher singlet state τ_{Sn} are estimated. The ESA cross-section (σ_2) from $T_1 \rightarrow T_n$ and ISC rate (τ_{ISC}) are estimated from the theoretical fit of the ns data. The estimated values from the theoretical fits, the widely used figures of merit, the ratios $\sigma_1/\sigma_0, \sigma_2/\sigma_0$, where σ_0 is the ground-state cross-section along with the parameters used for the estimation of these parameters are shown in Table 1. τ's are the lifetimes of the levels and $\varnothing_{\mathrm{fl}}$ is the fluorescence yield. The higher figure of merit σ_1/σ_0 for $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}\mathrm{Cl}_2]^+$ than $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{OH})_2]^+$ confirms that enhancement in the nonlinear absorption at lower fluences with ps pulses is more due to ESA from $S_1 \rightarrow S_n$. In case of $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}\mathrm{Cl}_2]^+$, though the onset of saturation started at slightly higher fluences than $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{OH})_2]^+$, saturation of the excited states is more predominant even with slight increase in the input fluence. This is due to the longer lifetime of the high lying excited states S_n [15] leading to saturation in the absorption from the first excited singlet state S_1 at higher fluences. Faster ISC rate observed in $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}\mathrm{Cl}_2]^+$ is in agreement with a similar observation made earlier for halogenated porphyrins [21,22], the difference being that in our case the substitution is in the axial site. The heavy atom effect arising from the spin–orbit coupling decreases the fluorescence quantum yield ($\varnothing_{\mathrm{fl}}$), hence increasing ISC. Even though the triplet lifetime is reduced, the ESA from T_1 is not reduced

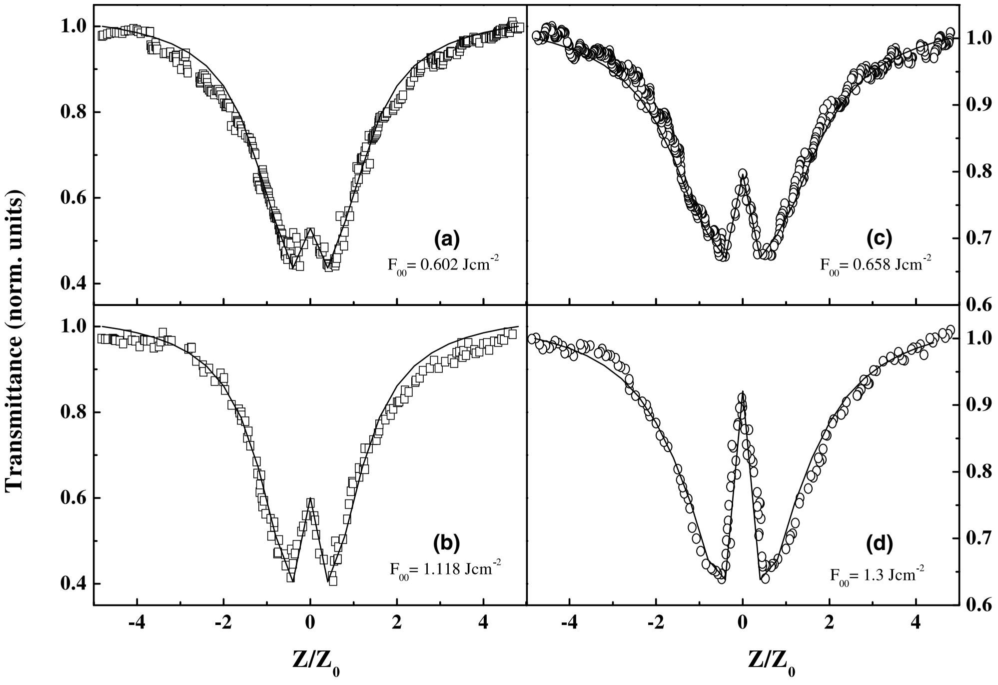

Fig. 4. Open aperture *Z*-scan curves of (a, b) $[(TTP)P^V(OH)_2]^+$ (squares) and (c, d) $[(TTP)P^VCl_2]^+$ (circles) showing SA followed by RSA with 25 ps pulse widths. Peak fluences F_{00} are also shown.

Table 1
Calculated figures of merit for optical limiting

	$[(TTP)P^V(OH)_2]^+$	$[(TTP)P^VCl_2]^+$
τ_{S1}	4.19 ns	4.22 ns
$\varnothing_{fl}$	0.056	0.036
τ_{T1}	68 μs	17 μs
τ_{Sn} [a]	450 fs	600 fs
σ_1/σ_0 [a]	2.67	3.56
σ_2/σ_0 [b]	2.086	12.15
τ_{ISC} [b]	1 ns	100 ps
F_{th} [b]	0.560 J cm^{-2}	0.618 J cm^{-2}

[a] Estimated from ps data.
[b] Estimated from ns data.

as its lifetime (τ_{T1}) is much larger than the exciting ns pulse duration.

4. Conclusions

In summary, we have obtained faster ISC and enhanced second hyperpolarizability of $[(TTP)P^VCl_2]^+$. In the ns regime, the observed large enhancement in the $\langle\gamma\rangle$ is attributed to the excited triplet states of the molecule. We observe a significant reduction in the limiting threshold both in the ps as well as ns regimes by a simple axial chloride substitution.

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