Enhanced optical limiting and nonlinear absorption properties of azoarene-appended phosphorus (V) tetratolylporphyrins

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Optical limiting performance, third-order nonlinearity $\chi^{(3)}$, and nonlinear absorption properties have been investigated in a new class of azoarene phosphorus (V) porphyrins with charge transfer (CT) states. The introduction of axial azoarene groups into the phosphorus porphyrin structure is found to reduce the limiting threshold by a factor of 2 and lead to a rise in the second hyperpolarizability by 1 order of magnitude in the picosecond time regime and by 2 orders of magnitude in the nanosecond regime. The experimental data show reverse saturation of absorption in the nanosecond time regime and a saturation of the nonlinear absorption above a fluence of 0.5 J/cm^2 in the picosecond regime. The presence of the CT state reduces saturation of excited-state absorption (ESA) in the $S_1 \rightarrow S_n$ transition through the $S_1 \rightarrow$ CT transition. Faster CT $\rightarrow T_1$ transition increases the ESA from $T_1 \rightarrow T_n$ states in the nanosecond regime. A self-consistent theoretical analysis based on rate equations is used to estimate the high-lying excited-state lifetimes and absorption cross sections from the experimental results. © 2002 Optical Society of America

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1. Introduction

Optical limiting devices are of interest for protection of sensors and eyes from high-intensity laser light. An ideal limiter exhibits a linear transmission below threshold, but above threshold the transmitted output power is constant. A wide range of materials that contribute to optical limiting and nonlinear absorption have been investigated.[1,2] The optical limiting devices rely on one or more of the nonlinear optical mechanisms[3] such as excited-state absorption (ESA), two-photon absorption (TPA), thermal defocusing and scattering, photorefraction, nonlinear refraction, and induced scattering. Optical limiting performance is enhanced by coupling two or more of the nonlinear optical mechanisms such as self-defocusing in conjunction with TPA in semiconductors[4] or TPA of one molecule with ESA in another molecule.[5] A cascaded optical limiter by use of a reverse saturable absorption (RSA) material along with CS$_2$ has also been reported to achieve better limiting performance.[6]

Porphyrins, a class of tetrapyrrolic chromophores that possess strong ESA from both the triplet as well as the singlet states, are among the most effective optical limiters in the visible region known to date.[7–14] The interest in metalloporphyrins is manyfold. These molecules were found to have strong nonlinearity and fast response times, the desired criteria for making useful photonic devices.[15] Porphyrins were also found to have strong RSA over a wide range in the visible region from 500 to 600 nm.[16] The architecture of the porphyrin macrocycles and the high π-electron density, resulting in an extended electron delocalization, is relevant to the development of materials with optimum optical nonlinearity and response times.[17,18] Since the mechanism of limiting in such materials depends on the absorption of excited molecules, it is important to characterize the excited-state dynamics and evaluate parameters such as absorption cross sections and lifetimes so as to optimize their properties for the real-

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ization of a functional device. Study of the optical nonlinearity and elucidation of the dynamics associated with excited states of such molecules is therefore important from a fundamental as well as a technological point of view. One way to modulate the excited-state properties would be to change the structural geometry and hence electronic structure of these macrocycles.

Structural modifications to the porphyrin ring can be expected to result in molecules with diverse photophysical and photochemical properties that would in turn affect their optical nonlinearity. This could possibly lead to a desirable change in a variety of excited-state processes including enhanced internal conversion and intersystem crossing (ISC), ion association, excitation energy transfer, and photoinduced electron transfer (PET). Such effects can be conveniently harnessed to enhance third-order nonlinearity and decrease limiting threshold compared with simple, unsubstituted porphyrins. Indeed, covalently or noncovalently bound porphyrin acceptor–donor conjugates can be used in the fabrication of molecular electronic and optical devices.[19] Photoinduced electron transfer, leading to excited charge transfer states, is a well-known phenomenon in porphyrins[20] and porphyrin derivatives.[21]

The tetratolylporphyrins (TTPs) synthesized by our group have high third-order nonlinearities and efforts are being made to attain large ESA cross sections through structural modifications.[22,23] Here we report our studies of the family of a new class of phosphorus (V) tetratolylporphyrins with axial azobenzene chromophores. In these porphyrins, donor–acceptor levels and a charge transfer (CT) state are introduced due to the introduction of azoarene (AZT = 4-hydroxy, 4′-methyl azobenzene, AZB = 4-hydroxy azobenzene, AZN = 4-hydroxy, 4′-nitro azobenzene) subunits in place of H in axial $(OH)^-$ in 5,10,15,20-(tetratolyl)porphyrinatophosphorous (V) dihydroxide $[(TTP)P^V(OH)_2]^+$. An intramolecular PET from the axial azoarene donors to the singlet excited state of the basal phosphorus (V) porphyrin is responsible for quenching of fluorescence in these complexes.[24] We observed stronger RSA in the nanosecond regime with the introduction of axial azoarene units. We also observed saturation of absorption of the S_1 states at higher fluence in the picosecond regime, whereas no such saturation of absorption behavior is observed with nanosecond pulses. The observed nonlinear absorption and the phenomenon leading to such behavior are explained by use of a self-consistent rate equation model. These results are compared with a reference porphyrin $[(TTP)P^V(OH)_2]^+$ without CT states.

2. Experimental Details

We synthesized and purified the samples according to the procedures reported in the literature.[24] Each sample was subjected to a column chromatographic purification process prior to the measurements. In all the experiments, sample solutions in chloroform were taken in 1-mm quartz cuvettes. The compounds remained stable even after exposure to laser pulses for a long period of time, which was confirmed by the identical absorption spectra recorded before and after exposure. Frequency-doubled Nd:YAG lasers with 25-ps and 6-ns pulse widths and 10-Hz repetition rate were used for the experiments. We employed standard backward degenerate four-wave mixing (DFWM) geometry[25] for the measurement of third-order optical nonlinearity $\chi^{(3)}$. We performed optical limiting studies using $f/5$ test bed[26,27] and we carried out open-aperture Z-scan[28] studies by focusing the input beam onto the sample with linear transmission of approximately 75% by use of 500- and 125-mm focal-length lenses for picosecond and nanosecond pulses, respectively. The transmitted light was collected with a fast photodiode. The peak fluences used in the Z-scan experiments with 25-ps and 6-ns pulses were approximately 0.25–1.2 and 3–4 J cm^{-2}, respectively. The studies were performed at the same concentration of $\sim 10^{-4}$ M to ensure identical experimental conditions for both the picosecond and the nanosecond regimes.

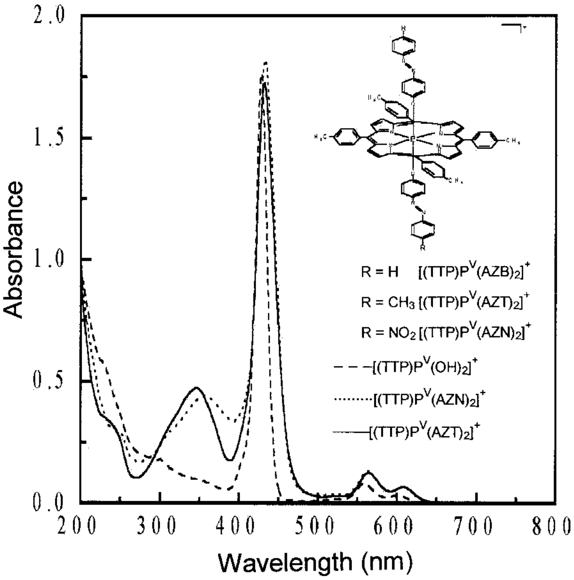

Fig. 1. Absorption spectra and molecular structure of phosphorus (V) azoarene porphyrins.

3. Results and Discussion

The absorption spectra and molecular structures of the axial azoarene-appended phosphorus (V) porphyrins are shown in Fig. 1. These molecules show linear absorption features typical of metalloporphyrins, with a high energy B (Soret) band and low energy Q bands. Each new molecule shows an additional moderately intense absorption band in the UV region (~350 nm) that is due to the axial azoarene chromophores. This band is absent in the spectrum of $[(TTP)P^V(OH)_2]^+$. The intensity dependence of the phase conjugate (PC) signal is shown in Fig. 2. The enhancement in the DFWM signal is quite obvious with the introduction of axial azoarene subunits. The solid curve represents the fit to the cubic depen-

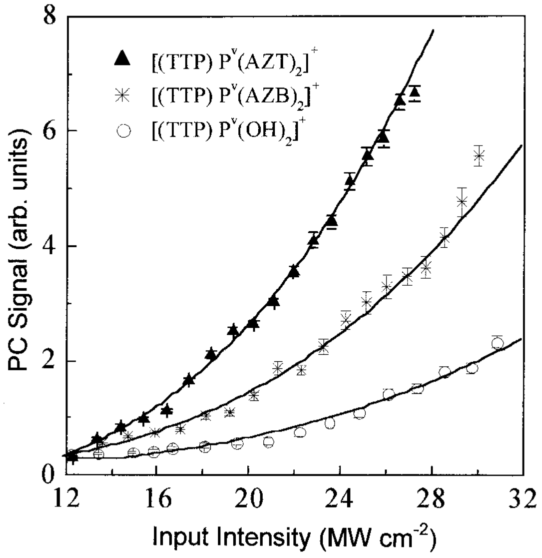

Fig. 2. Intensity dependence of the PC signal for azoarene porphyrins with 25-ps pulses. Solid curves represent the cubic fit of the input intensity to the PC signal.

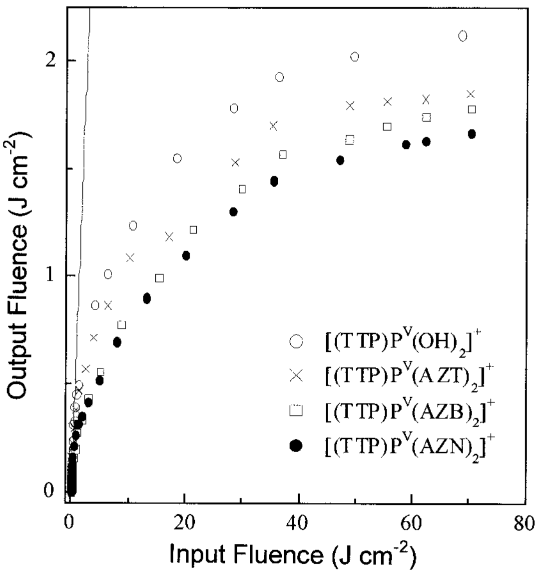

Fig. 3. Optical limiting curves of azoarene porphyrins at 75% linear transmittance (solid curve).

dence of this signal with input intensity. The ratio of the signals for the conjugate beam in a nanosecond DFWM experiment for parallel and perpendicular probe polarizations dropped down by approximately one third, indicating that the nonlinearity is predominantly electronic in origin. The values of the effective microscopic second hyperpolarizability ⟨γ⟩ with 25-ps pulses and 6 ns for the samples are listed in Table 1. The second hyperpolarizability of these molecules is higher than that of the reference molecule without CT states[23] {i.e., $[(TTP)P^V(OH)_2]^+$}, by 1 order of magnitude in the picosecond regime and by 2 orders of magnitude in the nanosecond regime. This clearly indicates that introduction of the azoarene groups into the phosphorus porphyrin structure leads to a rise in the measured ⟨γ⟩ values. These findings are consistent with the fact that greater polarization emanates from electron donation or withdrawal and also that the presence of the CT states enhances the second hyperpolarizability.[29]

The optical limiting curves for these molecules with 6-ns pulses are shown in Fig. 3 for a linear transmittance of 75%. The limiting threshold is reduced in azoarene-appended porphyrins by a factor of 2 as can be seen from the threshold values $I_{1/2}$ listed in Table 1. The throughputs of these molecules are limited to 1.66–2.20 J cm^{-2} for incident fluences as high as approximately 70 J cm^{-2}. Figure 4 shows the optical limiting curves for one of the representative azoarene molecules $[(TTP)P^V(AZT)_2]^+$ at 80%, 60%, and 40% linear transmittance. The clamping levels can be seen to reduce linearly with an increase in ground-state absorption. PET from the excited state of conjugated polymers onto C_{60} is well known, leading to enhanced nonlinearity and optical limiting performance.[30] In our molecules the population from the first singlet state S_1 can relax to triplet T_1 or to ground state S_0 by means of a nonfluorescent CT state in addition to $S_1 \rightarrow S_0$ and $S_1 \rightarrow T_1$ transitions. To determine the contribution of each channel that

Table 1. Second Hyperpolarization of Phosphorus (V) Azoarene Porphyrins with 25-ps and 6-ns Pulses[a]

Porphyrin	⟨γ⟩ (*10^{-30} esu) 25 ps	⟨γ⟩ (*10^{-28} esu) 6 ns	$I_{1/2}$ (J/cm^2) 6 ns
$[(TTP)P^V(OH)_2]^+$	0.286	3.2550	3.00
$[(TTP)P^V(AZT)_2]^+$	3.13 ± 0.2	123.42 ± 12	2.02
$[(TTP)P^V(AZB)_2]^+$	1.60 ± 0.2	149.56 ± 16	1.52
$[(TTP)P^V(AZN)_2]^+$	4.01 ± 0.3	252.94 ± 20	1.30

[a] $I_{1/2}$ is the limiting threshold.

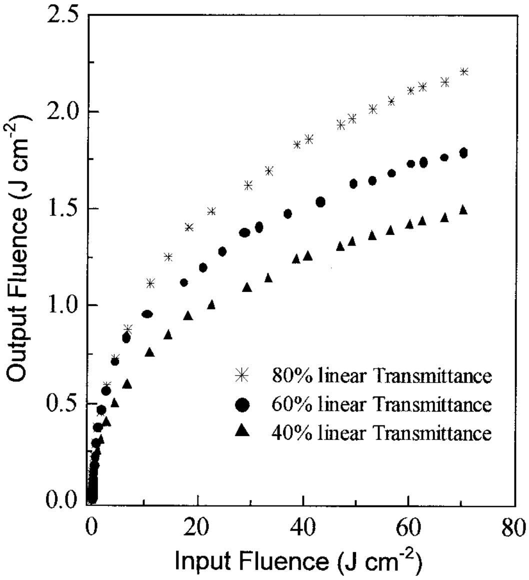

Fig. 4. Optical limiting curves of $[(TTP)P^V(AZT)_2]^+$ at different linear transmittances.

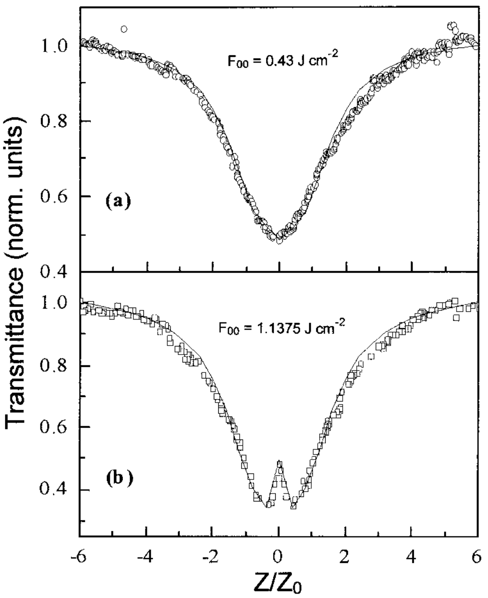

Fig. 5. Open-aperture Z-scan curves of (a) $[(TTP)P^V(AZN)_2]^+$ and (b) $[(TTP)P^V(AZB)_2]^+$ with 25-ps pulses at different peak fluences (F_{00}). Solid curves represent the theoretical fit by use of an energy-level diagram.

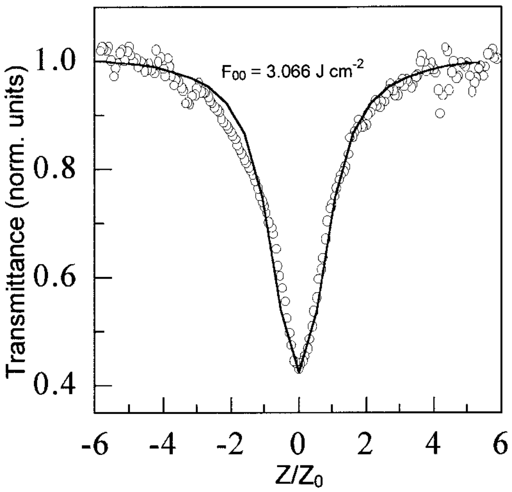

Fig. 6. Open-aperture Z-scan curve of $[(TTP)P^V(AZN)_2]^+$ with 6-ns pulses. Solid curve represents the theoretical fit by use of an energy-level diagram. The peak fluence (F_{00}) is also shown.

leads to enhanced limiting, we performed open-aperture Z scan for these molecules. With picosecond pulses, these molecules show RSA to fluences of approximately 0.43 J/cm^2. But above these fluences gradual saturation in the nonlinear absorption evolved (Fig. 5). The open-aperture Z-scan curves for $[(TTP)P^V(AZN)_2]^+$ and $[(TTP)P^V(AZB)_2]^+$ with 25-ps pulses at lower and higher peak fluences (F_{00}) are shown in Fig. 5. Similar behavior was also observed for other samples. Even though saturable absorption was found in the RSA curve, there is a slight reduction in the saturable absorption within the RSA curves for these complexes compared with the ones without CT states.[23] The detailed behavior of nonlinear absorption depends on absorption cross sections, lifetimes of excited states of the material, and the laser pulse width. Saturation in absorption at high fluences based on higher ESA was reported earlier for a cadmium texaphyrin solution,[8] 1,1′,3,3,3′,3′-hexamethylindotricarbocyanine iodide (HITCl)[31] and in chloroaluminum phthalocyanine dye.[32] The Z-scan data with 6-ns pulses for $[(TTP)P^V(AZN)_2]^+$ is shown in Fig. 6 with a normalized transmittance at focus (T_0) of 0.431. Peak fluences used for the experiment are also shown in Fig. 6. $[(TTP)P^V(AZB)_2]^+$ and $[(TTP)P^V(AZT)_2]^+$ also show similar behavior with a T_0 of 0.476 and 0.521, respectively, at peak fluences of 3.43 J/cm^2. In the nanosecond regime open-aperture Z-scan curves show only RSA even at high fluences, indicating the dominance of ESA from $T_1 \rightarrow T_n$ through ISC from CT $\rightarrow T_1$.

For our attempts to explain the results of the nanosecond and the picosecond experiments, we constructed a six-level model (Fig. 7). We developed a self-consistent theoretical analysis based on rate equations that describe the different mechanisms in the molecule and the output transmittance. We solved the rate equations numerically by using the Runge–Kutta fourth-order method. The differential equations were first decoupled and then integrated over time, length, and along the radial direction. The limits of integration for r, t, and z varied from 0 to ∞, from $-\infty$ to $+\infty$, and from 0 to L (length of the sample), respectively. The typical number of slices used for r, t, and z were 60, 30, and 10, respectively.[33] Solid curves in Figs. 5 and 6 show the theoretical fits.

Laser light excites molecules from the ground state S_0 into the vibrational–rotational states in the first excited singlet state $S_0 \rightarrow S_1$ (σ_1), which relaxes very rapidly (approximately picoseconds) to the lowest level of this electronic state. This level relaxes either by nonradiative decay into the CT state and from there to the first triplet state (ISC) or by both radiative and nonradiative decay within the singlet system. ESA can occur from the singlet state S_1 up to a higher singlet state S_n (σ_1) and from the triplet

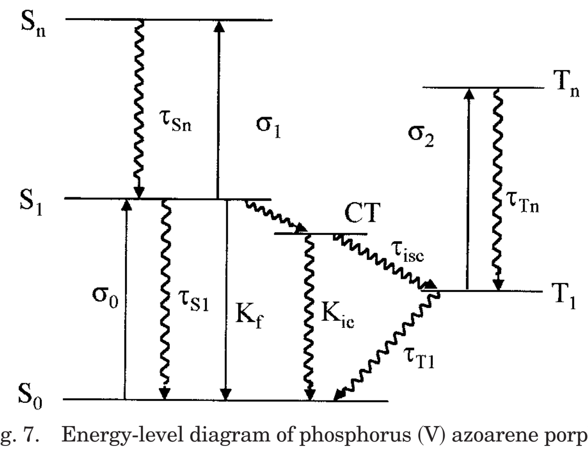

Fig. 7. Energy-level diagram of phosphorus (V) azoarene porphyrins.

Table 2. Lifetimes of Higher Excited State, ISC Times, and Saturation Threshold of the Phosphorus (V) Azoarene Porphyrins

Porphyrin	τ_{S_n} (fs)^a	τ_{ISC} (ps)^b	S_{th}(J cm^{-2})^a
$[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{AZB})_2]^+$	440	750	0.802
$[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{AZT})_2]^+$	415	620	0.628
$[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{AZN})_2]^+$	375	500	0.712

Estimated from Z-scan curves with 25-ps pulses^a and from 6-ns pulses.^{b} S_{th} is the saturation threshold.

state up to a higher triplet state $T_n(\sigma_2)$. For picosecond pulse excitation, triplet level contribution to the nonlinear absorption can be neglected because the slower ISC rate and absorption that are due to the CT states are included in the σ_1 cross section. Whereas with nanosecond pulses the triplet levels do play an important role.[33] In the picosecond regime only three singlet levels (S_0, S_1, and S_n) along with the CT level play a major role and hence the six-level model effectively becomes a four-level model. In the nanosecond regime, S_0, S_1, T_1, T_n and CT states including ISC from CT $\rightarrow T_1$ play a dominant role. The parameters that lead to enhanced limiting performance and nonlinear absorption with nanosecond pulses and picosecond pulses, along with the parameters used for the estimation are listed in Tables 2 and 3. Also listed are lifetimes of the higher excited singlet state and the ISC obtained from theoretical modeling. The fluence at which the saturation of excited states has started, saturation threshold (S_{th}), which is one of the important parameters necessary to decide the capability of a material as optical limiter, is also given in Table 2. S_{th} (0.628–0.802 J cm^{-2}) for the these molecules was found to be larger than that for $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{OH})_2]^+$ (0.56 J cm^{-2}). The figures of merit (σ_1/σ_0 and σ_2/σ_0) for our molecules are compared with reference porphyrin $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{OH})_2]^+$ (Table 3). The enhancement in σ_1/σ_0 and σ_2/σ_0 that is due to the presence of an additional CT state can be clearly seen compared with the reference porphyrin. The values of σ_1/σ_0 and σ_2/σ_0 for these porphyrins was found to be higher than some of the earlier reported molecules and comparable to some of the earlier reports.[8–10,14,34] The $\sigma_{\mathrm{ex}}/\sigma_0$ for C_{60} and C_{70} solutions were reported as 2.865 and 2.062, respectively.[35]

The presence of a CT state and internal conversion from a CT state to singlet S_0 and ISC from CT to triplet T_1 play a significant role in enhanced RSA in the nanosecond regime. In the picosecond regime, since population from S_1 can relax faster to S_0 by means of CT states, the saturation of ESA in the $S_1 \rightarrow S_n$ transition, which leads to saturable absorption in RSA at higher intensities, is also reduced considerably when we increase S_{th}.

Table 3. Figures of Merit for Optical Limiting for the Phosphorus (V) Azoarene Porphyrins^a

Porphyrin	σ_1/σ_0	σ_2/σ_0
$[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{OH})_2]^+$	2.67	2.086
$[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{AZB})_2]^+$	2.93	4.76
$[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{AZT})_2]^+$	2.88	8.44
$[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{AZN})_2]^+$	3.07	9.28

^{a}Estimated from Z-scan curves with 25-ps and 6-ns pulses. Values for $[(\mathrm{TTP})\mathrm{P}^{\mathrm{V}}(\mathrm{OH})_2]^+$ (from Ref. 22) are also given for comparison.

4. Conclusions

Enhancement of the optical limiting performance and nonlinear absorption has been achieved for the investigated phosphorus (V) porphyrins that are due to the contribution of a nonfluorescent CT state and by an increase in the intersystem crossing to triplet, which, in turn, enhanced the excited-state absorption from $T_1 \rightarrow T_n$. The $\langle\gamma\rangle$ for these molecules increased by 1 order of magnitude in the picosecond regime and by 2 orders of magnitude in the nanosecond regime. The RSA increased considerably in the nanosecond regime, whereas in the picosecond regime the saturation of ESA decreased considerably in addition to enhanced RSA. These molecules with charge transfer states from axial ligands can easily be doped into polymers to increase stability and hence are promising materials for optical limiting purposes.

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References

1. R. C. Hollins, "Materials for optical limiters," Curr. Opin. Solid State Mater. Sci. **4,** 189–196 (1999).
2. Y.-P. Sun and J. E. Riggs, "Organic and inorganic optical limiting materials. From fullerenes to nanoparticles," Int. Rev. Phys. Chem. **18,** 43–90 (1999).
3. L. W. Tutt and T. F. Boggess, "A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors and other materials," Prog. Quantum Electron. **17,** 299–338 (1993).
4. E. W. Van Stryland, H. Vanherzeele, M. A. Woodall, M. J. Soileau, A. L. Smirl, S. Guha, and T. F. Boggess, "Two-photon absorption, nonlinear refraction, and optical limiting in semiconductors," Opt. Eng. **24,** 613–623 (1985).
5. M. P. Joshi, J. Swiatkiewicz, F. Xu, P. N. Prasad, B. A. Reinhardt, and R. Kannan, "Energy transfer coupling of two-photon absorption and reverse saturable absorption for enhanced optical power limiting," Opt. Lett. **23,** 1742–1744 (1998).
6. F. E. Hernandez, S. Yang, E. W. Van Stryland, and D. J. Hagan, "High-dynamic-range cascaded-focus optical limiter," Opt. Lett. **25,** 1180–1182 (2000).
7. W. Blau, H. Byrne, W. M. Dennis, and J. M. Kelly, "Reverse saturable absorption in tetraphenyl porphyrins," Opt. Commun. **56,** 25–29 (1985).
8. J. Si, M. Yang, Y. Wang, L. Zhang, C. Li, D. Wang, S. Dong, and W. Sun, "Nonlinear excited state absorption in cadmium texaphyrin solution," Appl. Phys. Lett. **64,** 3083–3085 (1994).
9. F. Z. Henari, W. J. Blau, L. R. Milgram, G. Yahioglu, D. Phillips, and J. A. Lacey, "Third-order nonlinearity in Zn (II) com-

plexes of 5,10,15,20-tetra aryl ethynyl-substituted porphyrins," Chem. Phys. Lett. **267,** 229–233 (1997).

10. W. Sun, C. C. Byeon, M. M. McKerns, C. M. Lawson, G. M. Gray, and D. Wang, "Optical limiting performances of asymmetric pentaazadentate porphyrin-like cadmium complexes," Appl. Phys. Lett. **73,** 1167–1169 (1998).
11. A. Krivokapic, H. L. Anderson, G. Bourhill, R. Ives, S. Clark, and K. J. McEwan, "Meso-tetrra-alkynyl porphyrins for optical limiting: a survey of group III and group IV metal complexes," Adv. Mater. **13,** 652–656 (2001).
12. J.-H. Chou, M. E. Kosal, H. S. Nalwa, N. A. Rakow, and K. S. Suslick, "Applications of porphyrins and metalloporphyrins to materials chemistry," in *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith, and R. Guilard, eds. (Academic, New York, 2000), Vol. 6, pp. 43–131.
13. I. E. Borissevitch, N. Rakov, G. S. Maciel, and C. B. de Araujo, "Changes in porphyrin nonlinear absorption owing to interaction with bovine serum albumin," Appl. Opt. **39,** 4431–4435 (2000).
14. A. Sevian, M. Ravikanth, and G. Ravindra Kumar, "Optical limiting in short chain baskethandle porphyrins," Chem. Phys. Lett. **263,** 241–246 (1996).
15. M. P. O'Neil, M. P. Niermczyk, W. A. Svec, D. Gosztola, G. L. Gaines III, and M. R. Wasielewski, "Picosecond optical switching based on biphotonic excitation of an electron donor–acceptor–donor molecule," Science **257,** 63–65 (1992).
16. N. K. M. Naga Srinivas, S. Venugopal Rao, D. V. G. L. N. Rao, B. K. Kimball, M. Nakashima, B. S. Decristofano, and D. Narayana Rao, "Wavelength dependent studies of non linear absorption in zinc *meso*-tetra(*p*-methoxyphenyl) tetrabenzoporphyrin (Znmp TBP) using *Z*-scan technique," J. Porphyrins Phthalocyanines **5,** 549–554 (2001).
17. D. Narayana Rao, S. Venugopal Rao, F. J. Aranda, D. V. G. L. N. Rao, M. Nakashima, and J. A. Akkara, "Ultrafast relaxation times of metalloporphyrins by time-resolved degenerate four-wave mixing with incoherent light," J. Opt. Soc. Am. B **14,** 2710–2715 (1997).
18. A. G. Bezerra, Jr., I. E. Borissevitch, R. E. de Araujo, A. S. L. Gomes, and C. B. de Araujo, "Investigation of picosecond optical nonlinearity in porphyrin metal complexes derivatives," Chem. Phys. Lett. **318,** 511–516 (2000).
19. S. Tsuchiya, "Intramolecular electron transfer of diporphyrins comprised of electron-deficient porphyrin and electron-rich porphyrin with photocontrolled isomerization," J. Am. Chem. Soc. **121,** 48–53 (1999).
20. K. Hirakawa and H. Segawa, "Excitation energy transfer and photo-induced electron transfer in axial bispyrenyl phosphorus porphyrin derivatives: factors governing the competition between energy and electron transfer processes under the existence of intramolecular π–π interaction," J. Photochem. Photobiol. A **123,** 67–76 (1999).
21. D. LeGourrierec, M. Andersson, J. Davidson, E. Mukhtar, L. Sun, and L. Hammarstrom, "Photoinduced electron transfer from a higher excited state of a porphyrin in a zinc porphyrin-ruthenium(II) tris-bipyridine dyad," J. Phys. Chem. A **103,** 557–559 (1999).
22. S. Venugopal Rao, N. K. M. N. Srinivas, D. Narayana Rao, L. Giribabu, B. G. Maiya, R. Philip, and G. R. Kumar, "Studies of third-order optical nonlinearity and nonlinear absorption in tetra tolyl porphyrins using degenerate four wave mixing and Z-scan," Opt. Commun. **182,** 255–264 (2000).
23. P. Prem Kiran, N. K. M. N. Srinivas, D. Raghunath Reddy, B. G. Maiya, A. Dharmadhikari, A. S. Sandhu, G. Ravindra Kumar, and D. Narayana Rao, "Heavy atom effect on nonlinear absorption and optical limiting characteristics of 5,10,15,20-(tetratolyl) porphyrinato phosphorus (V) dichloride," Opt. Commun. **202,** 347–352 (2002).
24. D. Raghunath Reddy and B. G. Maiya, "A molecular photoswitch based on an 'axial-bonding' type phosphorus (V) porphyrin," Chem. Commun. Issue 1, 117–118 (2001).
25. R. L. Sutherland, *Handbook of Nonlinear Optics* (Marcel Dekker, New York, 1996).
26. D. B. James and K. J. McEwan, "Bubble and refractive processes in carbon suspensions," Nonlinear Opt. **21,** 377–390 (1999).
27. T. J. McKay, J. Staromlynska, J. R. Davy, and J. A. Bolger, "Cross sections for excited-state absorption in a Pt:ethynyl complex," J. Opt. Soc. Am. B **18,** 358–362 (2001).
28. M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, "Sensitive measurement of optical nonlinearities using a single beam," IEEE J. Quantum Electron. **26,** 760–769 (1990).
29. M. Ichida, T. Sohda, and A. Nakamura, "Third-order nonlinear optical properties of C_{60} CT complexes with aromatic amines," J. Phys. Chem. B **104,** 7082–7084 (2000).
30. M. Cha, N. S. Sariciftci, A. J. Heeger, J. C. Hummelen, and F. Wudl, "Enhanced nonlinear absorption and optical limiting in semiconducting polymer/methanofullerene charge transfer films," Appl. Phys. Lett. **67,** 3850–3852 (1995).
31. S. N. R. Swatton, K. R. Welford, S. J. Till, and J. R. Sambles, "Nonlinear absorption of a carbocyanine dye 1,1′,3,3,3′,3′-hexamethylindotricarbocyanine iodide using a *z*-scan technique," Appl. Phys. Lett. **66,** 1868–1870 (1995).
32. T.-H. Wei, T.-H. Huang, H.-D. Lin, and S.-H. Lin, "Lifetime determination for high-lying excited states using *Z* scan," Appl. Phys. Lett. **67,** 2266–2268 (1995).
33. S. Venugopal Rao, D. Narayana Rao, J. A. Akkara, B. S. DeCristofano, and D. V. G. L. N. Rao, "Dispersion studies of non-linear absorption in C_{60} using Z-scan," Chem. Phys. Lett. **297,** 491–498 (1998).
34. P. Chen, I. V. Tomov, A. S. Dvornikov, M. Makashima, J. F. Roach, D. M. Alabran, and P. M. Rentzepis, "Picosecond kinetics and reverse saturable absorption of meso-substituted tetrabenzoporphyrins," J. Phys. Chem. **100,** 17507–17512 (1996).
35. F. Henari, J. Callaghan, H. Stiel, W. Blau, and D. J. Cardin, "Intensity-dependent absorption and resonant optical nonlinearity of C_{60} and C_{70} solutions," Chem. Phys. Lett. **199,** 144–148 (1992).