ISRAPS

ISRAPS Bulletin

A Publication of Indian Society for Radiation and Photochemical Sciences

Volume 16, Number 3-4

November, 2004

Prof. Bhaskar G. Maiya Memorial Issue



Born : June 20, 1956 Died : March 21, 2004

CONTENTS

Editorial	2
Secretary's Desk	2
Tetratolylporphyrins as Optical Limiters (D. Narayana Rao*, P. Prem Kiran, N.K.M. Naga Srinivas and S. Venugopal Rao ^{a)}	3
Interaction of porphyrins with plant lectins: Absorption and fluorescence spectroscopic studies (Musti J. Swamy)	9
Excited State Properties of Certain Ruthenium(II) Polypyridyl Complexes Bound to DNA : Molecular Light Switches	
(P. Uma Maheswari and M. Palaniandavar*)	15
Expanded Corrole: synthesis, properties and receptor behaviour (Rajneesh Misra, Rajeev Kumar, Viswanathan PrabhuRaja and Tavarekere K. Chandrashekar*	⁺) 20
The Intrinsic Fluorescence Decay of Folded Cytochrome c: Fluorescene Resonance Energy Transfer from the Single Tryptophan to the Heme	
(Tapan Kanti Das ¹ , Shyamalava Mazumdar*)	25

Tetratolylporphyrins as Optical Limiters

D. Narayana Rao*, P. Prem Kiran, N.K.M. Naga Srinivas and S. Venugopal Rao*

School of Physics, University of Hyderabad, Hyderabad - 500 046

*e-mail: dnrsp@uohyd.ernet.in

^a Centre for Ion Beam Applications, Department of Physics, National University of Singapore, Singapore 117652

ABSTRACT

Metalloporphyrins are promising materials for optical limiting possessing strong nonlinear absorption and high third order optical nonlinearities combined with ultrafast response time in the picosecond and femtosecond time scales. Structural modifications like heavy atom effect and introduction of donor-acceptor groups are known to vary the excited state properties in these molecules. We discuss the effects of these modifications on the optical limiting properties and excited state dynamics in phosphorous(V) tetratolylporphyrin and tin(IV) tetratolylporphyrin.

1. Optical Limiting (OL) and Nonlinear Absorption

With the advent of high power laser sources over wide range of wavelengths and pulse widths, protection of sensors and eyes has posed a major challenge in the last decade. In this context optical limiters have received significant attention. Optical limiters are devices that strongly attenuate optical beams at high intensities while exhibiting high transmittance at low intensities, thus providing safety to sensors in general and to human eyes in particular. An ideal limiter exhibits a linear transmission below a threshold and a constant above it. Optical limiting (OL) has been achieved by means of various nonlinear optical mechanisms. Although there are a great variety of processes leading to optical limiting, most of them can be divided into two categories. First one is the energy-spreading type of processes and the other are the energy-absorbing type of processes. The mechanisms like self-focusing, self-defocusing, induced scattering, induced-refraction, induced aberration, and photorefraction result in spreading of the incident energy. The processes like excited state absorption, two-photon absorption, and free-carrier absorption result in the absorption of the energy [1]. Among the above mentioned processes nonlinear absorption is very promising for the development of materials for optical limiting. Nonlinear absorption is defined as an increase/decrease in the absorption coefficient with increasing intensity. The nonlinear increase in absorption coefficient is termed as reverse saturation of absorption (RSA) while the decrease in absorption coefficient is termed as saturation of absorption (SA). Recent investigations indicate that materials with RSA behavior are one of the potential candidates for optical limiting applications [2,3] as they give a response that is closer to that of the ideal optical limiter. SA in various materials has been studied for applications in laser pulse compression and laser amplification [4]. The optical limiting capability of different materials is characterized by the parameter known as limiting threshold ($I_{1/2}$). Limiting threshold is defined as the input intensity at which the transmittance of the material becomes half of the linear transmittance.

An intense laser pulse redistributes the molecular population between the ground and excited states causing a transient modification in the optical properties of the material. The dependence of transmission in organic molecules on light intensity can yield considerable information on the molecular level system that can lead to variety of nonlinear optical processes like limiting, switching and bistability. Organic materials with delocalized electrons are of a great deal of importance because of their large nonlinear optical absorption coefficients, architectural flexibility, and ease of fabrication. Metalloporphyrins form an important class of electronic materials because of the large π -electron conjugation over two-dimensional molecular structure [5]. In organic molecules, RSA arises mainly due to two different processes named excited state absorption (ESA) and two-photon absorption (TPA). 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 like excited state absorption cross-sections, lifetimes etc. so as to optimize their properties for the realization of a functional device [6,7]. 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 [8]. Porphyrins, owing to strong RSA arising from the ESA from both singlet and triplet states, are among the most effective optical limiters in the visible region [9,10]. In our search for better optical limiting materials, we have improvised the present porphyrin systems using various structural modifications as introduction of heavy-atom, charge transfer (CT) states. These modifications would 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 (EET), photoinduced electron transfer (PET). Such effects can be conveniently harnessed to enhance the third order nonlinearity, and hence to develop promising materials for optical limiting. One of the key structural modifications in this regard, is the introduction of heavy atoms in the porphyrin ring, which in turn, due to faster ISC reduces the fluorescence yield, increase triplet formation and hence further enhancing absorption from $T_1 \rightarrow T_p$. PET and EET are the other phenomena that come into play due to the presence of additional donor/acceptor units in the molecule. This paper explains the effect of structural modifications on the limiting behavior of Phosphorus (V) tetratolylporphyrins and hybrid porphyrin arrays based on tin (IV) tetratolylporphyrin scaffold.

2. Porphyrin media for OL and Nonlinear Absorption

Strong nonlinearity and fast response times are the desired criteria for making porphyrins useful for photonic devices. Because of the two-dimensional delocalization of the π -electrons throughout the macrocycle ring, porphyrins are interesting chromophores for second and third order nonlinear optical (NLO) properties. Porphyrins have been studied extensively for their second order NLO properties using various techniques like HRS, EFISHG etc. Third-order NLO properties are also studied in variety of porphyrin molecules, like tetraphenylporphyrins (TPP), tetrabenzoporphyrins (TBP), tetrakispentadecylphenylporphyrins, octaethylporphyrins (OEP), Octaphenyltetraazaporphyrin (OPTAP), baskethandle porphyrins, conjugate polymers, tetratolylporphyrins (TTP) to name a few. These molecules are among the most effective third-order NLO materials possessing high second hyperpolarizabilities. Porphyrins were also studied extensively for the optical limiting and nonlinear absorption properties. After the first report of RSA in porphyrins by Blau et. al. [9], the interest in various porphyrins to enhance the RSA has increased greatly. Porphyrins, owing to strong ESA from both singlet and triplet states, are among the most effective optical limiters in the visible region [11].

The nonlinear absorption behavior in the porphyrin molecules can be explained using a generalized five-level energy diagram (Jablonski diagram) containing three singlet states (S_0 , S_1 and S_n) and two triplet states (T₁ and T_n). Laser light excites molecules from the ground state So into the vibrationalrotational states in the first excited singlet state via $S_0 \rightarrow S_1$ with a cross-section of σ_0 , which relaxes very rapidly (approximately picoseconds) to the lower vibronic levels of this state. This level relaxes either by both radiative and nonradiative decay within the singlet system or to the first triplet state via ISC. ESA can occur from the singlet state S, up to a higher singlet state S with cross-section s, and from the triplet state up to a higher triplet state $T_1 \rightarrow T_n$ with a cross-section of σ_2 . The ratio of the absorption cross-sections σ_1/σ_0 and σ_2/σ_0 indicate the material's capability as an optical limiter and are known as material figure of merit. For picosecond pulse excitation, triplet level contribution to the nonlinear absorption can be neglected because of the slower ISC rate and the singlet levels So, S, and Sn play a dominant role, whereas with nanosecond pulses the ESA from the triplet levels associated by the ISC from S₁ to T₁ play an important role in the optical limiting behavior. Though some of the porphyrins show good RSA with ps pulse excitation, at higher input intensities saturation of absorption takes over thus reducing the optical limiting behavior. Our attempt is to have materials that work as good optical limiters in both ns and ps timescales.

3. Experimental techniques

The processes ESA and TPA leading to optical limiting behavior are studied in the nanosecond and picosecond regime. Frequency doubled Nd:YAG lasers at 532 nm with 25 ps and 6 ns pulse widths, 10 Hz repetition rate are used for the experiments. We have employed two different experimental techniques known as optical limiting test bed (figure 1) and open aperture Z-scan [12] and using f/5 and f/30 optical geometries respectively, and the transmitted light is collected with a fast photodiode, which was given to data acquisition system. The peak intensities used in the Z-scan experiments with 25 ps pulses are approximately in the range of 500 MWcm⁻² to 53 GWcm⁻². The input fluence (energy density) is varied in the range of 30 µJcm⁻² to 70 Jcm⁻² in the ns regime. The linear transmission is approximately 70-75% for 1-mm path length of the sample. The optical limiting and Z-scan studies are performed at the same



Fig. 1: (a) Schematic of optical limiting setup and (b) response of ideal optical limiter.

concentration of $\sim 10^{-4}$ M ensuring identical experimental conditions for both ps and ns regimes.

4. Effect of Structural modification on OL properties

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 [10] and efforts are being made to attain large excited state absorption cross-sections through structural modifications. We have taken two molecular systems based on P(V)TTP and Sn(IV)TTP scaffold as the starting molecules for structural modifications.

The first modification is the introduction of heavy atom in the P(V)TTP macrocycle. With introduction of heavier chlorine in place of OH in the axial position of 5,10,15,20-(tetratolyl) porphyrinato phosphorous (V) dihydroxide [(TTP)P^v(OH)₂]⁺, we have observed stronger RSA in both the ps and ns regimes. With the nanosecond excitation, the ISC has increased by 10 times leading to the enhancement in the limiting behavior by approximately 30 times and in the picosecond timescales the limiting behavior is enhanced by approximately 3 times [13]. Among the various factors that can be invoked to explain the improvement of the optical limiting performance due to heavy atom effect coming because of the axial chloride substitution ([(TTP)P^vCl₂]⁺) in the ns time regime, faster intersystem crossing rate is the most important as it plays a significant role by enhancing the population of the triplet state. The long lifetime of the T, state compared to the ns pulse duration, leads to larger effective ESA from $T_1 \rightarrow T_n$, leading to reduction in optical limiting



Fig. 2: Optical limiting curves of modified Phosphorous(V) tetratolylporphyrins.

threshold. With picosecond pulse excitation, we have observed saturation of absorption (SA) at higher input fluences (> 0.5 Jcm²) after the initial RSA at lower input fluences. Even though such behavior is not useful for optical limiting purposes, the extent of saturation gives an insight into the excited state dynamics of the molecule. Based on the rate equation model explaining the various processes taking place in the molecule, we found that the saturation at higher intensities is a result of the competition between ESA from S₁ to S_n and the lifetime of the excited singlet state S_n[13].

In our attempt to reduce SA at higher intensities with ps pulse excitation we have taken up the molecules having azoarene subunits axially linked to the central Phosphorous of the P(V)TTP. In these systems, the axial azoarene subunits act as electron donors leading to PET from axial subunits to the central porphyrin. In these porphyrins, donor/acceptor levels and a charge transfer (CT) state is 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) porphyrinato phosphorous (V) dihydroxide [(TTP)P^v(OH)₂]⁺ without any chargetransfer states. An intra-molecular 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. An additional energy level known as charge-transfer (CT) state is introduced leading to more delocalization of the singlet levels. With nanosecond excitation, limiting threshold has lowered by a factor of 2 due to enhanced ISC. With ps pulse excitation, at lower intensities only RSA is observed, but at higher intensities we observed SA within RSA due to saturation of higher excited states. But the observed saturation has reduced greatly compared to that observed in [(TTP)P(V)Cl_] + as shown in figure 3. Table 1 summarizes the excited state parameters obtained for modified phosphorus(V)



Fig. 3: Open aperture Z-scan curves of (a) $[(TTP)P(V)Cl_2]^+$ and (b) $[(TTP)P(V)(AZB)_2]^+$ with 25 ps pulse excitation.

Table 1: Figures of merit for optical limiting, Lifetimes of higher excited state and ISC times for the modified phosphorus (V) tetratolylporphyrin molecules estimated from Z-scan curves with *25 ps pulses and from ^b6 ns pulses. Values for [(TTP)P^V(OH),]⁺ are also given for comparison.

Porphyrin	I _{1/2}	$a\sigma_1/\sigma_0$	${}^{a}\mathcal{T}_{Sn}$	^b σ ₂ /σ ₀	${}^{b}\tau_{isc}$
	(J cm ⁻²)	Ind ones	(fsec)		(psec)
[(TTP)P ^v (OH) ₂] ⁺	3.0	2.67	450	2.086	1000
[(TTP)P ^v Cl ₂]+	0.1	3.56	600	12.15	100
[(TTP)P ^v (AZB) ₂] ⁺	2.02	2.93	440	4.76	750
[(TTP)P ^v (AZT) ₂]+	1.52	2.88	415	8.44	620
[(TTP)P ^v (AZN) ₂]*	1.30	3.07	375	9.28	500

tetratolylporphyrins. Excited state parameters of the starting porphyrin are also given for comparison. Both the heavy atom effect and the PET played an important role in enhancing the optical limiting properties with the nanosecond excitation [14]. PET has resulted in the reduction of saturation at higher intensities with ps excitation.

In order to control the excited state dynamics to achieve better optical limiting properties, we extended our studies to porphyrin oligomers. We studied the 'axial-bonding' type hybrid porphyrin trimer and hexamer arrays based on tin(IV) tetratolylporphyrin scaffold. The architecture of the trimer arrays [15] is such that Sn^{IV} complex of *meso*-5,10,15,20-(tetratolyl)porphyrin forms the basal scaffolding unit, the free-base, Ni^{II} porphyrins occupy the two axial sites via an aryloxy bridge. The architecture of hexamers [16] is based on a covalently linked Sn^{IV} porphyrin dimer, with each of the two Sn^{IV} porphyrins centers trans-axially ligated to two free-base, zinc(II) porphyrins. The effect of different central metal atoms



Fig. 4: Nonlinear transmittance curves of hybrid arrays based on Sn(IV)TTP scaffold.

substituted adjacent to the tin(IV) porphyrin in the oligomer structure is studied. In these systems in addition to the PET from the axially linked porphyrins to the central Sn(IV)TTP, excitation energy transfer (EET) from the central Sn(IV)TTP to the axial porphyrins is operative. Both the PET and EET lead to further delocalization of the singlet states.

With 6 ns pulse excitation very good enhancement in the optical limiting properties due to RSA is observed. OL curves for monomer SnTTP, trimer Sn₂-(H₂)₂ (TTP)₃ and hexamer Sn₂-(H₂)₄ (TTP)₆ at ~75% linear transmission at 532 nm shown in Fig. 4 clearly indicates the enhanced limiting behavior as one moves to higher homologues. With the introduction of heavier metalloporphyrin in the axial position in place of freebase porphyrin, in trimer and hexamer donor-acceptor homologues, lead to slightly reduced limiting response. Though the limiting threshold has not varied greatly, the onset of limiting varies certainly, with lower values for the oligomers. Throughput fluences from these hybrids are as low as 35 - 52 mJcm⁻² with input fluences in the range of ~ 26 - 74 Jcm⁻² making these arrays very good optical limiters at higher intensities. Table 2 summarizes the material figure of merits and the ISC times.

With ps pulse excitation the nonlinear absorption behavior is totally different from that of observed with ns excitation. At lower intensities for ps pulses these materials show only RSA. With increasing intensity an interesting changeover from RSA to SA and then back to RSA is observed. At higher intensities the ESA saturates and SA followed by RSA is observed. At still higher intensities the nonlinear absorption shows a sudden transition to RSA at higher intensities within SA behavior (Fig. 5(a)).

In the case of trimers and hexamers with Sn(IV)TTP surrounded by freebase porphyrin (H,TTP),

Porphyrin	Í _{1/2}	^a σ ₁ /σ ₀	τ _{sn}	β	^b σ₂/σ₀	τ _{isc}	
	(J cm ⁻²)	And S. S. Steen	(psec)	(cm/GW)	(psec)		
Sn(TTP)	12.30	18.32	60	0.45	3.24	1000	
$Sn-(H_2)_2(TTP)_3$	2.91	3.13	500	Laid H Convin	7.26	380	
Sn-Ni ₂ (TTP) ₃	3.46	35.7	50	1.45	6.21	550	
Sn ₂ -(H ₂) ₄ (TTP) ₆	0.46	1.93	500	inives D <u></u> C.esvini	19.45	220	
Sn ₂ -Zn ₄ (TTP) ₆	1.16	2.39	15	0.9	6.73	600	

Table 2: Excited state parameters $\sigma_1 \sigma_0$, τ_{sn} and TPA coefficient β with 25 ps pulse excitation and $\sigma_2 \sigma_0$, τ_{ISC} with ns pulse excitation.



Fig. 5: Open aperture Z-scan curves of (a) Sn_2 - Zn_4 hexamer and (b) Sn-Ni, trimer with 25 ps pulse excitation.

at lower input intensities RSA is observed and with increasing intensity, saturation of the higher excited states due to the $S_1 \rightarrow S_2$ transition is observed. While replacing H_aTTP in axial position with NiTTP lead to a total reversal in the nonlinear absorption behavior. For Sn-Ni, (TTP), at lower input intensities saturation of absorption alone is observed. With gradual increase in the input intensity RSA followed by initial SA is observed. As the intensity is increased further, RSA started to take over and at higher intensities RSA completely dominates due to TPA (Fig. 5(b)). However, Sn₂-Zn₄(TTP)₆ has shown an interesting nonlinear absorption behavior with varying input intensities. At lower intensities (~ 29 GWcm-2), saturation of absorption due to excited states is observed (similar to Fig 3a) with transmittance at focus going up to 0.84 and the curves appear slightly broader indicating the confribution of ESA. As the intensity increased to ~ 53 GWcm⁻²RSA is observed after saturation of absorption due to TPA (similar to that shown in Fig. 5(a)). Such a crossover from RSA to SA and then back to RSA with 25 ps pulses can be utilized to make these arrays desirable materials for nonlinear optical switching purposes. Though the ESA, TPA and the lifetimes of the higher excited states appears to play an important role in the nonlinear absorption of all these oligomers, TPA is more predominant in oligomers having metalmetal interactions (Sn-Ni, Sn-Sn, Sn-Zn) and is lower in molecules having metal-freebase interaction. In metalloporphyrins, N and L bands exist at higher energies (317 nm) in addition to the low energy B and O bands. The N and L bands are more prominent in SnTTP compared to NiTTP and ZnTTP, whereas in H.TTP, N and L bands are not prominent. At higher excitation intensities, the possibility of two-photon transition to the N, L bands from the lower singlet states increases[17].

5. Summary

To summarize we have studied the effect of introduction of halogen atom leading to increased ISC, donor-acceptor units leading to PET, and the hybrid arrays with both the heavy atom, PET and additional EET on the optical limiting properties. With these structural modifications we are able to identify the materials that show RSA at both the nanosecond and picosecond pulse regimes.

Acknowledgements

Authors thank financial support from DAE-BRNS and DRDO. Authors are grateful to Late Prof. Bhaskar G. Maiya, for his invaluable discussions and the porphyrins.

6. References

- 1. L. W. Tutt and T.F. Boggess, *Prog. Quant. Elcetron.* 17, 299 (1993).
- R. Sutherland, R. Pachter, P. Hood, D. Hagan, K. Lewis, J.W. Perry, eds., *Materials for Optical limiting II*, Vol.479 of Mater. Res. Soc. Proc. (MRS, Pittsburrgh).

- R.C. Hollins, Current Opinion in Solid State & Mat. Sc. 4, 189 (1999).
- 4. M. Hercher, Appl. Opt. 6, 947 (1967).
- T.E.O. Screen, K.B. Lawton, G.S. Wilson, N. Dolney, R. Ispasoiu, T. Goodson III, S.J. Martin, D.D.C. Bradley, and H.L. Anderson, J. Mater. Chem. 11, 312 (2001).
- D.N. Rao, S.V. Rao, F.J. Aranda, D.V.G.L.N. Rao, M. Nakashima, and J.A. Akkara, J. Opt. Soc. Am. B 14, 2710 (1997).
- S. V. Rao, N.K.M.N. Srinivas, D.N. Rao, L. Giribabu, B.G. Maiya, R. Philip, and G.R. Kumar, *Opt. Commun.* 192, 123 (2001).
- S. V. Rao, N.K.M.N. Srinivas, D.N. Rao, L. Giribabu, B.G. Maiya, R. Philip, and G.R. Kumar, *Opt. Commun.* 182, 255 (2000).
- W.J. Blau, H. Byrne, W.M. Dennis and J.M. Kelly, Opt. Commun. 56, 25 (1985).
- 10. A. Krivokapic, H.L. Anderson, G. Bourhill, R. Ives, S. Clark,

and K. J. McEwan, Adv. Mater. 13, 652 (2001).

- N.K.M.N. Srinivas, S.V. Rao, D.V.G.L.N. Rao, B.K. Kimball, M. Nakashima, B.S. DeCristofano, D.N. Rao, J. Porphyrins Phthalocyanines, 5, 549 (2001).
- M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, and E.W. Van Stryland, *IEEE J. Quant. Electron.* QE-26, 760 (1990).
- P.P. Kiran, N.K.M.N. Srinivas, D.R. Reddy, B.G. Maiya, A.S. Sandhu, A.K. Dharmadhikari, G.R. Kumar and D.N. Rao, *Opt. Commun.* 202, 347 (2002).
- P.P. Kiran, D.R. Reddy, B.G. Maiya, A.K. Dharmadhikari, G.R. Kumar and D.N. Rao, Appl. Opt. LPEO 41, 7631 (2002).
- L. Giribabu, T.A. Rao, and B.G. Maiya, *Inorg. Chem.*, 38, 4971 (1999).
- A.A. Kumar, L. Giribabu, D.R. Reddy, and B.G. Maiya, Inorg. Chem., 40, 6757 (2001).
- P.P. Kiran, D.R. Reddy, B.G. Maiya, A.K. Dharmadhikari, G.R. Kumar and D.N. Rao, Manuscript submitted to Opt. Commun.



About the Author

D. Narayana Rao is a Professor in the School of Physics at University of Hyderabad. He obtained his Ph. D. in 1979 from IIT Kanpur. His areas of interest are experimental nonlinear optics and spectroscopy.