Chapter 4

Axial-Bonding Type Hybrid Porphyrin Arrays with basal Tin (IV) Tetratolyloporphyrin Scaffold

Optical limiting properties of 'axial-bonding' type hybrid porphyrin arrays - trimers and hexamers based on a Tin (IV) scaffold are studied. The effect of different central metal atoms substituted in the adjacent porphyrin ring in the oligomer structure is discussed in the nanosecond and picosecond regime. In the nanosecond regime the optical limiting performance has increased considerably with increasing number of porphyrins in the array and ESA from singlet and triplet states found to play a major role. However, in the ps regime the higher order nonlinear processes takeover at higher intensities leading to interesting switching behaviour of nonlinear absorption. The second hyperpolarizability \(<\gamma>\) is three orders of magnitude higher compared to the monomer Sn(IV) TTP.

4.1 Conjugated molecules / arrays for NLO applications

Organic materials with delocalized electrons have got a great deal of importance because of their large nonlinear optical susceptibilities, architectural flexibility, and ease of fabrication. The relation between the molecular structures and the third-order nonlinear optical susceptibilities (\(\chi^{(3)}\)) has been the main interest in these molecules [1,2]. Generally the delocalization of an electron in the molecular frame will enhance the optical nonlinearity and it has been one of the most successful strategies for designing the molecules. The optical and electronic properties of many oligomeric conjugated systems have been thoroughly investigated [3] for better understanding of both the basic physics in small, well-defined molecular systems as well as to determine structure/property relations applicable to the corresponding polymers. Conjugated organic materials have been widely investigated in search of suitable chromophores for all-optical applications like switching, and limiting [4]. Simple conjugated polymers such as poly(p-phenylene) and poly(p-phenylenevinylene) exhibit useful properties, like semiconductivity and electroluminescence [5]. Metalloporphyrin and metallophthalocyanines form an important class of electronic materials because of the large re-electron system with two-dimensional conjugated molecular
structure [6]. At the same time, another class of organic systems, conjugated polymers, shows promise as suitable materials due to an expected large nonlinearity that is caused by one-dimensionally delocalized electrons [7]. Interest in advanced electronic and photonic materials recently has led to the exploration of conjugated polymers of more complex units, such as porphyrins [8]. The high polarizability and optical oscillator strength of the porphyrin macrocycles gives these materials remarkable nonlinear optical (NLO) behaviour, making them potentially useful for ultra-fast switching technologies. High values of the nonlinear refractive index, \( n_r \) (which is proportional to the real part of the third order susceptibility, \( \chi^{(3)} \)) are essential for electro-optical and all-optical switching [9], whereas high nonlinear absorption coefficients, \( \beta \) (proportional to the imaginary part of \( \chi^{(3)} \)) are important for optical limiting [10]. High values of \( \chi^{(3)} \) are associated with large, polarizable \( \pi \)-systems, long conjugation lengths and small HOMO-LUMO gaps [11], making porphyrins good building blocks for such materials. The possibilities of substitution around the porphyrin periphery and of varying the metal at the center of the porphyrin provide extra ways of optimizing the performance of these materials [12]. Although number of studies have focused on the third-order nonlinear properties of porphyrin based materials [13], the majority of these involve macrocycle chromophores that are electronically uncoupled or weakly coupled to one another. Several alkync-linked [14] and edge-fused [15] conjugated dimers and trimers have been investigated [16]. In this chapter we discuss the optical limiting and nonlinear optical properties of 'axial-bonding' type hybrid trimer and hexamer arrays based on Sn\textsuperscript{IV}TTP scaffold; in which photoinduced electron transfer (PET) and excitation energy transfer (EET) play a significant role in modifying the singlet state properties.

### 4.2 Molecular Structure and linear optical properties

The molecular structures of monomer and dimer are shown in Fig. 4.1. The nomenclature of monomer and dimer molecule is *meso*-5,10,15,20-(tetratolyl)porphyrinato tin(IV) dihydroxide: \([\text{TTP} \text{Sn}^{IV} \text{OH}_2]\) and \([\mu-\text{[5,10,15-}\)
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Tri(p-toly)-20-[4-[4-[10,15,20-tri(p-toly)-5-porphyrinyl] phenoxy] ethoxy] phenyl[porphyrinato]] di(tin) (IV)Tetrahydroxide; [(TriTP)-Sn\textsuperscript{IV}(OH)\textsubscript{2}O(CH\textsubscript{2})\textsubscript{2}O-TriTP]Sn (OH)\textsubscript{2}] respectively. Dimer molecule has two monomers linked at meso position with ethoxy spacer. Monomer and dimer are synthesized following the procedure reported in the literature [17,18]. For the sake of simplicity we mention them as SnTTP and Sn-Sn(TTP)\textsubscript{2} in this chapter. Sn\textsuperscript{IV} porphyrin based, "axial-bonding" type hybrid trimers and hexamers are constructed by employing 'building-block' approach. The approach involves simple inorganic reactions such as axial bond formation of main group element containing porphyrins and insertion of metal/metalloid ions into the porphyrin cavity. The architecture of the trimer arrays [19] is such that Sn\textsuperscript{IV} complex of meso-5,10,15,20-(tetratolyl)porphyrin forms the basal scaffolding unit, the free-base, Ni porphyrins occupy the two axial sites via an aryloxy bridge. The nomenclature of the porphyrin trimer arrays discussed here is as follows: (free-base porphyrin)\textsubscript{2} (tin(IV)porphyrin) = [(TTP)-Sn\textsuperscript{IV}(H\textsubscript{2}TriTP(O))]\textsubscript{2} and (nickel (II) porphyrin)\textsubscript{2} (tin(IV)porphyrin) s [(TTP)-Sn\textsuperscript{IV}(NiTriTP(O))]\textsubscript{2}. For simplicity these trimers are referred as Sn-(H\textsubscript{2})\textsubscript{2}(TTP)\textsubscript{3} and Sn-Ni\textsubscript{2}(TTP)\textsubscript{3} respectively.

![Sn(IV)TTP](image1)

![Sn(IV)TTP dimer](image2)

Fig. 4.1: Molecular structure of Sn\textsuperscript{IV} monomer and dimer
The scheme of construction of hexamer arrays employs a synthetic protocol involving sequential "organic" and "inorganic" reactions conducted, respectively, at the peripheral meso- phenyl ring and the central Sn\textsuperscript{IV} ion of the porphyrin scaffold. The architecture of hexamers [18] are based on a covalently linked Sn\textsuperscript{IV} porphyrin dimer, with each of the two Sn\textsuperscript{IV} porphyrins centers trans-axially ligated to two free-base, zinc(II) porphyrins. The nomenclature of the hexamers is given as follows: [(TTP)-Sn\textsuperscript{IV}(H\textsubscript{2}TriTP(O))\textsubscript{2}]-O(CH\textsubscript{2})\textsubscript{2}O-[(TTP)-Sn\textsuperscript{IV}(H\textsubscript{2}TriTP(O))\textsubscript{2}] and [(TTP)-Sn\textsuperscript{IV}(ZnTriTP(O))\textsubscript{2}]-O(CH\textsubscript{2})\textsubscript{2}O-[(TTP)-Sn\textsuperscript{IV}(ZnTriTP(O))\textsubscript{2}]. These arrays are referred as Sn\textsubscript{2}-(H\textsubscript{2})\textsubscript{4}(TTP)\textsubscript{6} and Sn\textsubscript{2}-Zn\textsubscript{4}(TTP)\textsubscript{6} arrays. The molecular structure of the trimers and hexamers are shown in Fig. 4.2 and 4.3 respectively. UV-VIS absorption spectrum of all these molecules is shown in Fig. 4.4.

Fig 4.2: Molecular structure of "axial-bonding"-type tin (IV) trimers. Arrows indicate the PET and EET.
A comparison of the UV-VIS spectrum of a given trimer and hexamer with the spectra of the corresponding monomeric porphyrins suggested that the $\lambda_{\text{max}}$ values of these array are in the same range as those of the reference compounds. In addition, the molar absorptivities at the peak maxima ($e$) values of the bands due to trimers and hexamers are nearly equal to the sum of those due to their constituent monomers. Minor variations in the spectral features of the trimers with respect to the corresponding monomers are ascribed to the 'substituent effects' i.e., differences in the axial ligands of Sn$^{IV}$ porphyrins and the meso substituents of the free-base porphyrins/ metalloporphyrins.

Fig 4.3: Molecular structure of Sn$_2$-(H$_2$)$_4$ hexamers

These indicate that there is minimal perturbation of the electronic structures of the individual macrocyclic $\pi$-systems in these arrays. Specifically
there exists no indication of the presence of exciton coupling between the porphyrin rings i.e., basal-basal, basal-axial, or axial-axial interaction in these arrays. Their redox potential data are also close to those of the corresponding constituent monomeric species. On the other hand, the singlet state activities of these oligomers are quite different from those of the precursor reference compounds as probed by steady-state fluorescence.

Fig 4.4: UV-Vis spectra of Sn(IV) oligomers.

In the case of trimers, fluorescence due to both the basal and axial porphyrins is considerably quenched in comparison with that due to the monomeric chromophores. Whereas, the spectral shapes and the wavelengths of
maximum emission for the individual chromophores of these arrays remains close to those due to the corresponding monomeric entities. Thus, the singlet state energy values ($E_{0,0}$ values of $H_2$, $Zn^{II}$ and $Sn^{IV}$ porphyrins are 1.94, 2.07 and 2.04 eV respectively) of the individual components of these arrays are assumed to be essentially similar to those of their constituent monomers.

In the case of hexamers, strong quenching of fluorescence is observed. The percent quenching is close to 100, with the band that is characteristic of $Sn^{IV}$ porphyrin emission being totally absent in the spectra. This is in contrast with the partial quenching observed in case of trimers. In trimer molecules, PET occurs from the axial porphyrin to the basal $Sn^{IV}$ porphyrin and EET occurs from basal $Sn^{IV}$ porphyrin to axial acceptors. In the case of hexamers, in addition to the EET from the basal $Sn^{IV}$ porphyrin to its own two axial free-base acceptors, additional energy transfer from a given $Sn^{IV}$ porphyrin to the free bases ligated at the neighbouring $Sn^{IV}$ centers i.e., “trans-axial” energy transfer is likely to occur leading to more efficient quenching. A very high efficiency of energy transfer from the basal $Sn^{IV}$ porphyrin to the axial acceptors is observed in these axial-bonding type donor-acceptor hexamer assemblies [18].

4.2.1 Fluorescence lifetimes

Fluorescence lifetimes and the respective quantum yields are given in Table 4.1. All these molecules have bi-exponential decays for $\tau_{S1}$ representing slow and fast decay. For $SnTTP$ the lifetime is between 0.562 to 1 ns. In the case of trimers, $\tau_{S1}$ has increased to 0.74 - 5.93 ns in $Sn-(H_2)_2(TTP)_3$ trimer and with metal substitution in case of $Sn-Ni_2(TTP)_3$ $\tau_{S1}$ is ~ 0.62 - 2.13 ns. As the array is becoming larger, the contribution of slowly decaying (long lived) component has increased. In case of $Sn_2-(H_2)_4(TTP)_6$ $S_1$ lifetime is 0.454-7.25 ns whereas for $Sn_2-Zn_4(TTP)_6$ it is 0.663-1.73 ns. The lifetimes of the first excited singlet state have varied considerably with the metal substitution in hexamers. Substitution of Zn as central metal atom in porphyrin ring is reported to vary the singlet state properties and triplet state formation quite significantly [18,19]. As the excitation pulse is 6ns, the longer $S_1$ lifetime of $Sn_2-(H_2)_4(TTP)_6$
will help in enhanced ESA and ISC, which lead to better optical limiting performance. Fluorescence decay curves for monomer, trimer and hexamer are shown in Fig. 4.5(a) and 4.5(b) respectively.

Table 4.1: Fluorescence lifetimes and % yields of Sn(IV) TTP oligomers

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>( \tau_{S1} ) ns, (% fluorescence yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(TTP)</td>
<td>0.562 (71), 1 (28)</td>
</tr>
<tr>
<td>Sn-Sn (TTP)</td>
<td>0.57 (95), 4.94 (5)</td>
</tr>
<tr>
<td>Sn-(H(_2))(_2) (TTP)(_3)</td>
<td>0.744 (71), 5.93 (28)</td>
</tr>
<tr>
<td>Sn-Ni(_2) (TTP)(_3)</td>
<td>0.62 (70), 2.13 (29)</td>
</tr>
<tr>
<td>Sn(_2)-(H(_2))(_4) (TTP)(_6)</td>
<td>0.454 (28), 1.95 (23), 7.25 (47)</td>
</tr>
<tr>
<td>Sn(_2)-Zn(_4) (TTP)(_6)</td>
<td>0.667 (30), 1.73 (69)</td>
</tr>
</tbody>
</table>

Fig 4.5: Fluorescence decay curves for (a) Sn(IV) TTP monomer, Sn-(H\(_2\))\(_2\) trimer and Sn-(H\(_2\))\(_4\) hexamer and (b) Sn\(_2\)-(H\(_2\))\(_4\) hexamer and Sn\(_2\)-Zn\(_4\) hexamer.
Excitation energy transfer (EET) and photoinduced electron transfer (PET) are found to be responsible for the observed variation in the singlet state properties. The number of acceptors (free-base porphyrins) in the neighborhood of a given donor (Sn(IV) porphyrin) increases as one moves from the lower homologue to the higher donor-acceptor assemblies. Thus in the case of hexamer arrays additional energy transfer, called trans-axial energy transfer, from a given Sn^{IV} porphyrin to the free bases ligated at the neighboring Sn^{IV} centers is likely to occur in addition to the EET from the basal Sn^{IV} porphyrin to its two axial free-base acceptors which is the case with trimers. PET from ground-state free-base porphyrin to the singlet-state Sn^{IV} porphyrin leads to a charge transfer state of Sn^{IV}P—H_{2}P^{+} and involves free-energy changes leading to formation of charge transfer states (Fig. 4.6). These charge transfer states lead to localization of singlet states and the spread in the singlet states is quite large and the fluorescence emission wavelength is red shifted quite considerably.

Fig 4.6: A generalized energy level diagram illustrating the singlet state dynamics and charge transfer states pertaining to the photoactive arrays of trimer and hexamer. The effect of PET, EET and the CT states formed in these oligomers are found to vary the singlet state properties and in these effects were considered while estimating the figures of merit.
4.3 Measurement of $\langle \gamma \rangle$ and higher order nonlinearities

DFWM-PC geometry is used to measure the second hyperpolarizability $\langle \gamma \rangle$ of these oligomers using 25 ps pulses. In the case of Sn(IV) oligomers $\langle \gamma \rangle$ has increased from monomer to dimer, trimer and hexamer arrays. However $\langle \gamma \rangle$ saturates for trimer arrays and decreases as one moves on to hexamer arrays. The $\langle \gamma \rangle$ value is three orders of magnitude higher for hexamers compared to that of monomer [20]. For dimer molecule, in which two SnTTP monomers were edge linked via ethoxy spacer, the $\langle \gamma \rangle$ value is four orders of magnitude higher. The log-log plot of input energy and phase conjugate signal for dimer and Sn$_2$-Zn$_4$ (TTP)$_6$ hexamer are shown in Fig. 4.7(a) and 4.7(b) respectively. These molecules show log-log slope of ~ 3 at lower intensities ($<10$ GW cm$^{-2}$) and above that the slope approaches ~ 5, suggesting contributions from the higher excited states and the presence of higher order nonlinearities to the observed nonlinearity. For dimer molecule higher order slope appeared at a relatively lower intensities (~ 9 GWcm$^{-2}$) compared to that for trimer and hexamer (~ 15 GWcm$^{-2}$) molecules. The values of $\langle \gamma \rangle$ measured from cubic fit of the phase conjugate signal at lower intensities where the slope is ~ 3 are given in Table 4.2.

The chain length dependence of $\chi^{(3)}$ for several molecular arrays and polymers has been investigated earlier and it is known that the magnitude depends on the number of monomer unit $N$ [1, 21]. Usually it is a function of power of the chain length [1],

$$\gamma \propto N^{a(N)} \quad (4.1)$$

For conjugate compounds with a small monomer unit such as polythiophene, $a(N)$ is almost constant in an intermediate region (3-7 units) and finally $a(N)$ becomes less than unity which indicates the saturation effect. For instance, in the case of thiophene oligomers, reported by Hein et al. absolute value of $\chi^{(3)}$ was enhanced with increasing the thiophene unit; however, $\gamma$ per monomer unit was saturated at about 4 units. It is also reported that the saturation of the oligothiophenes occurs at about 7-8 units [1]. It is interesting to
note that for the oligomers and arrays of larger monomer unit such as porphyrin, the enhancement is more drastic and it saturates at a much shorter length [22]. Effects of alternation and saturation of $y$ have been reported earlier for cyanines [23].

Fig 4.7: Log-log plot of phase conjugate signal and the input energy for (a) Sn-Sn dimer and (b) Sn$_2$-Zn$_4$ hexamer with 25 ps pulses.
Table 4.2: Second hyperpolarizability $<\gamma>$ of Sn(IV)TTP oligomers

<table>
<thead>
<tr>
<th>Compound</th>
<th>$&lt;\gamma&gt;$ (x 10 esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(TTP)</td>
<td>$0.368 \times 10^{-3}$</td>
</tr>
<tr>
<td>Sn-Sn(TTP)$_2$</td>
<td>$2.99 \pm 0.4$</td>
</tr>
<tr>
<td>Sn-(H$_2$)$_2$(TTP)$_3$</td>
<td>$0.9328 \pm 0.06$</td>
</tr>
<tr>
<td>Sn-Ni$_2$(TTP)$_3$</td>
<td>$0.6142 \pm 0.04$</td>
</tr>
<tr>
<td>Sn$_2$-(H$_2$)$_4$(TTP)$_6$</td>
<td>$0.333 \pm 0.02$</td>
</tr>
<tr>
<td>Sn$_2$-Zn$_4$(TTP)$_6$</td>
<td>$0.385 \pm 0.03$</td>
</tr>
</tbody>
</table>

Large third-order electronic polarizabilities in porphyrin oligomers [22,24] and polymers [25] are reported earlier. The deviations from the cubic behaviour of the phase conjugate signal where the log-log slope approaching ~ 5 are observed earlier in tetramer, pentamer and polymers of porphyrin [25]. In isolated molecules in solution, strongly coupled pairs of excitations created by a TPA or ESA processes would create a two-photon grating that would produce a scattering proportional to the fifth power of the laser intensity, and an effective $\chi^{(5)}$ process. The nonlinearity would be expected to be rapid on the time-scale of the pulse duration because $S_n$ excited states of organic molecules commonly decay rapidly to $S_1$. Ultrafast measurements [26] of the dynamics of $S_2 \rightarrow S_1$ in analogous meso-linkedethynyl bridged porphyrin oligomers show the relaxation occurs in a sub 100 fs timescale. Similar results of the fifth-order nonlinearity are reported in stilbazolium derivative [27] due to TPA and TPA generated ESA.

Four-wave description of the DFWM interaction specifies only the number of beams involved and does not constrain the interaction to a third-order nonlinearity. The most general form of the third-order polarization density for the backward DFWM geometry can be expressed as

$$P^{(3)} = \chi^{(3)}_{ff'} (\vec{e}_f \cdot \vec{e}_{f'}^*) \vec{e}_b + \chi^{(3)}_{bf} (\vec{e}_b \cdot \vec{e}_{f'}^*) \vec{e}_f + 2C \chi^{(3)}_{fp} (\vec{e}_f \cdot \vec{e}_p^*) \vec{e}_p$$

The first two terms are identified as spatial grating terms and the third term corresponds to the scattering of the probe wave from a spatially uniform
two-photon coherence. The susceptibility $C$ is usually negligible unless there is a strong resonant enhancement from a two-photon transition. Depending on the polarization state of the input waves and the conjugated signal different terms contribute to the nonlinear polarization. In our experimental setup all the four waves are linearly polarized and all the three terms contributing to $P^{(3)}$ will be present [28]. The order of the susceptibilities and the specific terms that contribute significantly to the DFWM signal, depend on the nonlinear interaction. For instance, when the nonlinear mechanism is due to two-photon transitions, terms involving both third order and fifth order nonlinear susceptibilities will generally be significant and the dominance of one over the other will depend on details such as the two-photon transition probability, the dephasing rate of the two-photon coherence. Even for the case of a single-photon transition, terms of higher than third order may contribute, but such conditions are usually negligible unless significant population changes are involved.

The polarization density terms leading to DFWM can be written as

\[ P_{NL(co)} - P^{(3)} + P^{(5)} + \text{(higher-order terms)} \]  

(4.3)

In contrast to the single-photon resonant terms in $P^{NL}$, in two-photon resonant media a much more significant contribution to the net polarization density $P^{NL}$ may occur from $P^{(5)}$ and higher order terms, even when the population changes are negligible. For DFWM interaction some of the terms that are phase matched to radiate in the conjugate-wave direction are shown in table 4.3 below.

In the presence of an intermediate state one can expect term $\chi_c^{(5)}$ to dominate, owing to the formation of a relatively long lived intermediate state population. If this intermediate state is already well saturated at the light intensities of interest, this term essentially reduces to a third order term. If the population relaxation times for the states are generally longer than the dephasing times of the coherences $\chi_a^{(5)}$, $\chi_b^{(5)}$ be significantly longer than $\chi_c^{(5)}$ and $\chi_e^{(5)}$, and the corresponding polarization terms may be expected to result in DFWM signals comparable to the third-order $2\omega$ coherence term. Each term in $P^{(5)}$ has
functional dependence on the amplitudes of the input waves. For instance \( \chi^{(5)}_b \) has a cubic dependence on the intensity of the backward beam. With appropriate polarization selection, and by intensity and angular dependence experiments, it is possible to study the individual contributions of these terms to the DFWM signal.

<table>
<thead>
<tr>
<th>Typical term in ( P^{(5)}(\omega) )</th>
<th>Physical sequence in the nonlinear polarization density</th>
</tr>
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<tbody>
<tr>
<td>( \chi^{(5)}_a \left( \vec{E}_f \cdot \vec{E}_f \right) \vec{E}_p \cdot \vec{E}_b )</td>
<td>2( \omega ) coherence ( \rightarrow ) spatial grating</td>
</tr>
<tr>
<td>( \chi^{(5)}_b \left( \vec{E}_f \cdot \vec{E}_b \right) \vec{E}_f \cdot \vec{E}_p \cdot \vec{E}_b )</td>
<td>2( \omega ) coherence ( \rightarrow ) spatial grating</td>
</tr>
<tr>
<td>( \chi^{(5)}_c \left( \vec{E}_f \cdot \vec{E}_b \right) \vec{E}_f \cdot \vec{E}_p \cdot \vec{E}_b )</td>
<td>Population of intermediate state ( \rightarrow ) spatial grating</td>
</tr>
<tr>
<td>( \chi^{(5)}_d \left( \vec{E}_f \cdot \vec{E}_b \right) \vec{E}_f \cdot \vec{E}_p \cdot \vec{E}_b )</td>
<td>2( \omega ) coherence only no spatial grating</td>
</tr>
<tr>
<td>( \chi^{(5)}_e \left( \vec{E}_f \cdot \vec{E}_b \right) \vec{E}_f \cdot \vec{E}_p \cdot \vec{E}_b )</td>
<td>2( \omega ) coherence only no spatial grating</td>
</tr>
</tbody>
</table>

Table 4.3: Nature of \( P^{(5)} \) terms in two-photon resonantly enhanced materials

The population distribution of porphyrins with 25 ps pulse excitation can be explained by the following rate equations

\[
\frac{dN_0}{dt} = \frac{\sigma_0 I N_0}{\hbar \omega} - \frac{\beta I^2}{2\hbar \omega} + \frac{N_1}{\tau_1} \quad (4.4)
\]

\[
\frac{dN_1}{dt} = \frac{\sigma_0 I N_0}{\hbar \omega} - \frac{\sigma_1 I N_1}{\hbar \omega} - \frac{N_1}{\tau_1} + \frac{N_2}{\tau_2} \quad (4.5)
\]

\[
\frac{dN_2}{dt} = \frac{\sigma_1 I N_1}{\hbar \omega} - \frac{\beta I^2}{2\hbar \omega} - \frac{N_2}{\tau_2} \quad (4.6)
\]

As the relaxations from the excited singlet state \( S_2 \) are very fast compared to the excitation pulse width the population \( N_2 \) can be assumed to be not changing at very high intensities

\[
i.e., \frac{dN_2}{dt} = 0. \Rightarrow \frac{N_2}{\tau_2} = \frac{\sigma_1 I N_1}{\hbar \omega} + \frac{\beta I^2}{2\hbar \omega} \quad (4.7)
\]

Substituting this in to eqn (4.6), gives
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\[
\frac{dN_i}{dt} = \frac{\sigma_0 I N_0}{h \omega} \frac{N_i}{\tau_i} + \frac{\beta I^2}{2h \omega} \tag{4.8}
\]

The effective population describing the nonlinear property

\[
\frac{dN_i}{dt} - \frac{dN_0}{dt} = 2 \frac{\sigma_0 I N_0}{h \omega} - 2 \frac{N_i}{\tau_i} + 2 \frac{\beta I^2}{2h \omega} \tag{4.9}
\]

\[
2 \frac{N_i}{\tau_i} = \frac{1}{\tau_i} \left[ (N_i - N_0) + (N_i + N_0) \right] = \frac{1}{\tau_i} \left[ N_{\text{eff}} + N_0 \right] 
\]

Where \( N_{\text{eff}} = N_i - N_0 \) is the effective population contributing to the nonlinear polarization and \( N_{\text{eff}}^0 - N_i + N_0 \) is the population at zero field, which is a constant \( N_0 \).

The effective population density leading to the nonlinear polarization properties can be given by

\[
\frac{dN_{\text{eff}}}{dt} = 2 \frac{\sigma_0 I N_0}{h \omega} - \frac{1}{\tau_i} \left[ N_{\text{eff}} + N_0 \right] + 2 \frac{\beta I^2}{2h \omega} \tag{4.10}
\]

The resulting nonlinear polarization source term \( P^{NL} \) is proportional to \( EN_{\text{eff}} \). At higher intensities the two-photon term have dominant contribution to the nonlinear polarization is

\[
N_{\text{eff}}(t) \propto \int_{-\infty}^{I^2} I_{\text{eff}}^2 dt' \tag{4.11}
\]

At higher intensities assuming TPA to be the dominant process and in the DFWM geometry \( I^2 - (E_p + E_h + E_f)^2 \). Concentrating only on the terms which contain \( E_p E_p^* \) and neglect the terms in \( |E_p|^2 E_p^* \) since \( |E_p| \ll |E_f|, |E_h| \). Then the component of \( I^2 \) producing a grating leading to the DFWM signal is \( I_{\text{eff}}^2 \times (|E_f|^2 + 2|E_h|^2)|2E_f E_p^* + c.c.| \). Note that while \( I_{\text{eff}}^2 \) is real, it has been broken down into the sum of two complex conjugate terms. The first gives rise to the
conjugate signal, the second to a term, which radiates with a wave vector of \( \mathbf{k}_p - 2\mathbf{k}_f \) and is not phase matched.

Assuming the phase distortions on \( E_p \) to be small, \( E_p^* = E_{p0} \exp\{+ik_p(z \cos\theta + x \sin\theta)\} \) and \( E_f = E_p \{-ik_f z\} \) so that \( N_{\text{eff}} \) can be written as

\[
N_{\text{eff}} \propto 2 \cos[K_g x] \int_0^1 |E_f(t')|^3 |E_p(t')| dt'
\]  

(4.12)

where \( K_g = k_f - k_p \) is the grating wave vector. In the limit of small \( G, K_g \sim 2\pi \theta/\lambda \), where \( \lambda \) is the free-space wavelength. Since \( E_{\text{opc}} \propto P^N \), the total irradiance dependence of the DFWM signal is

\[
I_{\text{opc}} \propto I_b I_p I_f^3
\]  

(4.13)

The observed fifth-order nonlinearity can be considered to be arising from a sequential \( \chi^{(3)} : \chi^{(1)} \) nonlinearity. Such sequential nonlinearities leading to fifth and seventh order contributions to phase conjugation are reported in semiconductors [29]. In case of Sn-Sn dimer the log-log slope of the phase conjugate signal to the input energy varied as 2.83 ± 0.10 and 4.92 ± 0.11 at lower and higher intensities respectively. Where as for trimer and hexamers the slopes are higher than 3 and 5 at lower and higher intensities respectively. At higher intensities slopes higher than 5 observed in trimers and hexamers may be due to the additional localization coming due to the presence of PET and EET, which localize the singlet states, in turn changing the population densities contributing to nonlinear polarization. Whereas in dimer molecule the possibility of PET and EET is absent and only conjugation is present. In general for a medium that is m-photon resonant (\( m > 1 \)) the lowest-order term that may contribute significantly to a DFWM signal is of order \( 2m + 1 \), whereas the lowest-order term with a spatial modulation is of order \( 2m - 1 \) [29].
4.4 Optical limiting and nonlinear absorption

Optical limiting and nonlinear absorption studies are performed for these samples both in ns and ps regime. The nonlinear absorption behaviour observed in these hybrid arrays is totally different at ns and ps timescales. In the nanosecond regime all these molecules show good RSA even at higher intensities. However, in the picosecond regime the behaviour switches from RSA to SA and then again to RSA as the intensity increases.

4.4.1 With 6 ns pulses

Optical limiting studies are done using 6 ns pulses with 10 Hz repetition rate from frequency doubled Nd: YAG laser. We have employed f/5 geometry. The linear transmission is approximately 70-75% for 1-mm path length of the sample. The input fluence is varied in the range of $30 \mu \text{J cm}^{-2}$ to $70 \text{J cm}^{-2}$. OL curves for monomer SnTTP, trimer Sn$_2$-(H$_2$)$_2$ (TTP)$_3$ and hexamer Sn$_2$-(H$_2$)$_4$ (TTP)$_6$ at ~75% linear transmission at 532 nm shown in Fig. 4.8 clearly indicates the enhanced limiting behavior as one moves to higher homologues.

![Optical limiting curves of Sn(IV) TTP monomer, trimer and hexamer at 75% linear transmission with 6 ns pulses. Lines show the fits to the limiting curves.](image)
Figure 4.9 (a) and (b) show the variation in the limiting curves for SnTTP and Sn-Sn(TTP)$_2$ at different linear transmissions of 85% and 70%. These oligomers start showing considerable limiting performances from the concentrations corresponding to 75% linear transmission at 532 nm and the limiting performance increases with increasing concentration (decreasing linear transmission at 532 nm).

Fig 4.9: OL curves of (a) Sn(IV)TTP monomer and (b) Sn-Sn dimer at 85% and 70% linear transmission. Solid lines show theoretical fits.
Fig 4.10: OL curves showing (a) the effect of heavier metalloporphyrin with in hexamer arrays. Solid lines show theoretical fits. (b) OL curves showing the effect of concentration in Sn$_2$-Zn$_4$(TTP)$_n$ array.

However, with the introduction of heavier metalloporphyrin in the axial position in place of free-base porphyrin, in trimer and hexamer donor-acceptor homologues, lead to slightly reduced limiting response. OL curves for hexamers
with free-base and Zn porphyrins in axial position are shown in Fig. 4.10. Though the limiting threshold has not varied greatly the onset of limiting is certainly at lower input fluences for the oligomers with freebase porphyrin. Throughput fluences from these hybrids are as low as 35 - 52 mJcm\(^{-2}\) with input fluences in the range of \(\sim 26 - 74\) Jcm\(^{-2}\) making them very good optical limiters at higher intensities. Decreasing linear transmission to \(\sim 60\%\), we are able to achieve much better limiting performance in all these molecules. With increase in the concentration the ESA increases, thereby leading to improved nonlinear absorption behaviour. At higher concentrations we have not observed any scattering due to thermal blooming of the solution as reported earlier in suspensions of carbon black and ink [30]. No aggregation in the porphyrin solutions is observed even at higher concentrations.

Limiting threshold values for the oligomers with 6ns pulses are shown in Table 4.4. Figure of merit \((\sigma_{\text{ex}}/\sigma_0)\), which describes the capability of a material for optical limiting, and \(\tau_{\text{ISC}}\) estimated from the theoretical fits is also given in Table 4.4. The contribution from all the processes like PET and EET and both the radiative and nonradiative processes towards the lifetimes are taken as the effective singlet lifetime used in the rate equations. The values of \(\sigma_{\text{ex}}/\sigma_0\) are estimated using a generalized five-level model and from the rate equations explained in section 2.11 of this thesis. The lifetime of the higher excited singlet state \(S_n (\tau_{S_n})\) and triplet \((\tau_{T_n})\) are taken as \(\sim 100\) fs and the lifetimes of the first excited singlet state is taken as given in Table 4.1.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>(I_{1/2} ) (0 ) cm(^{-2})</th>
<th>(\sigma_{\text{ex}}/\sigma_0)</th>
<th>(\tau_{\text{ISC}}) (psec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnTTP</td>
<td>12.30</td>
<td>3.24</td>
<td>1000</td>
</tr>
<tr>
<td>Sn-Sn (TTP)(_2)</td>
<td>0.16</td>
<td>21.53</td>
<td>1x0</td>
</tr>
<tr>
<td>Sn-(H(_2))(_2)(TTP)(_3)</td>
<td>2.91</td>
<td>7.26</td>
<td>3x0</td>
</tr>
<tr>
<td>Sn-Ni(_2)(TTP)(_3)</td>
<td>3.46</td>
<td>6.21</td>
<td>550</td>
</tr>
<tr>
<td>Sn(_2)-(H(_2))(_4)(TTP)(_6)</td>
<td>0.46</td>
<td>19.45</td>
<td>220</td>
</tr>
<tr>
<td>Sn(_2)-Zn(_4)(TTP)(_6)</td>
<td>1.16</td>
<td>6.73</td>
<td>600</td>
</tr>
</tbody>
</table>

Table 4.4: Limiting threshold with 6 ns at 75% linear transmission at 532 nm.
Singlet state lifetime and the ESA from $S_1 \rightarrow S_n$ in addition to $T_1 \rightarrow T_n$ are found to be responsible for the enhanced limiting performance of higher homologues. Simultaneous occurrence of strong EET and less prominent PET lead to a drastic change and stabilization of $S_1$ states in these molecules, making the $S_1$ state metastable in comparison with the excitation laser pulse width. The effective ESA cross-sections from both singlets and triplet states is taken as $\sigma_{ex}$.

Even though the contribution due to ESA from $S_1$ to $S_n$ is present in these molecules as the lifetime of $S_1$ is longer and comparable to laser pulse width, due to the low fluorescence yields most of these molecules seem to transfer to $T_1$ with a time given by the longer decay. However high triplet yields in these molecules indicates that intersystem crossing plays an important role in these systems at the nanosecond timescales. Such a longer intersystem crossing has been reported in the unaggregated solutions of edge linked zinc porphyrin oligomers [31] and in monomer, dimer and polymer films [32]. The intersystem crossing time obtained from the theoretical fits is around 180 ps to 600 ps for these oligomers. Similar decay times are reported in zinc porphyrin oligomers [32] obtained from pump-probe measurements using a 0.8 ps pulse. Highly efficient triplet-triplet energy transfer and enhanced intersystem crossing is reported in rigidly linked metal and free-base porphyrin hybrids [33] and also in porphyrins linked via Ruthenium complex [34]. As the excitation pulse is of 6 ns duration, the longer lifetimes of $S_1$ in these arrays will help in enhanced ESA from the $S_1$ states, in addition to the ESA from the triplet states, which lead to better optical limiting performance. With the introduction of ZnTTP in case of hexamer and NiTTP in case of trimer in the place of the free-base TTP, we have observed reduced limiting performance of the molecule, due to the variation in the singlet state properties. When compared with the $H_2$TTP, NiTTP and ZnTTP monomers these oligomers show a better limiting performance under the similar experimental conditions. Substitution of Zn as central metal atom in porphyrin ring is reported to vary the singlet state properties and triplet state formation quite significantly [35]. Population relaxation times studied using DFWM-ps technique has been reported to have faster relaxations for ZnTTP and NiTTP compared to that of SnTTP and $H_2$TTP [36]. Population relaxation times studied using DFWM-ps technique has
shown just the autocorrelation trace that is similar to that obtained for CS$_2$ shows that the relaxations are certainly fast < 25 ps.

4.4.2 With 25 ps pulses

With 25 ps pulse excitation the nonlinear absorption behaviour is completely different compared to that observed with 6 ns pulses. SnTTP monomer shows a regular RSA behaviour at lower concentrations (corresponding to 75-80% linear transmission at 532 nm) and at lower intensities. At higher intensities the ESA saturates and SA followed by RSA is observed as shown in Fig.4.11 (a). At higher concentrations the nonlinear absorption shows a sudden transition to RSA at higher intensities within SA behaviour (Fig.4.11 (b)).

Fig 4.11: Sn monomer at (a) low (~14 GW cm$^{-2}$) and (b) high input intensities (~38 GW cm$^{-2}$) at lower concentration. Solid line is guide to the eye.
In the case of dimer at lower intensities only RSA (Fig. 4.12 (a)) is observed and as the intensity increases, the switching of the nonlinear absorption from RSA to SA and then back to RSA (Fig. 4.12 (b)) with intensity is observed. As the intensity increases the SA behaviour after RSA goes down as the RSA behaviour becomes more dominant (Fig. 4.12 c).

Fig 4.12: Sn dimer at low concentration, at (a) 5.6 GW cm\(^{-2}\) (b) 19 GW cm\(^{-2}\) and (c) 46 GW cm\(^{-2}\). Solid line is guide to the eye.

In the case of trimers, at lower concentrations and at lower intensities RSA is observed and with increasing intensity saturation of the ESA is observed. The saturation has increased with increasing input intensity. The open aperture Z-scan curves for Sn-(H\(_2\))\(_2\) (TTP)\(_3\) are shown in Fig. 4.13. For Sn-Ni\(_2\) (TTP)\(_3\), the substitution of NiTTP in axial position in place of H\(_2\)TTP lead to a total reversal
in the nonlinear absorption behaviour. At lower concentrations and at lower intensities SA is observed (Fig 4.1 a). With gradual increase in the input intensity the RSA phenomenon started taking over as RSA followed by SA is observed (Fig 4.14b) and at higher intensities pure RSA was observed (Fig 4.14c). At higher concentrations (60% linear transmission at 532 nm) the behaviour remained pure RSA similar to as shown in Fig 4.14c. As the intensity is increased the behaviour of RSA (Fig 4.14 (b)) started to take over and at higher intensities completely RSA dominates (Fig 4.14 (c)) probably due to TPA assisted ESA.

Fig 4.13: Sn-(H$_2$)$_2$ trimer at low concentration and at (a) 26.2 GW cm$^{-2}$ and (b) 44.5 GW cm$^{-2}$. Solid line is guide to the eye.

For Sn-Ni$_2$(TTP)$_3$ with 532 nm excitation that falls in the edge of the absorption band, we have observed SA behaviour (Fig 4.14 (a)) at lower
intensities. With 532 nm excitation, the lowest of the $S_1$ energy levels get excited and therefore one expects more localization of the energy [37], which thereby leads to saturation at lower intensities. When the pump excitation is into the lower side of the absorption band, there is more localization of the energy before it decays to the ground state, leading to resonant TPA.

Fig 4.14: Sn-Ni$_2$ trimer at low concentration and at intensities (a) 4.5 GW cm$^{-2}$ (b) 24.3 GW cm$^{-2}$ and (c) 47.5 GW cm$^{-2}$

In the case of Sn-(H$_2$)$_2$ (TTP)$_3$ and Sn$_2$-(H$_2$)$_4$ (TTP)$_6$, both at lower and higher concentrations and at higher intensities saturation due to the excited states...
is observed (Fig 4.13 and 4.15). At higher intensities the saturation has increased quite considerably. However in Sn₂-Zn₄(TTP)₆ at lower concentrations and at lower intensities a transition from SA to RSA due to two-photon/multi-photon absorption is observed (Fig 4.16). At higher concentrations and at lower intensities saturation of absorption due to excited states is observed (Fig. 4.17 (a)). As the intensity increased to ~ 52.5 GWcm⁻² RSA is observed after saturation of absorption due to the excited states (Fig 4.17 (b)).

Fig 4.15: Sn₂-(H₂)₄ hexamer at 75% linear transmission and at I₀₀ ~ 22.5 GWcm⁻²

Fig 4.16: Sn₂-Zn₄ hexamer at 75% linear transmission and at I₀₀ ~ 27.0 GWcm⁻². Solid line is guide to the eye.
Fig 4.17: Sn₂-Zn₄ hexamer at high concentration (60% linear transmission) at intensities of (a) 28.5 GW cm⁻² and (b) 52.5 GW cm⁻² respectively. Solid line is guide to the eye.

Depending on the input pulse duration, nonlinear absorption in these materials normally occurs through transitions from \( S_0 \to S_n \) states by instantaneous TPA or from \( S_0 \to S_1 \to S_n \) states by a two-step resonant ESA (if \( S_1 \to S_n \) occurs after vibrational transitions or diffusion within the singlet states) or \( T_1 \to T_n \) states by means of ESA. From the equilibrium level \( S_1 \) the molecules may relax radiatively or nonradiatively to the ground state or transfer to the lower level of triplet manifold, \( T_1 \). Efficient RSA for picosecond pulses requires that the recovery rate from the \( S_1 \) state be slow compared to the optical pumping rate. Intra-band vibrational relaxation times also play an important role for RSA. The higher excited states of the singlet manifold relax to the lower vibrational states,
leading to absorption of the pump from the lower singlet level to the higher excited states through ESA. At the intensities and the pulse width used one need to consider the effect of multi-photon absorption (MPA) process also. Two-photon and Three-photon processes leading to optical limiting are well reported in various organic compounds [38]. Presence of MPA is generally resolved using upconverted fluorescence [39], transient absorption [40] using pump-probe and four-wave mixing experiments with femtosecond pulses [41]. For porphyrins the intersystem crossing time (\(t_{\text{isc}}\)), which is of the order of few nanoseconds in general and few hundreds of picoseconds in some specific cases, is of minor consequence because of the 25 ps pulse width of the laser. For the ps excitation we therefore can neglect intersystem crossing and hence the contribution of the \(T_1\) state, which makes the singlet states responsible for the observed behaviour at these time scales.

At the wavelength of excitation, 532 nm, the lowest of the \(S_1\) energy levels get excited, and therefore one expects more localization of the energy, which thereby leads to saturation at lower intensities. As the intensity increased, the behavior switched to RSA, as shown in Fig. 4.14 (b)&(c). The intensities used are \(4.5 \times 10^9\) and \(24.3 \times 10^9\) W cm\(^{-2}\) for a concentration corresponding to 70% linear transmission at 532 nm. For increasing intensities (>34 \(\times 10^9\) W cm\(^{-2}\)) the behavior shows a complete switchover from SA to RSA, which could probably be due to either TPA or step-wise ESA, TPA generated ESA or multi-photon absorption. At very large intensities the behavior was completely dominated by RSA.

Behavior of RSA followed by initial SA has been observed earlier for zinc meso-tetra (p-methoxyphenyl) tetrabenzo porphyrin (ZnmpTBP) [42], polymethine dye [43], and coordination compounds [44] and in Rhodamine B [45]. In ZnmpTBP [38] the behavior was attributed to the excitation of population into higher excited states (\(T_n\)) at higher intensities, giving rise to RSA; and the SA behavior was given as due to the saturation of the \(T_1\) state. In polymethine dye [43] this behavior was attributed to irreversible damage induced by the input pulses. For ruthenium and osmium complexes of modified terpyridines [44], the saturation curve was explained as being due to the
compounds and the RSA portion as being due to TPA of the solvent. In RhB [45] the cross over from SA to RSA is observed with increasing concentrations and intensities in methanol when excitation is at near resonance with the absorption band and for RhB in water transition from RSA to SA is observed. The cross over is attributed to the formation of aggregates at higher concentrations that vary the singlet state lifetimes greatly. Zhan et al. [46] observed a transition from RSA to SA in a charge-transfer salt of with increasing intensity that was attributed to the fifth-order nonlinearity, as the excitation wavelength was 1064 nm and absorption peaked near 532 nm for their sample. Transition from RSA to SA with intensities and concentration depends on the higher excited state relaxation times. The most plausible explanation for the observed behavior in our case is that due to the PET and EET processes occurring simultaneously the excited singlet states become more and more localized thereby causing considerable changes in the absorption from the $S_1$ to the $S_n$ states, which follows the square law for intensity dependence, leading to enhanced TPA. Though PET is reported to lead to saturation of excited states, the contribution from the lifetimes also plays a crucial role [47].

4.5 Ultrafast relaxation - DFWM-ps results

Population relaxation from the excited states becomes very important parameter in these molecules. Relaxation of the molecules out of the excited states occurs rapidly (<1ps) into an equilibrium level in the highest singlet $S_1$ state. The relaxation of $S_n$ state would be unresolvable in our case due to the laser pulse width being larger than the expected lifetime. Population relaxation times studied using DFWM-ps technique has shown just the autocorrelation trace that is similar to that obtained for CS$_2$ shows that the relaxations are certainly faster < 25 ps. The recovery of the ground-state population can occur in times shorter than the measured fluorescence decay times under high laser fluence. This has been attributed to exciton-exciton annihilation. The rapid ground state recovery is common for porphyrin and phthalocyanine based systems in which
the excitons are strongly coupled [32]. This process could also lead to a rapid excited-state nonlinearity.

Ultrafast relaxations of the order of few hundred femtoseconds are well known in porphyrin-acceptor systems due to electron transfer [48]. Photoinduced charge separation, thermal charge recombination electron transfer due to porphyrin localized charge transfer character in a directly linked pyromellitimide-(porphyrinato) Zn(II) complex and similar donor-acceptor systems are reported to be in the timescales of 770 and 5200 fs [49]. Competition between internal conversion and energy transfer in the upper excited singlet state of the porphyrin-ruthenium complexes are also reported [50]. Lammi et al. [51] reported energy and charge transfer between the adjacent states leading to excited state quenching at timescales < 11 ps and between different sites by super exchange assisted energy transfer at timescales of < 55 ps in diphenyl ethyne linked porphyrin dyads and triads and the relaxation rates can be tuned using the porphyrin-linker connection motif. Ultrafast excitation energy transfer processes are reported to be in the order of 12 ± 3 ps in Zn(II) porphyrin box [52]. Increasing number of porphyrin units has also reported to accelerate the relaxation dynamics of the lowest excited states from 4.5 ps for dimer to 0.3 ps for hexamer [53]. O’Keefe et al. [54] reported a two-component decay, of approximately 700 fs and 170±50 ps due to exciton-exciton annihilation and exciton diffusion to recombination centers on the polymer chain from femtosecond transient photoinduced transmission measurements on Zinc conjugated porphyrin polymer. Similar faster decay of 13 ± 5 ps is also reported for dimer [54] due to the rotational diffusion of the excited molecule in solution. Relaxations of ~ 6 ps are also reported in ethylene bridged side-to-side OEP porphyrin dimer [55]. Excited-state energy transfer is reported to be operative at timescales of 3.5 ps and 10 ps in \textit{p-phenylene} linked porphyrin dimers [56], which varies with the bridge linker. Ultrafast fast kinetics of a hexameric benzo-porphyrin compound investigated by femtosecond transient absorption spectroscopy shows that in the hexamer a 20 ps decay component is present which is attributed to an intramolecular interchromophoric excited-state process [57]. In cofacial lanthanide porphyrin macrocycles two relaxation processes with time constants of ~1.5 and 10 ps are
reported [58]. Energy transfer to the nearest porphyrin in chelate assembly separated by approximately 15-18.5 Å is reported to occur in ~ 10 ps, which varies with the separation [59]. The transition from SA due to the excited states to RSA observed in the Sn^{IV} oligomer arrays at higher intensities and the contribution from different nonlinear absorptive processes can be better understood with the help of relaxation/decay dynamics from the higher excited singlet states/energy transfer in these molecules.

4.6 Conclusions

- In the ns regime OL performance increases as one moves to higher homologues.
- Within trimers and hexamers, substitution of heavier metalloporphyrin reduced limiting performance slightly.
- Linearly linked Sn-Sn dimer shows a better OL performance than the axial-bonding type trimers and hexamers.
- In the ps regime these molecules show SA at higher intensities after initially showing RSA at lower intensities. At very high intensities RSA again takes over.
- Higher order nonlinearities in the ps regime indicate the presence of two-photon/ multi-photon absorption process.
- Ultrafast relaxations show a very fast relaxation < 25 ps in these molecules.

4.7 References


Chapter 4 Axial-bonding type hybrid porphyrin arrays ...


Chapter 4 Axial-bonding type hybrid porphyrin arrays ...