Photophysical and Optical Limiting Properties of Axially Modified Phthalocyanines

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Abstract: As one of the most investigated organic compounds, phthalocyanines (Pcs) exhibit a stronger optical limiting response that can be used to protect human eyes, optical elements, and sensors from intense laser pulses, however, they tend to aggregate at high concentration. This aggregation usually adds relaxation pathways, shorten the excited state lifetime, and reduce the effective nonlinear absorption. A best strategy for reducing the intermolecular interactions between Pc molecules is to introduce more or less bulky axial substituents with which it would be expected to alter the electronic structure of the Pc compounds, to introduce a dipole moment perpendicular to the macrocycle, and to alter both intermolecular interactions as well as spatial relationships between neighboring molecules. As a result, a whole series of new highly soluble axially substituted MPc (M= In, Ga, Ti) compounds have been synthesized by us in recent years. Of interest is that their limiting response can be tailored over a very broad range due to the high architectural flexibility of the Pc structure. Future work will be focused on in-depth studies of the Pc–based solution and solid state systems to provide a detailed understanding of the factors affecting the optical limiting response.

Keywords: Nonlinear optics, optical limiting, phthalocyanines, axially modification, photophysical properties.

INTRODUCTION

Aside from numerous civilian applications of lasers, they have evolved to numerous modern battlefield weapons. Some are designed to dazzle or permanently disable humans by blinding, while others are used to destroy optical sensors, missiles, and other targets. Laser target designators and range finders used on the M series tanks and some artillery are in the inventories of all major armies, and their numbers are increasing. For examples, a laser designed to blind the optical and Electronic-Optical (E-O) devices of enemy tanks and armored fighting vehicles were deployed in the Gulf war by the Army but not used [1]. This device weighs only about 160 kilograms. A 30-pound hand-held laser weapon used to damage enemy sensors and human eyes has also been developed. This device may operate on three-different wavelengths. ABC news [2] of Dec. 30, 2004 reported that on Dec. 25 there were three reported laser incidents at airports in Houston; Medford, Ore.; and Washington, It's thus obvious that the need for passive laser protectors to protect human eyes and all optical sensors from intense laser beams is not limited to the military, but is rather a growing societal problem that can only escalate [3]. In the past decade, significant research effort has been invested into optical limiting materials and processes in an attempt to achieve some measure of protection from such laser beams [4-8]. Table **1** compares the various optical protection methods, of which nonlinear optical (NLO) principle-based optical limiter has been recognized to be one of the best optical protection methods. To achieve simultaneous protection against both pulsed and continuous wave (CW) or quasi-CW lasers, broadband optical limiting chromophores needed to be designed for multimechanistic function. In all probability, effective optical limiting devices, whatever their final design, will also require focusing optics to be effective [3].

Table 1. Comparison of the Various Optical Protection Methods. Optical Limiter and Switcher can only be Placed at Intermediate Focal Plane, while the Latter Three Devices can be Located at Anywhere within the Sensor's Optical Path

	Optical Limiter	Optical Switcher	Filter	Mechanical Shutter	Tunable Filter
Passive	Yes	Yes	Yes	No	No
Active	No	No	No	Yes	Yes
Response time	Fast	Fast	Fast	Slow	Slow
Potential for broadband protection against wavelength-agile lasers	Yes	Yes	No	Yes	No
Detection affected upon protection activated	No	Yes	No	Yes	No

Optical limiting is an important application of nonlinear optics, useful for the protection of human eyes, optical elements and optical sensors from intense laser pulses. Studies of the NLO properties of organic functional materials have resulted in the identification of materials that are among the most promising optical limiting materials available. Fullerenes, carbon nanotubes, porphyrins, phthalocyanines, carbon black suspensions and other materials have been widely studied to develop practical passive optical limiters that can protect against laser radiation exposure. An example is provided in Fig. (**1**). An important term in the optical limiting measurement is the limiting threshold. It is defined as the input fluence (or energy) at which the transmittance is 50% of the linear transmittance. It is obvious that the lower the optical limiting threshold, the better the optical limiting material.

Among the large number of NLO materials that have been identified, phthalocyanines(Pcs) have emerged as the most promising materials owing to their large nonlinearities, ultrafast response times, and easy processability [4-8]. Similar to C_{60} and its organic

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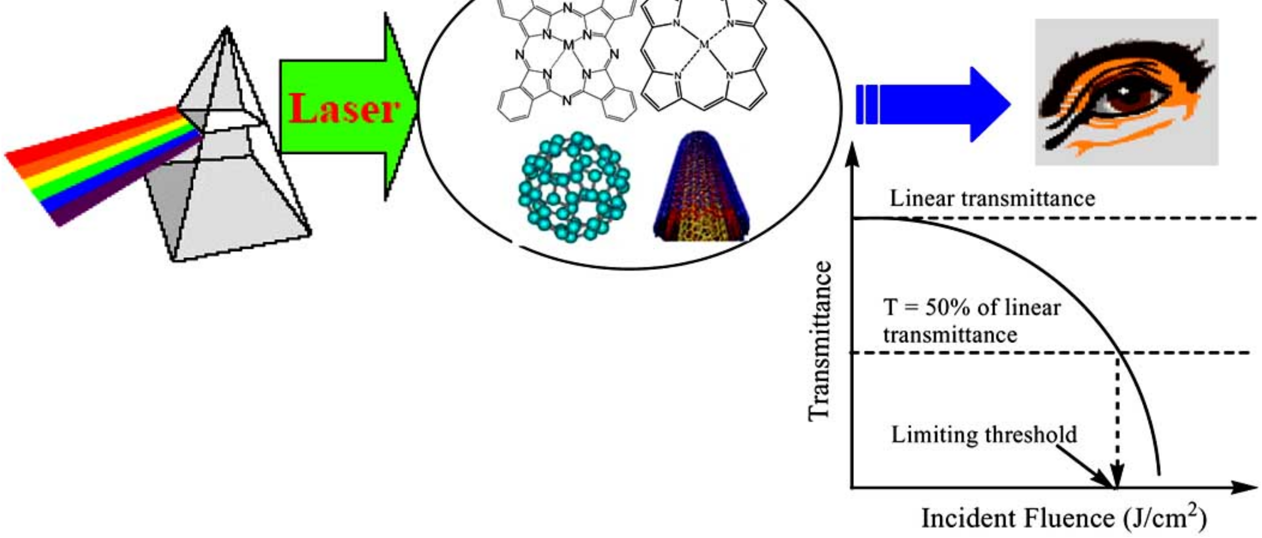

Fig. (1). The response of an optical limiter. An ideal material limits the output energy to some specified value. Suitable materials (in black circle) include phthalocyanines, porphyrins, carbon nanotubes, and fullerenes.

and polymeric derivatives, Pcs are materials that optically limit nanosecond light pulses in a fairly wide range of the UV/Vis absorption spectrum *via* excited state absorption processes, and have been extensively investigated as one of the most promising NLO materials due to their architectural flexibility, which allows tailoring of their physical, optoelectronic and chemical parameters in a broad range, exceptional stability and processability features. This review would lay special stress on describing our own work on the photophysical and optical limiting properties of axially modified phthalocyanines.

THEORETICAL BACKGROUND

Linear Absorption

Under ambient light irradiation (low intensity) materials typically exhibit a constant linear absorption coefficient α_0 usually described by the Lambert-Beer law as:

$$\frac{dI}{z} = -\alpha_0 I \quad (1)$$

This simple differential equation can be solved by integrating with limits on dz going from $z = 0 \rightarrow L$ and the limits on dI going from $I = I_{In} \rightarrow I_T$. If one defines the transmission as a function of the incident intensity as $T(I_{In}) = I_T/I_{In}$ then the solution to Equation (1) is

$$T = \exp(-\alpha_0 L) = \exp(-\sigma_0 N L) \quad (2)$$

where L denotes the sample length, σ_0 represents the absorption cross section of the ground state to first excited singlet state transition ($S_0 \rightarrow S_1$ transitions) and N represents the total population under excitation. Thus, in this operating regime the transmission T is independent of the excitation intensity. In this regime the ground state population never gets significantly depopulated and consequently as the population has to be conserved the excited state never achieves a significant population either. Thus, the light irradiating the sample experiences an approximately homogeneous population distribution as it propagates through the medium. As the excitation intensity increases to levels where the photon density is comparable to the population density an induced regime transition may occur where the absorption coefficient is depleted or enhanced corresponding to increases or decreases in the transmission respectively. The resultant regime depends upon the absorption cross sections of the ground and excited state levels and the lifetimes of the various allowable transitions in the system.

The electronic absorption spectra of Pcs are characterized by intense Q-band in the red end of the visible spectrum of light between 600-700 nm, with a molar absorption often exceeding 10^5 cm^2/mol, and a B-band at 300-400 nm in the blue end of the visible spectrum. In the spectra of metal phthalocyanine solutions, the intense Q-band arises from a doubly degenerate π-π* transition between the $A_{1g}(a_{1u}^2)$ ground state to the first excited single state, which has $E_u(a^1{}_{1u}e^1{}_g)$ symmetry. The second allowed π-π* transition (B-band) is due to a transition between either an a_{2u} or a b_{2u} orbital to the e_g orbital (LUMO). In the case of metal-free phthalocyanine all states are non-degenerated, due to the reduced D_{2h} molecular symmetry. The Q-band transition is polarized in either the x or y direction, and is therefore split into two bands. In the spectra of phthalocyanines with open d-shell metal as central atoms, metal to ligand or ligand to metal charge transfer transitions can be observed [9]. Intermolecular interactions like aggregation give rise to effects like band broadening, blue shift of the Q- and B-band or to an observed splitting of the Q-band [10-13]. In the solid state, coupling between dye molecules creates an exciton band structure with much broader absorption bands, often covering about half the solar spectrum. In contrast to phthalocyanines, naphthalocyanines compounds, which are almost transparent in the red light region (600-700 nm) where phthalocyanines have a considerable linear absorption coefficient due to the Q-bands, have a B-band in the region of 350 nm, but conversely the Q-bands are red-shifted by about 100 nm to around 800 nm. The UV/Vis absorption spectra of the highly conjugated porphyrin compounds usually exhibit an intense feature (extinction coefficient > 200000) at about 400 nm (B- band), followed by several weaker absorptions (Q-bands) at higher wavelengths (from 450 to 800 nm). Fig. (**2**) compared electronic absorption properties of porphyrin, phthalocyanine and naphthalocyanine.

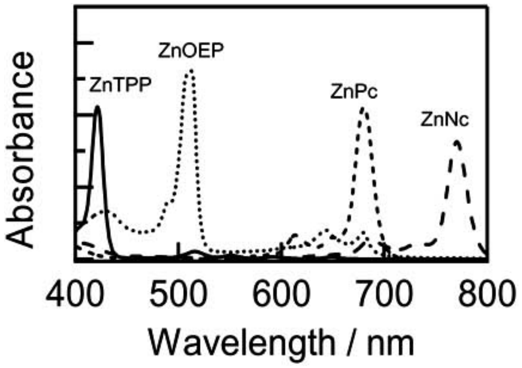

Fig. (2). Steady-state absorption spectra of zinc tetraphenylporphyrin (ZnTPP), zinc octaethylporphyrin (ZnOEP), zinc phthalocyanine (ZnPc) and zinc naphthalocyanine (ZnNc).

TWO-PHOTON ABSORPTION

Two photon absorption is the simultaneous absorption of two photons of energy $h\nu$ to span an energy bandgap of energy approximately equal but more likely slightly less 2 $h\nu$. One can consider an incident optical beam, with frequency ν irradiating a material with, for example, an $S_0 \rightarrow S_1$ transition of energy ≈ 2 $h\nu$ with sufficient intensity such that two photons may be simultaneously absorbed through a virtual energy level lying between S_0 and S_1. This hypothetical system is sketched in Fig. (**3**). After a small vibrational relaxation the excited population may then occupy the S_1 orbital from where it may subsequently re-radiate or irrationally relax back to the ground state. This is the same principle by which second harmonic generation(SHG) operates where two photons of frequency ν are absorbed simultaneously in a crystal and reradiated as a single photon of frequency 2 $h\nu$ or with wavelength equal to half that of the initial excitation.

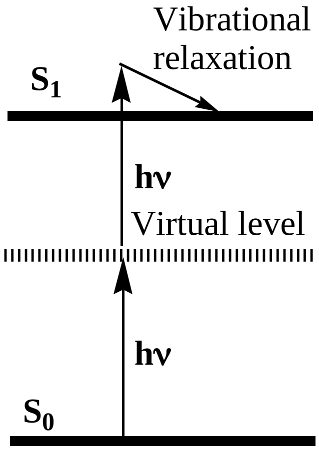

Fig. (3). Sketch of two-photon absorption process. In the hypothetical system the $S_0 \rightarrow S_1$ transition is of energy ≈ 2 hν, where hν is the energy of a single incident photon.

EXCITED STATE ABSORPTION

Saturable absorption refers to the case of excited state absorption (ESA), where the transmission increases with incident intensity, and indicates that the ground state absorption has bleached. Conversely, the opposite situation, where the trans-mission decreases with increasing incident intensity, is termed reverse saturable absorption (RSA). This occurs when the excited-state absorption cross-section is greater than that of the ground-state, and was initially discussed by Guiliano and Hess in 1967 [14].

Hercher conducted a general analysis of saturable absorbers using a three level scheme [15]. Under the steady state approximation, where the populations of energy levels remain constant for the duration of the pulse, he derived a general expression for the absorption coefficient in terms of a parameter called the saturation intensity, I_{Sat}.

$$\alpha = \frac{\alpha_0}{1 + \frac{I}{I_{Sat}}} \tag{3}$$

where $I_{Sat} = h\nu / (\sigma_0 \tau_{10})$, and τ_{10} refers to the excited-state relaxation time of the bleaching transition. I_{Sat} is the intensity at which the absorption coefficient drops to half of its linear value. Hercher also investigated the effect of excited-state absorption on the transmission of a saturable absorber, noted that it precluded the possibility of the absorption bleaching totally, and termed this residual absorption.

To discuss the importance of the various parameters that influence RSA in the phthalocyanine system, a general model of a five-level system, such as that shown in Fig. (**4**), has been investigated, and approximations suitable for the phthalocyanine system under nanosecond irradiation have been applied. Laser rate equations were used to simulate the excitation and subsequent relaxation of the system. The vibrational levels of the electronic states are ignored, and for the sake of simplicity the laser pulse width is assumed to be longer than any of the lifetimes associated with the levels. As such this is still a complicated system, and in an effort to further simplify matters it can be assumed that relaxation from states S_2 and T_2 is very rapid, so that the population of these two levels may be neglected.

Generally after initial excitation of this five-level system the first excited singlet state S_1 is populated. From here the electrons may be subsequently excited into S_2 within the pulse width of the laser. Once in S_2 they rapidly relax to S_1 again. From S_1 the population may undergo an intersystem crossing to the first excited triplet T_1 with a time constant τ_{isc}, and thereafter be excited into T_2. Simi-

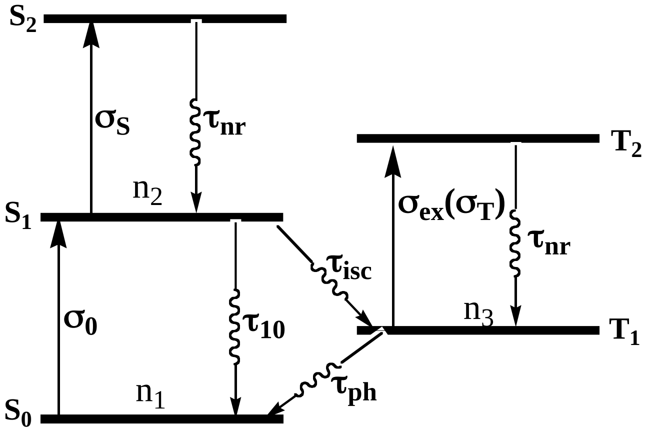

Fig. (4). Generalized five-level system used in deriving the excited state absorption model used to simulate RSA in the phthalocyanine system. S_i represents singlet levels and T_i represents triplet levels. Solid arrows imply an excitation resulting from photon absorption and jagged arrows represent relaxations.

larly to S_2 this state relaxes rapidly, and the population is exchanged between T_1 and S_1 cyclically since the lifetime of T_1 (τ_{ph}) is very long in comparison to τ_{isc}. The long lifetime of T_1 is one of the prerequisites for a large positive nonlinear absorption coefficient. Furthermore, stimulated emission from S_1 is excluded due to the small fluorescence quantum yield. The system now reduces to the following set of three differential rate equations:

$$\frac{\partial n_1}{\partial t} = -\frac{\sigma_0 I}{h\nu} n_1 + \frac{n_2}{\tau_{10}} + \frac{n_3}{\tau_{ph}} \tag{4}$$

$$\frac{\partial n_2}{\partial t} = \frac{\sigma_0 I}{h\nu} n_1 - \frac{n_2}{\tau_{isc}} - \frac{n_2}{\tau_{10}} \tag{5}$$

$$\frac{\partial n_3}{\partial t} = \frac{n_2}{\tau_{isc}} - \frac{n_3}{\tau_{ph}} \tag{6}$$

where n_1, n_2 and n_3 refer to the populations of S_0, S_1, and T_1, respectively. Attenuation of the laser beam is governed by a propagation equation where the absorption coefficient now includes the excited state absorption from S_1 and T_1:

$$\frac{\partial I}{\partial z} = -\alpha I = -\left(\sigma_0 n_1 + \sigma_S n_2 + \sigma_T n_3\right) I \tag{7}$$

Under the steady state approximation, which is valid when the pulse width is much longer than any relaxation time, all the time derivatives may be set to zero. This is a valid assumption for nanosecond pulses, as the lifetimes in phthalocyanines are typically on the order of pico-seconds [16]. In this case, the equation can be easily solved analytically and the intensity dependent absorption coefficient becomes:

$$\alpha(I) = \frac{\sigma_0 N}{1 + \frac{I}{I_{Sat}}} \left(1 + \frac{\sigma_S}{\sigma_T} \cdot \frac{\tau_{isc}}{\tau_{ph}} \cdot \frac{I}{I_{Sat}} + \frac{\sigma_T}{\sigma_0} \cdot \frac{I}{I_{Sat}}\right) \tag{8}$$

Noting that $\alpha_0 = \sigma_0 N$ (N is the total number density of dissolved molecules), defining $\kappa = \sigma_T/\sigma_0$, noting that σ_T and σ_S are probably of approximately the same order when $\tau_{isc} << \tau_{ph}$, and as the triplet yield approaches unity for phthalocyanines anyway, one is in a position to eliminate the term with σ_S in the numerator. This effectively reduces the five- level model to a three-level model, with the intensity-dependent absorption coefficient defined as:

$$\alpha(I, I_{Sat}, \kappa) = \frac{\alpha_0}{1 + \frac{I}{I_{Sat}}} \left(1 + \kappa \frac{I}{I_{Sat}}\right) \tag{9}$$

where in this case the excited state absorption cross section (σ_{ex}) is due almost entirely to σ_T, and thus $\kappa = \sigma_T/\sigma_0$. It can be noted that the intensity (I) and the pulse energy density (defined as $F = E_{Pulse}/(\pi\omega(z))^2$, where E_{Pulse} is the energy per pulse and $\pi\omega(z)^2$ is the surface area through which the pulse is propagating at any position denoted by z), are directly related to each other. Consequently the parameter I/I_{Sat} can be replaced with F/F_{Sat} in equation 9, where in this case F_{Sat} is the energy density saturation. Whenever the excited-state absorption cross section is greater than that of the ground state (i.e., $\kappa > 1$), RSA is observed as an increase in the normalized intensity-(or energy-density) dependent absorption coefficient ($\alpha(F, F_{Sat}, \kappa)/\alpha_0$) with respect to increasing normalized pulse energy density F/F_{Sat}. Whenever the converse is true, $\kappa < 1$, saturable absorption is observed as a reduction in $\alpha(F, F_{Sat}, \kappa)/\alpha_0$ with increasing F/F_{Sat}. This model, though simple, reproduces the gross effects of RSA, and highlights the crucial role that the excited-state absorption plays in the overall absorption coefficient. This steady-state model approximates to a dynamic model in the limit of temporally long pulse widths (i.e., nanosecond irradiation) when all other lifetimes in the material are of the order of pico-seconds. A full dynamic model cannot be approached analytically as the rate equations involved make up a set of coupled partial differential equations that must be numerically integrated over time and space.

OPTICAL LIMITING MECHANISMS

In 1939, Miles A. Dahlen wrote about phthalocyanines being the "first new chromophore of commercial importance developed in a quarter of a century [17]. With the invention of the laser in the 1960's [18], began the merging of structural material engineering and quantum physics leading to such research areas as nonlinear optics. Numerous investigations began into novel NLO properties including nonlinear absorption, scattering, 2nd order and 3rd order NLO properties, etc [19]. As a consequence, diverse NLO processes including RSA [14] began to acquire much industrial attention and interest. It is this NLO property which leads to the concept of *Optical Limiting*: Strong attenuation of high intensity light and potentially damaging light such as focused laser beams, whilst allowing for the high transmission of ambient light [20,21]. Industrial interest in this field has been driven by the need to protect expensive optical equipment, most importantly the human eye. This delicate yet robust "instrument" is a remarkable sensor, exhibiting multiple optical broadband responses, the ability to self-adjust to varying optical environments and a dynamic range in excess of 100 dB.

Several mechanisms giving rise to NLO responses can operate in a system. A perturbation of the electronic distribution in the material as a response to the electric field of the incident (low intensity) light is reason for normal linear polarization to occur. At high intensities, the electronic distribution no longer follows the applied field, resulting in both second- and third-order non-linearities. The second common mechanism that can contribute to the NLO response is molecular reorientation. This mechanism can lead to nonlinear refractive indices with a picosecond response time but it will not contribute to the third harmonic generation signal. In general, an orientational nonlinearity can be larger than an electronic nonlinearity. Another important mechanism for a third-order NLO response is optical pumping. In this case the incident laser frequency approaches a transition frequency in the molecule. The light is absorbed causing transitions to an excited state. The optical properties of the excited state differ substantially from those of the ground state. The higher the population in the excited state is, the larger the changes in the optical properties of the material and the larger the optical nonlinearities are. Optical pumping involves real transitions to excited states. This is a big difference compared to the small perturbations of the electronic cloud mentioned above. This mechanism is the most important mechanism giving rise to saturable and reverse saturable absorption. Like the second mechanism, the response time for optical pumping is too slow to give rise to frequency mixing and harmonic generation but it does give useful nonlinear absorption and refraction.

Usually, the most important mechanism for optical limiting is nonlinear absorption and nonlinear refraction and nonlinear scattering as well. A negative nonlinear refractive index giving rise to self-defocussing of a light beam can cause substantial amounts of the energy of the incident light to be absorbed by an exit aperture in the optical system. Materials with a positive nonlinear absorption coefficient exhibit reverse saturable absorption (RSA), and are characterized by a high transmission at normal light intensities and a decrease in transmission under high intensity or high fluence illumination. Conversely, the opposite situation, where the transmission increases with increasing incident intensity the process is termed saturable absorption (SA). The materials with SA usually have a negative nonlinear absorption coefficient. For optical limiters that rely on RSA from rapidly photogenerated transient states [19,22,23], they are almost transparent for weak light but opaque for the intense light. An efficient RSA material has a high ratio of excited state ($T_1 \rightarrow T_2$) to ground state ($S_0 \rightarrow S_1$) absorption cross section (>> 1), a rapid intersystem crossing rate ($\tau_{isc} << \tau$), a long internal conversion lifetime, a high intersystem crossing quantum yield ($\phi_{S1\rightarrow T1} \sim 1$) and a long triplet lifetime ($\tau_{T1} >> \tau$), the triplet state of the material absorbs the incoming laser so effectively that the laser can be greatly attenuated and the sensors can be protected. Two-photon absorption (TPA) [3], associated with the imaginary part of the third-order susceptibility, may also account for optical limiting. Basically in the visible region organic chromophore RSAs tend to have their primary absorption, $\lambda_{max}(\pi\text{-}\pi^*)$, at 400 nm, or below, to give reasonable transmission for solution or thin film measurements. Two-photon absorbers, on the other hand, would tend to depend on absorption in the 600-800 nm region to give rise to optical limiting effects in the visible [3]. TPA chromophores which limit between 600 and 800 nm via enhanced two-photon absorption would complement chromophorese which limit between 400 and 600 nm by RSA. It would thus be very desirable if one can design OL chromophores that might function in a bimechanistic fashion: (1) RSA behavior at the high energy end of the visible, and (2) TPA behavior at the low energy end of the visible [3].

In the case when the incident light is sufficiently intense so that a significant population accumulates in the excited state and if the material has an excited state absorption cross section σ_{ex} that is larger than the ground state cross section σ_0, the effective absorption coefficient of the material increases. To achieve the largest nonlinear absorption, both a large excited state absorption cross section and a long excited state lifetime are required. When the lifetime of the excited state being pumped is longer than the pulse width of the incident light, the changes in the absorbance and the refractive index are fluence (J cm^{-2}), not intensity (W cm^{-2}) dependent. Therefore, in materials with long upper state lifetimes, it is the fluence rather than the intensity that is limited. Limiting the fluence is usually desirable, since damage to optical devices is also often fluence dependent. Some criteria necessary for a large, positive nonlinear absorption are apparent including a large excited state cross section σ_{ex} and a large difference between the ground and excited state absorption cross sections (σ_{ex}-σ_0). A variety of organic and organometallic materials, including porphyrins, metallophthalocyanines, fullerenes, organometallic cluster com-pounds and other materials have been found to fulfill these conditions [24-28]. For porphyrins and metallophthalocyanines, they can exhibit strong excited-state absorption, high triplet yields and long excited-state lifetime, while their ground-state absorption is mostly confined to a few narrow regions (B and Q bands), allowing high transmission in the spectral window between these bands [27]. The spectral bandwidth or window over which the limiter operates, and the ground-state and excited-state spectra and lifetimes, can be controlled or engineered by altering the axial or peripheral substituents, central metal cations and the structure of the main rings.

A practical optical limiter must operate over the wide range of incident intensities that might be encountered. The condition that σ_{ex} is greater than σ_0 is necessary, but it is not sufficient for a useful OL material. The nonlinear response should possess a low threshold and remain large over a large range of fluences before the nonlinearity saturates. High saturation fluence normally requires a high concentration of the nonlinear material in the optical beam. For an organic material, this means it must be highly soluble in common organic solvents, or it is a pure liquid or a solid film that can be prepared with good optical quality. From the device point of view, the use of several successive limiters (tandem strategy) seems useful to optimize both the overall limiting and damage thresholds in phthalocyanines [7,8]. It should be noted that the response time of the nonlinear absorption and refraction in thin films of Pc materials may be strongly affected by intermolecular interations [29]. The use of a heavy metal-Pc material together with an appropriate nonhomogeneous concentration profile along the beam path leads to greatly improved optical limiting devices [27,30].

LINEAR OPTICAL AND EXCITED-STATE PROPERTIES

To obtain device-quality optical limiting materials, three stringent issues must be addressed: (1) Design and optimization of novel conjugated organic and/or polymeric functional materials to perform nonlinear optical processes under laser irradiation; (2) Maintenance of long-term stability toward the environment such as heat, light, oxygen, moisture and chemical during the fabrication and measurement of NLO devices; and (3) Effectively suppression of the aggregation of conjugated materials e.g. phthalocyanines in solutions and in the solid states. Third-order optical nonlinearities of phthalocyanines are of great interest due to their highly delocalized aromatic 18 π-electron systems giving rise to strong nonlinearities. Like many of the organic dyes used as nonlinear optical (including optical limiting) materials, however, phthalo-cyanine-based organic compounds tend to aggregate at high concentration. These aggregates are usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes, and are driven by enhanced Van der Waal's attractive forces between phthalocyanine rings [31]. For a NLO material, this aggregation is generally undesirable since strong intermolecular interactions usually add relaxation pathways, shorten the excited state lifetime, and reduce the effective nonlinear absorption [16]. This has been a primary barrier to further improvement of the optical limiting performance of the Pc-based organic materials. A best strategy for reducing the intermolecular interactions between Pc molecules is to introduce more or less bulky axial substituents, with which it would be expected to alter the electronic structure of the Pc compounds, to introduce a dipole moment perpendicular to the macrocycle. and to alter both intermolecular interactions as well as spatial relationships between neighboring molecules. Each of these effects can influence the NLO properties of the Pcs with respect to an improved optical limiting performance. The major goals of our work are therefore to design and synthesize a series of new highly soluble axially substituted metallophthalocyanine compounds with respect to an increase of the photophysical properties relevant for optical limiting of nanosecond pulses, specifically nanosecond nonlinear absorption; to characterize the linear and nonlinear optical properties of these organic compounds using the Z-scan, steady-state and time-resolved spectroscopic techniques, and to establish a clear relationship between the fundamental structural parameters and photophysical properties of materials. Based on past theoretical studies of organic materials which exhibit noted nonlinear absorption an in depth study into the resulting properties for solution- and solid state-based systems (by embedding in guest host polymer) would be undertaken in the near future.

Many of the central metal elements, for example, Ga^{3+}, In^{3+}, Ti^{4+} and others, have one or two sites which can coordinate to a variety of axial ligands. Such possibility to introduce different substituents into the axial position of phthalocyanines with these central metal elements promoted us to investigate the effect of a structural variation on the linear and nonlinear optical properties of the materials. The exploitation of the chemical reactivity of the M-Cl [M = Ga^{3+}, In^{3+}] and M=O [M= Ti^{4+} etc.] bonds can thus allow the preparation of a series of highly soluble axially substituted and bridged Pc-based organic compounds. We successfully developed a convenient and novel synthetic method that can be used to strongly suppress the aggregation of the macrocycles in solution and in the solid state, and to significantly improve the optical limiting performance and nanosecond nonlinear absorption of materials in the past several years. As a result, a series of highly soluble novel axially substituted indium-, gallium- and titanium phthalocyanine

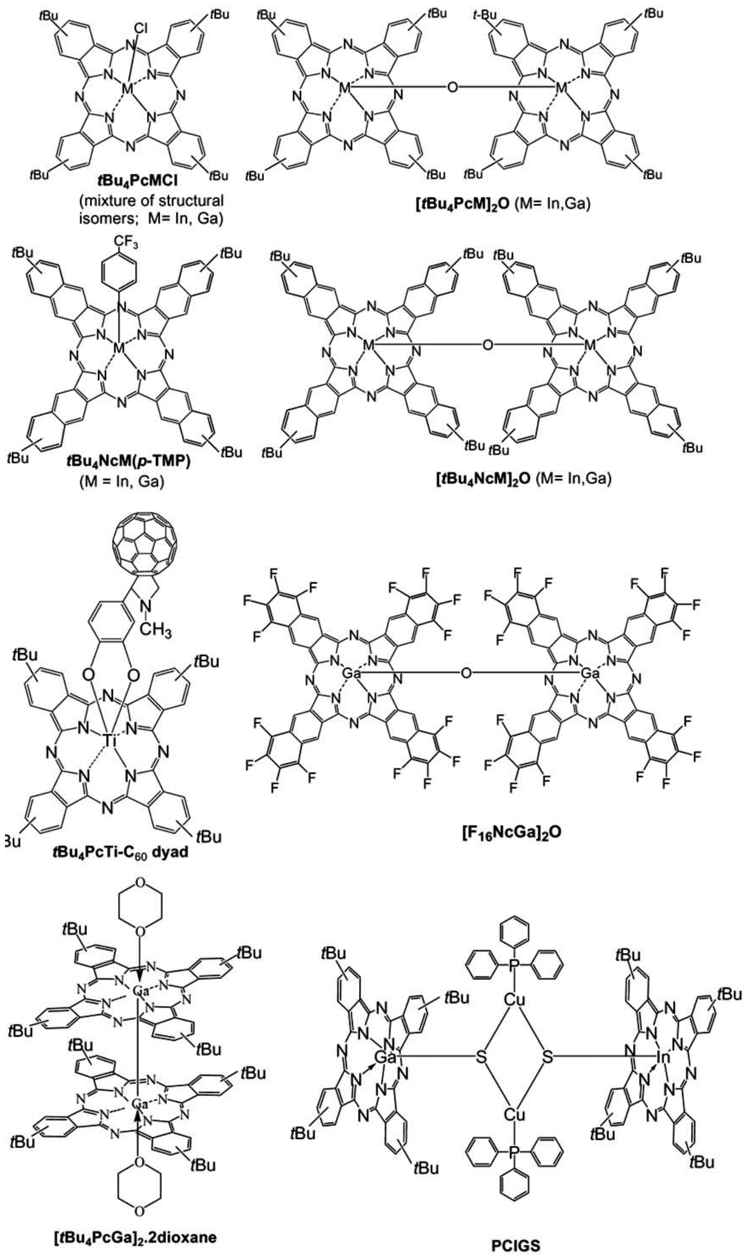

Fig. (5). Molecular structures of several typical Pc compexes.

monomers, dimers and polymers, all of which exhibit very good optical limiting response, have been synthesized by us in recent years [32-66]. For the first time we synthesized two new indium- and gallium phthalocyanine dimers with a direct indium-indium bond [32] and gallium-gallium bond [33], respectively. These dimers display optical limiting properties with improved features with respect to the single Pc ring coordinated by one single metal atom [34]. We also reported the first soluble indium- and gallium phthalocyanines-based nanoscale light-harvesting complex PCIGS [35], and the first axially substituted titanium Pc-C_{60} dyad [36] in the international highly rated journals. Our experimental results have demonstrated that axial substitution in Pc complexes provokes relevant changes on the electronic structure of the molecule by altering the π-electronic distribution due to the dipole moment of the central metal-axial ligand bond. In terms of optical limiting effectiveness in the visible range, axial substitution can improve the efficiency of excited state absorption through the inhibition of the decay of the excited state formed in a nonlinear optical regime. Moreover, axial substituents in Pc's influence favorably nonlinear optical absorption for the presence of a dipole moment perpendicular to the macrocycle in the axially substituted phthalocyanines. In comparison with octasubstituted Pc, tetrasubstituted Pc exhibits the much higher solubility mainly due to a lower degree of order in the solid state, which facilitates dissolution by the more pronounced interaction with solvent molecules. Also, the less symmetric isomers possess a higher dipole moment caused by the more asymmetric arrangement of the substituents in the periphery of the macrocycle.

Fig. (**5**) gives the molecular structures of several typical axially substituted indium-, gallium- and titanium phthalocyanines and their derivatives we synthesized. The enhanced solubility of the axially substituted phthalocyanine monomers and dimers, compared

Table 2. Photophysical Properties of Some Indium and Gallium Phthalocyanines in Deaerated Anhydrous Toluene. (τ_f: Fluorescence Lifetime at Emission Peak Wavelength, λ_{ex} = 410 nm; τ_T: Triplet Excited State Lifetime, λ_{ex} =355 nm)

Samples	λ_{max}^{abs} (nm)	λ_{max}^{fluo} (nm)	$\Delta\bar{\nu}^{stokes}$ (cm^{-1})	τ_f (ps)	λ_{max}^{T} (nm)	τ_T (μs)
tBu$_4$PcInCl	695	705	204	470	520	46
tBu$_4$PcIn(p-TMP)	696	701	103	280	520	22
[tBu$_4$PcIn]$_2$O	694	705	225	638	520	42
[tBu$_4$PcIn]$_2$(TFP)	694	705	225	350	520	35
[tBu$_4$PcInCl]$_2$.dib	692	703	226	470	520	38
tBu$_4$PcGaCl	693	702	185	2570	520	257
tBu$_4$PcGa(p-TMP)	696	701	103	2480	520	200
[tBu$_4$PcGa] $_2$O	692	701	186	3570	520	357
[tBu$_4$PcGa] $_2$.SDPO	692	712	406	3460	520	667
[tBu$_4$PcIn]$_2$.2tmed	697	710	262	380	520	4.5 (40%) 40(60%)
[tBu$_4$PcGa]$_2$.2dioxane	---	---	144	180(42%) 2480(58%)	520	2.1 (39%) 71(61%)

to the chloro analogues, shows that the usual tendency of phthalocyanines to form aggregates can be effectively suppressed by axial substitution. The axial ligand induces asymmetry and provides the molecule with an axial electric dipole moment, *i.e.* perpendicular to the macrocycle plane. The dipole moments associated with the axial substitution in tBu$_4$PcInCl and tBu$_4$PcIn(p-TMP) [p-TMP : p-trifluoromethylphenyl] were quite large being in the order of 10 Debye. The influence of different axial substituents on the electronic structure of the macrocycles is very small. The intense absorption band at ca. 700 nm with weak shoulder bands at 625 and 670 nm was attributed to the Q-band, while weak band at 375 nm was assigned to B-band. The steady-state absorption spectra are quite similar for almost all monomers and dimers. The shape of the UV/Vis absorption spectra of the aryl substituted phthalocyanines is almost independent of the concentration of the solution, whereas for the chloroindium(gallium) phthalocyanine a concentration dependent increase of the absorption on the red side of the Q-band indicates a somewhat larger degree of aggregation. In contrast to phthalocyanines, naphthalocyanines (Ncs) with their even larger delocalized π-electron system usually have their Q-band shifted to the near infrared, so that the absorption of visible red light is very low [40,41,67,68]. The color of such a complex is dominated only by the B-band absorption in the blue region of the visible spectrum, which gives the naphthalocyanine a yellow color. They have transmission windows in the yellow and red region of the spectrum.

The photophysical data of some indium and gallium phthalocyanines [42-46] are summarized in Table **2**. For all compounds, steady-state fluorescence spectra in deaerated toluene (λ_{ex} = 410 nm) show the mirror image of the corresponding UV/Vis absorption bands with small Stokes-shifts, suggesting that the structure change between the ground state and excited singlet state is small. The values of fluorescence lifetime (τ_f) of the PcGa derivatives are the order of ns, while the τ_f values of the PcIn derivatives are quite short. Compared with monomers, the μ-oxo- and 4,4′-sulfonyldiphenoxy(SPDO)- bridged dimers exhibit longer τ_f values. The decrease in the τ_f value was observed for the dimer with 2,3,5,6-tetrafluorophenylene(TFP)-spacer [44]. The PcGa dimer with a direct gallium-gallium bond, i.e. [tBu$_4$PcGa]$_2$.2dioxane, may exist in two different conformations: one in which the two phthalocyanines are poorly interacting and the other one in which they are very close and strongly interacting [45]. In the former case, the emission lifetime is quite close to that of the monomer model compounds; for the latter, it is much shorter due probably to different radiative and non-radiative deactivation constants compared to the monomers. Because no significant difference in the absorption spectra of the monomer and dimer has been observed in the photophysical experiments, implying no ground-state interaction can be assessed, the results regarding triplet excited state lifetimes of [tBu$_4$PcGa]$_2$.2dioxane can be due to strong intramolecular interactions existing only in the excited state. The deactivation processes of the excited singlet state of [tBu$_4$PcIn]$_2$.2tmed (tmed: *N,N,N′,N′*-tetramethylethylenediamine, (Fig. **6**)] dimer are apparently faster than that of μ-oxo-bridged PcIn dimer [tBu$_4$PcIn]$_2$O [46]. Molecular orbital calculation on the PcIn dimer shows no node between two indium atoms was found in the HOMO-2 of the PcIn-InPc dimer, suggesting that bonding electrons distribute between indium atoms.

The transient absorption spectra were observed by the excitation of the Pc derivatives with 355 nm laser light in deaerated toluene. On addition of O$_2$, the decay of the transient absorption band at 520 nm, which is attributed to triplet-triplet (T-T) absorption of the Pc compounds, was accelerated, suggesting that the energy transfer takes place from the triplet excited states of the Pc compounds to O$_2$, yielding probably ^{1}O$_2$. Fig. (**7**) gives ^{1}O$_2^*$ emission spectra generated by energy transfer processes from ^{3}C$_{60}^*$, ^3tBu$_4$PcGaCl* and ^3tBu$_4$PcInCl* to O$_2$. Among these three samples, the intersystem cross quantum yield of tBu$_4$PcGaCl is lowest, about 50% of the value of that for the tBu$_4$PcInCl. The decay of the 520 band in the presence of O$_2$ obeys first-order kinetics, giving the $k_{\text{first-order}}$, which increases with the concentration of added O$_2$; from the pseudo-first-order relation, the second-order rate constants for the reaction with O$_2$ (k_{O2}) were evaluated. Dimers and monomers have the almost same k_{O2} values, nevertheless they are all less than the diffusion controlled limit (k_{diff} = 1.1 x 10^{10} mol^{-1} dm^3 s^{-1} in toluene). In the absence of O$_2$, the decay rates depend on the laser powers. Fast decay observed at high laser power is attributed to the T-T annihilation due to the collision between the highly concentrated triplet states.

$$2\ {}^3[t\mathrm{Bu_4PcM}]_n\mathrm{X}^* \xrightarrow{k_{TT}} [t\mathrm{Bu_4PcM}]\mathrm{nX} + {}^1[t\mathrm{Bu_4PcM}]_n\mathrm{X}^* \quad (10)$$

The rate constants of first– and second– order kinetics were separately evaluated using the following equation:

$$-d[\ln(\Delta A_0)]/dt = \Delta k_{1st} = k_T^0 + (2k_{TT}/\varepsilon_T)\Delta A_0 \quad (11)$$

Where ΔA_0, k_T^0, and ε_T are T-T absorbance at t = 0, intrinsic first-order decay rate of the triplet excited state of Pc's, and extinction coefficient of the triplet absorption band, respectively. Plot of Δk_T to ΔA_0 shows a linear correlation. The intercept gives the k_T^0, from which the lifetimes of the triplet state was calculated ($\tau_T = 1/ k_T^0$).

	N	*r*, Å	*σ*, Å
In-(N_1)	4	2.12 ± 0.02	0.067 ± 0.010
In-(N_2)	2	2.59 ± 0.03	0.050 ± 0.005
In-(C_2)	8	2.90 ± 0.03	0.102 ± 0.025
In-(N_3)	4	3.05 ± 0.03	0.074 ± 0.011
In-(In‘)	1	3.24 ± 0.03	0.092 ± 0.002
In-(N_1‘)	4	3.40 ± 0.03	0.122 ± 0.018
η [°]		14.5 ± 2.0	
$In_{(out)}$ [Å]		0.78 ± 0.3	

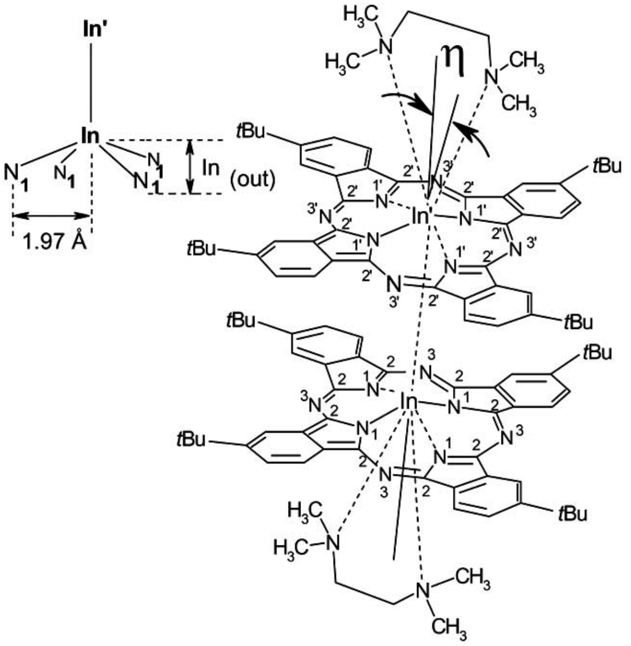

Fig. (6). EXAFS-Determined Structural Data and structure of $[tBu_4PcIn]_2$.2tmed [32].

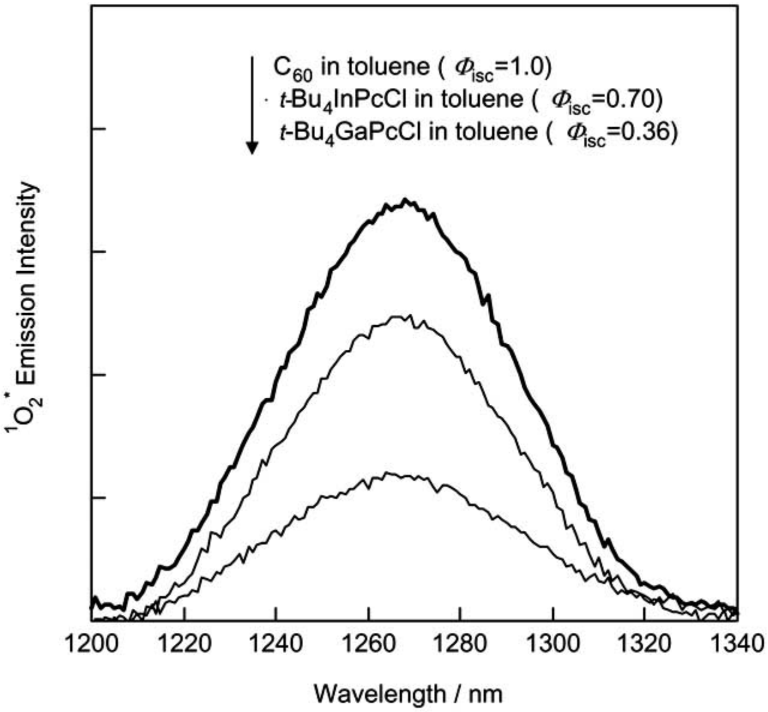

Fig. (7). $^1O_2^*$ emission spectra generated by energy transfer processes from $^3C_{60}^*$, $^3PcGa^*$ and $^3PcIn^*$ to O_2.

The τ_T values of indium phthalocyanines are shorter than those of gallium phthalocyanines by a factor of about 1/10. Among all Pc compounds, 4,4´-Sulfonyldiphenoxy-axially bridged gallium-phthalocyanine dimer {$[tBu_4PcGa]_2$.SDPO} exhibits the longest triplet excited state lifetime, up to 667 μs. The intersystem crossing rate from the excited singlet state to the excited triplet state was reported as 0.18×10^9 s^{-1} for PcGaCl without peripheral substituents and 2.4×10^9 s^{-1} for PcInCl at room temperature in chloronaphthalene. The longer lifetime of the excited triplet state observed for gallium phthalocyanines should be associated with the intersystem crossing rate. In the indium phthalocyanine monomers, the *p*-trifluoromethylphenyl (*p*-TMP) substituent introduces steric crowding and a dipole moment perpendicular to the macrocycle, and decreases the τ_T values compared with the Cl ligand. However, this effect diminished for the PcGa compounds in comparison with PcIn compounds. From the slope and the estimated ε_T value, the k_{TT} value was evaluated. The k_{TT} values for dimers are slightly smaller than those of monomers, implying that the excited triplet state localized in one Pc ring, which decreases the frequency factor for the energy transfer.

OPTICAL LIMITING PROPERTIES IN SOLUTIONS

Although axial ligands did not apparently affect the linear optical properties of phthalocyanines, but resulted in the considerable enhancement in optical limiting response [32-71]. The nanosecond nonlinear absorption and the optical limiting response of indium-, gallium- and titanium phthalocyanines seem to be dominated by a strong triplet state absorption in the optical region comprised between the Q- and B-bands in their UV/Vis absorption spectra. A very convenient and fast experimental method to assess materials for NLO (including optical limiting) is the z-scan experiment. This measures the total transmittance through the sample as a function of incident laser intensity while the sample is gradually moved through the focus of a lens (along the z-axis). Effective absorption coefficients were calculated by fitting theory. As an example, the nanosecond open aperture and 40% aperture Z-scans for a 22 mM solution of $t\mathrm{Bu_4PcInCl}$ in chloroform at 532 nm showed that the relative transimission decreases with rising incident fluences. $t\mathrm{Bu_4PcInCl}$ has a positive nonlinear absorption coefficient and is a reverse saturable absorber over this range of fluences. When the sample was far away from focus, experiments were performed with an exit aperture that gave approximately 40% transmission. Dividing these data by the open aperture transmission data gives a measure of the nonlinear refraction in the sample. Basically there is a negative (thermal) and a positive (excited state) contribution to the nonlinear refractive response of the materials. A negative contribution to the nonlinear refractive index, which leads to the well known peak-valley signature of the data, becomes apparent at a fluence of 2.7 $\mathrm{mJ/cm^2}$ and dominates the data with increasing fluence of the incident beam. This negative change in the refractive index has its origin in the decrease of the number density of molecules in the sample, due to thermal expansion of the solution that arises when the absorbed energy is converted to heat. A second positive contribution to the nonlinear refraction appears in the highest fluence scan (28 $\mathrm{mJ/cm^2}$). This response is assigned to an excited state nonlinearity, which is instantaneous compared to the duration of the nanosecond pulse and was found to be positive in the DFWM experiments. It becomes apparent in a larger distance to the focuse at z ~ 75 μm [68].

Similar to $t\mathrm{Bu_4PcInCl}$, all the phthalocyanine complexes synthesized by us exhibit strong reverse saturable absorption at 532 nm excitation. This effect is a consequence of the increase of absorbance of phthalocyanine compounds in the triplet excited state in the optical window comprised between Q- and B-bands, as verified upon laser irradiation with ns pulses at 355 nm. This indicates that both resonance and nonlinear off-resonance irradiation of all Pc compounds used with nanosecond pulses generate analogous excited states whose absorptivity is larger than in the ground state in the spectral window. The nonlinear response (including optical limiting response) of $t\mathrm{Bu_4PcMCl}$ [M =In, Ga] is obviously improved by axial substitution and dimerization. In the aryl-axially substituted indium phthalocyanine complexes e.g. $t\mathrm{Bu_4PcIn}$(*p*-TMP) the nonlinear absorption begins at a lower fluence than for $t\mathrm{Bu_4PcInCl}$. Furthermore, it was found that in the Z-scan experiments the materials in toluene were stable to ambient light over the course of the experiment, and even to the laser, so long as the samples were away from the focus. If chloroform was used as solvent instead of toluene, TFP-bridged indium phthalocyanine dimer $[t\mathrm{Bu_4PcIn}]_2$(TFP) in $\mathrm{CHCl_3}$ was not stable to multiphoton excitation at high laser intensities at the focus. The reactions might occur with multiphoton excitation. The photochemical reactions at focus are generally multi-photon processes. They often result from a second photochemical excitation of an already excited molecule [69].

Optical measurements were carried out on axially substituted gallium naphthalocyanines(Ncs) $t\mathrm{Bu_4NcGaCl}$, $t\mathrm{Bu_4NcGa}$(*p*-TMP) and $[t\mathrm{Bu_4NcGa}]_2\mathrm{O}$ in chloroform solution [40,41]. These compounds display RSA behavior at 532 nm excitation, and their transient absorption spectra recorded under 350 nm laser excitation exhibit a positive variation of absorption coefficient in the excited state in the spectra rang 500-700 nm. The substitution of axial chlorine by *p*-TMP group results in an increased value of the ratio of the excited-state absorption cross section to that of the ground-state ($\kappa = \sigma_{ex} / \sigma_0$) for the studied gallium naphthalocyanines almost by a factor of 2 due to the decreased linear absorption at 532 nm. The dimeric species $[t\mathrm{Bu_4NcGa}]_2\mathrm{O}$ exhibits the lowest value of κ (4.1± 0.1) but, as well, the lowest saturation density F_{Sat} among this series of gallium naphthalocyanines. In comparison with analogous gallium-phthalocyanines all reported NcGa compounds show lower κ and F_{Sat} values.

Electron-withdrawing groups in conjugated moleculars are known to increase the oxidation potential of the substituted molecules thus increasing the chemical stability of these systems against, e.g., oxidation due to intense light or oxygen [70]. The observation of the very low transmission of high intensity radiations through solutions of fluorine-substituted phthalocyanines e.g. $\mathrm{F_{16}PcTiO}$, $\mathrm{F_{16}PcVO}$, $\mathrm{F_{16}PcVO}$, $\mathrm{F_{16}PcInCl}$ and $\mathrm{(CF_3)_4PcTiO}$ poses new different issues like the effect of fluorine on the polarizability of the electronic cloud (nonresonant dynamic effect) under variable electric fields, and /or the modification of the optical absorption in the ground and, more important, in the excited electronic states of the substituted phthalocyanines and naphthalocyanines (molecular resonance effect). The optical limiting performance exhibited by phthalocyanines substituted with electron withdrawing atoms such as F and $\mathrm{CF_3}$, results considerably enhanced with respect to the optical limiting effect produced by unsubstituted or differently substituted phthalocyanines. The remarkable variations of the nonlinear transmittance of perfluorinated phthalocyanines in solution indicates the strong influence that electron-withdrawing group exhibit upon the variations of the transition dipole moments involved in the electronic transition, which effectively limits the intense radiation [70]. We developed a novel approach for naphthalocyanine (Nc) modification, namely introducing fluorine atoms on the peripheral positions of the Nc ring [41]. The first examples of peripherally fluorine substituted naphthalocyanines, $\mathrm{F_{16}NcGaCl}$ and $[\mathrm{F_{16}Nc\ Ga}]_2\mathrm{O}$ were reported by us. The high photostability of these two compounds is attributed to the electron-withdrawing property of the fluorine atoms, which reduces the electron density in the Nc ring and make its oxidation more difficult when irradiated. In comparison with $\mathrm{C_{60}}$ and nonfluorinated NcGa compounds $t\mathrm{Bu_4NcGaCl}$ and $[t\mathrm{Bu_4NcGa}]_2\mathrm{O}$, $[\mathrm{F_{16}NcGa}]_2\mathrm{O}$ displayed a much better optical limiting performance. The optical limiting thresholds for $[\mathrm{F_{16}NcGa}]_2\mathrm{O}$, $\mathrm{C_{60}}$, $[t\mathrm{Bu_4NcGa}]_2\mathrm{O}$ and $t\mathrm{Bu_4NcGaCl}$ are 450, 1248, 2150, and 3945 $\mathrm{mJ/cm^2}$, respectively. The possible reason for the enhancement of the optical limiting behavior in $[\mathrm{F_{16}NcGa}]_2\mathrm{O}$ is probably due to the involvement of the strong electron-withdrawing nature of the fluorine substituents, improved dipole moments and a higher effective σ_{ex} / σ_0 ratio [41].

SUMMARY

Axial substituents in phthalocyanines influence favorably nonlinear optical absorption for the presence of a dipole moment perpendicular to the macrocycle in the axially substituted phthalocyanines. In terms of optical limiting effectiveness in the visible range, axial substitution can improve the efficiency of excited state absorption through the inhibition of the decay of the excited state formed in a nonlinear optical regime. The spectral bandwidth or window over which the NLO device operates, and the ground-state and excited-state spectra and lifetimes, can be molecularly engineered by altering the axial or peripheral substituents, central metal cations and the structure of the main rings. For the development of the materials required for high-performance NLO devices, except for the further improvement of the NLO response of the known functional materials via molecular modification, the design, synthesis and evaluation of SupraRSA, such as the phthalocyanine- and fullerene-based donor-acceptor dyads, triads and/or supramolecular systems, and preparation of nanoscale NLO materials are also a rapidly growing new field.

The majority of optical limiting research has focused on solution based studies, with fewer reports investigating passive solid state nonlinear optical devices. A practical optical limiter based on the nonlinear optical response from phthalocyanines would almost inevitably require the casting of the optically active compounds in the solid state. Polymerizing the Pc's, or embedding them as inclusions in a polymer host to form a composite material, would allow traditional methods such as spin casting to be employed to produce suitable films for these solid-state applications [48,49,58,60,71]. The further work will be focused on in-depth studies of the Pc–based solution and solid state systems to provide a detailed understanding of the factors affecting the optical limiting response.

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