Phthalocyanines as Active Materials for Optical Limiting

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This work gives an overview concerning the optical limiting processes in phthalocyanines. In particular, the synthesis and the relevant optical properties of a series of axially substituted indium(III)– and titanium(IV)–phthalo- and -naphthalocyanines are described. Several techniques, such as transient absorption, *Z*-scan, and degenerate four-wave mixing, have been used for assessing the optical properties and optical limiting performance of the investigated compounds.

Introduction

Phthalocyanines (Pcs) and metallophthalocyanines (PcMs) (see Figure 1) have been studied in great detail for many years, mostly in terms of their uses as dyes and catalysts.[1] Recently, the chemistry of Pcs has been undergoing a renaissance, because Pcs and many of their derivatives exhibit properties of interest for applications in materials science,[2−12] especially in nonlinear optical (NLO) devices,[2] liquid crystals,[3] Langmuir−Blodgett films,[4,5] electrochromic devices,[7] gas sensors,[11] and photosensitizers,[12] among others.[1,13,14]

Substituted derivatives of Pcs can also function as active components in various light-driven processes, such as photoredox reactions,[1−3] photoelectrochemical reactions,[2−5] electrophotography [1] and photodynamic activity in cancer therapy.[1−3] Pcs, PcMs, and naphthalocyanines (Ncs) (see Figure 1) are interesting for a variety of reasons: They possess extended networks of π-electrons, have planar structures in many cases, and show high thermal stabilities. Moreover, Pcs, PcMs, and their derivatives can be synthesized in high yields and purities by several methods.[1,15]

Many of these Pcs and Ncs are insoluble in the common organic solvents; however, their solubilities can be improved by incorporation of substituents in their peripheral positions. These substituents may be either alkyl or alkoxy groups of different chain lengths, or branched systems. Substitution of Pcs and Ncs with one, two, or more substituents, for example, can result in structural isomers that can be separated by conventional chromatographic techniques if necessary.[16]

This review is focused on the optical properties of In^{III}− and Ti^{IV}−phthalocyaninato and −naphthalocyaninato compounds. In particular, our research has concentrated on

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Danilo Dini (right) was born in Rome (Italy) in 1968. He graduated in Chemistry at the University of Rome "La Sapienza", where he received his Ph.D. degree in Materials Science under the direction of Prof. Franco Decker. After a postdoctoral appointment at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin-Dahlem, under the supervision of Prof. Gerhard Ertl, he joined the research group of Prof. Michael Hanack at the University of Tübingen as associate researcher. His main interests are the electrochemical characterization of functional materials and the preparation of organic molecules for advanced optical applications.

Markus Barthel (left) was born in Chemnitz in 1971. He studied chemistry at the University of Tübingen and was awarded his diploma in 1999. Since then he has been working on his doctoral thesis in the field of the optical limiting properties of phthalocyanines in the group of Professor Hanack.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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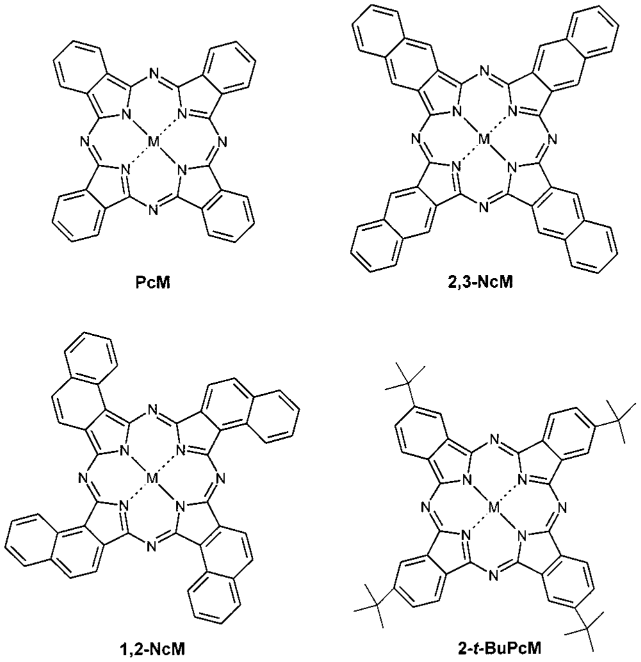


Figure 1. Metallophthalocyanine and its derivatives; PcM: metallophthalocyanine; 2,3-NcM: 2,3-metallonaphthalocyanine; 1,2-NcM: 1,2-metallonaphthalocyanine; 2-*t*BuPcM: 2-tetra-(*t*Bu)metallophthalocyanine (C_{4h} isomer)

the study of nonlinear optical (NLO) properties of Pcs and Ncs for their possible use in NLO applications. This effort has been motivated by the fact that Pcs and Ncs can show fast response times, large nonlinearities, small losses, and small dielectric constants. In addition they offer the potential to be processed and fabricated into waveguides and integrated optical devices more easily and economically than inorganic materials can. Among the NLO applications of Pcs and Ncs, optical limiting represents one of the most promising.[17] Optical limiters are of practical importance, due to the possibility of their being usable for protection of light-sensitive elements such as the human eye, optical apparatus, sky analyzers, and light sensors against intense sources of radiation (lasers or stellar radiation), which can irreversibly damage such elements when a safety threshold is exceeded.[11d,11e]

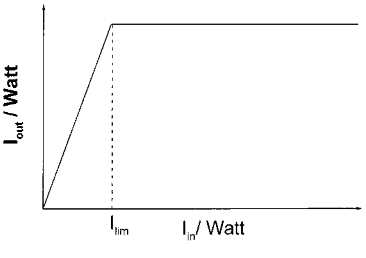


Figure 2. Trend in the light intensity I_{out} transmitted by an ideal optical limiter versus incoming light intensity I_{in}; the threshold intensity I_{lim} at which I_{out} saturates is indicated in the abscissa

What is Optical Limiting?

The phenomenon of optical limiting is observed when the intensity of a light beam is strongly attenuated by a system acting as optical limiter once the input intensity exceeds a threshold value, indicated here as I_{lim}. The ideal behavior of an optical limiter, or saturable filter, is represented by the trend shown in the plot I_{out} vs. I_{in} (see Figure 2). I_{out} and I_{in} are the intensity of the light beam transmitted by the optical limiter and the intensity of the incoming light, respectively. This is a case of an NLO effect, as the response of the system is not directly proportional to I_{in} over the whole range of I_{in}.

Observation of variable transmission as a function of incident light intensity implies the existence of different processes in the mechanism of light absorption in the system at the various irradiation levels.[18] An adequate model accounting for the variable transmission effect is the four-levels system,[19] in which the absorption of an excited state is considered.[20] The scheme of the energy levels for a four-levels system is presented in Figure 3.

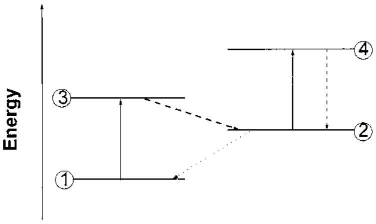


Figure 3. Energy diagram of a four-levels system; solid lines indicate absorption from ground [1 → 3] and excited states [2 → 4]; dashed lines represent intersystem crossing [3 → 2] and excited-state fluorescence [4 → 2] (fast processes); dotted line indicates phosphorescence [2 → 1] (slow process)

Absorption occurs for the transitions [1 → 3] and [2 → 4], with ($h\omega_{1,3}/2\pi$) being equal to ($h\omega_{2,4}/2\pi$), where $\omega_{i,j}$ indicating the frequency of absorption for the transition [$i \rightarrow j$] and h being the Planck constant. The mechanism of absorption in the model presented therefore involves a process with two-photon absorption, due to the consecutive electronic transitions [1 → 3] and [2 → 4].[21] The intersystem crossing (ISC) transition [3 → 2] (it is assumed that the pairs of states 1,3 and 2,4 are singlet and triplet states, respectively), and the fluorescence from the upper excited state [4 → 2] are assumed to be fast processes, with $\tau_{3,2} = \tau_{4,2} \approx 0$ ($\tau_{i,j}$ here indicates the lifetime of the transition [$i \rightarrow j$]). This assumptions are based on the fact that effective optical limiting requires fast intersystem crossing in order to populate the excited state $i = 2$ and a high value of the absorption cross-section for the transition [2 → 4] in order to absorb the second photon efficiently. In this model it is then found that when the system is in a steady state the net absorption coefficient α is given by Equation (1).[19,21,22]

$$\alpha = \alpha_{1,3} + \alpha_{NL} I_{in} \qquad (1)$$

The threshold value of the intensity is given by Equation (2).

$$I_{\lim} = h\omega^*/(2\,\pi\,\sigma_{1,3}\,\tau_{2,1}) \qquad (2)$$

In Equation (1) and (2) $\alpha_{i,j}$ and $\sigma_{i,j}$ are the absorption coefficient and the absorption cross-section for the transition between the levels [$i \rightarrow j$]. The relationship shown in Equation (1) implies a modification of the Lambert−Beer law according to Equation (3) in order to include the second photon absorption [z in Equation (3) is the direction of light propagation].

$$-(\mathrm{d}I_{\mathrm{in}}/\mathrm{d}z) = \alpha_{1,3}\,I_{\mathrm{in}} + \alpha_{\mathrm{NL}}\,I_{\mathrm{in}}^2 \qquad (3)$$

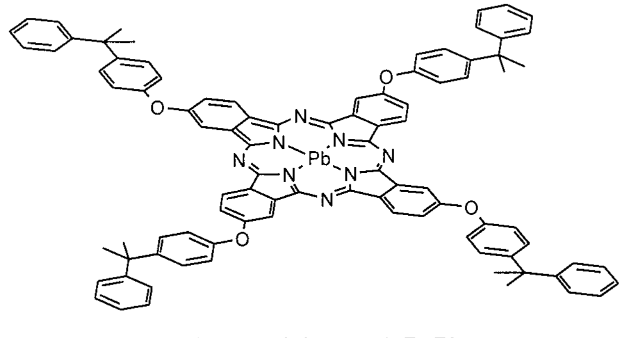
Therefore the four-levels model accounts for the variation of α with I_{in} and predicts that the saturation threshold $I_{\lim}$ should decrease with an increase in the absorption cross-section for the transition from the ground state, and with the lifetime of the decay [2 → 1]. The coefficient α is directly correlated with the imaginary part of the third order optical susceptibility Im[$\chi^{(3)}$].[23,24] This implies that there are no symmetry restrictions for the system in showing optical limiting, unlike in the case of second order nonlinear optical effects, which are symmetry dependent.[25,26] Another relevant consequence of third order nonlinear optical effects is the fact that their observation does not necessarily require the occurrence of resonance at the frequency of excitation. An important feature of interest for evaluation of the optical limiting properties of a saturable absorber is the temporal response for a given pulse of incident light. In fact, the response time should be short enough to counter possible disruptive effects from the incoming intense light.[18] According to the outline shown in Figure 3, the lifetime of the excited state $i = 2$ should be longer than the duration of the light pulse in order to produce an accumulation of the population in this state. Moreover, the system should switch to a transparent state shortly after the light pulse ends.[27] Useful criteria for estimation of large, positive nonlinear absorptivities involve the magnitude of excited state cross-section σ_{ex} and the difference between the ground and excited state absorption cross-sections ($\sigma_{\mathrm{ex}} - \sigma_0$).[17]

The phenomenon of saturable absorption has been reported for several classes of organic chromophores, including Pcs,[17,28,29] porphyrins,[18,30−33] charge-transfer complexes,[34−36] cluster compounds,[36−41] and − more recently − fullerenes[22,42,43] and carbon nanotubes[44] (among others[45−52]), with the goal of the development of optical limiting devices for the protection of sensors and eyes from energetic light pulses.[53] A comparative table of Im[$\chi^{(3)}$] values for different classes of materials is given below.[54−60]

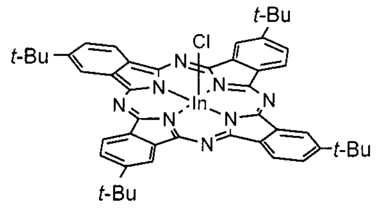
From Table 1 it is evident that the most interesting nonlinear optical properties are shown by the class of Pcs.[61−65] Moreover, this class is one of the most thoroughly investigated, thanks to the concomitant remarkable facility for modulation of Pcs′ physical properties in a controlled fashion through appropriate chemical derivatization of the Pc skeleton[56,57,66−68] or variation of the central substituent M−X (see substituted Pcs in Figure 4).[69,70] The main reason for the existence of large optical nonlinearities in Pc-based systems is the presence of extended networks of conjugated π-electrons, the main characteristics of which are a high electrical polarizability and the ability to give rise to several transitions in the UV/Vis range.[71] Such features, then, render possible a nonlinear response through different mechanisms, the relevance of which depends mainly on the pattern of modification of the Pc.[65]

Table 1. Values of Im[$\chi^{(3)}$] for different classes of compounds

Compound	Im[$\chi^{(3)}$]/esu	Ref.
RSiPc	$2.0\cdot10^{-9}$	[54]
Sc(Pc)2	$1.5\cdot10^{-9}$	[54]
PtPc	$2.0\cdot10^{-10}$	[54]
ClInPc	$1.5\cdot10^{-10}$	[54]
FAlPc	$5.0\cdot10^{-11}$	[54]
$Ni[S_2C_2(C_6H_5)_2]_2$	$3.5\cdot10^{-11}$	[55]
$[(t\mathrm{Bu})_4PcGe(OH)]_2$	$2.5\cdot10^{-11}$	[56]
$[(t\mathrm{Bu})_4PazGe(OH)]_2$	$1.5\cdot10^{-11}$	[56]
C_{60}	$1.0\cdot10^{-11}$	[21]
Poly(phenylenevinylene)	$8.0\cdot10^{-12}$	[55]
Poly(methylphenylsilane)	$7.5\cdot10^{-12}$	[55]
NiPc	$7.0\cdot10^{-12}$	[57]
PdPc	$6.5\cdot10^{-12}$	[57]
$Pt[S_2C_2(CN)_2]_2$	$4.0\cdot10^{-12}$	[55]
Poly(di-*n*-hexylsilane)	$1.5\cdot10^{-12}$	[55]
C_{70}	$1.5\cdot10^{-12}$	[58]
CS_2	$4.5\cdot10^{-13}$	[59]
$Ni[Se_2C_2(CF_3)_2]_2$	$1.5\cdot10^{-13}$	[55]
cis-$Mo(CO)_4[P(C_6H_5)_3]$	$9.0\cdot10^{-14}$	[36]
$C_6H_5CH_3$	$1.0\cdot10^{-14}$	[60]
SiO_2	$4.0\cdot10^{-15}$	[59]



(β-cumylphenoxy)$_4$PcPb



(t-Bu)$_4$PcInC

Figure 4. Some substituted PcM complexes for optical limiting

For a useful optical limiting material, the condition that σ_{ex} should be greater than σ_0 is necessary, but not sufficient. A practical optical limiter must operate over the wide range of incident intensities that might be encountered. The nonlinear response should possess a low threshold and remain large over a large range of fluences before the nonlinearity saturates. A high saturation fluence normally requires a high concentration of the nonlinear material in the optical beam. For an organic material, this means it must either be highly soluble in common organic solvents, or be a pure liquid or a solid film that can be prepared with good optical quality.

The Pcs used as nonlinear absorbers tend to aggregate at high concentrations. The intermolecular interactions caused by aggregation can often be deleterious, resulting in the decay of the upper triplet state. The effect of molecular aggregation is particularly relevant when highly concentrated solutions of PcMXs or solid state configurations are adopted for the determination of PcMXs' nonlinear optical properties.[72−74] In fact, the spectral properties of PcMX thin films differ from those of dilute solutions, in broadening of the absorption bands and a slight red-shifting of the wavelengths corresponding to the absorption peaks.[75,76] Such features are expected as a consequence of aggregation in which intermolecular interactions are of the van der Waals type.[77] The influence of molecular aggregation upon optical susceptibility of PcMXs manifests itself in an increase of $\chi^{(3)}$ with increasing PcMX concentration, as experimentally determined by several authors.[78,79] Extensive aggregation of Pcs has to be suppressed by modification of molecular shape and electronic distribution, in order to diminish van der Waals interactions between the large π-systems. In addition, the material must possess a high level of linear transmission and large nonlinear absorption over a broad spectral bandwidth, as well as a high threshold for damage. Furthermore, the nonlinear absorption must appear within a sub-nanosecond response time. Meeting all these criteria is a significant chemical challenge in synthesis. Of the large number of nonlinear absorbers that have been identified, (β-cumylphenoxy)$_4$PcPb,[80,81] tetra-*tert*-butylPcInCl,[17,65,75,76] (see Figure 4) and some substituted porphyrins,[18,31] have been used for the construction of optical limiters approaching the characteristics necessary for a practical device.

Addition of axial ligands X to the central atom M represents a further tool for fine modulation of nonlinear optical properties in the resulting PcMXs.[76] This is due to several effects associated with the presence of the MX entity, such as the introduction of a dipole moment oriented perpendicularly to the Pc ring plane, which alters the electronic structure of the macrocycle,[82] and the introduction of new steric effects that modify the packing properties of the PcMXs.[75] Data collected from several working groups,[17,72,75,82−84] show that the presence of an axial ligand brings about a considerable improvement in third order Pc optical properties. This is especially true for $\chi^{(3)}$ in the case of PcMXs with MX = VO or InCl, as compared with $\chi^{(3)}$ of simple metal-substituted Pcs.[17,75,76,84] In these particular cases, the reason for such large variations resides mostly in the fact that central moieties such as VO and InCl possess the favorable combination of high dipole moments, associated with paramagnetism and the presence of a central heavy atom.[17,75] Such molecular features result in improved performances in MXPc-based optical absorbers, due to enhancement of the ISC process [3 → 2] (see Figure 3) through the so-called heavy-atom and paramagnetic effects.[85]

In the following sections the NLO properties of InPcs, InNcs, and TiPcs are presented in detail, together with the analysis of those molecular features that produce relevant effects on optical limiting properties of these systems.

Indium Phthalocyanines

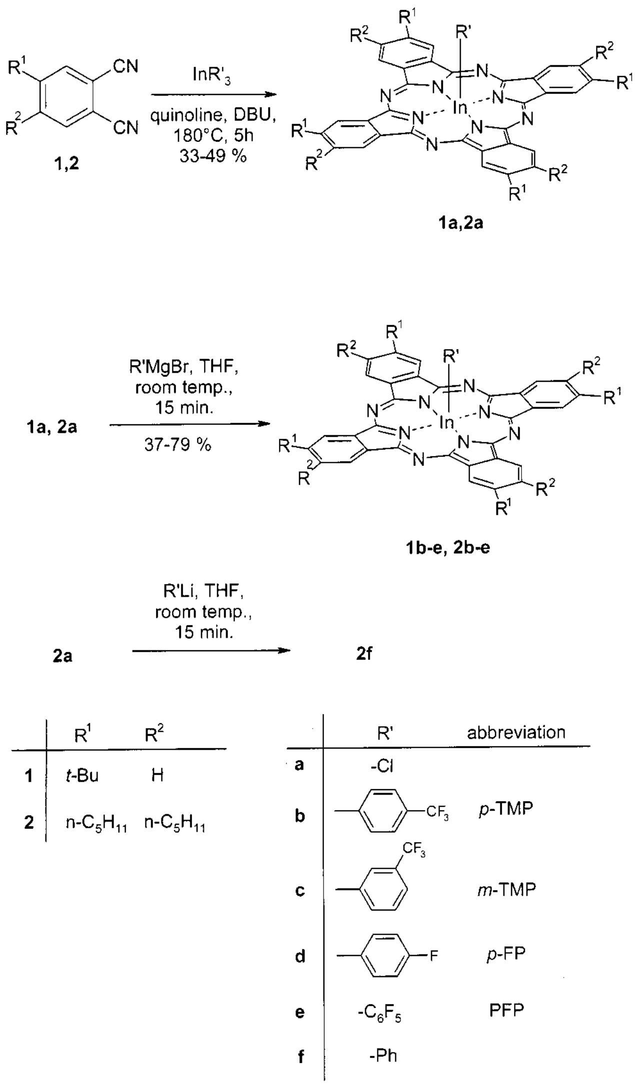
Spectral Properties

Diversity of structural features[1,15,86−88] in Pcs, enabling effective tuning of the resulting optical properties to be accomplished, can be achieved through adoption of different synthesis procedures. We have synthesized several PcInXs and have studied the effect of the axial substituent X on the optical limiting behavior of the resulting complexes. As previously stated, axial substitution can alter the electronic structure of the Pc through the presence of an additional dipole moment oriented perpendicularly to the macrocycle. Moreover, thanks to steric effects, the axial substitution can change the packing properties between neighboring molecules, thus modifying the aggregation properties in solution. Both of these effects can have an influence on the NLO properties.[75,82]

In 1998, we prepared highly soluble alkyl- and arylphthalocyaninatoindium complexes with X = Cl, *p*-trifluoromethylphenyl (*p*-TMP), *m*-TMP, *p*-fluorophenyl (*p*-FP), phenyl, and pentafluorophenyl (PFP)[88] (see Scheme 1).

The aryl-substituted InPcs were prepared from the soluble chloro(phthalocyaninato)indium(III) complexes **1a**, **2a**, and RMgBr, by means of Grignard methodology (see Scheme 1). The resulting compounds were the stable, σ-bonded aryl(phthalocyaninato)indium(III) complexes **1b−e** and **2b−e**, which were highly soluble in common organic solvents and displayed low tendencies towards aggregate formation. The dipole moments associated with the axial substitution in compounds **1a** and **1b** were quite large, being in the order of 10 Debye.[70] The axially *p*-TMP- and PFP-substituted (tBu)$_4$PcIn complexes (**1a**,**1b**) were found to have better solubilities than their chloro analogues, together with higher nonlinear absorption coefficients, lower limiting thresholds, and lower transmission at high fluences.[75]

By comparison of the UV/Vis absorption spectra of solutions of **1a** and **1b** at different concentrations (see Figure 5), it is apparent that there is a modification in the spectra with the concentration of **1a**. This is not so for the aryl-substituted compound, as shown by the unchanging nature of the absorption profile with variation of the concentration over three orders of magnitude (see Figure 5b).



Scheme 1. Synthesis of chloro- and arylindium(III)−phthalocyanine complexes

In dilute solutions, the spectra of **1a** and **1b** are characterized by the strong Q band near 700 nm and the strong B band near 340 nm. There is a shift in the position of the Q-band of less than 1 nm between **1a** and **1b**. The range of interest for optical limiting is the high transmission region between 420 nm and 600 nm, that is, between the two intense Q and B bands. Compound **1a** has an absorption cross-section of about 2×10^{-18} cm^2 in the ground state, which corresponds to a molar extinction coefficient of 500 L/(mol × cm) over the range 460 to 533 nm. The measured absorption cross-sections of the aryl analogues **1b**−**e** are very similar to the values found for **1a** in the same wavelength range.

NLO Properties

The photophysical processes and the dynamics associated with optical limiting phenomena have been studied for different axially substituted compounds by several techniques.[75] For each of the compounds **1a**, **1b**, and **1e**, transient absorption studies showed that incident light in the visible range first induces excitation of the system to a singlet state, which rapidly evolves into a triplet state with an ISC time of about 300 ps and a quantum yield close to unity. Consequently, the triplet state absorption should dominate the nanosecond nonlinear response. The triplet state lifetime was found to be longer than 5 ns. In both the excited singlet and triplet states, the absorption cross-section of **1a** is larger than the cross-section of the ground state. The variations in the absorption cross-section of **1a** in both ground and triplet excited states, as measured in a transient absorption study, are shown in Figure 6. The material thus behaves as a reverse saturable absorber in the 420−600 nm range.

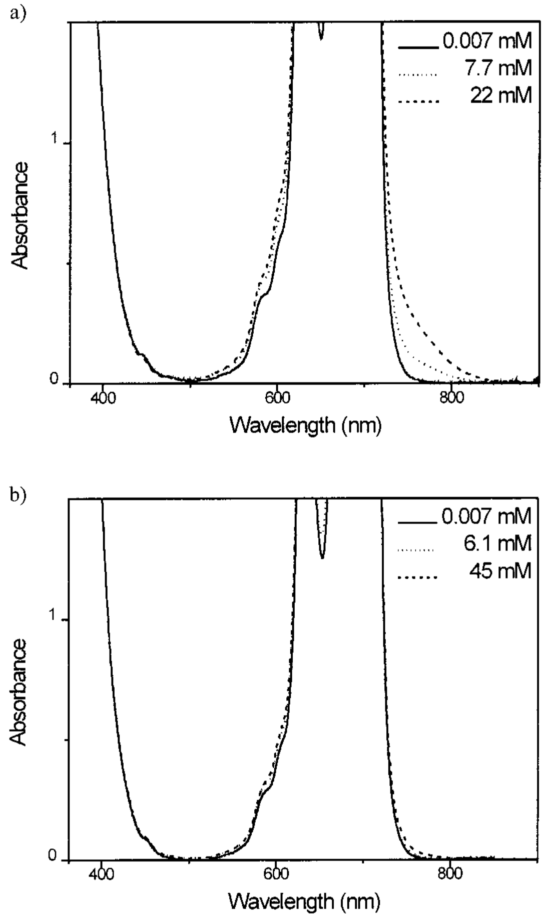


Figure 5. Absorption spectra of: (a) $(t\mathrm{Bu})_4\mathrm{PcInCl}$ (**1a**), and (b) $(t\mathrm{Bu})_4\mathrm{PcIn}(p\text{-}\mathrm{CF_3C_6H_4})$ (**1b**) in $CHCl_3$ at different concentrations

The nonlinear absorption coefficients α, expressed in terms of fluence, were determined by measurement of the nanosecond nonlinear transmission between 500 and 620 nm (see Figure 7). The values of α were generally large for all of the complexes. In particular, the aryl-substituted Pcs **1b** and **1e** showed the highest values of α at $\lambda > 550$ nm. The larger values of α resulted in lower optical limiting thresholds in the aryl-substituted materials (see Figure 7).

Samples displaying a low-intensity transmission $T_0 = 0.80$ at $\lambda = 532$ nm showed different saturation energy

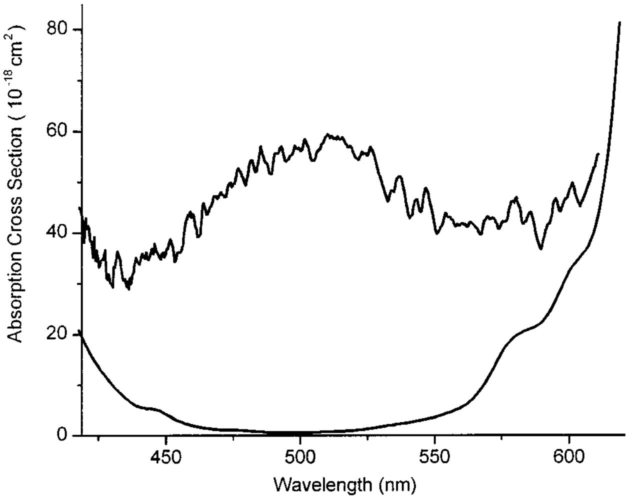


Figure 6. The ground and excited triplet state absorption spectra of (tBu)$_4$PcInCl (**1a**)

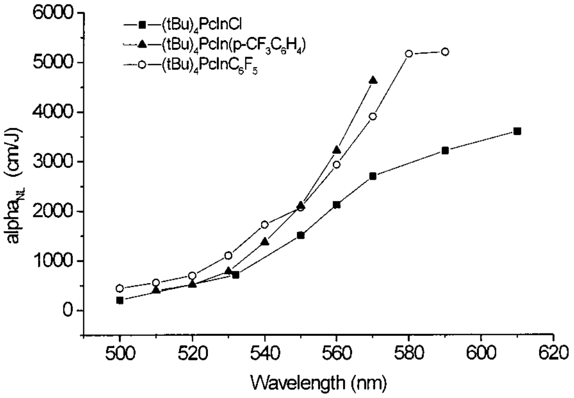


Figure 7. Nonlinear absorption coefficients as a function of wavelength for (tBu)$_4$PcInCl (**1a**, squares), (tBu)$_4$PcIn(p-CF$_3$C$_6$H$_4$) (**1b**, triangles) and (tBu)$_4$PcIn(C$_6$F$_5$) (**1e**, circles)

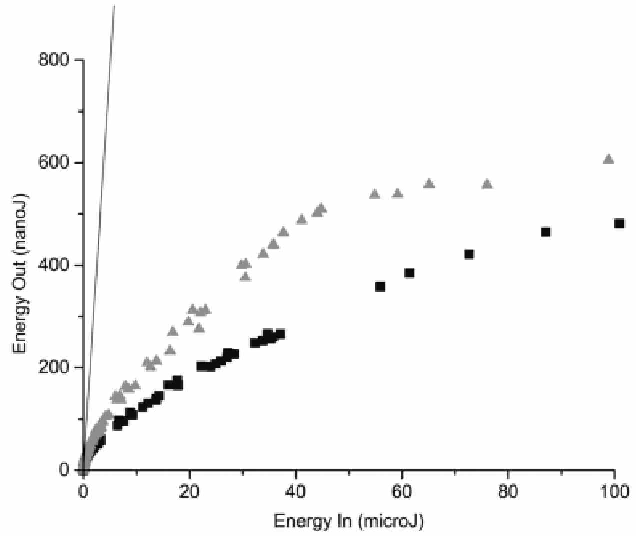


Figure 8. Optical limiting at 532 nm by (tBu)$_4$PcInCl (**1a**, triangles), and (tBu)$_4$PcIn(p-CF$_3$C$_6$H$_4$) (**1b**, squares)

thresholds E_{lim}, where E_{lim}(**1b**) $= 0.5 \cdot E_{\mathrm{lim}}$(**1a**) as determined from f/5 experiments.[75,80] The transmission is substantially lower for the aryl compound **1b** than for the chloro-substituted material **1a**. It can be seen from Figure 8 that **1b** showed a lower transmission than **1a** over a wide range of incoming energy E_{in}, except at high values ($E_{\mathrm{in}} > 8 \cdot 10^{-5}$ J), at which the differences tended to decrease.

Indium Naphthalocyanines

Spectral Properties

Extension of the Pc core by linear benzannelation affords the related 2,3-Nc group (see Figure 1). The more extended π-electron systems provide more pronounced nonlinear optical properties than seen in the Pc analogues, due to the higher levels of electronic susceptibility. In addition, 2,3-Ncs have their Q-bands shifted to the near IR at about 800 nm, the hue of Nc solutions being determined by the B-band absorption in the blue region at about 400 nm. Dilute Nc solutions, then, have a green-yellowish color. These absorption properties of Ncs offer new opportunities for applications in which the blue color of Pcs might result in ineffective optical limiting at certain wavelengths of interest. In, for example, an environment in which it was necessary to be able to see conventional red light signals or displays, the strongly red-absorbing phthalocyanines would be unsuitable for use in eye protection, although their performance in limiting high light intensities would still be good, due to excited state absorption. Ncs are almost transparent in the red region, with a transmission window of 530−650 nm. We therefore focused on the synthesis of substituted, highly soluble In$^{\mathrm{III}}$−Ncs with different axial ligands. We developed a new, unsymmetrical, peripheral, eightfold substitution pattern, with alkyl and alkoxy substituents in the 2- and 4-positions of the Ncs (see Figure 9). The resulting compounds are in general more soluble than the symmetrically octasubstituted 2,3-Ncs.[89]

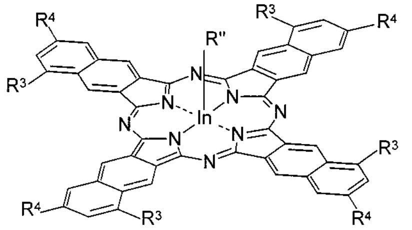
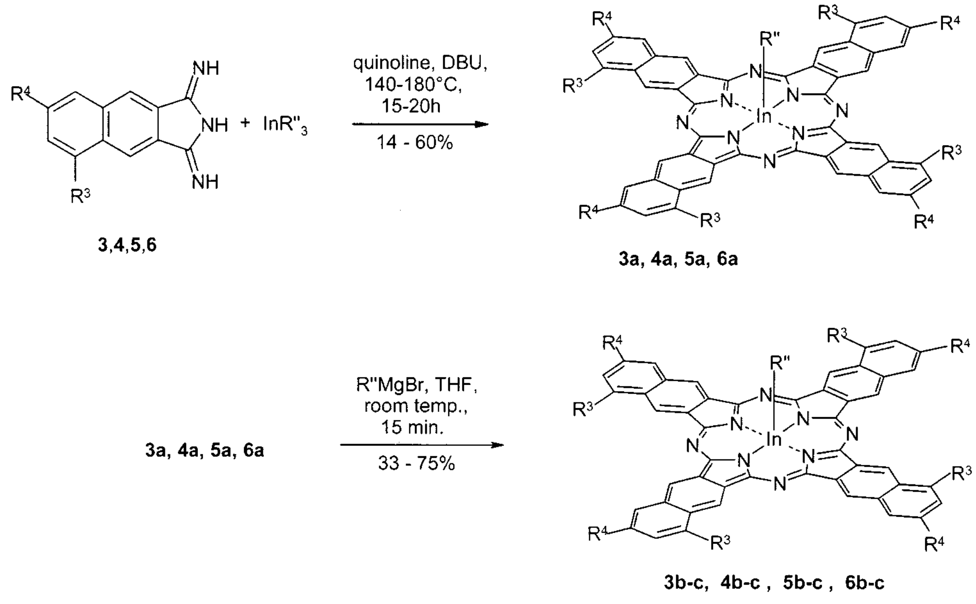


Figure 9. 2,4-Octasubstituted indium(III)−naphthalocyanines

The synthesis of (octa-tBu)- (**4a**), {(tetra-tBu)[tetra-2-ethylhexyloxy (EHO)]}- (**5a**), (octa-EHO)- (**6a**) and (tetra-tBu)-substituted NcInCl (**3a**) is shown in Scheme 2.[89] The bulky tBu group and the long chain EHO were chosen as substituents because they imparted solubility as a result of their steric demand. Moreover, the electron-donating natures of these groups shift the Q-band absorptions further into the near IR.



	R3	R4
3	H	*t*-Bu
4	*t*-Bu	*t*-Bu
5	EHO	*t*-Bu
6	EHO	EHO

	R"
a	-Cl
b	*p*-TMP
c	PFP

Scheme 2. Synthesis of different octa- and tetrasubstituted 2,3-indium(III)−naphthalocyanines

The resulting axially aryl-substituted Ncs **3b−c**, **4b−c**, **5b−c**, and **6b−c** do not change very much either in color or in stability upon ligand exchange. Dilute solutions of the compounds possessing *t*Bu groups exclusively (**3b−c** and **4b-c**) are still greenish yellow, and the others, with the EHO groups (**5b−c** and **6b-c**), range from yellow to orange. Ligand exchange also has only slight influence on the electronic properties of the Ncs. UV/Vis spectra (not shown here) of dilute samples of the Ncs **3b−c**, **4b−c**, **5b−c**, and **6b−c** show slightly bathochromically shifted B-bands (3−13 nm) and hypsochromically shifted Q-bands (0.5−4 nm) in comparison with their chloro analogues.

From the variation of absorption profiles with concentration of Ncs in solution it can be deduced that the tetra-*t*Bu-substituted Ncs **3a−c** have a stronger tendency to aggregate than the mixed octasubstituted Ncs **5a−c**. This is consistent with expectations based on steric considerations. For the octasubstituted species, the *t*Bu peripheral substituent was more effective than the EHO substituent in blocking aggregation. The mixed substituted $(t\mathrm{Bu})_4(\mathrm{EHO})_4$ Ncs with large axial substituents showed very little evidence of aggregation even at very high concentrations.

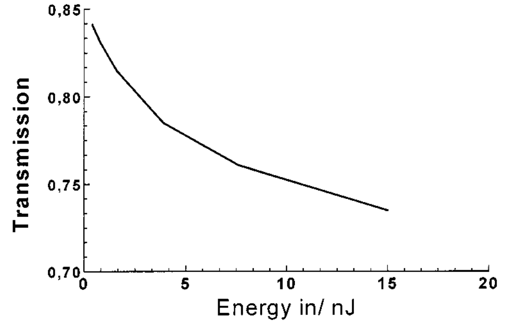


Figure 10. Optical limiting by a 2.4 mM solution of $(t\mathrm{Bu})_4\mathrm{NcInCl}$ (**3a**) at 640 nm

NLO Properties

The NLO properties, photophysical processes, and their dynamics in the different Ncs were studied using the same techniques as had been adopted for Pcs.[75,76] Optical limiting measurements were carried out using the *Z*-scan method on a 2.4 mM solution of $(t\mathrm{Bu})_4\mathrm{NcInCl}$ (**3a**) in $\mathrm{CHCl_3}$ at 640 nm, and the results are presented in Figure 10.

The value of α_{NL} for compound **3a** derived from *Z*-scan experiments proved inferior to expectations, due to the fact that a fraction of the material in solution formed aggregates during the relaxation times of the excited state. A reduction of the deleterious effects on nonlinear absorption associated with aggregation was an important goal, and it was achieved through the synthesis of new Ncs bearing eight peripheral substituents (**4a**, **5a**, **6a**). The octa-EHO-substituted Ncs (**6a−c**) showed a stronger tendency to aggregate than (tetra-*t*Bu)(tetra-EHO)-substituted Ncs (**5a−c**) did. These latter materials showed only slight aggregation tendencies, even in quite concentrated solutions. Of these compounds, the species with axial *p*-TMP groups were more resistant to aggregation over time. *Z*-scans were performed on $(t\mathrm{Bu})_4(\mathrm{EHO})_4\mathrm{NcIn}(p\text{-TMP})$ (**5b**) at different wavelengths in the transmission window of this complex. It was confirmed that this material is a nonlinear absorber between 550 nm and 640 nm.

Among the Ncs, $(t\mathrm{Bu})_4(\mathrm{EHO})_4\mathrm{NcIn}(p\text{-TMP})$ (**5b**) was the most promising. This material had a large excited state cross-section and an excited state lifetime longer than 10 ns. This resulted in large nonlinear absorption coefficients and effective optical limiting. This material undergoes an interesting, and as yet unexplored, reversible photochemical reaction upon irradiation at high fluences. This reaction, which produces a material with a strong absorption coefficient, may prove useful in practical optical limiters. The optical limiting behavior of 40 mM $(t\mathrm{Bu})_4(\mathrm{EHO})_4\mathrm{NcIn}(p\text{-TMP})$ (**5b**) solution (sample thickness 20 µm) is shown in Figure 11.

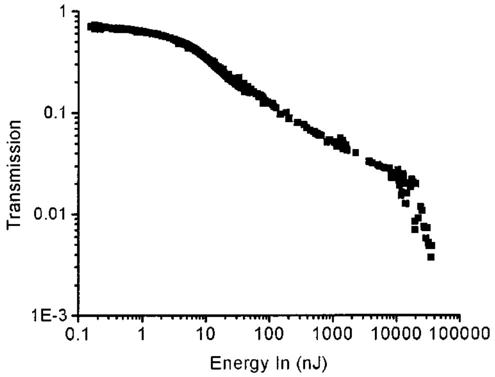


Figure 11. Optical limiting by a 40 mM solution of $(t\mathrm{Bu})_4(\mathrm{EHO})_4\mathrm{NcIn}(p\text{-TMP})$ (**5b**) at 580 nm; the sample was 20 µm thick and had T_0 = 76%

The transmission T_0 through **5b** solution at low levels of incidence is 76%. The observed energy threshold at which transmission reduces to 50% of T_0 is 10 ± 2 nJ. The slope change at ca. 10^4 nJ is coincident with formation having a lifetime of longer than 1 s. Such changes indicate the onset of system damage due to degradation of the active limiting material. Unlike other examples of photochemical damage in limiter materials, however, the system based on **5b** shows partial reversibility, with recovery of limiting properties at energy values lower than 10^4 nJ. Partial reformation of the original material within 1 h was observed.

Titanium Phthalocyanines

The NLO properties of some oxotitanium−Pcs − namely PcTiO, $(\mathrm{CH_3})_4\mathrm{PcTiO}$, $(\mathrm{CH_3O})_4\mathrm{PcTiO}$, and $(\mathrm{CH_3O})_8\mathrm{PcTiO}$ − have previously been investigated in order to study how the different substituents and substitution patterns of the rings can influence the reverse saturable absorption (RSA) of the respective oxotitanium Pc solutions.[57] The results suggested that functionalization of the edges of the conjugated rings might permit fine-tuning of the NLO properties of Pcs in which TiO constituted the central metal−ligand combination. Our approach, then, was to study NLO properties in PcTiXs as a function of changes in the substituent at an axial aromatic ligand. In particular, the NLO properties of a series of PcTiXs with catechol-based axial ligands, synthesized with the goal of characterization of the RSA induced by modification of the axial dipole moment, are reported. The PcTiXs investigated for optical limiting are shown in Figure 12.[82] The synthesis of the various axially substituted PcTiXs is shown in Scheme 3.[90] The typical absorption spectra of the PcTiXs (see Figure 13) show the characteristic Pc Q and B bands centered at 700 and 360 nm, respectively, together with a series of absorption shoulders in the 590−670 nm range.

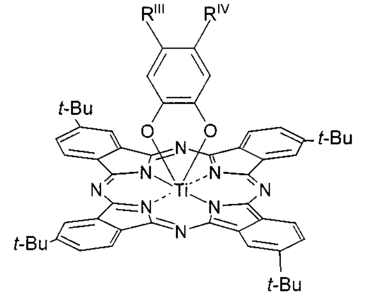
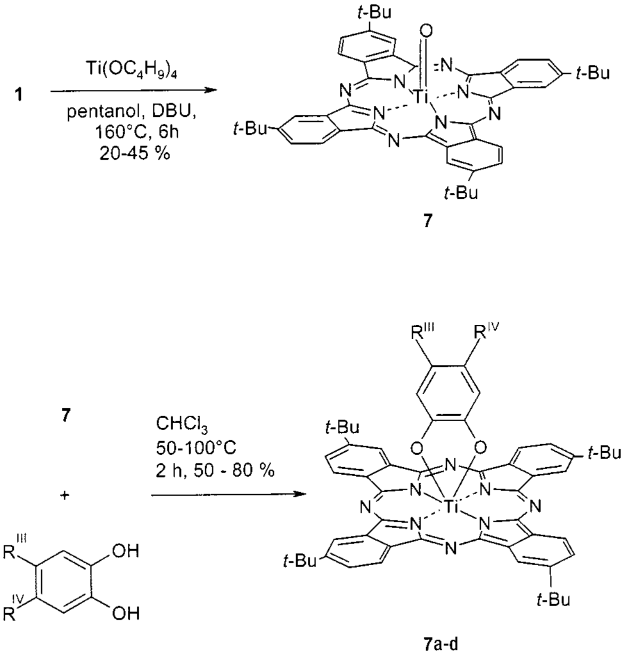


Figure 12. Structure of the axially catechol-substituted $t\mathrm{Bu_4PcTi}$



	R^{III}	R^{IV}
a	H	t-Bu
b	H	CHO
c	H	$\mathrm{CH_2CN}$
d	CN	CN

Scheme 3. Synthesis of the $\mathrm{PcTi^{IV}}$−catechol complexes[90]

The optical limiting performance of **7a**−**7d** at 532 nm (Figure 14) varies markedly with the different electron-withdrawing characters (EWC) of the substituents at the aromatic ligand.[91] The EWC of the axial ligand increases over the range from **7a** to **7d**, and a corresponding reduction in the limit transmission is observed. Such a correlation is not trivial, because changes in limit transmission in PcTiX solutions are mainly due to electronic effects associated with the dipole moment of the axial ligand. In these cases, in fact, steric effects associated with the different catechol-based ax-

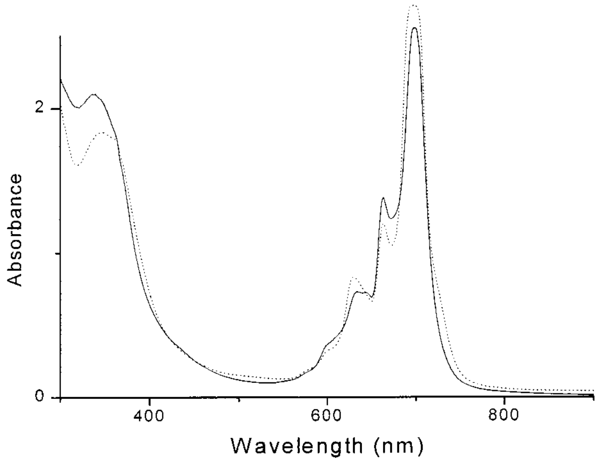


Figure 13. Absorption spectrum of compounds **7a** (solid line) and **7d** (dotted line) in toluene

ial ligands do not play any significant role in determining the optical limiting performance. This is probably because the sizes and packing properties of the different PcTiXs **7a**−**7d** considered here are the same. Such results represent the first clear demonstration that substituents with EWT at the axial ligand improve the optical limiting performance of Pcs in a fashion analogous to that of electron-withdrawing substituents at the conjugated Pc ring.[17]

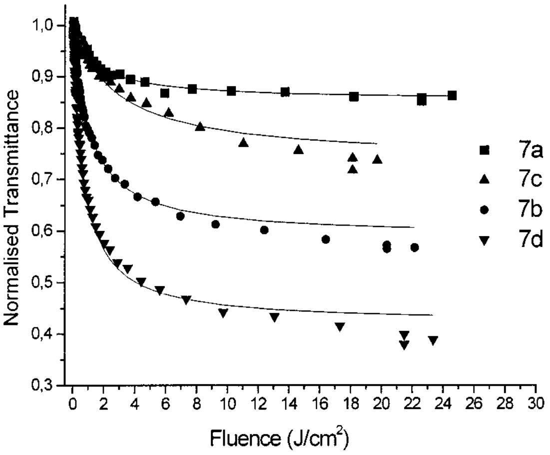


Figure 14. Nonlinear transmission of compounds **7a**−**7d**

Summary

The synthesis of a variety of new chloro- and aryl-substituted indium− and titanium−phthalocyanines and −naphthalocyanines is described. Among the indium−phthalocyanines, molecules with tetra-*tert*-butyl peripheral substitution and axial (*para*-trifluoromethyl)-phenyl, and perfluorophenyl substituents have been found to be sufficiently soluble to be effective in optical limiting.

For each of the indium−phthalocyanines studied, excitation in the visible range initially gives an excited singlet state, which rapidly and efficiently evolves into a triplet state. The relatively long lifetime of the triplet state implies that its absorption kinetics fall in the nanosecond range.

For indium−phthalocyanines, it is generally found that the excited state cross-section in the transparent region is larger than the ground state cross-section. Among the indium−phthalocyanines, the aryl-substituted representatives generally showed larger values of α, with resulting decreases in optical limiting thresholds.

In a series of phthalocyanines with titanium−catechol as the central metal−ligand combination, it has been found that the optical limiting performance improves with increasing electron-withdrawing character in the catechol substituents. This represents the first observation of a direct influence of axial dipole moment upon the nonlinear optical properties of the corresponding phthalocyanines.

Expansion of the ring structure to a naphthalocyanine proved to be a successful strategy for moving the transmission window and the range of effective optical limiting to higher wavelengths. In order to be effective limiters, however, the indium−naphthalocyanines must be designed to resist aggregation. In indium naphthalocyanines it was found to be possible to inhibit aggregation by incorporation of eight peripheral *tert*-butyl substituents or a mixture of *tert*-butyl and ethylhexyloxy moieties. Among the naphthalocyanines, (tBu)$_4$(EHO)$_4$NcIn(p-TMP) showed the largest excited state cross-section and an excited state lifetime of longer than 10 ns. This resulted in large nonlinear absorption coefficients and effective optical limiting. Moreover, this material showed a reversible photochemical reaction upon irradiation at high fluences, forming a product with a strong absorption coefficient. Such unique properties may offer new opportunities in the field of photochemically driven optical limiting.

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